ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 36, No. 1, 1–148, September 1966

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

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)

Manuscripts

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).

Figures should be drawn in Indian ink on drawing or tracing paper with all lettering in **thin** pencil. Standard symbols should be used in line drawings; the following are available to the printers:

▼ ▽ ■ □ ● ◎ ■ ◘ ⊖ ▣ ▪ + ×

Photographs should be submitted as clear black and white glossy prints. Figures and photographs should be of the same size as the typed pages. Legends for figures should be **typed on a separate page**. Figures should be numbered in Arabic numerals in the order in which they are mentioned in the text.

References should be given at the end of the paper and should be numbered in the order of their appearance in the text (**not** arranged alphabetically). Abbreviations of journal titles should conform to those adopted by the *Chemical Abstracts List of Periodicals*, 1961 Edition and supplements. The recommended form for references to journal papers and books is as follows:

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.

For multi-author references, **all** authors must be named, and initials given, in the reference list, although the use of, for example, Smith *et al.*, is desirable in the text.

Summaries are published in English, French and German; authors must always provide a summary in the language of the paper, and are encouraged to supply translations where convenient. No summaries are needed for Short Communications.

Reprints

Fifty reprints will be supplied free of charge. Additional reprints (minimum 100) can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

Analytica Chimica Acta has four issues to the volume, and three volumes appear per year. Subscription prices: $ 17.50 or £ 6.6.— or Dfl. 63.— per volume; $ 52.50 or £ 18.18.— or Dfl. 189.— per year, plus postage (per year): 11 s. or $ 1.50 or Dfl. 5.40. Additional cost for copies by airmail available on request. For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands

Announcing an important new Elsevier Journal

POWDER TECHNOLOGY

An International Journal

The Journal publishes original research papers, review articles, and short communications dealing with the results of research into the fundamental properties and behaviour of powders and the exploitation of this knowledge for handling and using them.

POWDER TECHNOLOGY provides a means of exchanging information between different industries and areas of knowledge where, in spite of apparent differences, the underlying problems are often very similar.

The following list, though not exhaustive, gives a general outline of the scope:

SCIENCE OF POWDERS

Properties of individual particles - physical, chemical, mechanical; and methods of determination

Properties of assemblies of particles - including dispersions in a variety of systems (e.g. solid/liquid, liquid/liquid, solid/gas, liquid/gas) and related interfacial phenomena; powder rheology, agglomeration, dispersion, etc.

TECHNOLOGICAL ASPECTS OF POWDERS

Powder production - crushing, grinding, precipitation, etc.

Size enlargement - agglomeration, sintering, etc.

Mixing - solid/solid, solid/liquid.

Separation of powders - (solid from solid, solid from liquid, solid from gas) including such methods as electrostatic separation, filtration, gas cleaning.

Handling and processing of powders - storage; conveying in bulk in liquids and in gases; drying; fluidisation.

INDUSTRIAL ASPECTS OF POWDERS

Powder problems in industry - both general and specific.

(see over)

Order form

POWDER TECHNOLOGY
An International Journal

8 x 11″, bi-monthly issues, one volume per year
Subscription price: £6.6.0, US$17.50 or Dfl. 63.00 per volume (plus postage: 5s., US$0.70, Dfl. 2.40 per year)

☐ Please enter my subscription to POWDER TECHNOLOGY as a *standing order/to be renewed yearly

☐ Cheque enclosed/please invoice

☐ Please send me a free specimen copy

☐ Please send me a copy of instructions to authors

Date:

Name: ______________________
(please print)
Address: ______________________
____

*** Delete where not applicable**

TYPES OF CONTRIBUTIONS

a. FULL-LENGTH PAPERS reporting results of original research work on any aspect of powder technology

b. SHORT COMMUNICATIONS giving a concise but complete description of an investigation which will not be included in a later paper

c. REVIEW ARTICLES on specialized topics within the scope of the journal

d. BOOK REVIEWS

e. NEWS ITEMS

SUBMISSION OF MANUSCRIPTS

Contributions may be in English, French or German and should be sent to any one of the three Regional Editors:

DR. B. H. KAYE, I.I.T. Research Institute, 0 W 3 Street, Chicago, Illinois 60616, U.S.A.

MR. D. F. KELSALL, C.S.I.R.O., Division of Chemical Engineering, P.O. Box 4331, Melbourne, Victoria, Australia.

MR. J. C. WILLIAMS, Department of Chemical Engineering, Bradford Institute of Technology, Bradford 7, Yorkshire, England

PUBLICATION AND SUBSCRIPTIONS

POWDER TECHNOLOGY is published bi-monthly, one volume per year. Subscription price: £6.6.0, US$17.50 or Dfl. 63.00 per volume, plus postage 5s., US$0.70 or Dfl. 2.40 per year

Subscriptions should be sent to ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands, or to your usual supplier.

ELSEVIER PUBLISHING COMPANY

Subscription Department

P.O. Box 211

AMSTERDAM

The Netherlands

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 36, No. 1, September 1966

AUTOMATED CHROMATOGRAPHY OF URONIC ACIDS ON ANION-EXCHANGE RESINS

An automatic system is described for the determination of various uronic and biouronic acids after chromatographic separation on an anion-exchange column. Elution is carried out with sodium acetate or acetic acid, and the colors developed with carbazole and after oxidation with chromic acid are determined in a multichannel photometer and recorded continuously.

S. Johnson and O. Samuelson,
Anal. Chim. Acta, 36 (1966) 1–11

SPECTROPHOTOMETRIC DETERMINATION OF FORMALDEHYDE, GLYCOLLIC AND GLYOXALIC ACIDS IN THE PRESENCE OF GLYOXAL AND SOME CARBOXYLIC ACIDS

A spectrophotometric procedure is described for determining glycollic acid, glyoxalic acid and formaldehyde in the presence of high concentrations of oxalic acid and ammonium oxalate, and in the presence of glyoxal, formic acid, tartaric acid, and dihydroxytartaric acid. Three known spectrophotometric methods required modification. The experimental error under the specified conditions does not exceed ±5%.

Lj. Josimović and O. Gal,
Anal. Chim. Acta, 36 (1966) 12–17

DETERMINATION OF RHENIUM BY NEUTRON ACTIVATION

A neutron activation method is proposed for the determination of rhenium in rocks and ores. After the irradiation, the radiochemical separation consists of a one-step anion exchange; β-activities of radiochemically pure ^{188}Re or ^{186}Re are counted. The chemical yield averaged 75% and there was a considerable saving of time in the radiochemical work. Results are quoted for the rhenium contents of the standard rock W-1, several molybdenites and pyrolusites.

K. Ishida, K. Kawabuchi and R. Kuroda,
Anal. Chim. Acta, 36 (1966) 18–24

INTENSITY OF THERMAL RADIATION OF METAL SPECTRA IN FLAME EMISSION SPECTROMETRY

A unified and well-referenced approach to the derivation of the total intensity of spectral lines of atoms excited by flame in thermal equilibrium is given. Expressions for the total intensity for atoms at low and high concentrations are given. The influence of self-absorption and self-reversal on the spectral line contour and on analytical curves is discussed. Application of the derived equations to emitting atoms in arcs and to molecules in flames is also considered.

J. D. Winefordner, W. W. McGee, J. M. Mansfield, M. L. Parsons and K. E. Zacha,
Anal. Chim. Acta, 36 (1966) 25–41

SOME CAUSES OF BENDING OF ANALYTICAL CURVES IN ATOMIC EMISSION FLAME SPECTROMETRY

Factors affecting the shape of analytical curves in atomic emission flame spectrometry are discussed. Equations are presented by which the effect on the analytical curve of self-absorption, ionization, compound formation, variation in solution flow rate and atomization efficiency, entrance optics, and multiple spectral lines can be considered quantitatively. Theoretical and experimental curves are compared for Na introduced as aqueous NaCl solution into H_2/air, H_2/O_2, and C_2H_2/O_2 flames. The portion dealing with the effect of ionization, compound formation, and variation in solution flow rate and atomization efficiency on the atomic concentration in the flame applies as well to atomic absorption and atomic fluorescence flame spectrometry.

T. J. Vickers, L. D. Remington and J. D. Winefordner,
Anal. Chim. Acta, 36 (1966) 42–56

THE DETERMINATION OF CALCIUM AND MAGNESIUM BY ATOMIC ABSORPTION SPECTROSCOPY

An examination of the atomic absorption spectroscopy of calcium and magnesium has been made and the results confirm that several anions and cations interfere. Simple and reliable means are suggested for overcoming these interferences. The possibility of the use of a 2% isopropanol medium for overcoming several interferences on magnesium is also presented.

T. V. Ramakrishna, J. W. Robinson and P. W. West,
Anal. Chim. Acta, 36 (1966) 57–64

USE OF A DIGITAL COMPUTER IN EQUILIBRIUM CALCULATIONS:
THE EFFECTS OF DILUTION AND IONIC STRENGTH ON THE BUFFER INDEX AND SHARPNESS INDEX IN THE TITRATION OF A MONOPROTIC ACID WITH A STRONG BASE

The effects of dilution and ionic strength on weak acid–strong base titration curves and on the buffer index, β, and sharpness index, η, for these titrations have been calculated. It has been shown that the approximate equations generally used to calculate β and η are often misleading.

J. Butcher and Q. Fernando,
Anal. Chim. Acta, 36 (1966) 65–76

EXTRACTIONS WITH β-DIKETONES AS CHELATING SOLVENTS

This study was undertaken to prepare a liquid compound with low water solubility which would form metal chelates readily and also act in the dual role of organic solvent in the solvent extractions of metal chelates. The compounds 7-methyl-2,4-octanedione and 1,1,1-trifluoro-7-methyl-2,4-octanedione were prepared and their P and K values determined. Radiotracer distribution studies with 9 metals indicate that the stated goal was reached. The observed distribution coefficients for the majority of the metals were much larger than those obtained with another pure β-diketone, acetylacetone. Also, extractions occur at lower pH values. Ion-pair phenomena are indicated in several cases. The principal general difference between the fluorinated and non-fluorinated β-diketones is a shift in the distribution curves towards the acid region for the fluorinated compounds.

G. K. Schweitzer and W. van Willis,
Anal. Chim. Acta, 36 (1966) 77–89

EXTRACTION OF CAESIUM WITH NITROBENZENE IN E PRESENCE OF PHOSPHOMOLYBDIC ACID

The main factors controlling the distribution of caesium be-een the aqueous phase and a nitrobenzene phase in presence of osphomolybdic acid were investigated. Data on the distribution of e heteropolyacid are given. The selectivity of caesium extraction was evaluated. The possiblity of separating caesium by this method for analytical purposes was demonstrated in isolating caesium from a mixture of long-lived fission products and in isolating caesium from rubidium by repeated extraction.

J. Rais, S. Podešva and M. Kyrš,
Anal. Chim. Acta, 36 (1966) 90–96

AN ION-EXCHANGE METHOD FOR THE DETECTION OF AMIDES, IMIDES AND ANILIDES

Ion-exchange resins are efficient catalysts for the acid hydrolysis of amides, imides and anilides; the ammonium ion or aniline so formed can be detected by the well-known specific tests for these species. In general, the proposed tests are simpler, faster and more selective than those already available. The amounts that can be detected are of the order of 0.05–5 μg depending on the compound.

P. W. West, M. Qureshi and S. Z. Qureshi
Anal. Chim. Acta, 36 (1966) 97–104

STEPWISE PHOTOMETRIC TITRATIONS

Stepwise titrations of several metals with photometric end-point detection are described. The equivalence points when 2 metal ions are titrated compleximetrically can be detected if the conditional stability constants are sufficiently high in value even if there are only slight differences between the colours of the different species of the indicator compounds.

The following systems were analysed by stepwise photometric titration using either metalphthalein or eriochrome black T as indicator: manganese–calcium; manganese–magnesium; calcium–magnesium; manganese–calcium–magnesium; zinc–magnesium. EDTA, DTPA and EGTA were used as titrants. A satisfactory accuracy was attained in each case. The results agreed with conclusions drawn from the theory of stepwise photometric titrations based on equilibrium calculations and absorbance values.

B. Skrifvars and A. Ringbom,
Anal. Chim. Acta, 36 (1966) 105–114

AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATION OF IRON AND/OR ALUMINUM WITH EDTA

Automatic derivative spectrophotometric EDTA titration procedures for the determination of iron and/or aluminum are described. Iron is automatically titrated in the presence of aluminum at pH 1.8–3.0 using 3,5-dinitrosalicylic acid as indicator. Total iron and aluminum, or aluminum alone, are determined by adding a small excess of standard EDTA, as visually indicated by the fluorescence of calcein W, with subsequent automatic titration of excess EDTA. The intense color of the iron–EDTA complex causes no difficulty in the automatic method, and macro as well as micro quantities of iron and/or aluminum can be determined with relative errors of 0.3% or less, even when the amount of aluminum is 4 times that of iron.

C. Vassiliadis, C. Th. Kawassiades, T. P. Hadjiioannou and G. Colovos,
Anal. Chim. Acta, 36 (1966) 115–121

NEW SPECTROPHOTOMETRIC THIOCYANATE DETERMINATION OF IRON IN METALS, ALLOYS, ACIDS AND SALTS

A rapid, sensitive and fairly selective spectrophotometric thiocyanate method for the determination of traces of iron in metals, alloys, acids and salts is described. The iron is isolated from the bulk of the sample by solvent extraction with methyl isobutyl ketone from 7 *N* lithium chloride solution or 7 *N* hydrochloric acid. The iron(III) thiocyanate color is developed directly in the ketone extract and then measured spectrophotometrically.

C. L. Luke,
Anal. Chim. Acta, 36 (1966) 122–129

AN ATTEMPT TO DETERMINE THE BORON NATURAL ABUNDANCE RATIO, $^{11}\text{B}/^{10}\text{B}$, BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

(Short Communication)

J. A. Goleb,
Anal. Chim. Acta, 36 (1966) 130–131

SOME EXPERIMENTAL OBSERVATIONS ON INTER-ELEMENT EFFECTS IN ATOMIC FLUORESCENCE SPECTROMETRY

(Short Communication)

G. I. Goodfellow,
Anal. Chim. Acta, 36 (1966) 132–134

SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM WITH THIOGLYCOLLIC ACID

(Short Communication)

E. Jacobsen and W. Lund,
Anal. Chim. Acta, 36 (1966) 135–137

INORGANIC CHROMATOGRAPHY ON IMPREGNATED ION-EXCHANGE PAPERS

(Short Communication)

J. Sherma,
Anal. Chim. Acta, 36 (1966) 138–141

A SELECTIVE SPOT TEST FOR SILVER WITH ARSENIC TRISULFIDE

(Short Communication)

F. Feigl and F. L. Chan,
Anal. Chim. Acta, 36 (1966) 141–144

ANALYTICA CHIMICA ACTA

Vol. 36 (1966)

ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

Editors
PHILIP W. WEST *(Baton Rouge, La., U.S.A.)*
A. M. G. MACDONALD *(Birmingham, Great Britain)*

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 36 (1966)

PRINTED IN THE NETHERLANDS

AUTOMATED CHROMATOGRAPHY OF URONIC ACIDS ON ANION-EXCHANGE RESINS

STIG JOHNSON AND OLOF SAMUELSON
Department of Engineering Chemistry, Chalmers Tekniska Högskola, Göteborg (Sweden)
(Received March 25th, 1966)

Anion-exchange chromatography in acetate media is a valuable tool in the analysis of mixtures containing several uronic acids. Acetic acid[1-3] and sodium acetate[4,5] have been used as eluants by various authors whose working conditions have differed in many respects. Acetic acid has also been used in preparative work. Some contradictory results have been reported.

The aim of this work was to devise an automated method for the determination of uronic acids after separation on anion-exchange resins. In addition to the 5 more common hexuronic acids, 4-O-methyl-D-glucuronic acid was included. For comparison, some biouronic acids and some other hydroxy acids of interest in carbohydrate chemistry were chromatographed. A detailed discussion of the optimum conditions for a mutual separation of these acids is, however, outside the scope of this work. Both acetic acid and sodium acetate were used as eluants.

The analysis system

In earlier work on anion-exchange separations of organic acids, fractions from a fraction collector were transferred into the sampling device of a Technicon Auto-Analyzer. The acids were oxidized with dichromate and the remaining dichromate determined automatically by its reaction with diphenylcarbazide[6]. Compared with the manual method of titration or colorimetric determinations, this method was much faster. In the present work the eluate was passed directly into a monitor which consisted of a peristaltic pump, reaction coils, and a multichannel photometer with a recorder.

By means of the peristaltic pump the eluate was divided into 3 streams. One of these was used for automatic determination of uronic acids by a carbazole method. The second stream of the eluate was oxidized by chromic acid to determine all oxidizable organic acids, and the rest went into an automatic fraction collector where fractions were taken for additional identification. This simultaneous recording of 2 different analyses from the same run is extremely valuable when other acids in addition to uronic acids are present. The information obtained from both these types of analysis is very useful[7], but with the old system much time was required to obtain it. The principle of the analytical system is given in Fig. 1.

Results reported by SWANN *et al.*[8] facilitated the choice of conditions for the carbazole reaction. The conditions were, however, simplified in various respects. Three tubings were used in the peristaltic pump, one with the eluate, one with the carbazole reagent and one with sulfuric acid. An excessively high sulfuric acid concentration resulted in a broadening of the elution curves. Under the conditions chosen, no excessive broadening of the curves recorded by the carbazole method was observed, as compared to that obtained with the dichromate channel.

To simplify the method involving dichromate oxidation, the final determination of remaining dichromate by diphenylcarbazide was omitted since it was found that a sufficiently high sensitivity could be obtained by a direct determination of remaining dichromate at 440 mμ under the conditions employed in this work. A typical chromatogram in which this method was used is given in Fig. 2.

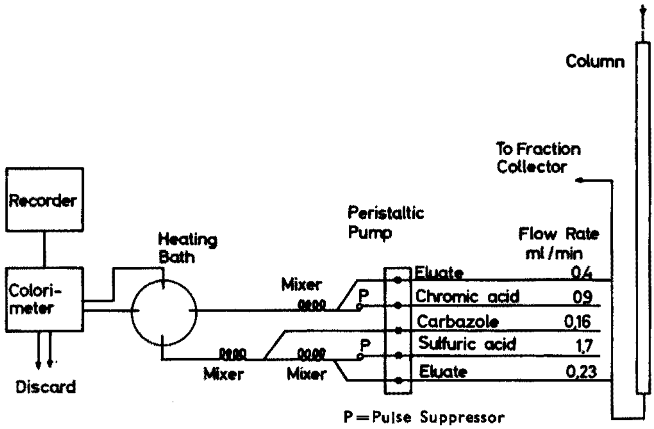


Fig. 1. Principle of the analysis system. Pump tubings. Eluate: Tygon; sulfuric and chromic acids: Acidflex; carbazole in 70% ethanol: Yellow Tygon.

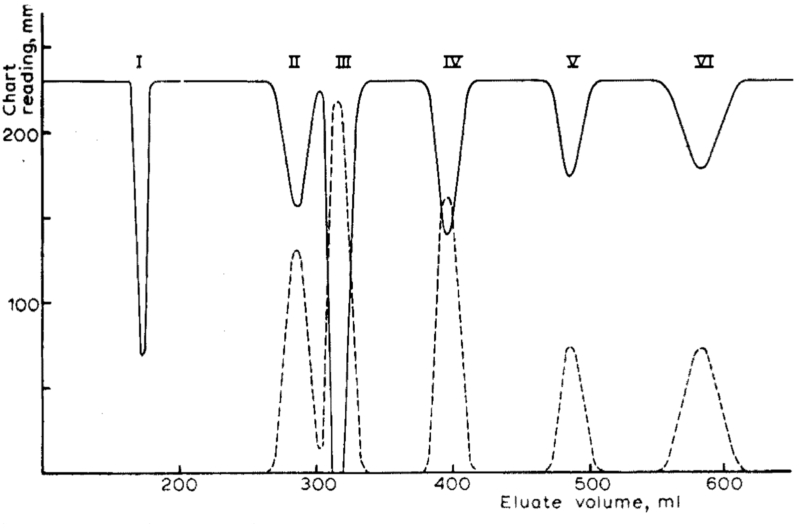


Fig. 2. Separation of D-gluconic acid (I), D-galacturonic acid (II), L-guluronic acid (III), L-iduronic acid (IV), D-mannuronic acid (V) and D-glucuronic acid (VI). Analysed by the carbazole method (dotted line) and by determination of remaining dichromate (full line) at 440 mμ in a 10-mm flow cell and with a scale expansion of 2. Eluant: 1 *M* acetic acid; flow rate: 0.94 ml/min.

In automated chromatography the evaluation of the chromatograms for quantitative purposes is more complicated, however, if the analysis is based upon the consumption of a reagent rather than upon the determination of a compound which is formed in the reaction. The possibility of using the green color resulting from the formation of chromium(III) ions as a measure of the dichromate consumption was therefore investigated. This color has a much lower intensity than that developed by carbazole, but by choosing different lengths of the flow cells and different scale expansions in the channels used for the 2 reactions it was possible to adapt the equipment to this determination.

Chromatographic separations

Uronic acids are unstable in alkaline solutions especially at elevated temperature. High pH and temperature must, therefore, be avoided in the chromatographic runs[9,10]. No complications could be detected with sodium acetate at 30° when only 4-O-methyl-glucuronic, galacturonic, glucuronic, and mannuronic acids were involved. The peak elution volumes of the acids (*cf.* Table I) were found to be the same as those in an eluant buffered at pH 5.9 with acetic acid. With iduronic acid some reactions leading to a decomposition of this acid occurred during the run in the unbuffered solution. For this reason it is recommended that sodium acetate solution buffered with acetic acid be used. All chromatograms in buffered sodium acetate medium reported in this paper were run at pH 5.9.

TABLE I

VOLUME DISTRIBUTION COEFFICIENTS (D_v) OF VARIOUS ORGANIC ACIDS IN SODIUM ACETATE BUFFERED WITH ACETIC ACID AT pH 5.9 AND IN ACETIC ACID

	D_v in various media			
	0.05 M NaAc	*0.08 M NaAc*	*0.08 M NaAc*[a]	*1.0 M HAc*
2-O-(4-O-Methyl-α-D-glucopyranosyluronic acid)-D-xylose	6.07		3.74	6.07
6-O-(β-D-Glucopyranosyluronic acid)-D-galactose	6.15		3.78	7.31
Cellobiouronic acid	9.48		5.82	12.0
2-O-(α-D-Glucopyranosyluronic acid)-D-xylose			6.19	8.31
D-Glucoheptonic acid	12.0			5.54
D-Gluconic acid				6.47
D-Arabinonic acid				7.47
Glycolic acid				9.88
4-O-Methyl-D-glucuronic acid	12.7		7.87	18.4
D-Galacturonic acid	15.3	9.40	9.36	11.1
D-Erythronic acid	18.6			
L-Guluronic acid	19.2	11.8		12.3
D-Glucuronic acid	20.7	13.0	13.0	22.8
L-Iduronic acid	22.7	14.2		15.5
D-Mannuronic acid	23.1	14.4	14.5	18.9

[a] No acetic acid added.

A typical separation of the simple uronic acids using a resin of low particle size (13–17 μ) is shown in Fig. 3. It is seen that the uronic acids appear in the following order: 4-O-methylglucuronic, galacturonic, guluronic, glucuronic and mannuronic acid. A slight overlapping was recorded between guluronic and glucuronic acids whereas the other acids were completely separated. This overlapping has no influence upon the evaluation of the chromatogram for quantitative purposes, however. From the peak elution volumes recorded in this and in several other runs the volume distribution coefficient (D_v), has been calculated as usual[11]. The results are summarized in Table I, which also contains D_v-values of some other organic acids run on the same column. In this medium iduronic acid appeared slightly before mannuronic acid and overlapped seriously with the mannuronic acid band. Iduronic acid was, therefore, not included in the run represented in Fig. 3.

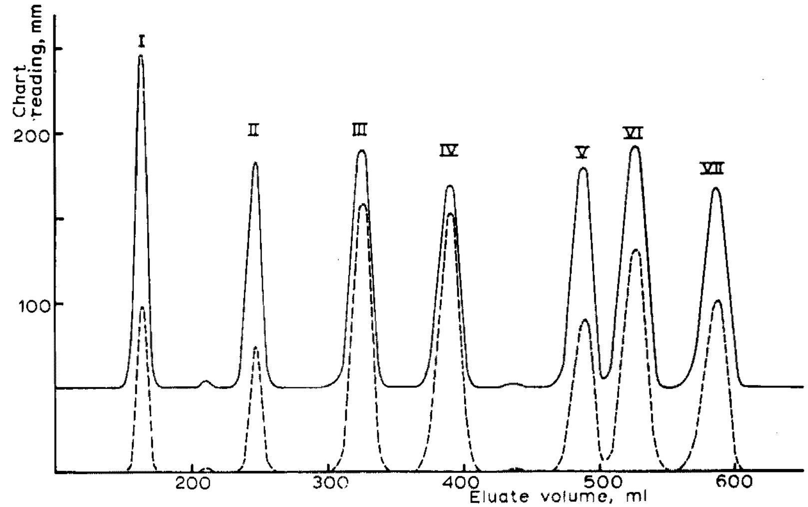


Fig. 3. Separation of 6-O-(β-D-glucopyranosyluronic acid)-D-galactose (I), cellobiouronic acid (II), 4-O-methyl-D-glucuronic acid (III), D-galacturonic acid (IV), L-guluronic acid (V), D-glucuronic acid (VI) and D-mannuronic acid (VII). Carbazole method: dotted line; dichromate method: full line. Eluant: 0.05 *M* sodium acetate, pH 5.9; flow rate: 1.06 ml/min.

The 2 aldobiouronic acids included in this run appeared as well separated bands before the simple uronic acids. In separations of more complicated mixtures of biouronic acids a lower acetate concentration can be used to advantage[4]. Two small impurities in the sample eluted at about 210 ml and 430 ml were recorded both by the dichromate and carbazole methods. Some of the acids studied in sodium acetate medium have been studied previously. The order of elution is in agreement with that reported earlier but better separations have been achieved in the present work. This is not due to improved separation factors, but can be entirely explained by a better column efficiency. The time required for the elution of the 7 acids in Fig. 3 was about 10 h. The pressure drop in the column was about 40 atmospheres. Since a great part of the pressure drop was caused by clogging of the porous teflon bottom with resin particles, the column could be run at a higher speed without an excessively high pressure drop if a more suitable bottom could be found. Experience gained in other experiments shows that, with a resin of this particle size, the overlapping increases only slightly if the rate of elution is increased by a factor of 2.

Some experiments were carried out with coarser (53–64 μ), but still very uniform resin particles, obtained by fractionation of the same batch received from the manufacturer. At a high elution rate (2.21 ml/min) there was serious overlapping of most elution bands. A combination of coarse resin particles and high flow rate can be used if, for example, only galacturonic and glucuronic acids are involved, but not with more complicated mixtures like those used in the run referred to in Fig. 3. Figure 4 shows a chromatogram with the coarser resin run at the same rate and with the same acids as those given in Fig. 3. Expectedly, the elution curves are much broader. The overlapping between the curves corresponding to guluronic and glucuronic acids is so serious that the chromatogram cannot be evaluated accurately for quantitative purposes. The results clearly demonstrate that small resin particles are desirable in order to obtain clean-cut separations of complicated mixtures of uronic acids.

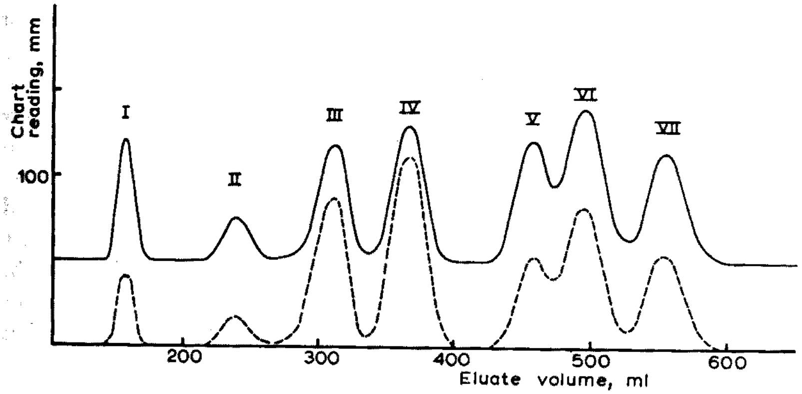


Fig. 4. Separation of the same acids as in Fig. 3. Carbazole method: dotted line; dichromate method: full line. Particle size of the resin: 53–64 μ; Eluant: 0.05 *M* sodium acetate, pH 5.9; flow rate: 1.06 ml/min.

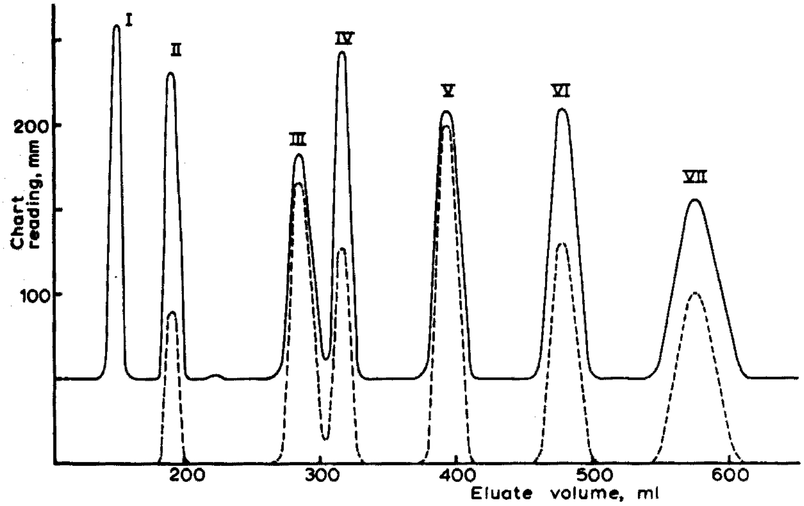


Fig. 5. Separation of D-glucoheptonic acid (I), 6-O-(β-D-glucopyranosyluronic acid)-D-galactose (II), D-galacturonic acid (III), L-guluronic acid (IV), L-iduronic acid (V), D-mannuronic acid (VI), and D-glucuronic acid (VII). Carbazole method: dotted line; dichromate method: full line. Eluant: 1 *M* acetic acid; flow rate: 0.97 ml/min.

The pressure drop decreases greatly when working at elevated temperature, but, as shown previously[10], there is a risk of decomposition of the uronic acids in sodium acetate solution. Experiments carried out in the present work showed that complications occurred at 80° also when working with acetic acid. Hence, working at high temperature cannot be recommended when the more unstable uronic acids are involved.

As already mentioned iduronic and mannuronic acids could not be separated by elution with sodium acetate. These acids were easily separated, however, by elution with 1 *M* acetic acid. A chromatogram demonstrating this separation is given in Fig. 5. Three other hexuronic acids, one biouronic acid and one aldonic acid were included in this run. The aldonic acid did not react with carbazole and the corresponding peak was recorded only in the dichromate channel. Hence aldonic acids can be easily distinguished from uronic acids. Galacturonic and guluronic acids, which among the hexuronic acids appeared first in the eluate, gave slightly overlapping curves. An accurate quantitative evaluation is, however, possible. If desired a complete separation can be achieved by increasing the column length. The other acids were separated completely in this run which was completed within 11 h. Galacturonic, guluronic, mannuronic and glucuronic acids have been studied earlier by LARSEN AND HAUG[2] by gradient elution in acetic acid. The same order of elution was obtained. The careful fractionation of the resin used and the greater length of the resin bed are probably the main factors explaining the improved separations obtained in our work.

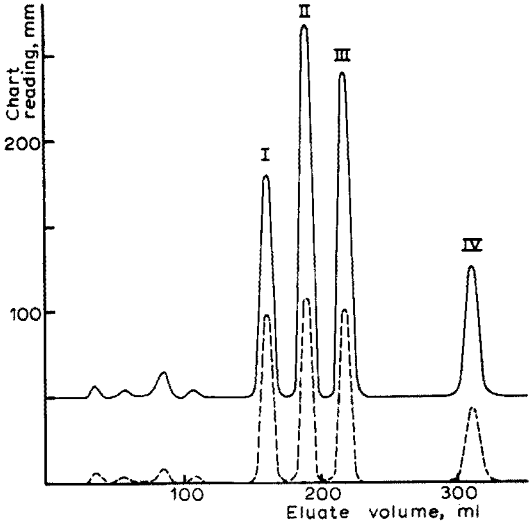


Fig. 6. Separation of 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylose (I), 6-O-(β-D-glucopyranosyluronic acid)-D-galactose (II), 2-O-(α-D-glucopyranosyluronic acid)-D-xylose (III) and cellobiouronic acid (IV). Carbazole method: dotted line; dichromate method: full line; eluant: 1 *M* acetic acid; flow rate: 0.94 ml/min.

As can be seen from Table I the peak elution volume of 4-O-methylglucuronic acid is only slightly lower than that of mannuronic acid. These 2 acids which showed a very different elution behavior in sodium acetate solution could therefore not be separated in 1 *M* acetic acid. Hence, the choice of eluant in the separation of complicated mixtures of uronic acids depends upon the acids present in the sample. If complicated or unknown mixtures containing several uronic acids are present it may be necessary to make separate runs in both eluants. Quite often it is safer to collect fractions from a run with one of the eluants and to rechromatograph the fractions in separate runs with the other eluant.

Finally, it should be mentioned that in separations of certain aldobiouronic acids, acetic acid is a more favorable eluant than sodium acetate. From Table I it is seen that 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylose and 6-O-(β-D-glucopyranosyluronic acid)-D-galactose cannot be separated in sodium acetate medium under the conditions used in these experiments. In acetic acid a complete separation was achieved on the same column (Fig. 6). The other 2 aldobiouronic acids included in this chromatogram show a reversed order of elution in acetic acid as compared with sodium acetate (Table I). Whereas in sodium acetate the curves overlapped, in the acetic acid run there was a large volume between the elution curves. The different elution behavior in the 2 eluants can be ascribed in part to different dissociation constants of various uronic acids (*cf.* ref. 11). The time required for the separation of the 4 aldobiouronic acids was about 6 h. The small elution peaks recorded ahead of peak I are explained by small amounts of impurities (higher uronic acids) in the aldobiouronic acids studied in this run.

Reproducibility of the chromatograms

The reproducibility of the peak elution volumes in this work was better than in our earlier work with organic acids in which fractions were taken in a fraction collector and transferred to the sampling device in an AutoAnalyzer. One explanation is that more reliable pumps were used in this work, but more important is that the risk of confusion which exists when several hundred fractions must be analysed is eliminated in the automated method. As an example, it can be mentioned that in 5 experiments with the hexuronic acids carried out with 0.05 *M* sodium acetate at pH 5.9 the maximum deviation from the average value was less than 1%. These 5 experiments were carried out within the course of one month and the equipment was used for other purposes between the various runs. Hence, it is evident that the peak elution volumes determined with this method provide more certain identification than those obtained with the earlier method. It is, of course, necessary that the eluant pump be in good condition and the flow rate be controlled carefully.

As reported earlier, the quantitative determination of organic acids in the eluate by the earlier method gave recoveries between 97 and 104%[6,12]. In these experiments very careful calibrations of the monitor were made in connection with the analysis of the eluate fractions. In order to obtain reliable results 3 sampling cups with the same standard solution were analysed in turn and the analysis of the chromatographic fractions interrupted several times by calibration. In unpublished experiments with the carbazole method less reliable results were obtained due to the tailing which occurred in the highly viscous solutions (*cf.* also ref. 8).

Whereas the reproducibility of the peak elution volumes is mainly dependent upon the eluant pump, the pumping rate in the various tubings in the peristaltic pump is the critical point as far as the areas of the elution curves (absorbance *versus* eluant volume) are concerned. An example of the reproducibility of the method is given in Table II in which the peak elution volumes as well as the areas of the elution curves, recorded both by the dichromate and the carbazole methods, are given. Both runs were carried out with the same tubings in the peristaltic pump. The deviations in peak elution volumes are negligible and the reproducibility of the peak areas is also very good. Both with the dichromate and carbazole methods the areas differ by 2% or less in these 2 runs.

In order to obtain good reproducibility it is essential that the tubings be changed before they are exhausted. This necessary precaution results in certain variations in flow rate and if the tubings are not well matched against each other the absolute magnitude of the areas is affected greatly. In amino acid analysis it is common practice to add a known amount of an internal standard to compensate for such variations and this technique is recommended also when the present method is used for quantitative purposes. One difficulty in analysis of uronic acids is that of finding a suitable standard substance. If samples must be analysed which contain all uronic acids available in a pure condition it is recommended that some other acid, *e.g.* an aldonic acid, be used and that the quantitative determination be based upon the dichromate method.

TABLE II

TEST OF REPRODUCIBILITY OF PEAK ELUTION VOLUMES ($\bar{v}$) AND PEAK AREAS OBTAINED BY DICHROMATE (A_d) AND CARBAZOLE(A_c) REACTIONS IN TWO CHROMATOGRAPHIC RUNS IN 1 *M* ACETIC ACID

Added acid	*Run A*				*Run B*			
	$\bar{v}$	A_d	A_c	A_c/A_d	$\bar{v}$	A_d	A_c	A_c/A_d
D-Galacturonic	285	0.271	1.96	7.23	285	0.271	2.00	7.38
L-Guluronic	317	0.239	0.898	3.76	317	0.236	0.916	3.88
L-Iduronic	393	0.231	1.80	7.79	393	0.228	1.83	8.03
D-Mannuronic	478	0.264	1.26	4.77	478	0.264	1.27	4.81
D-Glucuronic	575	0.329	1.77	5.38	576	0.330	1.76	5.33

The direct introduction into the monitor of standard solutions containing the substances present in the sample immediately before and after the chromatogram can also be used for calibration purposes and for control of irregularities in the analysis system. This method is recommended if the sample solution contains so many acids that it is impossible to find a suitable internal standard. This method is also employed if a sample whose constituents are unknown must be analysed quantitatively.

The experience gained hitherto indicates that for quantitative purposes also, the automated method devised in this paper is more reliable than the earlier semi-automated technique. The new method requires a careful control of the working conditions *e.g.* pumping rates, but this holds true also for the older method.

It has been previously shown that the carbazole reaction gives varying color intensities with different uronic acids[8,13,14]. This holds true also under the conditions used in this work. Advantage can be taken of this fact in the identification of the elution peaks. A convenient index used for identification is the ratio between the area recorded in the carbazole channel and that recorded in the dichromate channel. Under the conditions used in the runs referred to in Table II this response index varies between 3.8 and 7.9 for the 5 hexuronic acids studied. If the presence of a certain uronic acid has been established in an unknown mixture and this index is found to be lower than that recorded with the pure known substance, some other compound which gives no (or a less intense) reaction with carbazole is present in the fractions corresponding to this elution peak. Quite often such mixtures can be resolved by anion-exchange chromatography by changing the eluant.

EXPERIMENTAL

Materials

2-O-(4-O-Methyl-α-D-glucopyranosyluronic acid)-D-xylose was kindly supplied by Professor TORE E. TIMELL, Syracuse, 2-O-(α-D-glucopyranosyluronic acid)-D-xylose by Dr. ADRIEN ROUDIER, Paris, and cellobiouronic acid by Professor BENGT LINDBERG, Stockholm.

6-O-(β-D-Glucopyranosyluronic acid)-D-galactose was prepared by acid hydrolysis of gum arabic[15]. L-Iduronic acid was obtained by epimerization of D-glucuronic acid as described by FISCHER AND SCHMIDT[16]. D-Mannuronic and L-guluronic acid were prepared by hydrolysis of commercial sodium alginate with sulfuric acid according to HAUG AND LARSEN[17].

The identity of the prepared guluronic acid was established by a comparison with an authentic sample obtained from Drs. A. HAUG AND B. LARSEN, Trondheim, using anion-exchange chromatography in sodium acetate and acetic acid as well as paper chromatography (ethyl acetate–pyridine–water–acetic acid, 5:5:3:1[18]). The same methods were used to identify mannuronic acid and the prepared biouronic acid. A sample obtained from A. ROUDIER was used for comparison.

4-O-Methyl-D-glucuronic and erythronic acids were prepared in previous work[4,7]. The other acids were obtained from commercial sources.

Anion-exchange columns

The chromatographic equipment was of the usual type with jacketed columns[11] with an inner diameter of 6 mm and a bed length of 880 mm. They were conditioned with the eluant before use. The eluant was boiled continuously under reflux before it was passed into the piston pump (Beckman Accu Flo) used for feeding the eluant onto the column. The temperature in the column was kept at 30° by means of circulating water. A strongly basic anion-exchange resin (Dowex 1X-8) was fractionated to obtain uniform particles. Unless otherwise stated the particle size was 13–17 μ.

In the chromatograms reproduced in this paper the loading of simple uronic acids was 1.5–2 mg whereas that of biouronic acids amounted to 0.8–1.3 mg of each component.

Conditions used in the analysis system

In the carbazole method concentrated sulfuric acid (purum grade; s.g. 1.84) was first tested for interfering substances, and only those carboys of acid which gave no green color in the carbazole reaction were used[8]. Sodium tetraborate was dissolved in the concentrated sulfuric acid to a final concentration of 0.025 M. No disadvantages were encountered in using sulfuric acid of purum grade instead of analytical grade.

The carbazole reagent was prepared as an 0.15% (by weight) solution of carbazole (Merck and Eastman Organic Chemicals) in 70% (w/w) ethanol. This ethanol concentration was used instead of absolute ethanol to decrease the attack upon the tubing (Yellow Tygon) used in the peristaltic pump. In order to prevent air bubbles in the analysis system the carbazole reagent was reboiled continuously. An experiment carried out manually showed that boiling of the carbazole reagent for 5 h had no appreciable influence upon the absorbance.

The chromic acid solution was prepared by mixing 5 volumes of sulfuric acid (purum grade) with 2 volumes of an aqueous solution containing 2.45 g of potassium dichromate per liter.

The peristaltic pump, the tubings used in this part of the analysis system and the pulse suppressors were from Technicon Instruments Co. Ltd., Chertsey. The teflon tubings used as mixing coils had a length of 0.8 m. The inner diameter was 0.8 mm in the coils used for mixing the eluate with sulfuric and chromic acids. The second coil used in the carbazole channel had an inner diameter of 1.2 mm. All fittings used were from LKB-Produkter AB, Stockholm.

After the eluate streams were mixed with the reagent solutions, the mixtures were passed through reaction coils of teflon with an inner diameter of 1.2 mm. These reaction coils were kept at 100°. In the carbazole method the length of this tubing was 5.5 m which corresponded to a time of reaction of 3 min. The color obtained in the carbazole method was measured at 531 mμ in a 2-mm flow cell using a 3-channel absorptiometer from LKB-Produkter, Stockholm. The recorder, which was purchased from the same firm, was run with a scale expansion of 2.

In the dichromate method the length of the reaction coil was 9 m which corresponded to a reaction time of 7.8 min. The green color formed in the reduction to chromium(III) was measured at 633 mμ in a flow cell with a length of 10 mm using the second channel in the same photometer. The corresponding channel in the recorder was run with a scale expansion of 10. The higher cell length and scale expansion in the dichromate method were chosen in order to compensate for the lower color intensity in this reaction compared with the carbazole method.

Calibration experiments carried out with glucuronic acid within the concentration interval 0–165 μg/ml showed that there is a linear relationship between the absorbance and the concentration. This holds true with both channels.

The third channel in the photometer was used in our work for monitoring the eluate from another chromatographic column by means of the dichromate method.

The financial support of the 1959 Års Fond för Teknisk och Skoglig Forskning samt Utbildning and the Swedish Technical Research Council is gratefully acknowledged.

SUMMARY

An automatic system is described for the determination of various uronic and biouronic acids after chromatographic separation on an anion-exchange column. Elution is carried out with sodium acetate or acetic acid, and the colors developed with carbazole and after oxidation with chromic acid are determined in a multichannel photometer and recorded continuously.

RÉSUMÉ

Un système automatique est décrit pour le dosage de divers acides uroniques et biouroniques après séparation chromatographique sur une colonne échangeuse d'anions. L'élution s'effectue avec l'acétate de sodium ou l'acide acétique. Les colorations développées avec le carbazole et après oxydation à l'acide chromique sont déterminées dans un photomètre à canaux multiples et enregistrement continu.

ZUSAMMENFASSUNG

Für die Bestimmung verschiedener Uron- und Biouronsäuren wird nach chromatographischer Trennung an einem Anionenaustauscher ein automatisches System beschrieben. Eluiert wird mit Natriumacetat oder Essigsäure. Die Farben die sich mit Carbazol entwickeln, werden in einem Multikanalphotometer bestimmt und kontinuierlich aufgezeichnet.

REFERENCES

1 J. KHYM AND D. G. DOHERTY, *J. Am. Chem. Soc.*, 74 (1952) 3199.
2 B. LARSEN AND A. HAUG, *Acta Chem. Scand.*, 15 (1961) 1397.
3 J. K. GILLHAM AND T. E. TIMELL, *Can. J. Chem.*, 36 (1958) 1467.
4 O. SAMUELSON AND L. WICTORIN, *Svensk Papperstidn.*, 67 (1964) 555.
5 D. DZIEWIATKOWSKI, *Biochim. Biophys. Acta*, 56 (1962) 167.
6 O. SAMUELSON AND R. SIMONSON, *Svensk Papperstidn.*, 65 (1962) 363.
7 I. NORSTEDT AND O. SAMUELSON, *Svensk Papperstidn.*, 68 (1965) 565.
8 K. BERNTSEN, E. A. BALAZS, J. KAROSSA AND D. SWANN, *Technicon 25th Anniversary International Symposium, London, 1964.*
9 I. R. SIDDIQUI AND C. B. PURVES, *Can. J. Chem.*, 41 (1963) 382.
10 U.-B. LARSSON, I. NORSTEDT AND O. SAMUELSON, *J. Chromatog.*, 22 (1966) 102.
11 O. SAMUELSON, *Ion Exchange Separations in Analytical Chemistry*, Almqvist and Wiksell, Stockholm; John Wiley and Sons, New York, 1963.
12 B. ALFREDSSON, S. BERGDAHL AND O. SAMUELSON, *Anal. Chim. Acta*, 28 (1963) 371.
13 Z. DISCHE, *J. Biol. Chem.*, 167 (1947) 189.
14 J. D. GREGORY, *Arch. Biochem. Biophys.*, 89 (1960) 157.
15 C. L. BUTLER AND L. H. CRETCHER, *J. Am. Chem. Soc.*, 51 (1929) 1519.
16 F. G. FISCHER AND H. SCHMIDT, *Chem. Ber.*, 92 (1959) 2184.
17 A. HAUG AND B. LARSEN, *Acta Chem. Scand.*, 16 (1962) 1908.
18 F. G. FISCHER AND H. DÖRFEL, *Z. Physiol. Chem.*, 301 (1955) 224.

SPECTROPHOTOMETRIC DETERMINATION OF FORMALDEHYDE, GLYCOLLIC AND GLYOXALIC ACIDS IN THE PRESENCE OF GLYOXAL AND SOME CARBOXYLIC ACIDS

LJ. JOSIMOVIĆ AND O. GAL
Radiation Chemistry Department, Boris Kidrich Institute of Nuclear Sciences, Beograd (Yugoslavia)

(Received January 3rd, 1966)

In studying the effects of irradiation on solid oxalic acid and ammonium oxalate, it was necessary to determine very small amounts of glycollic acid, glyoxalic acid, formaldehyde and glyoxal in the presence of similar concentrations of tartaric acid, dihydroxytartaric acid, and a large excess of oxalic acid or ammonium oxalate. 2,7-Dihydroxynaphthalene[1], resorcinol[2] and phenylhydrazine[3] are suitable for spectrophotometric determinations of glycollic acid, glyoxalic acid and formaldehyde. The procedures are fairly well established for pure compounds, but little information is available on interferences of the compounds mentioned above. The present systematic investigation was therefore carried out.

Glycollic acid was determined with 2,7-dihydroxynaphthalene because this reagent is selective and sensitive. However, formaldehyde also reacts, so that a method for formaldehyde with which glycollic acid would not interfere had to be chosen; the phenylhydrazine procedure appeared to be most suitable. Since glyoxalic acid was measured simultaneously with formaldehyde, the resorcinol method was used to determine glyoxalic acid alone; none of the compounds mentioned above interfered with this method.

A systematic investigation of these spectrophotometric methods allowed us to develop a procedure for simultaneous determinations of formaldehyde, glycollic acid and glyoxalic acid. The presence of a large excess of oxalic acid or ammonium oxalate, as well as the occasional presence of other compounds, such as formic acid, tartaric acid, and dihydroxytartaric acid does not interfere.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP. 500 spectrophotometer, with 10-mm optical cells was used for absorption measurements. If not specifically stated, the procedures used were those recommended in the literature. Where possible, analytical reagent-grade chemicals were used.

Measurements of absorption spectra

The absorption spectra for the pure compounds with 2,7-dihydroxynaphthalene were measured. Glycollic acid gave an absorption maximum at 540 mμ as described in the literature[1]. The same absorption band was obtained with formaldehyde, glyoxal and glyoxalic acid. Tartaric acid showed some absorption in the same region but without a characteristic maximum. Ammonium oxalate and oxalic acid, with the same reagent, showed no absorption in this region.

When resorcinol was used as reagent, glyoxalic acid gave an absorption maximum at 560 mμ, whereas 550 mμ is the reported maximum[2]. In the same region glyoxal and tartaric acid showed slight absorption, whereas ammonium oxalate did not. Oxalic acid formed a precipitate after adding the reagents.

With phenylhydrazine, the maximum absorption for formaldehyde and glyoxalic acid was found at 510 mμ, instead of 520 mμ[3]. In this spectral region, glyoxal caused some absorption but there was no pronounced maximum. No absorption was observed for ammonium oxalate, glycollic acid, tartaric acid, dihydroxytartaric acid or oxalic acid.

*Determinations of percentage absorptivity and validity of Lambert–Beer's law**

The percentage absorptivity for each of 3 reagents used in the present work was determined. Special attention was paid to the influence of those compounds which might interfere in the measurements. The values for the percentage absorptivities are listed in Table I.

When 2,7-dihydroxynaphthalene was used as a reagent, glyoxalic acid gave a value 10 times lower than those for glycollic acid and formaldehyde, but it was experimentally checked that its presence in equivalent amounts had practically no effect on the determination of glycollic acid or formaldehyde.

The percentage absorptivities in the resorcinol method for the determination of glyoxalic acid were in very good agreement within one set of experiments, but the agreement between different sets of experiments was poor. The irreproducibility may be due to differences in temperature between ambience and sample when adding the reagent, or to variations in the time interval between the end of the liquid–liquid extraction and further treatment under routine working conditions. This problem was accounted for by determining the *A* value in each series of sample determinations. Glyoxal did not interfere when the concentration was approximately the same as that of glyoxalic acid, but even in a 0.1 *M* oxalic acid solution a precipitate was formed after addition of potassium hydroxide; therefore a preliminary precipitation of oxalic acid with calcium chloride was always performed. The presence of the calcium chloride did not affect the absorbance. A standard sample was a solution of glyoxalic acid in 0.1 *M* oxalic acid.

The high value of the percentage absorptivity for glyoxalic acid with phenylhydrazine as reagent confirmed that it could also be determined by this method in approximately the same concentration ranges as formaldehyde. For glyoxal the percentage absorptivity could be estimated only roughly, because glyoxal precipitated with phenylhydrazine at concentrations above 10^{-5} *M*. The presence of a high concentration (0.1 *M*) of oxalic acid caused a considerable decrease in the absorbance value for formaldehyde and glyoxalic acid, whereas 0.1 *M* ammonium oxalate had no effect whatsoever. This confirmed that change in absorbance is a function of pH. By adjust-

---

* For the purpose of comparing results for different components in mixtures, $A^{1\%}_{1\,\mathrm{cm}}$ values (percentage absorptivity) are given; the values were calculated from the formula $A_{\mathrm{m}} = A^{1\%}_{1\,\mathrm{cm}} \cdot d \cdot c$ where A_{m} is the absorbance measured, *d* the cell length, and *c* the initial concentration in percentage by weight of the substance measured.

TABLE I

EXPERIMENTAL DATA FOR SOME ACIDS AND ALDEHYDES

Compound	*2,7-Dihydroxynaphthalene*		*Phenylhydrazine hydrochloride*		*Resorcinol*	
	$\lambda = 540\ m\mu$ $A^{1\%}_{1cm} \cdot 10^{-3}$	*Lambert–Beer's law range (M)*[a]	$\lambda = 510\ m\mu$ $A^{1\%}_{1cm} \cdot 10^{-3}$	*Lambert–Beer's law range (M)*[a]	$\lambda = 560\ m\mu$ $A^{1\%}_{1cm} \cdot 10^{-3}$	*Lambert–Beer's law range (M)*[a]
Glycollic acid	22	$0.5–3 \cdot 10^{-5}$	—	—	—	—
Glyoxalic acid	1.75	$0.4–1 \cdot 10^{-3}$	12.5	$1–5 \cdot 10^{-5}$	9–16	$0.5–6 \cdot 10^{-5}$
Dihydroxytartaric acid	0.58	—	—	—	—	—
Tartaric acid	0.58	—	—	—	—	—
Formic acid	—	—	—	—	—	—
Formaldehyde	22	$0.5–3 \cdot 10^{-5}$	24.7	$0.3–3 \cdot 10^{-5}$	—	—
Glyoxal	10.5	$0.1–1 \cdot 10^{-4}$	1.5	—	—	—
Oxalic acid	—	—	—	—	—	—
Ammonium oxalate	—	—	—	—	—	—

[a] The concentrations refer to the solution measured.

ing the pH of formaldehyde in oxalic acid solution to the same acidity as that with pure formaldehyde, a reproducible value for the percentage absorptivity could be obtained. The adjustment of pH was achieved by keeping the solution in an ammonia atmosphere, the neutralization process being monitored by a pH meter.

Determinations of glyoxal

The 2,7-dihydroxynaphthalene method did not give satisfactory results, and the phenylhydrazine and resorcinol methods showed no absorption bands; the determination of glyoxal with chromotropic acid[4] or with phenylhydrazine in an acidic medium[5] was therefore examined. The former method gave only very small absorbances even after reduction with magnesium. The phenylhydrazine method[5] gives a maximum absorbance at 415 mμ with glyoxal, whereas with glyoxalic acid the maximum occurs at 520 mμ and glycollic acid shows no absorption. However, no satisfactory results could be obtained by these methods, possibly because of the tendency of glyoxal to form various condensation products in aqueous solutions.

Procedure for determination in mixtures

The experimental data obtained as described above made it possible to develop a procedure for the determination of small amounts of glycollic and glyoxalic acid even in the presence of high concentrations of oxalic acid or ammonium oxalate, as well as in the presence of glyoxal, formic acid, tartaric acid, and dihydroxytartaric acid.

The procedure is as follows: an aliquot of the sample solution is taken, and glyoxalic acid alone is determined by the resorcinol method[2]. The reference solution, which contains pure glyoxalic acid in 0.1 *M* oxalic acid, is treated similarly.

Another aliquot of the sample solution is neutralized by exposure to ammonia gas, and then analysed by the phenylhydrazine method[3]. The absorbance measured is the sum of the absorbances of formaldehyde and glyoxalic acid. Since the glyoxalic acid concentration is known from the resorcinol method, the formaldehyde concentration can be calculated. For control purposes the absorbance was read not only at the maximum but at at least one other suitable wavelength. Since the absorbance measured is the sum of absorbances of formaldehyde and glyoxalic acid, an equation can be derived for each of the 2 wavelengths. In these 2 equations only the concentrations of formaldehyde and glyoxalic acid are unknown and the other values can be determined or measured.

A third aliquot of the solution is analysed by the 2,7-dihydroxynaphthalene method. The absorbance obtained is the sum of the absorbances of formaldehyde, glyoxal, and glycollic acid. Since the concentration of formaldehyde is known from the phenylhydrazine determination, the concentration of glycollic acid can be obtained by difference. The possible error in determining glycollic acid depends on the concentrations of the glyoxal present; the presence of glyoxal and its interference can be checked by reading the absorbance of glycollic acid at different wavelengths.

RESULTS

This procedure was carefully checked on several mixtures of known composition (Table II). The composition of these mixtures is typical of those expected in irradiated samples of oxalic acid and some oxalates. As can be seen fairly good results were obtained when the concentration of glyoxal was about 20 times smaller than those of the other components. In that case glyoxal did not interfere in the determinations of glyoxalic acid and formaldehyde, and did not precipitate with phenylhydrazine. The maximum deviation in determining glycollic acid was 2%. It should be pointed out that in glycollic-acid measurements the glyoxalic–glycollic molar ratio should not exceed 2. Reference samples should always be used, *i.e.* the absorbance of pure solutions should be measured under the same conditions.

TABLE II

ANALYSIS OF MIXTURES

The composition of mixtures[a]	*Present concn.* · 10^3 *(M)*	*% Error found*[b]
A Glyoxalic acid	20	+1[c]
Glycollic acid	27	—
Formaldehyde	6.1	—
Tartaric acid	410	—
Dihydroxytartaric acid	20	—
B Glyoxalic acid	20	−1[c]
Glyoxal	0.1	—
C Glyoxalic acid	20	−5[c]
Glycollic acid	27	—
Formaldehyde	6.1	−2.5[d]
Glyoxal	0.9	—
Tartaric acid	410	—
Dihydroxytartaric acid	20	—
D Glyoxalic acid	25	−0.2[c]
Glycollic acid	9	−2[e]
Formaldehyde	9	−2.5[d]
Tartaric acid	12	—
E Glyoxalic acid	25	−0.5[c]
Glycollic acid	9	+2[e]
Formaldehyde	9	−5[d]
Glyoxal	1.4	—
Tartaric acid	2	—

[a] Percentage error is given as a mean value for 6 determinations.
[b] 0.1 M oxalic acid present in all solutions.
[c] Resorcinol method.
[d] Phenylhydrazine method.
[e] 2,7-Dihydroxynaphthalene method.

The authors wish to thank Dr. I. G. DRAGANIĆ for helpful discussions and criticism of this work. Thanks are also due to Mrs. LJ. MARKOVIĆ for technical assistance.

SUMMARY

A spectrophotometric procedure is described for determining glycollic acid, glyoxalic acid and formaldehyde in the presence of high concentrations of oxalic acid and ammonium oxalate, and in the presence of glyoxal, formic acid, tartaric acid, and dihydroxytartaric acid. Three known spectrophotometric methods required modification. The experimental error under the specified conditions does not exceed ±5%.

RÉSUMÉ

Un dosage spectrophotométrique est décrit pour le dosage de l'acide glycollique, de l'acide glyoxalique et du formaldéhyde, en présence de fortes concentrations d'acide oxalique et d'oxalate d'ammonium, et en présence de glyoxal, d'acide formique, d'acide tartrique et d'acide dihydroxytartrique. Pour ces besoins trois méthodes spectrophotométriques connues ont été modifiées. L'erreur expérimentale dans les conditions spécifiées ne dépasse pas ±5%.

ZUSAMMENFASSUNG

Es wird ein spektralphotometrisches Verfahren beschrieben zur Bestimmung von Glykolsäure, Glyoxalsäure und Formaldehyd sowohl in Gegenwart hoher Konzentrationen von Oxalsäure und Ammoniumoxalat als auch von Glyoxal, Ameisensäure, Weinsäure und Dihydroxyweinsäure. Dazu werden 3 bekannte spektralphotometrische Methoden modifiziert. Der experimentelle Fehler überschreitet unter den angegebenen Bedingungen ±5% nicht.

REFERENCES

1 F. Snell and C. Snell, *Colorimetric Methods of Analysis*, Van Nostrand, New York, 1953.
2 M. Pesez and J. Bartos, *Bull. Soc. Chim. France*, 3 (1960) 481.
3 M. Tanenbaum and C. E. Bricker, *Anal. Chem.*, 23 (1951) 354.
4 C. E. Bricker and W. A. Vail, *Anal. Chem.*, 22 (1950) 720.
5 D. N. Kramer, N. Klein and R. A. Baselike, *Anal. Chem.*, 31 (1959) 250.

DETERMINATION OF RHENIUM BY NEUTRON ACTIVATION

KOJI ISHIDA AND ROKURO KURODA
Laboratory of Analytical Chemistry, Faculty of Engineering, The University of Chiba, Chiba (Japan)
KAZUAKI KAWABUCHI
Chemistry Laboratory, Faculty of Education, Ehime University, Matsuyama (Japan)

(Received January 24th, 1966)

The abundance of rhenium is very low[1-3] in materials of geochemical interest except for molybdenites in which considerable enrichment of rhenium has long been known[4]. In nature there are 2 stable isotopes of rhenium, ^{185}Re and ^{187}Re, which possess large neutron activation cross-sections of 100 and 75 barns, respectively, so that a highly sensitive determination of rhenium is possible by neutron activation. Nuclear data relevant to the activation analysis are listed in Table I. Neutron activation analysis has previously been applied to the determination of rhenium in ores[5], rocks[2,3,6], meteorites[7-9] and tektites[1], and such organic materials as enzymes[10] and marine organisms[11,12]. These methods mostly involve complicated chemical separations including coprecipitation, distillation and solvent extraction, leading to low chemical yields. In addition, most of the previous purification procedures do not afford clear separation of radioactive rhenium and ^{99m}Tc, which is produced by uranium fission or comes from the ^{98}Mo(n,γ) ^{99}Mo reaction followed by a β-decay. Therefore, it is of primary importance to remove the conversion electron arising from ^{99m}Tc by using a thick aluminum absorber or to use γ-spectrometry to remove the contribution of ^{99m}Tc. These precautions inevitably cause a loss of sensitivity.

TABLE I

NUCLEAR DATA

Target nuclide	*Natural abundance (%)*	*Cross-section (barns)*	*Nuclide formed*	*Half-life (h)*	*Energy (MeV)*	
					β	γ
^{185}Re	37.07	100	^{186}Re	88.8	1.07,0.93 0.3	0.768, 0.631, 0.137, 0.123, 0.063
^{187}Re	62.93	75	^{188}Re	16.7	2.12,1.96	0.931, 0.828, 0.633, 0.478, 0.155, 0.062, 0.034

In this work a very effective radiochemical procedure was developed for rhenium; the single-step anion exchange involved allows a variety of samples to be rapidly analyzed with a high chemical yield. ^{99m}Tc can be completely separated to achieve direct β- or γ-counting of rhenium activities without a loss of sensitivity.

EXPERIMENTAL

Reagents and apparatus

Standard solution of rhenium. Dissolve *ca.* 1 g of potassium perrhenate (99.0% purity) in 150 ml of 0.5 *M* hydrochloric acid. Standardize gravimetrically by a tetraphenylarsonium method. This solution served both as a carrier and as a comparative standard after appropriate dilution. All other chemicals used were of analytical grade quality.

Ion-exchange column. Dowex 1-X10, 200–400 mesh, Cl form, was used. The resin was converted to the thiocyanate form and stored as described previously[13]. Slurry the resin (2 g) with water and pour into a conventional column of diameter 1.0 cm to form a bed *ca.* 5 cm long. Before use pass several column volumes of 0.025 *M* ammonium thiocyanate–0.5 *M* hydrochloric acid solution through the column.

Irradiation and activity measurement

Weigh out a powdered sample of molybdenite (50 mg) or pyrolusite (200 mg) and seal in a polyethylene tube. Impregnate a small piece of filter paper placed in a polyethylene bag with an aliquot of the rhenium standard solution (0.0906 μg Re) and seal. For rock samples, weigh *ca.* 150 mg in a quartz tube and seal. Prepare a comparative standard for rock samples (0.0906 μg Re) by placing an aliquot of the standard solution in a separate quartz tube, evaporating to dryness under an infrared lamp, and sealing as before. Pack the sample and the comparative standard with aluminum foil and position in an aluminum capsule along with aluminum packing foil.

Ore samples were irradiated for 6 h in the TRIGA II reactor of St. Paul's University (Yokosuka) at a neutron flux of $5 \cdot 10^{11}$ n/cm^2/sec. Rock samples were irradiated for 130 h at a neutron flux of $2 \cdot 10^{13}$ n/cm^2/sec in the Japan Research Reactor, JRR-II. After appropriate cooling (*ca.* 4 h for ores, 210 h for rocks) the sample and standard were mixed with the rhenium carrier and processed chemically to isolate a pure rhenium fraction as a rhenium phenylarsonate. The precipitate was mounted on a thick paper card. β-Counting was performed using a standard end-window G.M. counter with a mica window thickness of 1.2 mg/cm^2. Appropriate decay, chemical yield and geometry corrections were applied. Radiochemical purity was checked with a TMC 400-channel multichannel analyzer coupled with a 1.5 × 1 in. NaI(Tl) crystal.

Dissolution of irradiated samples

Molybdenite. Transfer the irradiated sample quantitatively to a 25-ml Kjeldahl flask containing 4.53 mg Re as carrier. Add 2 ml of nitric acid and warm. Add 1 ml of fuming nitric acid and boil gently until a clear solution results. Treat several times with 5-ml portions of hydrochloric acid to expel nitric acid and finally evaporate to *ca.* 5 ml. Dilute to 20 ml with water and add 5 mg of Fe(III) carrier. Precipitate iron(III) hydroxide by adding ammonia and centrifuge. Discard the precipitate. Continue as described under *Radiochemical separation of rhenium.*

Pyrolusite. Transfer the irradiated sample to a 25-ml Kjeldahl flask containing 4.53 mg of rhenium as the carrier. Add 5 ml of hydrochloric acid and warm to complete the decomposition. Neutralize by dropwise addition of 1:1 ammonia and centrifuge. Discard the precipitate. Follow the procedure as described for *Radiochemical separation of rhenium.*

Silicate rock. Fuse the irradiated sample with 1 g of sodium peroxide in a nickel crucible. After cooling place the crucible in a beaker containing 4.53 mg Re. Add 10 ml of water to leach the melt. Remove the crucible and centrifuge. Neutralize the supernate with hydrochloric acid, centrifuge and discard the precipitate. Treat the supernate as described below.

Radiochemical separation of rhenium

Adjust the supernate obtained to 0.025 *M* in ammonium thiocyanate and 0.5 *M* in hydrochloric acid. Do not exceed a total volume of 35 ml. Allow the acidic thiocyanate solution to pass through the ion-exchange column at a flow rate of about 0.5 ml/min. Discard the eluate. Wash the column with 20 ml of the same acidic thiocyanate solution and discard the eluate. Remove the rhenium by elution with 30 ml of 0.5 *M* thiocyanate–0.5 *M* hydrochloric acid solution. Collect the whole eluate. Add to this 8 ml of hydrochloric acid, 1 ml of 35% tin(II) chloride solution in 6 *M* hydrochloric acid, and 2 ml of 20% potassium thiocyanate solution. Transfer to a separatory funnel and extract the rhenium by shaking with 20 ml of ethyl ether for 1 min. Transfer the ether layer to a conical beaker and evaporate to dryness. Add 10 ml of 6 *M* hydrochloric acid to the residue and warm. While shaking, add 30% hydrogen peroxide dropwise to the solution to decompose the thiocyanate. If a yellowish brown or blackish brown precipitate appears, make the solution alkaline with ammonia and warm until the precipitate turns yellow. Add a few drops of methyl orange solution and neutralize with ammonium hydroxide or hydrochloric acid, depending on the previous step. Digest for 5 min on a steam bath and filter. Add 2 ml of aqueous 1% tetraphenylarsonium chloride solution to the filtrate and digest for 10 min. Cool and filter through a weighed small filter paper. Wash with water and then with ethanol. Dry at 110° for 10 min, cool and weigh. Mount for the activity measurements. Treat the comparative standard in a similar way.

RESULTS AND DISCUSSION

Although several radiochemical procedures are available for rhenium, a specific method is still lacking. ^{99m}Tc, produced by uranium fission or by decay of activated molybdenum, behaves very similarly to rhenium in most radiochemical separations. Aluminum absorbers must be employed in radiometric assays to absorb conversion electrons arising from the isomeric transition (e/γ very large) and γ (e/γ, 0.11) decay of ^{99m}Tc. With γ-spectrometry, the 0.14-MeV γ-peak of ^{99m}Tc interferes with the primary γ-peaks at 0.137 MeV for ^{186}Re and at 0.155 MeV for ^{188}Re. Strong bremsstrahlung also makes it difficult to measure γ-rays.

A very selective anion-exchange chromatographic method for the separation of rhenium in acidic thiocyanate media was developed previously in this laboratory[13,14], and was tested in the present work in the radiochemical procedure for rhenium. Under the conditions indicated in the radiochemical procedure above, rhenium can be quantitatively separated from more than 40 elements including Li, Na, K, Be, Mg, Ca, Ba, Cu, Zn, Cd, Co, Ni, Mn(II), Al, Y, trivalent rare earths, Cr(III), As(III), Ga, In, Sb(III), Bi, Fe(III), Sn(IV), Ge, Te(IV), Se(IV), Th, Zr, V(V), W(VI), Mo(VI), U(VI), Tc(VII). One can thus expect to be able to isolate a pure rhenium fraction in a single step by this anion-exchange process. Table II shows the results for the determination of rhenium in several molybdenites, pyrolusites, molybdenum sulfide (of chemically pure quality) and the standard rock W-1 from Centerville, Virginia. The errors reported are the standard deviations based on the final result not on the counting data. Colorimetric values for the Yamanashi molybdenite and molybdenum sulfide are included in Table II; agreement of the average values between colorimetry and activation analysis is satisfactory. MORRIS AND FIFIELD[2,6] and MORGAN[3] found, for rhenium in W-1 by neutron activation, values of 0.0007 p.p.m. (av. of 5 determinations) and $4.2 \cdot 10^{-10}$ g/g (av. of 2 determinations), respectively. Because of the extremely low abundance concerned, there is probably no significant difference between the value found in the present work and those given previously.

TABLE II

DETERMINATION OF RHENIUM IN ORES AND ROCK

Sample	*Locality*	*Re (p.p.m.)*	
Molybdenite	Yamanashi, Japan	137, 130, 115, 113	av. 124 ± 12[a]
Molybdenite	Kokura, Japan	25, 26, 25, 26, 24	av. 25.2 ± 1.0
Molybdenite	Korea	5.1, 4.3, 6.5, 4.5, 5.2	av. 5.12 ± 0.86
Molybdenite	Korea	0.13, 0.13, 0.14	av. 0.133 ± 0.006
Molybdenite	Gifu, Japan	3.3, 2.8, 2.0	av. 2.70 ± 0.66
Molybdenite	Unknown, Japan	51, 56, 54	av. 53.7 ± 2.5
W-1	Virginia, U.S.A.	0.00026, 0.00024	av. 0.00025
Pyrolusite	Saitama and Ehime, Japan	$< 1 \cdot 10^{-3}$	
(Composite of two individual samples)			
Pyrolusite	Shizuoka, Japan	$< 1 \cdot 10^{-3}$	
Hausmannite	Shiga, Japan	$< 1 \cdot 10^{-3}$	
Chemicals (MoS_2)		9.3[b]	

[a] Values of 139 and 138 p.p.m. Re found spectrophotometrically.
[b] A value of 14 p.p.m. Re found spectrophotometrically.

Figure 1 shows a representative γ-ray spectrum of ^{188}Re isolated from an irradiated molybdenite along with that of the reference standard. No extraneous γ-activities were found in either spectra.

In Fig. 2 a typical β-decay curve is illustrated for induced rhenium activities obtained from the irradiated molybdenite sample. The gross decay curves consist of 2 components with half-lives of 16.7 h and 88.8 h, respectively; each half-life is consistent with the literature value.

Because the radiochemical procedure consists primarily of a one-step anion exchange, the chemical yield averages 75% and a considerable saving of time is possible. Multiple analyses are quite feasible, for 5–7 samples can be treated at the same time; in this case the average time needed to complete the whole procedure is only 2 h.

The effect of neutron shielding in the comparative standard appears to be significant because of the large cross-sections for thermal neutrons and greater abundance of 2 isotopes giving rise to the activities. There is also a strong possibility of neutron shielding in the epithermal energy range as a consequence of strong

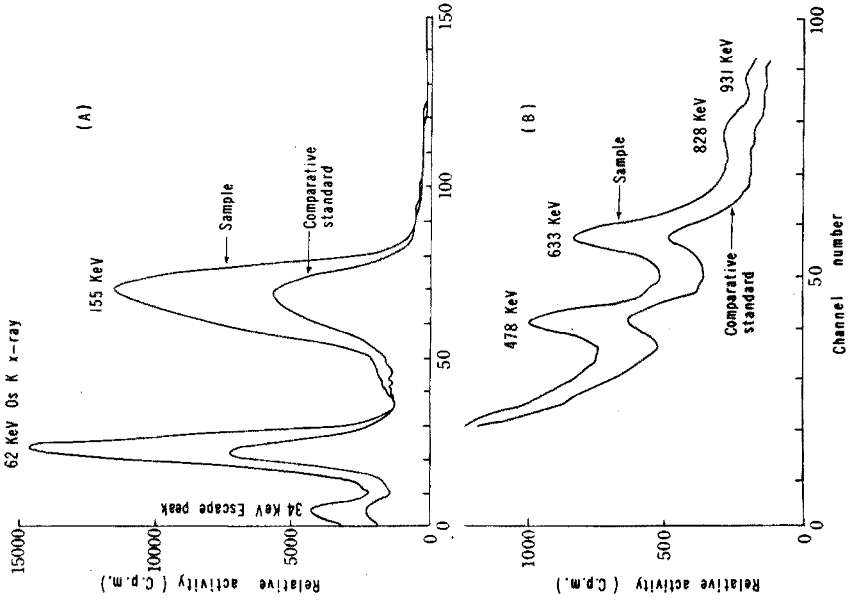


Fig. 1. γ-Spectra of ^{188}Re separated from molybdenite. (A) Lower energy range; (B) higher energy range.

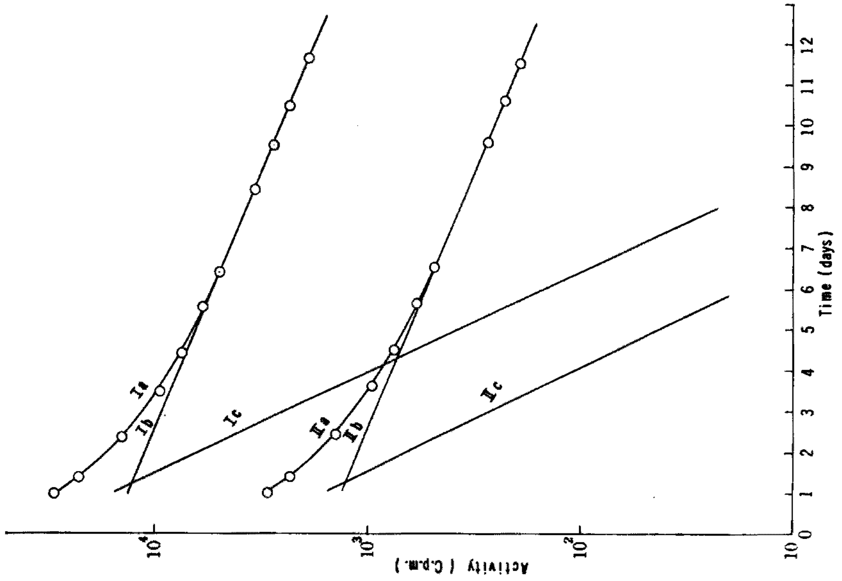


Fig. 2. Decay curve of induced rhenium activities obtained from the irradiated molybdenite. (Ia, IIa) Gross decay of rhenium activities obtained from the sample and comparative standard, respectively. (Ib, IIb) Decay of ^{186}Re (88.8 h) obtained from the sample and comparative standard, respectively. (Ic, IIc) Decay of ^{188}Re (16.7 h) obtained by subtraction of the long-lived ^{186}Re fraction in the sample and comparative standard, respectively.

resonance capture. However no sign of neutron shielding was found experimentally, so far as the specific activities produced on less than 0.1 μg Re were concerned. The effect of neutron self-shielding in the samples does not appear to be significant, because of the small sample size used and the low absorption cross-section of the major matrix materials. However, if the samples contain appreciable amounts of rhenium, possible interference arising from self-shielding must be considered. This will be the case for molybdenites. Experimentally, 50-mg portions of commercially available molybdenum disulfide containing 9.3 p.p.m. Re, each spiked with varying amounts of rhenium ranging 1 μg to 90 μg, were irradiated and the induced specific activities of rhenium were calculated; the specific activities thus obtained were uniform for the rhenium concentrations tested. Therefore, the effect of neutron self-shielding in the molybdenites is not considered significant. Additional evidence on this point is provided by the reasonably good agreement between the values obtained colorimetrically and by the activation method for the molybdenite of high rhenium content as stated above (see Table II). Possible interfering nuclear reactions leading to the formation of ^{186}Re and ^{188}Re are summarized by MORRIS AND FIFIELD[2] as follows:

$$^{184}\mathrm{W}(\mathrm{n},\gamma)^{185}\mathrm{W} \xrightarrow{\beta} {}^{185}\mathrm{Re}(\mathrm{n},\gamma)^{186}\mathrm{Re}$$

$$^{186}\mathrm{W}(\mathrm{n},\gamma)^{187}\mathrm{W} \xrightarrow{\beta} {}^{187}\mathrm{Re}(\mathrm{n},\gamma)^{188}\mathrm{Re}$$

$$^{186}\mathrm{Os}(\mathrm{n,p})\,^{186}\mathrm{Re}$$

It can be shown by calculation[15] that under the neutron irradiation conditions for rocks in the present work, the ^{186}Re activity produced by 1 μg of tungsten corresponds to $4 \cdot 10^{-8}$ μg of rhenium; 50 p.p.m. of tungsten in rocks, which is extremely rare in actual cases, can cause ^{186}Re activity equivalent to only $2 \cdot 10^{-6}$ p.p.m. of Re. In the same way, 1 μg of tungsten can cause ^{186}Re and ^{188}Re activities equivalent to only $3 \cdot 10^{-6}$ μg Re and $3 \cdot 10^{-6}$ μg Re, respectively, on the basis of the irradiation conditions used for the ores. The error is likely to be insignificant unless the minerals and ores contain large amounts of tungsten. The ^{186}Os(n, p) ^{186}Re reaction will also not contribute to the result for rhenium to any significant extent because of the low abundance of osmium[1,3,8,9] coupled with the low average cross-section of the reaction (0.04 mb) in a fission neutron spectrum[16].

SUMMARY

A neutron activation method is proposed for the determination of rhenium in rocks and ores. After the irradiation, the radiochemical separation consists of a one-step anion exchange; β-activities of radiochemically pure ^{188}Re or ^{186}Re are counted. The chemical yield averaged 75% and there was a considerable saving of time in the radiochemical work. Results are quoted for the rhenium contents of the standard rock W-1, several molybdenites and pyrolusites.

RÉSUMÉ

On propose une méthode par activation au moyen de neutrons pour le dosage du rhénium dans des roches et des minerais. La séparation radiochimique consiste en un échange d'anions; on compte les activités-β de ^{188}Re ou ^{186}Re, radiochimiquement purs. Le rendement chimique est en moyenne de 75%; le gain de temps est considérable. Des résultats sont donnés pour des teneurs en rhénium de roche standard W-1, plusieurs molybdénites et pyrolusites.

ZUSAMMENFASSUNG

Die Neutronenaktivierungsanalyse wird für die Bestimmung von Rhenium in Gesteinen und Erzen vorgeschlagen. Die radiochemische Trennung geschieht durch Anionenaustausch. Die β-Aktivitäten des radiochemisch reinen ^{188}Re oder ^{186}Re werden gezählt. Die chemische Ausbeute beträgt etwa 75%. Das Verfahren ist zeitsparend.

REFERENCES

1 J. F. LOVERING AND J. W. MORGAN, *Geochim. Cosmochim. Acta*, 28 (1964) 761.
2 D. F. C. MORRIS AND F. W. FIFIELD, *Geochim. Cosmochim. Acta*, 25 (1961) 232.
3 J. W. MORGAN, *Anal. Chim. Acta*, 32 (1965) 8.
4 L. PAGANELLI, *Geochim. Cosmochim. Acta*, 27 (1963) 401.
5 G. W. LEDDICOTTE AND A. P. GRIMANIS, unpublished work, cited in G. W. LEDDICOTTE, *The Radiochemistry of Rhenium*, U.S. At. Energy Comm., NAS-NS 3028, 1961.
6 D. F. C. MORRIS AND F. W. FIFIELD, *Talanta*, 8 (1961) 612.
7 E. D. GOLDBERG AND H. BROWN, *Anal. Chem.*, 22 (1950) 308.
8 W. HERR, W. HOFFMEISTER AND J. LANGHOFF, *Z. Naturforsch.*, 15a (1960) 99.
9 J. W. MORGAN AND J. F. LOVERING, *Science*, 144 (1964) 835.
10 W. A. BROOKSBANK, G. W. LEDDICOTTE AND J. E. STRAIN, *Nuclear Eng. Sci. Congress, Cleveland, U.S.A., December, 1955*, Preprint No. 308.
11 R. FUKAI AND W. W. MEINKE, *Nature*, 184 (1959) 815.
12 R. FUKAI AND W. W. MEINKE, *Limnol. Oceanog.*, 4 (1959) 398.
13 H. HAMAGUCHI, K. KAWABUCHI AND R. KURODA, *Anal. Chem.*, 36 (1964) 1654.
14 K. KAWABUCHI, H. HAMAGUCHI AND R. KURODA, *J. Chromatog.*, 17 (1965) 567.
15 W. ROBINSON, *J. Chem. Phys.*, 17 (1949) 542.
16 J. C. ROY AND J. J. HAWTON, AECL-1181, Chalk River, Ontario, 1960.

INTENSITY OF THERMAL RADIATION OF METAL SPECTRA IN FLAME EMISSION SPECTROMETRY

J. D. WINEFORDNER, W. W. McGEE, J. M. MANSFIELD, M. L. PARSONS AND K. E. ZACHA
Department of Chemistry, University of Florida, Gainesville, Fla. 32601 (U.S.A.)

(Received February 15th, 1966)

A simple yet comprehensive discussion and derivation of the intensity of spectral lines of atoms excited in flames which are in thermal equilibrium has not been previously given. The final expressions derived in this paper have been used in a large number of papers, theses and books, but generally the procedure for obtaining the expressions is unclear and the references incomplete. In this paper, a unified and well-referenced qualitative and quantitative approach to the derivation of equations for the total intensity of a spectral line of atoms excited by a flame in thermal equilibrium is given (over a small region of the outer cone of most analytical flames, the flame gases are approximately in thermal equilibrium[1-3]).

The signal produced and recorded by most flame spectrometers is proportional to the total intensity, I, rather than the intensity, I_ν, which is the intensity for a small frequency interval around the peak frequency, ν_0, of the spectral line. The reason for this is that the half-intensity widths of atomic lines in flames are generally less than 0.1 Å and the spectral band widths of most monochromators used in flame spectrometers are greater than 0.1 Å[4]. The total intensity of a spectral line from atoms in analytical type flames is derived in this manuscript as a function of atomic concentration, flame temperature, spectral characteristics and flame size using the Einstein coefficient of spontaneous emission in conjunction with a dimensional analysis and the classical black body approach. The effects of self-absorption and self-reversal on the spectral line contour and on analytical curves are discussed, and application of the derived equations to molecular emission is considered.

THEORY AND DISCUSSION

Intensity of spectral lines—Use of Einstein's coefficients for low atomic concentrations[1-3,5]

The approach used in this section to find the total (integrated) intensity of a spectral line is similar to the one often used in physics and physical chemistry text books. A metal atom, M, emits a photon when undergoing a radiational transition from an energy level E_m to a lower energy level E_n. The peak frequency, ν_0, of the spectral line is determined by the energy balance of $h\nu_0 = E_m - E_n$ where h is Planck's constant. If the transition is to the ground state, then $E_n = 0$, and the spectral line is called a resonance line, *i.e.*, $h\nu_0 = E_m$. The most prominent lines of any element are generally the resonance lines from low lying excited states. This results because the energy of excitation, E_m, is sufficiently small to be supplied by collisional processes within the flame gases and because the transition probabilities of such transitions are appreciable.

The total energy emitted per second, P, in watts from a small volume ΔV of flame gases and at a frequency ν_0 can be simply and logically derived using a dimensional analysis, *i.e.*

$$\text{watts} \Leftrightarrow \left(\frac{\text{ergs}}{\text{transition}}\right)\left(\frac{\text{watts}}{\text{erg/sec}}\right)\left(\frac{\text{excited atoms}}{\text{cm}^3}\right)(\text{cm}^3)\left(\frac{\text{transitions}}{\text{excited atom}\cdot\text{sec}}\right),$$

and so

$$P = (h\nu_0)(10^7)(N_M{}^*)(\Delta V)(A_t)\ (\text{watts}) \tag{1}$$

where $h\nu_0$ is the energy in ergs of the transition, the 10^7 is a factor to convert from ergs/sec to watts, $N_M{}^*$ is the number of excited atoms per cm^3 of flame gases, ΔV is the volume in cm^3 and is as defined above, and A_t is the Einstein spontaneous transition probability, in sec^{-1}, *i.e.*, transitions per second. For eqn. (1) to be valid, ΔV must be sufficiently small that self-absorption is negligible, induced emission is insignificant, and T and $N_M{}^*$ are constant throughout the flame gases (in ΔV). The power emitted, P, can be converted into a total intensity, I, in watts per cm^2 of flame gas area per steradian by dividing P by the flame area, α_f, and by 4π (the number of unit solid angles in a sphere is 4π steradians). The ratio $\Delta V/\alpha_f$ is just the flame path length, L, in cm in the direction of the monochromator entrance slit. Therefore,

$$I = \frac{P}{4\pi\alpha_f} = \frac{10^7}{4\pi} L h\nu_0 N_M{}^* A_t \left(\frac{\text{watts}}{\text{cm}^2\,\text{ster}}\right) \tag{2}$$

In the above derivation, it is assumed that all photons have the same frequency ν_0. Actually all spectral lines have a finite line width because of natural, Doppler, collisional and other types of broadening. However, for a dilute gas, the integrated intensity, I, obtained by eqn. (2) is valid whatever the broadening factors (refer to Appendix I).

In the above equations, A_t and ν_0 are parameters characteristic of the atom in concern. The parameter $N_M{}^*$, however, depends not only on the atomic structure but also on the total atomic concentration of metal atoms available, *i.e.*, the equilibrium concentration of the species M at the temperature T (in °K) of the flame gases. If the flame gases are in complete thermal equilibrium, then the concentration of atoms in the excited state depends upon the absolute flame temperature, T. The value of $N_M{}^*$ is given by the Boltzmann equation, namely,

$$N_M{}^* = (N_M)_T \frac{g_m}{B(T)} \exp(-E_m/kT) \left(\frac{\text{excited atoms}}{\text{cm}^3}\right) \tag{3}$$

where k is the Boltzmann constant ($8.6\cdot 10^{-5}$ eV/°K), g_m is the statistical weight of the excited state (no units), $B(T)$ is the partition function of M over all states, and $(N_M)_T$ is the total concentration of atoms in all states. The term $B(T)$ is defined by

$$B(T) = g_n + g_m e^{-E_m/kT} + g_l e^{-E_l/kT} + \ldots, \tag{4}$$

where n is considered the ground state and m and l are excited states. If the transition is a resonance transition and if the excited states are more than 1.5 to 2.0 eV above the ground state, then

$$B(T) \approx g_n \quad \text{and} \quad (N_\mathrm{M})_\mathrm{T} \approx N_\mathrm{M} \tag{5}$$

where N_M is the concentration of atoms in the ground state (n). Therefore, the Boltzmann equation can be simplified and written as

$$N_\mathrm{M}{}^* = N_\mathrm{M} \frac{g_m}{g_n} \exp(-h\nu_0/kT) \left(\frac{\text{excited atoms}}{\text{cm}^3}\right) \tag{6}$$

where g_m and g_n are the statistical weights of the excited (m) and ground (n) states and $E_m = h\nu_0$. Equation (6) also applies to a transition from one excited state to another as long as the approximations of eqn. (5) are valid and $h\nu_0$ is the energy of the transition involved. Therefore, the total intensity of a spectral line (generally a resonance line in flame emission spectrometry) is given by combining eqns. (2) and (6), and so

$$I = \frac{h\nu_0 N_\mathrm{M} A_\mathrm{t} L g_m}{4\pi 10^7 g_n} \exp(-h\nu_0/kT) \left(\frac{\text{watts}}{\text{cm}^2\ \text{ster}}\right) \tag{7}$$

Equation (7) is valid only if self-absorption and induced emission are negligible, *i.e.*, at low atomic concentrations; values of N_M less than that correspond to the intersection point, N_Mi, of a plot of I *vs.* N_M[6].

Equation (7) is also valid for the intensity of molecular emission. The transition probability A_t for molecules, however, is more complex than for atoms. If the reader is interested in an exact evaluation of total intensities of molecular emission (*i.e.*, A_t can be evaluated in terms of spectral characteristics), then the treatise by PENNER[7] should be consulted.

Intensity of spectral lines—Classical black body approach for low atomic concentrations

Equation (7) can also be derived from the classical black body approach. Flames containing an atomic vapor of an emitting species, M, are light sources which selectively emit and absorb radiation over the narrow frequency interval of the spectral line. If the flame emits as a black body at any given frequency then the absorptivity and emissivity factors will both be unity for that frequency. In other words, all radiation emitted is absorbed, and all absorbed radiation is emitted. If the radiating body is not black but gray, then the intensity as a function of frequency, ν (I_ν has units of ergs per second (or watts) per steradian per unit surface area per unit frequency interval), is given by Kirchhoff's Law[3,7,9-12], namely,

$$I_\nu = I_\nu{}^\mathrm{B} A_\nu \left(\frac{\text{watts}}{\text{cm}^2\ \text{ster}\ \text{sec}^{-1}}\right) \tag{8}$$

where $I_\nu{}^\mathrm{B}$ is the intensity of a black body radiator at frequency, ν, and A_ν is the atomic absorptivity at frequency ν. The factor A_ν is a parameter to account for the fact that the spectral line over its frequency range does *not* act as a black body radiator, *i.e.*, $A_\nu = 1.0$ for a black body, but $A_\nu < 1$ for a gray body. The parameter A_ν, which tells how close an atomic vapor approaches black body intensities for various parts of the line, has values between 0 and 1.0 and is defined by

$$A_\nu = 1 - \exp(-k_\nu L) \quad \text{(no units)} \tag{9}$$

where k_ν is the atomic absorption coefficient, in cm^{-1}, at frequency ν and L is the flame path length, in cm, in the direction of observation.

If the emitting and absorbing atoms are uniformly distributed in the flame gases (such as exists in most flames over the central portion of the flame or exists in most flames in which the flame used for excitation is surrounded by a nonluminous flame), if the flame gases are in thermal equilibrium, and if the spectral line in concern is isolated, then the total intensity, I, is given by integrating Kirchhoff's equation over the line width,

$$I = \int_0^\infty I_\nu \mathrm{d}\nu = \int_0^\infty I_\nu{}^{\mathrm{B}} A_\nu \mathrm{d}\nu = I_{\nu_0}{}^{\mathrm{B}} \int_0^\infty A_\nu \mathrm{d}\nu = I_{\nu_0}{}^{\mathrm{B}} A_{\mathrm{T}} \left(\frac{\text{watts}}{\text{cm}^2\,\text{ster}}\right) \tag{10}$$

where $I_{\nu_0}{}^{\mathrm{B}}$ is the intensity of a black body radiator at frequency ν_0, the frequency of the line center, and A_{T} is the so-called total absorption of the spectral line. Because the value of $I_\nu{}^{\mathrm{B}}$ does not vary appreciably over the width of the spectral line, $I_\nu{}^{\mathrm{B}}$ can be removed from within the integral and replaced by $I_{\nu_0}{}^{\mathrm{B}}$, the black body intensity at ν_0, the peak frequency of the line. This is done in the latter two equations in expression (10). This approximation is valid for spectral lines resulting from atomic excitation in the flames[1,10,13].

The term $I_{\nu_0}{}^{\mathrm{B}}$ can be evaluated[7] from Planck's equation,

$$I_{\nu_0}{}^{\mathrm{B}} = \frac{2h\nu_0{}^3}{10^7 c^2} \left[\exp(h\nu_0/kT) - 1\right]^{-1} \left(\frac{\text{watts}}{\text{cm}^2\,\text{ster}}\right) \tag{11}$$

where c is the speed of light ($3.0 \cdot 10^{10}$ cm/sec). For the case of analytical flames and spectral lines of importance in atomic emission flame spectrometry, $\exp(h\nu_0/kT) \gg 1$, and so $I_{\nu_0}{}^{\mathrm{B}}$ is given with good accuracy[7] by Wien's Law

$$I_{\nu_0}{}^{\mathrm{B}} = \frac{2h\nu_0{}^3}{10^7 c^2} \exp(-h\nu_0/kT) \left(\frac{\text{watts}}{\text{cm}^2\,\text{ster}}\right) \tag{12}$$

Wien's Law is a good approximation and does not introduce any errors greater than 0.1% for the U.V.-visible regions (*i.e.*, wavelengths less than 8500 Å) and for flames at temperatures below 4000°K.

The total absorption factor, A_{T}, represents the fraction of radiation absorbed by the spectral line from a black body radiator and is defined[7-10,12,14] by

$$A_{\mathrm{T}} = \int_0^\infty \left[1 - \exp(-k_\nu L)\right] \mathrm{d}\nu \,(\text{sec}^{-1}) \tag{13}$$

where the integration is taken from 0 to ∞, *i.e.*, over the entire spectral line which is assumed to be single and isolated. In Fig. 1, a graphical representation of A_{T} is given. In Fig. 2, a graphical representation of the effect of increasing atomic concentration on the line shape and on A_{T} is given.

The atomic absorption coefficient, k_ν, is determined by the factors causing a spectral line to broaden. When the broadening of a spectral line is primarily a result of contributions from the Doppler effect and from the damping effect due to natural, collisional and resonance broadening, then (assuming the pressure shift in frequency and line asymmetry due to collisional effects are small) the atomic absorption co-

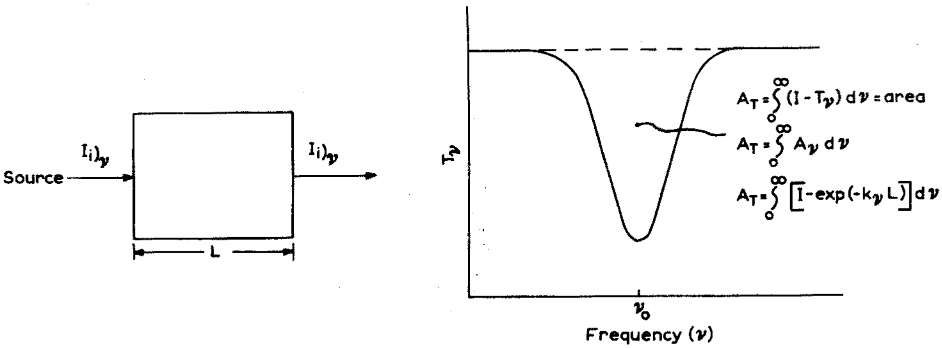


Fig. 1. Graphical representation of the total absorption for an isolated spectral line. Ordinate is fraction of radiation from a continuous (black body) radiator transmitted by a spectral line; abscissa is frequency. T_ν = fraction transmitted $= (I_t)_\nu/(I_i)_\nu \cdot A_\nu = 1 - T_\nu = 1 - \exp(-k_\nu L)$.

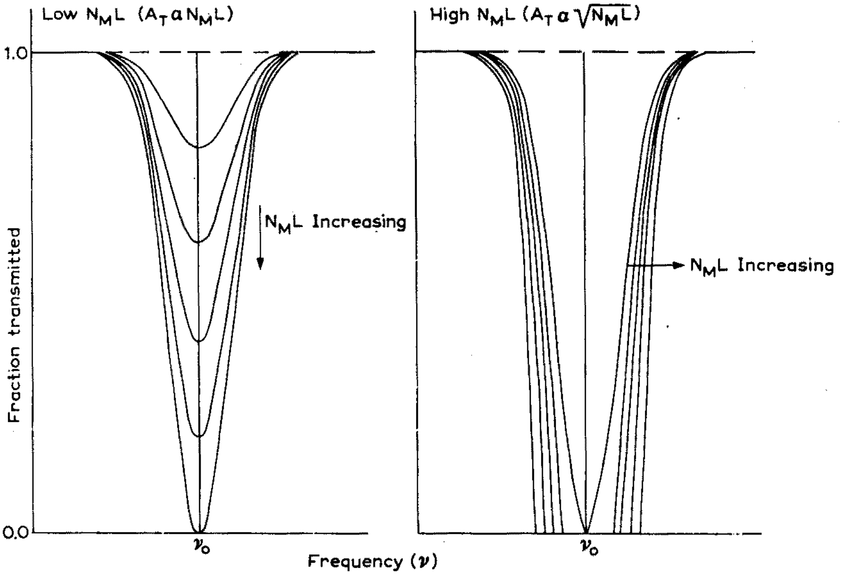


Fig. 2. Graphical representation of the effect of increasing atomic concentration, N_M, on line shape and on total absorption. See Fig. 1 for definition of symbols.

efficient, k_ν, is given[7,12,14] by the well-known Voigt profile expression

$$k_\nu = k^0 \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-y^2)\, dy}{a^2 + (v - y)^2} = k^0 \varrho \, (\text{cm}^{-1}) \tag{14}$$

where

$$y = \frac{2\delta}{\Delta\nu_D} \sqrt{\ln 2} \quad \text{(no units)} \tag{15}$$

$$v = \frac{2(\nu - \nu_0)}{\Delta\nu_D} \sqrt{\ln 2} \quad \text{(no units)} \tag{16}$$

$$a = \frac{\Delta\nu_N + \Delta\nu_c + \Delta\nu_R}{\Delta\nu_D} \sqrt{\ln 2} \quad \text{(no units)} \tag{17}$$

and k^0, the atomic absorption coefficient at the line center for the case of pure Doppler broadening, is given (14) by

$$k^0 = \frac{2\sqrt{\ln 2}\,\lambda_0{}^2 g_m N_{\mathrm{M}} A_{\mathrm{t}}}{8\pi^{\frac{3}{2}} \Delta\nu_{\mathrm{D}} B(T)} = \frac{2\sqrt{\ln 2}\,\pi e^2}{\sqrt{\pi}\;\Delta\nu_{\mathrm{D}} mc}\; N_{\mathrm{M}} f (\mathrm{cm}^{-1}) \tag{18}$$

where $\Delta\nu_{\mathrm{D}}$ is the half-intensity width in sec^{-1} due only to Doppler broadening, $\Delta\nu_{\mathrm{N}}$ is the half-intensity width in sec^{-1} due only to natural broadening, $\Delta\nu_{\mathrm{c}}$ is the half-intensity width in sec^{-1} due only to collisional broadening by foreign species, $\Delta\nu_{\mathrm{R}}$ is the half-intensity width due only to collisions with the same species (*i.e.*, resonance broadening), δ is a variable distance from the point $(\nu - \nu_0)$, ν is the frequency in sec^{-1}, ν_0 is the peak frequency in sec^{-1}, λ_0 is the peak wavelength in cm, e is the charge of an electron, m is the mass of an electron, c is the speed of light, and f is the oscillator strength of the transition, *i.e.*, the number of classical oscillators which reproduce the absorbing action of one atom in the given line and which is related[14] to A_{t} by $f = mc\, g_m \lambda_0{}^2 A_{\mathrm{t}}/8\pi^2 e^2 g_n = 1.51\, g_m \lambda_0{}^2 A_{\mathrm{t}}/g_n$. The second expression for k^0 results from the classical electron theory of dispersion, and the first expression for k^0 results from the Einstein theory of radiation[12].

Doppler broadening is due to thermal agitation of the absorbing or emitting atoms with respect to the point of observation, and for temperatures between 1500°K and 3000°K, the Doppler halfwidth in wavelength units (*i.e.*, $\Delta\nu = (c/\lambda_0{}^2)\Delta\lambda$) is of the order of 0.01–0.1 Å for most spectral lines of most elements. The Doppler half-intensity width, $\Delta\nu_{\mathrm{D}}$, is given[14] by

$$\Delta\nu_{\mathrm{D}} = \frac{2\sqrt{2R\ln 2}}{c}\,\nu_0 \sqrt{\frac{T}{M}} = 7.15\cdot 10^{-7}\nu_0 \sqrt{\frac{T}{M}}\,(\mathrm{sec}^{-1}) \tag{19}$$

where M is the atomic weight of the emitting or absorbing atom in atomic mass units, R is the gas constant, and $7.15\cdot 10^{-7}$ results from evaluation of the constant term $2\sqrt{2R\ln 2}/c$.

Collisional broadening is due to a perturbation of the energy levels of the absorbing or emitting atoms by foreign gas particles during the process of absorption or emission. As the pressure of foreign gas particles is increased, the spectral line is broadened, and the line is shifted, in most cases, to longer wavelengths. Also, the spectral line usually becomes asymmetrical. For resonance lines of most elements, the collisional half-intensity widths in wavelength units are of the order of 0.01–0.1 Å for analytical flames at one atmosphere pressure. The collisional half-intensity width, $\Delta\nu_{\mathrm{c}}$, in sec^{-1} is given[14] by

$$\Delta\nu_{\mathrm{c}} = \frac{2\sigma_{\mathrm{c}}{}^2 N_f}{\pi}\sqrt{2\pi RT\left(\frac{1}{M}+\frac{1}{M_f}\right)} = 1.38\cdot 10^{23}\sigma_{\mathrm{c}}{}^2 P_f \sqrt{\frac{1}{T}\left(\frac{1}{M}+\frac{1}{M_f}\right)}\,(\mathrm{sec}^{-1}) \tag{20}$$

where $\sigma_{\mathrm{c}}{}^2$ is the average collisional cross section for collisional broadening in cm^2, N_f is the concentration of foreign particles in particles per cm^3, M_f is the average molecular weight of the foreign particles in atomic mass units, P_f is the pressure in mm of foreign gas particles (P_f is related to N_f by the ideal gas law, *i.e.*, $N_f = P_f/kT = 9.74\cdot 10^{18}\, P_f/T$). KOHN *et al.*[15,16], and ALKEMADE *et al.*[17,18] have evaluated $\sigma_{\mathrm{c}}{}^2$ and a value for a number of resonance lines of a number of elements. More work of this type is necessary before reasonable estimates of $\Delta\nu_{\mathrm{c}}$ values of atoms in flames can be obtained.

Resonance broadening[14] is similar to collisional broadening but differs in that interactions occur between the same type of absorbing or emitting atoms. Resonance broadening does not become important in analytical flames until extremely concentrated solutions are introduced into the flame, *e.g.*, solutions more concentrated than 1 *M* may result in significant resonance broadening. Resonance broadening can be calculated from eqn. (20), if σ_c is replaced by σ_R, the average resonance cross section in cm, if M_f is replaced by M and N_f is replaced by N_M, and so

$$\Delta\nu_R = \frac{2\sigma_R{}^2 N_M}{\pi}\sqrt{\frac{\pi RT}{M}}\,(\text{sec}^{-1}) \tag{21}$$

Natural broadening is a result of the finite lifetime of an atom in the excited state. The natural half-intensity width, $\Delta\nu_N$, is given[14] by

$$\Delta\nu_N = \frac{A_t}{2\pi} = \frac{1}{2\pi\tau}\,(\text{sec}^{-1}) \tag{22}$$

where τ is the lifetime of the excited state and is inversely related to the transition probability. The natural half-intensity width in wavelength units is generally in the range of 0.001–0.0001 Å.

Other types of line broadening such as Stark and Zeeman broadening are not significant for atoms in flame sources and so will be neglected. Hyperfine structure due to nuclear spin or to the presence of several isotopes is generally insignificant in flame emission spectrometry. Each hyperfine component, if isolated and sharp, can be treated in the same manner as the isolated spectral lines. If the hyperfine components overlap, then the total intensity expression is considerably more complicated. Because the separation of hyperfine components is small compared to the spectral band width, *s*, of the monochromator generally used in flame spectrometry, the total intensity should have approximately the same value whether hyperfine structure is considered or whether it is not. An excellent discussion of the effect of hyperfine splitting on the value of A_T is given by MITCHELL AND ZEMANSKY[14].

The total line width of a spectral line, $\Delta\nu_T$, in sec^{-1} for atoms in flames is approximately given[19] by

$$\Delta\nu_T = \sqrt{\Delta\nu_D{}^2 + (\Delta\nu_N + \Delta\nu_c + \Delta\nu_R)^2}\,(\text{sec}^{-1}) \tag{23}$$

if it is assumed that hyperfine splitting is small compared to the half widths in eqn. (23). In most flame emission studies, $\Delta\nu_c \gg \Delta\nu_N + \Delta\nu_R$, and so

$$\Delta\nu_T \cong \sqrt{\Delta\nu_D{}^2 + \Delta\nu_c{}^2}\,(\text{sec}^{-1}) \tag{24}$$

It should be pointed out that the damping broadening terms add linearly, but the damping terms and Doppler broadening add quadratically because they are independent types of broadening[14].

If the atomic concentration is low, then the total absorption, A_T, is given by

$$A_T = \int_0^\infty [1 - \exp(-k_\nu L)]\mathrm{d}\nu \cong L\int_0^\infty k_\nu \mathrm{d}\nu\,(\text{sec}^{-1}) \tag{25}$$

Assuming the spectral line for atoms in a dilute atomic gas is broadened primarily by

Doppler broadening (actually in most flames collisional broadening will be comparable to Doppler broadening, but it should be noted that even if the exact expression for k_ν were used, the same low concentration value of A_T would still result, *i.e.*, at small values of $N_M L$ the values of A_T for a given $N_M L$ are the same for any a value which is evident from astrophysical growth curves[17,18]; also see Appendix I). A_T is then given[12] by

$$A_T = \frac{\sqrt{\pi}\,\Delta\nu_D k^0 L}{2\sqrt{\ln 2}} \left[1 - \frac{k^0 L}{2!\sqrt{2}} + \frac{(k^0 L)^2}{3!\sqrt{3}} - \ldots\right] (\mathrm{sec}^{-1}) \tag{26}$$

and if $k^0 L \ll 1$, *i.e.*, a low atomic concentration, then the limiting law expression results, namely,

$$A_T = \frac{\sqrt{\pi}\,\Delta\nu_D k^0 L}{2\sqrt{\ln 2}} \tag{27}$$

The mathematical derivation of the low concentration value of A_T involves substituting for k_ν and $d\nu$ in terms of k^0 and v, *i.e.*, $v = (\nu - \nu_0) 2\sqrt{\ln 2}/\Delta\nu_D$, and so $d\nu = \Delta\nu_D dv/2\sqrt{\ln 2}$ and $k_v = k^0 \exp(-v^2)$. Expansion of the integral into a series and integrating gives eqn. (26).

Substituting for k^0 from eqn. (18) results in the following expression for A_T,

$$A_T = \frac{g_m \lambda_0^2 N_M A_t L}{8\pi B(T)} = \frac{\pi e^2}{mc} N_M f L \tag{28}$$

where the first expression results from the Einstein theory of radiation, and the second expression results from the classical theory of electron dispersion. The total intensity of a spectral line, I, can be found by substituting the value A_T from eqn. (28), and $I_{\nu_0}{}^B$ from eqn. (11) into eqn. (10), and so eqn. (7) results,

$$I = \frac{h\nu_0 N_M A_t L g_m}{4\pi 10^7 g_n} \exp(-h\nu_0/kT) = \frac{2h\pi e^2}{mc^3} N_M f L \exp(-h\nu_0/kT) \left(\frac{\text{watts}}{\text{cm}^2\ \text{ster}}\right) \tag{7}$$

which is valid for spectral lines of M atoms present in a dilute gas. The first expression has been derived using the Einstein theory of radiation and the second using the electron dispersion theory. The above equations have been derived using the classical black body approach. Equation (7), as previously stated, should be valid for molecular emission as well as atomic emission.

Equation (7) results for low values of $N_M L$ whatever the broadening process, *i.e.*, as long as self-absorption is not present, the total intensity I which is the area under the emission line ($I = \int I_\nu d\nu$) will be a constant value for a given flame type and flame temperature and a given atomic concentration (see Appendix I).

Intensity of spectral lines—Classical black body approach for high atomic concentrations

At high atomic concentrations, the spectral line is influenced by *self-absorption* (refer to Fig. 3). According to eqn. (8), I_ν, *i.e.*, the intensity in a very narrow frequency interval around ν_0, would not be expected to grow indefinitely as the atomic concentration, N_M, increases and/or the flame diameter, L, increases, because A_ν approaches unity, and so I approaches a constant value at high values of the product $N_M L$. However, it is well-known that the total intensity, I, increases linearly with $N_M L$ at low concentration and with $\sqrt{N_M L}$ at high concentrations. This phenomenon must therefore be due to the spectral line broadening because the peak intensity is a constant, *i.e.*, $I = I_{\nu_0}{}^{\mathrm{B}} \int A_\nu \mathrm{d}\nu$, and because $A_\nu \rightarrow 1.0$ at high concentrations, I can increase only if $\mathrm{d}\nu$ increases.

Radiation emitted by excited M atoms can be reabsorbed by M atoms in the lower energy state (usually ground) corresponding to the transition. This phenomenon which results in broadening of the spectral line and in an increase in the total intensity is called self-absorption. The absorption is greatest for radiation emitted at the line center and tapers off to zero in the wings of the line. The parameter A_{T} (defined by eqn. (13)) can be used to account for self-absorption. For high atomic concentrations, A_{T} can be approximated by assuming that the spectral line is broadened completely by collisional broadening[8,12,17]. From eqns. (12) and (14), the total absorption factor, A_{T}, is given by the well-known square root relationship

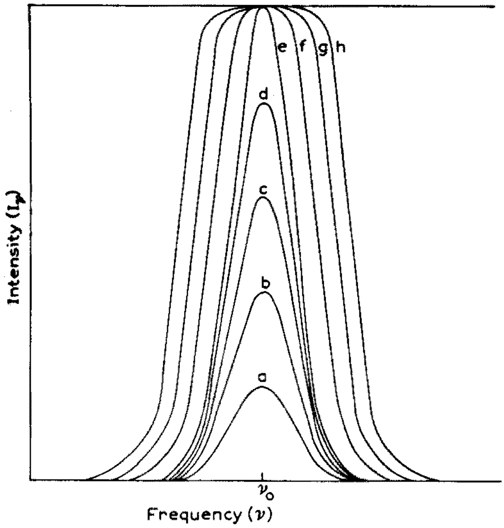


Fig. 3. Schematic representation of the contour of a spectral line as a function of atomic concentration, N_{M}. Atomic concentration increases in curves from a to f.

$$A_{\mathrm{T}} = \frac{\sqrt{\pi}\, \Delta\nu_{\mathrm{D}}}{\sqrt{\ln 2}} \sqrt{\frac{k^0 L a}{\pi}} \;(\mathrm{sec}^{-1}) \tag{29}$$

The mathematical derivation of the high concentration value of A_{T} involves substituting for k_ν and $\mathrm{d}\nu$ in terms of k^0 and $\mathrm{d}v$, *i.e.*, $\mathrm{d}\nu = \Delta\nu_{\mathrm{D}} \mathrm{d}v / 2\sqrt{\ln 2}$ and $k_\nu = k^0 \exp(-v^2)$. Therefore the total intensity, I, for a concentrated atomic gas of M atoms is obtained by substituting A_{T} from eqn. (29) and $I_0{}^{\mathrm{B}}$ from eqn. (11) into eqn. (10), and so

$$I = \frac{h\nu_0{}^2}{c\, 10^7} \exp(-h\nu_0/kT) \sqrt{\frac{g_m \Delta\nu_{\mathrm{D}} N_{\mathrm{M}} A_{\mathrm{T}} L a}{\pi\sqrt{\ln 2}\, g_n}} = \frac{2h\nu_0{}^2}{10^7 c^2} \sqrt{\frac{2\pi \mathrm{e}^2 \Delta\nu_{\mathrm{D}} N_t L a}{mc\sqrt{\ln 2}}} \left(\frac{\mathrm{watts}}{\mathrm{cm}^2\, \mathrm{ster}}\right) \tag{30}$$

where the first expression results from the Einstein theory of radiation and the second from the classical dispersion theory.

Qualitatively the effect of self-absorption can be explained by considering the atomic absorption coefficient, k_ν. At high atomic concentrations, the atomic absorption coefficient at the line center is so large that the flame becomes opaque to its own radiation at the line center. At $\nu = \nu_0$ and in each volume increment across the flame, nearly all radiation is absorbed and re-emitted. This process is so complete that the absorptivity A_ν at the line center is nearly unity, and so the intensity, I_ν, at the line center approaches the value $I_{\nu_0}{}^{B}$, *i.e.*, the intensity of a black body radiator whose temperature is that of the atomic vapor cloud. Therefore, as the concentration of the atomic vapor increases, the increase in I is due to an increase in k_ν in the line wings which results in an increase in A_ν in the line wings and an increase in A_T for the spectral line. The increase in k_ν in the line wings is due to an increase in collisional broadening which is the major factor in determining the line shape at high atomic concentrations. Self-absorption, therefore, results in a spectral line contour with a flat top and wings (see Fig. 3). In fact, in the case of an atomic vapor of sodium, the self-absorption broadening could theoretically continue until the Na-D lines begin to overlap (however, spectral lines in flames seldom exceed 1 Å).

It should be pointed out that the total intensity of molecular emission will be linear with molecular concentration (N_M) over a wide range. Molecular emission should be almost completely unaffected by self-absorption because the most intense molecular emission is generally at much longer wavelengths than the most intense excitation, *i.e.*, emission in molecules generally occurs from the lowest vibrational state of the excited state to various vibrational states of the ground electronic state, whereas excitation in molecules generally occurs from the lowest vibrational states of the ground electronic state to various vibrational states of the excited electronic state; therefore, absorption requires more energy than is usually emitted.

Intensity of spectral lines—Classical approach to the influences of self-reversal[11]

Self-reversal of spectral lines is impossible in a homogeneous flame, *i.e.*, if T is the same throughout. However, if the radiation from the hot flame gases passes through an atomic cloud of lower temperature, then selective absorption will occur, and not as much radiation will be added back by the lower temperature vapor as was absorbed by the lower temperature vapor. Therefore, very little of the radiation at the line center gets through, but in the wings essentially all of the radiation is transmitted. Simultaneously the cool vapor adds its own radiation to the beam which is much less bright than the hot flame gases at any given frequency. The final intensity contour is therefore made up of radiation from the hot cloud transmitted through the cool atomic vapor in addition to the radiation emitted by cool atomic vapor. In Fig. 4, the effect of self-reversal on line contour is illustrated.

In this section, it will be convenient to consider the flame gases as composed of two distinct parts (see Fig. 5) in which the central part is at a higher temperature, T_h, and has a path length of L_h, and the outer part is at a lower temperature, T_c, and has a path length of L_c. No exact expression for the total intensity I of a self-reversed line will be given here. Since a flame actually consists of a gradient in temperature from room temperature to that of the central part of the flame gases, the expressions to be derived would not be exact anyway. Also, extremely concentrated solutions are ordinarily diluted sufficiently to be on the linear portion of the analytical curve where self-reversal is not a problem. However, a qualitative and semiquantitative discussion of self-reversal and its effect on I_ν is instructive and useful in terms of its effect on spectral line shape and analytical curve shape.

Self-reversal can be considered in the following way. Refer to Fig. 5 for the geometry of the system under consideration. The resultant intensity I_{ν_R} at any frequency ν per unit frequency interval is given by the summation of the intensity I_{ν_c} of the cool vapor plus the intensity I_{ν_m} of the hot vapor modified by passage through the cool flame gases, *i.e.*

$$I_{\nu_R} = I_{\nu_c} + I_{\nu_m} \tag{31}$$

The intensity of radiation from the cool flame can be found from eqn. (8) and is given by

$$I_{\nu_c} = I_{\nu_{oc}}{}^{B} A_{\nu_c} \tag{32}$$

where $I_{\nu_c}{}^{B}$ is the intensity of a black body at frequency ν and flame gas temperature T_c ($I_{\nu_{oc}}{}^{B}$ can be evaluated using eqn. (11)) and A_{ν_c} is the atomic absorptivity at frequency ν, path length L_c, and temperature T_c (A_{ν_c} can be evaluated using eqn. (9)

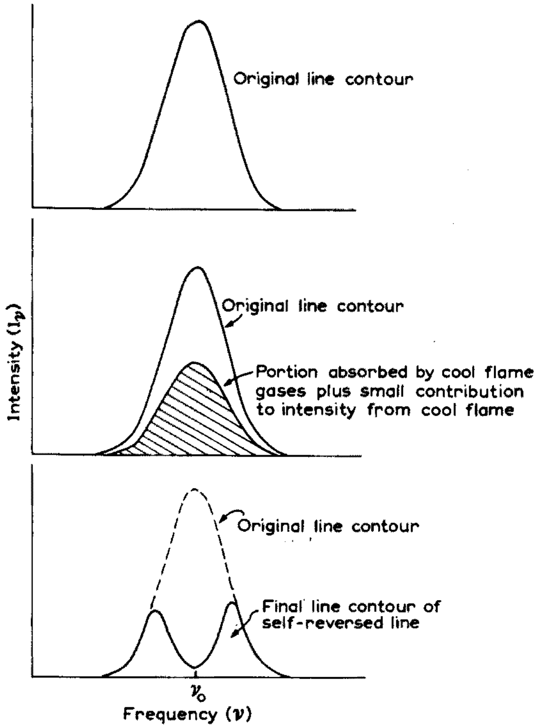


Fig. 4. Schematic representation of effect of self-reversal on spectral line.

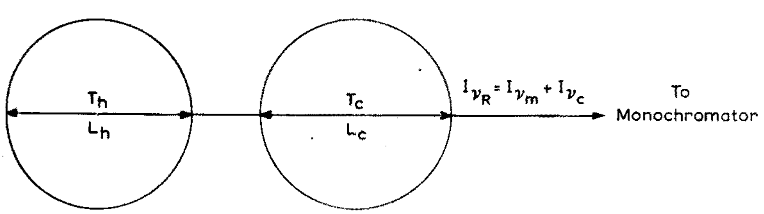


Fig. 5. Schematic representation of flame in which self-reversal can occur.

plus the appropriate expression for k_ν). The modified intensity, I_{ν_m}, is given by

$$I_{\nu_m} = I_{\nu_h} \exp(-k_{\nu_c} L_c) \tag{33}$$

where I_{ν_h} is the intensity from the hot flame, *i.e.*,

$$I_{\nu_h} = I_{\nu_h}{}^{B} A_{\nu_h} \tag{34}$$

where $I_{\nu_h}{}^{B}$ and A_{ν_h} have the same definitions as for $I_{\nu_c}{}^{B}$ and A_{ν_c} except that they are defined for flame temperature T_h, path length L_h and frequency ν. The term k_{ν_c} is the atomic absorption coefficient for the cool vapor, and the entire exponential term of $\exp(-k_{\nu_c} L_c)$ merely corrects for the transmission of the cool flame for radiation from the hot flame. Therefore, the resultant intensity at any frequency ν is given by

$$I_{\nu_R} = I_{\nu_c}{}^{B} A_{\nu_c} + I_{\nu_h}{}^{B} A_{\nu_h} \exp(-k_{\nu_c} L_c) \tag{35}$$

Substituting for $I_\nu{}^{B}$ and A_ν using eqns. (12) and (13), respectively, results in

$$I_{\nu_R} = \frac{2h\nu_0{}^3}{10^7 c^2} \left[1 - \exp(-k_{\nu_c} L_c)\right] \exp(-h\nu_0/kT_c) + \left[1 - \exp(-k_{\nu_h} L_h)\right] \exp(-k_{\nu_c} L_c) (\exp - h\nu_0/kT_h) \tag{36}$$

Equation (36) can be evaluated in terms of N_M by substituting the proper equation for k_ν and for the total intensity I by integrating over the range 0 to ∞ using eqn. (10). However, for reasons given above, this will not be done, but rather the effect of self-reversal on I_{ν_R} and on I will be discussed qualitatively.

Certainly I_{ν_R} can never be as great as I_{ν_h} for a uniformly hot flame gas with a path length of $L_h + L_c$. Also, it can be seen from eqn. (36) that if the atomic concentration is high, then I_{ν_R} can be quite small; in fact, in the extreme case, I_{ν_R} can approach I_{ν_c}, because I_{ν_m} approaches zero at large N_M values. From eqn. (36), it can also be seen that in the other limiting case of very low atomic concentrations, I_{ν_R} can approach $I_{\nu_c} + I_{\nu_h}$, *i.e.*, $\exp(-k_{\nu_c} L_c)$ becomes essentially unity. Although no expression for I for a self-reversed line is given here, it is easy to see that I also decreases as the cool vapor becomes more strongly absorbing, *i.e.*, as N_M increases.

Intensity corresponding to point of intersection of analytical curve

An analytical curve in flame emission spectrometry normally consists of a plot of a photodetector signal *versus* sample concentration. To avoid problems associated with non-linearity of detector response and loss of atoms via incomplete compound dissociation or metal ionization in the hot flame gases, the analytical curve of I *vs.* N_M will be considered here. The point of intersection[6] of the high and low concentration asymptotes occurs at a value of N_{M_i}, where the total intensity given by eqn. (7) just equals the total intensity given by eqn. (30). If these equations are equated and solved for N_{M_i}, then for a resonance line

$$N_{M_i} = \frac{16\pi a \Delta\nu_D g_n}{\sqrt{\ln 2}\, g_m \lambda_0{}^2 A_t L} = 60\, \frac{a \Delta\nu_D g_n}{g_m \lambda_0{}^2 A_t L} \left(\frac{\text{atoms}}{\text{cm}^3}\right) \tag{37}$$

where all values have been previously defined and where the 60 in the second half of the equation is $16\pi/\ln 2$ evaluated. The value of the total intensity at the intersection point, I_i, then is given by substituting eqn. (37) for N_{M_i} into eqn. (7) or (30). Therefore,

I_l for a resonance line is given by

$$I_l = \frac{4a\Delta\nu_D h\nu_0^3}{10^7\sqrt{\ln 2}\, c^2} \exp(-h\nu_0/kT) \left(\frac{\text{watts}}{\text{cm}^2\,\text{ster}}\right) \tag{38}$$

Of course, analytical curves of log I_l *versus* log N_M do not actually consist of two straight segments of slopes 1 and 1/2 which intersect at an I_l equal to eqn. (38) but rather consist of two segments which are straight at great distances from the intersection region but which curve in the region of intersection. Even so, I_l calculated using eqn. (38) allows one to estimate the linear region over which the slope will be approximately unity and the self-absorption region where the slope will be approximately one-half.

Shapes of analytical curves of I vs. N_M

With eqns. (7) and (30), I *vs.* N_M can be plotted. The analytical curve plots of I *vs.* N_M for specified a values will be essentially identical in shape to the famous growth curves of astrophysics[12,20], *i.e.*, growth curves (see Fig. 6) are generally plots of some function of A_T *versus* some function of $N_M fL$; the shape of such curves will be identical to curves of I *vs.* N_M. In fact, from experimental analytical curves, it is possible to calculate values of the a-parameter from the shapes of the curves and from the intersection point of the 2 asymptotes. From values of a and values of $\Delta\nu_c$, values of σ_c^2 can then be calculated. If the flame temperature is accurately known, then $\Delta\nu_D$ can be obtained using eqn. (19). The calculated values of I should be quite accurate for all values of N_M as long as the a-value is between 0.3 and 10; for this range of a-values the greatest error in I will come at the atomic concentration, N_{M_1} (see Fig. 6). Calculated values of I will be subject to considerable errors in the region surrounding the intersection concentration, N_{M_1} for a-values less than 0.3. It should be emphasized

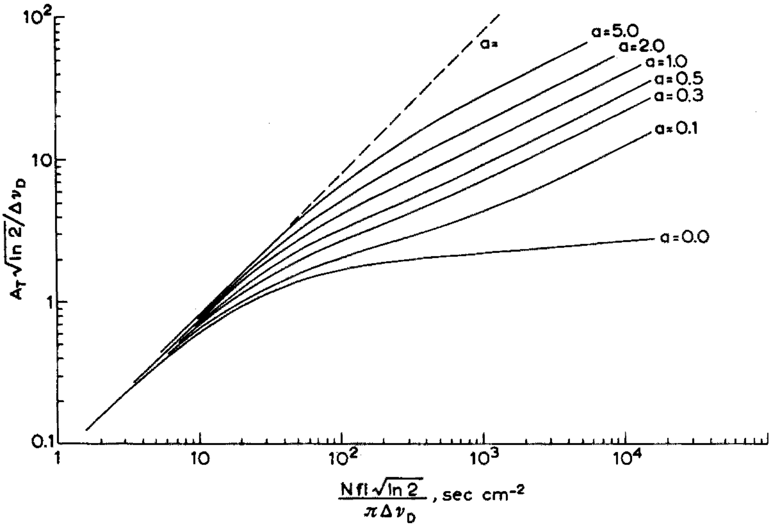


Fig. 6. Shapes of analytical curves.

that eqn. (7) for a dilute atomic gas is exact only for very low atomic concentrations and that eqn. (30) for a concentrated atomic gas is exact only for very high atomic concentrations. However, as long as a is between 0.3 and 10, eqns. (7) and (30) for I should be quite accurate. Values of a measured by KOHN *et al.*[15,16] for the prominent lines of a number of elements in an acetylene–air flame at 2500°K and in an acetylene–nitrous oxide flame at 2760°K are all greater than 0.3 and less than 5. Values of a calculated by an approximation method for a number of elements in acetylene–oxygen and hydrogen–oxygen flames also are greater than 0.3 and less than 5, in nearly all cases. Therefore, the exact evaluation of I using k_ν from eqn. (14) is not usually necessary. The exact evaluation of I can be obtained by substituting in the complete Voigt profile expressions for k_ν from eqn. (14) into eqn. (13) for A_T, integrating by an approximation method, and finding I from eqn. (10). This process is extremely complex and certainly not necessary for this manuscript. It should be pointed out that accurate values of A_T as a function of N_M and for a wide variety of experimental conditions of interest in flame spectrometry ($a = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 1.0, 2.0, 3.0, 4.0, and 5.0 and $N_t L\sqrt{\ln 2}/\pi\Delta\nu_D = 2$ to 9600 sec/cm^2) can be calculated using a computer program described in the thesis of HOLLANDER[18]. In this way, accurate analytical curves of I *vs.* N_M for various a values may be plotted. These curves would coincide with the ones calculated using eqns. (7) and (30) except for a small region near the intersection of the two segments and for some elements at high atomic concentrations where self-reversal may occur if the flame is nonhomogeneous (*i.e.*, if the flame containing the high atomic concentration of emitters is not surrounded by a clear outer flame of approximately the same temperature as the inner flame). Self-reversal will cause the analytical curve of I *vs.* N_M to curve back down at high N_M values.

Therefore, if the spectral parameters of a given line of a given atom are known (ν_0, E_M, g_m, g_n, A_t, $\Delta\nu_D$ and a) and if the flame gas characteristics are known (T and L), then analytical curves of I *vs.* N_M can be accurately calculated (assuming a is between 0.3 and 10) by using eqns. (7) and (30). It should be emphasized, however, that the analytical curves of signal *versus* sample concentration experimentally measured in flame emission spectrometry may deviate greatly from the I–N_M analytical curves for the following reasons[17,18,21–23]: (*a*) the measured signal may not be directly proportional to I (actually this will not be a problem for large values of I); (*b*) the atomic concentration N_M may not be linear with sample concentration, C_M in moles per liter [*i.e.*, if the salt introduced into the flame is not completely dissociated at the flame temperature T, then N_M will not vary linearly with C_M; in addition, if the metal atom, M, undergoes compound formation with flame gas products, such as O, OH, H, etc., then N_M will vary nonlinearly with C_M and will also depend greatly on flame temperature, sample introduction rate, and aspiration efficiency; finally, if the metal atom, M, undergoes ionization, then N_M will vary nonlinearly with C_M and will also depend on the additional factors listed above for compound formation (generally, most salts introduced into flames will be almost completely dissociated for the flame conditions in concern, but most metal atoms are quite prone to ionization at high flame temperatures, particularly if N_M is small and also to compound formation at low temperatures, particularly if N_M is large)]; (*c*) sample flow rate and aspiration efficiency may vary with C_M, particularly at large C_M values, causing N_M to vary nonlinearly with C_M; and (*d*) if the entrance optics consist of a mirror back of the flame to increase the measured signal, curvature in the analytical plot will occur at large values of C_{M} because of absorption of the reflected radiation by the M atoms in the flame.

Intensity of spectral lines of atoms in arcs

The low and high concentration expressions for the total intensity of spectral lines derived in this manuscript should also apply directly to spectral lines of atoms excited in arcs which are in thermal equilibrium and meet the criteria listed above for flames.

Intensity of spectral lines of atoms not in thermal equilibrium

Non-thermal equilibrium in flames exists in the reaction zone of most flames where abnormal excitation occurs. Abnormal excitation is the basis for the analytical technique developed by GILBERT[24] called Chemiluminescence Flame Spectrometry. Non-thermal equilibrium also occurs in spark sources. It is impossible to give exact expressions for the intensity of spectral lines of atoms not in thermal equilibrium unless the type of excitation distribution is known (a Boltzmann distribution applies only to the case where thermal equilibrium exists). However, if the atomic vapor is dilute, the total intensity, I, will still generally[2] be linear with N_{M} no matter what the atomic (or molecular) distribution happens to be.

APPENDIX I

Influence of broadening on the low concentration expression for I

The total intensity, I, of a spectral line is given by eqn. (10), namely,

$$I = I_{\nu_0}{}^{\mathrm{B}} \int_0^\infty A_\nu \mathrm{d}\nu \,. \tag{10}$$

The integral $\int A_\nu \mathrm{d}\nu$ for low values of $k_\nu L$ can be replaced by

$$\int_0^\infty A_\nu \mathrm{d}\nu = \int_0^\infty [1-\exp(-k_\nu L)]\,\mathrm{d}\nu = L\int_0^\infty k_\nu \mathrm{d}\nu \tag{39}$$

According to MITCHELL AND ZEMANSKY[14], the integral of $\int k_\nu \mathrm{d}\nu$ is given by

$$\int_0^\infty k_\nu \mathrm{d}\nu = \frac{\lambda_0{}^2}{8\pi}\,\frac{g_m}{g_n}\,N_{\mathrm{M}}L\left(1 - \frac{g_n}{g_m}\,\frac{N_{\mathrm{M}}{}^*}{N_{\mathrm{M}}}\right) \tag{40}$$

In flame gases, the ratio $N_{\mathrm{M}}{}^*/N_{\mathrm{M}}$ is much, much less than unity and so eqn. (40) is given with good accuracy by

$$\int_0^\infty k_\nu \mathrm{d}\nu = \frac{\lambda_0{}^2 g_m N_{\mathrm{M}} L}{8\pi g_n} \tag{41}$$

Equation (41) is of great importance since it implies that whatever processes are responsible for broadening a spectral line, the integral of the atomic absorption coefficient remains constant when $N_{\mathrm{M}}L$ is a constant. Combination of eqns. (10) and (41) and substitution for $I_{\nu_0}{}^{\mathrm{B}}$ from eqn. (12) results in eqn. (7) for I.

Qualitatively, it can be seen from observing astrophysical growth curves that $\int_0^\infty k_\nu \mathrm{d}\nu$ is a constant whatever the value of a, *i.e.*, whatever the relationship of damping to Doppler broadening; as long as $N_{\mathrm{M}}L$ is small. Therefore, the assumption of pure

Doppler broadening in the black body approach to I is valid as well as being convenient and simple to follow.

This research was sponsored by AFOSR(SRC)-OAR, U.S.A. F. Grant No. AF-AFOSR-1033-66 with supplementary funds from Edgewood Arsenal, Md.

SUMMARY

A unified and well-referenced approach to the derivation of the total intensity of spectral lines of atoms excited by flame in thermal equilibrium is given. Expressions for the total intensity for atoms at low and high concentrations are given. The influence of self-absorption and self-reversal on the spectral line contour and on analytical curves is discussed. Application of the derived equations to emitting atoms in arcs and to molecules in flames is also considered.

RÉSUMÉ

Les auteurs ont examiné la dérivation de l'intensité totale des lignes spectrales d'atomes excités par flamme en équilibre thermique. Des expressions sont données pour l'intensité totale d'atomes à faibles et fortes concentrations. On considère également une application d'équations dérivées pour les atomes émis dans les arcs et les molécules dans les flammes.

ZUSAMMENFASSUNG

Es wird eine Näherung angegeben für die Ableitung der Gesamtintensitäten von Spektrallinien von in der Flamme bei thermischem Gleichgewicht angeregten Atomen sowohl für niedrigere als auch hohe Konzentrationen. Der Einfluss der Selbstabsorption und Selbstumkehr auf die Spektrallinienform und die analytischen Kurven wird diskutiert. Die Anwendung der abgeleiteten Gleichungen auf emittierende Atome in Bögen und auf Moleküle in Flammen wird geprüft.

REFERENCES

1 C. T. J. ALKEMADE, in E. R. LIPPINCOTT AND M. MARGOSHES, *Proc. Xth Colloquium Spectroscopicum Internationale*, Spartan Books, Washington, D. C., 1963, pp. 143–170.
2 R. MAVRODINEANU AND H. BOITEUX, *Flame Spectroscopy*, John Wiley, New York, 1964.
3 R. HERRMANN AND C. T. J. ALKEMADE, *Flammenphotometrie*, 2nd Edn., Springer Verlag, Berlin, 1960; *Chemical Analysis by Flame Photometry*, translated by P. T. GILBERT, John Wiley, New York, 1963.
4 J. D. WINEFORDNER, *Appl. Spectry.*, 17 (1963) 109.
5 G. HERZBERG, *Atomic Spectra and Atomic Structure*, Dover Publications, New York, 1944.
6 J. D. WINEFORDNER, T. J. VICKERS AND L. D. REMINGTON, *Anal. Chem.*, 37 (1965) 1216.
7 S. S. PENNER, *Quantitative Molecular Spectroscopy and Gas Emissivities*, Addison–Wesley, Reading, Mass., 1959.
8 M. BORN, *Optik*, Springer Verlag, Berlin, 1933.
9 R. D. COWAN AND G. H. DIEKE, *Rev. Mod. Phys.*, 20 (1948) 418.
10 A. C. KOLB AND E. R. STREED, *J. Chem. Phys.*, 20 (1952) 1872.
11 H. M. STRONG, F. P. BUNDY AND D. A. LARSON, *Third Symposium on Combustion Flame, and Explosion Phenomena*, Williams and Wilkins, Baltimore, Md., 1949, pp. 641–647.
12 A. UNSÖLD, *Physik der Sternatmosphären*, Springer Verlag, Berlin, 1955.
13 N. S. POLUEKTOV, *Techniques in Flame Photometric Analysis*, translated by C. N. TURTON AND T. I. TURTON, Consultants Bureau, New York, 1961.

14 A. C. G. MITCHELL AND M. W. ZEMANSKY, *Resonance Radiation and Excited Atoms*, University Press, Cambridge, 1961.
15 E. HINNOV AND H. KOHN, *J. Opt. Soc. Am.*, 47 (1957) 156.
16 F. W. HOFMANN AND H. KOHN, *J. Opt. Soc. Am.*, 51 (1961) 512.
17 C. T. J. ALKEMADE, *A Contribution to the Development and Understanding of Flame Photometry*, Ph.D. thesis, University of Utrecht, The Netherlands, 1954.
18 T. HOLLANDER, *Self-Absorption, Ionization and Dissociation of Metal Vapor in Flames*, Ph.D. thesis, University of Utrecht, The Netherlands, 1964.
19 M. DANOS AND S. GESCHWIND, *Phys. Rev.*, 91 (1953) 1159.
20 V. A. AMBARTSUMYAN, *Theoretical Astrophysics*, Pergamon Press, London, 1958.
21 T. J. VICKERS, *The Calculation of Limits of Detectability and Optimum Conditions for Atomic Emission and Absorption Flame Spectrometry*, Ph.D. thesis, University of Florida, Gainesville, Florida, 1964.
22 L. D. REMINGTON, *Factors which Influence the Signal-to-Noise Ratio in Atomic Emission Flame Spectrometry*, Ph. D. thesis, University of Florida, Gainesville, Florida, 1966.
23 T. J. VICKERS, L. D. REMINGTON AND J. D. WINEFORDNER, *Anal. Chim. Acta*, 36 (1966) 42.
24 P. T. GILBERT, JR., in E. R. LIPPINCOTT AND M. MARGOSHES, *Proc. Xth Colloquium Spectroscopicum Internationale*, Spartan Books, Washington, D. C., 1963, pp. 171–215.

SOME CAUSES OF BENDING OF ANALYTICAL CURVES IN ATOMIC EMISSION FLAME SPECTROMETRY*

T. J. VICKERS
Physical Sciences Laboratory, Directorate of Research and Development, U. S. Army Missile Command, Redstone Arsenal, Ala. (U.S.A.)
L. D. REMINGTON
Asheville-Biltmore College, Asheville, N. C. (U.S.A.)
AND
J. D. WINEFORDNER
Department of Chemistry, University of Florida, Gainesville, Fla. (U.S.A.)

(Received February 15th, 1966)

Recently papers have appeared elucidating some of the causes of bending of analytical curves in atomic absorption flame spectrometry[1,2]. Surprisingly little has been published concerning the causes of bending of analytical curves in the older flame analytical technique, atomic emission flame spectrometry. It is well known that self-absorption, incomplete dissociation, ionization, and compound formation all play a part in determining the shape of atomic emission analytical curves, and several authors[3-5] have, at least qualitatively, discussed these effects. It is less well recognized that other spectral and instrumental factors also play a part.

In this paper equations are developed by which a number of factors affecting the shape of atomic emission analytical curves can be quantitatively considered. These factors include self-absorption, ionization, compound formation, variation in solution flow rate and atomization efficiency, entrance optics, and the effect of measuring spectral line multiplets.

Self-absorption

The most important and the most readily discussed factor in accounting for the bending of analytical curves in atomic emission flame spectrometry is that of self-absorption. At low concentrations the emitted intensity of a spectral line in a flame, I_L, assuming thermal equilibrium, is given[6] by

$$I_L = \frac{10^{-7}}{4\pi} h\nu_0 \frac{g_u}{B(T)} N A_t L \exp(-E_u/kT) \qquad (1)$$

where I_L is the integrated intensity in watts/cm^2 ster, h is Planck's constant in erg-sec, ν_0 is the frequency at the line center in sec^{-1}, g_u is the statistical weight of the upper state (no units), $B(T)$ is the partition function over all states (no units), N is the

---

* This paper was taken in part from the Ph.D. thesis of T. J. VICKERS, *The Calculation of Limits of Detectability and Optimum Conditions for Atomic Emission and Atomic Absorption Flame Spectrometry*, University of Florida, April, 1964.

atomic concentration in atoms/cm^3 of flame gases, A_t is the transition probability in sec^{-1}, L is the flame thickness viewed by the monochromator in cm, E_u is the excitation energy of the upper state in eV, k is the Boltzmann constant ($8.62 \cdot 10^{-5}$ eV °K^{-1}), T is the flame temperature in °K, and the 10^{-7} factor is needed to convert ergs/sec to watts. At low atomic concentrations, for a given spectral line and constant flame conditions, the intensity is directly proportional to N, and the slope of a curve plotting logarithm of intensity *versus* logarithm of N would be 1. At high concentrations, where self-absorption occurs, the emitted intensity is given[6] by

$$I_H = \frac{10^{-7} h\nu_0{}^2}{c} \exp(-E_u/kT) \left\{ \frac{\Delta\nu_D g_u}{\pi\sqrt{\ln 2}\, B(T)} \, aNA_tL \right\}^{\frac{1}{2}} \tag{2}$$

where I_H is the integrated intensity in watts/cm^2 ster, c is the speed of light in cm/sec, $\Delta\nu_D$ is the Doppler half-width of the absorbing line in sec^{-1}, and a is the damping constant (no units) which accounts for line broadening other than Doppler broadening. At high concentrations, for a given spectral line and constant flame conditions, the intensity is directly proportional to $N^{\frac{1}{2}}$, and the slope of a curve in which logarithm of intensity, I_H, *versus* logarithm of N is plotted would be $\frac{1}{2}$. The effect of self-absorption on the shape of analytical curves may be accounted for by use of the proper intensity expression, eqn. (1) or eqn. (2). WINEFORDNER, VICKERS AND REMINGTON[7] have equated eqns. (1) and (2) in order to find the atomic concentration corresponding to the point of intersection of the high and low concentration asymptotes of the *I vs. N* analytical curve.

Incomplete dissociation of salt introduced and ionization and compound formation of atomic species in the flame gases

Other factors than self-absorption can also affect the shape of experimental curves. Experimentally measured intensity, or more often, some measured quantity proportional to intensity, *versus* solution concentration of the species of interest is plotted. The atomic concentration, N, is dependent not only on the solution concentration, C, but also on such effects as incomplete dissociation of the salt introduced into the flame, ionization of the atomic species and compound formation of the atomic species with flame gas products, such as O, OH, H, etc. An expression relating N to C has been given by WINEFORDNER AND VICKERS[8]. In slightly altered form, this equation is

$$\frac{N}{\beta} = 3 \cdot 10^{21} \left(\frac{n_{298} \varepsilon C \phi}{n_T Q T} \right) \tag{3}$$

where ϕ is the solution flow rate in cm^3/min, n_{298} is the moles of flame gas present at 298°K, n_T is the moles of flame gas products at flame temperature T, Q is the flow rate of unburned gases in cm^3/sec, ε is the atomization efficiency (no units), and β is a factor (no units) to account for atomic losses due to ionization and incomplete dissociation of the salt introduced and compounds formed between the atomic species of interest and various flame gas products.

In the discussion to follow, it will be more convenient to relate C to P_T, the total pressure in atmospheres of the species of interest present in all forms, *i.e.*, in the atomic, molecular, and ionic forms. The term N/β is the total concentration, N_T, in particles/cm³, of the species of interest in all forms. Because N_T is small compared to the concentration of flame gas products for most flame spectrometric studies, N_T may be related to P_T by means of the ideal gas expression[5], $P_T = N_T kT$, where P_T is in atmospheres, k is the Boltzmann constant in cm³-atm/°K ($1.38 \cdot 10^{-22}$), and T is the flame temperature in °K. The desired expression is, therefore,

$$P_T = \frac{3 \cdot 10^{21} k \phi n_{298} \varepsilon C}{Q n_T} \tag{4}$$

For a given value of P_T, the equilibrium concentration of atoms of the species of interest present in the flame is dependent upon the dissociation of the aspirated salt, the formation of compounds with the flame gases, and ionization of the species of interest. If chemical equilibrium is assumed in the flame (this assumption should be valid for the outer cone of most flames used in flame spectrometry), it is possible to calculate the concentration of atoms of the species of interest present in the flame by consideration of the processes of dissociation, ionization, and compound formation. The required equations will be derived for a *sample case* in which both ionization and the formation of a flame gas compound must be considered, that is, the case in which an aqueous solution of sodium chloride is aspirated into the flame. However, only one flame gas compound, namely, NaOH, must be considered[9].

The following equilibria expressions and their corresponding material balance expressions for sodium aspirated into flame gases as sodium chloride may be written as shown below. The dissociation of the aspirated salt, is given by

$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na} + \mathrm{Cl}$$

and has an equilibrium constant K_1 given by

$$K_1 = \frac{p_{\mathrm{Na}} p_{\mathrm{Cl}}}{p_{\mathrm{NaCl}}} \tag{5}$$

where p_{Na}, p_{Cl}, and p_{NaCl} are the partial pressures in atmospheres of Na, Cl, and NaCl, respectively. Assuming that Cl in the flame comes only from the dissociation of the salt, and that the pressure of HCl formed in the flame gases is a small fraction of the total pressure of Cl in the flame, and further assuming that $p_{\mathrm{NaCl}} \ll P_T$, then p_{Cl} is given by

$$p_{\mathrm{Cl}} = P_T - p_{\mathrm{NaCl}} \cong P_T \tag{6}$$

When using H_2/O_2, H_2/air, and C_2H_2/O_2 flames, aspiration rates less than about 3 ml/min, and HCl concentrations less than approximately 0.2 M, 3.2 M and 14 M, respectively, for the 3 flames (see Appendix), the above assumptions are valid. The stability of HCl is low[10], and so dissociation (see Appendix) should be nearly complete. The stability of NaCl, as will be evident, is also low, and so the assumption $p_{\mathrm{NaCl}} \ll P_T$ is also valid. Substituting for p_{Cl} in eqn. (5) and solving for p_{NaCl} gives

$$p_{\mathrm{NaCl}} = \frac{p_{\mathrm{Na}} P_T}{K_1} \tag{7}$$

For the ionization reaction, the equilibrium is

$$\mathrm{Na} \rightleftharpoons \mathrm{Na}^+ + e^-$$

and the equilibrium constant, K_2, is given by

$$K_2 = \frac{(p_{\mathrm{Na}^+})P_e}{p_{\mathrm{Na}}} \tag{8}$$

where p_{Na^+} is the partial pressure in atmospheres of sodium ions in the flame, and P_e is the partial pressure in atmospheres of electrons in the flame. The partial pressure of electrons in the flame is the sum of the partial pressures of electrons due to ionization of the flame gases and due to ionization of the metal, *i.e.*,

$$P_e = p_e + p_{\mathrm{Na}^+} \tag{9}$$

where p_e is the partial pressure in atmospheres of the flame gas electrons, and may include electrons due to ionization of metals other than sodium introduced with the NaCl sample. Substituting for P_e in eqn. (8) gives

$$K_2 = \frac{(p_{\mathrm{Na}^+})p_e + (p_{\mathrm{Na}^+})^2}{p_{\mathrm{Na}}} \tag{10}$$

Solving for p_{Na^+} by the quadratic expression gives

$$p_{\mathrm{Na}^+} = \frac{-p_e + (p_e^2 + 4K_2 p_{\mathrm{Na}})^{\frac{1}{2}}}{2} \tag{11}$$

For the dissociation reaction of the flame gas compound NaOH,

$$\mathrm{NaOH} \rightleftharpoons \mathrm{Na} + \mathrm{OH}$$

the equilibrium constant K_3 is given by

$$K_3 = \frac{p_{\mathrm{Na}} p_{\mathrm{OH}}}{p_{\mathrm{NaOH}}} \tag{12}$$

where p_{OH} and p_{NaOH} are the partial pressures in atmospheres of OH and NaOH, respectively, present in the flame. Solving for p_{NaOH} gives

$$p_{\mathrm{NaOH}} = \frac{p_{\mathrm{Na}} p_{\mathrm{OH}}}{K_3} \tag{13}$$

Because P_T is the total pressure in atmospheres of the species of interest present in all forms, P_T is given by the material balance expression of

$$P_T = p_{\mathrm{Na}} + p_{\mathrm{Na}^+} + p_{\mathrm{NaCl}} + p_{\mathrm{NaOH}} \tag{14}$$

It may appear that the forms of NaH and NaO should also be present in eqn. (14), but it was theoretically verified from the dissociation constants of NaH and NaO that even in flames of relatively large partial pressures of H and O, the NaH and NaO species are essentially completely dissociated. The influence of H atoms from the flame gases on the formation of HCl in the flame has not been considered, because, as will be shown, the dissociation of NaCl is essentially complete, and this effect will not produce any changes in the results of the theory. In the Appendix, the effect of introduction of an excess of Cl into the flame is considered, *i.e.*, introduction of NaCl into the flame in the presence of HCl. Substituting for p_{NaCl}, p_{Na^+}, and p_{NaOH} from eqns. (7), (11), and (13), results in the following expression for P_T

$$P_T = p_{Na} + \frac{-p_e + (p_e^2 + 4K_2 p_{Na})^{\frac{1}{2}}}{2} + \frac{p_{Na} P_T}{K_1} + \frac{p_{Na} p_{OH}}{K_3} \tag{15}$$

Clearing fractions and combining terms results in the expression below.

$$2(K_1K_3 + K_3P_T + K_1p_{OH})p_{Na} + K_1K_3(p_e^2 + 4K_2p_{Na})^{\frac{1}{2}} - K_1K_3(2P_T + p_e) = 0 \tag{16}$$

In order to use eqn. (16), the equilibrium constants K_1, K_2, and K_3 must be known at several temperatures over the temperature ranges of the flames of interest. The partial pressure of OH, p_{OH}, and the partial pressure of flame gas electrons, p_e, must also be known for the flames of interest. These factors, p_{OH} and p_e, are characteristic of the particular flames and vary somewhat with temperature. However, in the calculations to follow, p_{OH} and p_e will be assumed to be constant over the temperature range of a particular flame.

Solving eqn. (16) for p_{Na} for a particular flame and a number of values of P_T is somewhat tedious (a graphical method seems to be the easiest), but fortunately *two limiting cases*, which are of practical importance, may be noted in which eqn. (16) can be greatly simplified. In most of the calculations reported in this paper, one or the other of the simplified forms can be used.

Case I. If ionization of the sodium atoms is unimportant, *i.e.*, $p_e^2 \gg 4K_2p_{Na}$, then eqn. (16) becomes

$$(K_1K_3 + K_3P_T + K_1p_{OH})p_{Na} - K_1K_3P_T = 0 \tag{17}$$

which is readily solved for p_{Na}

$$p_{Na} = \frac{K_1K_3P_T}{K_1K_3 + K_3P_T + K_1p_{OH}} \tag{18}$$

Case II. If the partial pressure of flame gas electrons becomes negligible when compared to those produced by ionization of the metal, then $(4K_2p_{Na})^{\frac{1}{2}} \gg p_e$, and so eqn. (16) becomes

$$(K_1K_3 + K_3P_T + K_1p_{OH})p_{Na} + K_1K_3K_2^{\frac{1}{2}}p_{Na}^{\frac{1}{2}} - K_1K_3P_T = 0 \tag{19}$$

Equation (19) is in the form of a quadratic expression. Solving for $p_{Na}^{\frac{1}{2}}$ and squaring eqn. (19) gives

$$p_{Na} = \left\{\frac{-K_1K_3K_2^{\frac{1}{2}} + [(K_1K_3K_2^{\frac{1}{2}})^2 + 4(K_1K_3 + K_3P_T + K_1p_{OH})K_1K_3P_T]^{\frac{1}{2}}}{2(K_1K_3 + K_3P_T + K_1p_{OH})}\right\}^2 \tag{20}$$

The partial pressure in atmospheres of Na, p_{Na}, can be converted by the ideal gas expression[5] to N, the atomic concentration of Na in the flame in atoms/cm³, *i.e.*,

$$N = p_{Na}/kT \tag{21}$$

where k is the Boltzmann constant in cm³-atm/°K. Therefore, multiplying either eqn. (16), eqn. (18), or eqn. (20) by $1/kT$ allows the calculation of N as a function of temperature for a number of flame types and a number of values of P_T (and because P_T is related to the solution concentration by eqn. (4), N can be calculated at any value of solution concentration).

The results of the calculation of N are shown in Fig. 1, where log N is plotted *versus* T for 7 values of P_T and 3 different flame types. From Fig. 1, the effects of compound dissociation and ionization may be seen, as well as how these competing factors change with P_T and with flame type. As P_T increases, the maxima of the curves, *i.e.*, the temperature at which ionization becomes more important than further compound dissociation, shift to higher temperatures. As p_{OH} decreases, *e.g.*, in going from the C_2H_2/O_2 flame to the H_2/O_2 flame, the maxima of the curves are seen to appear at lower temperatures.

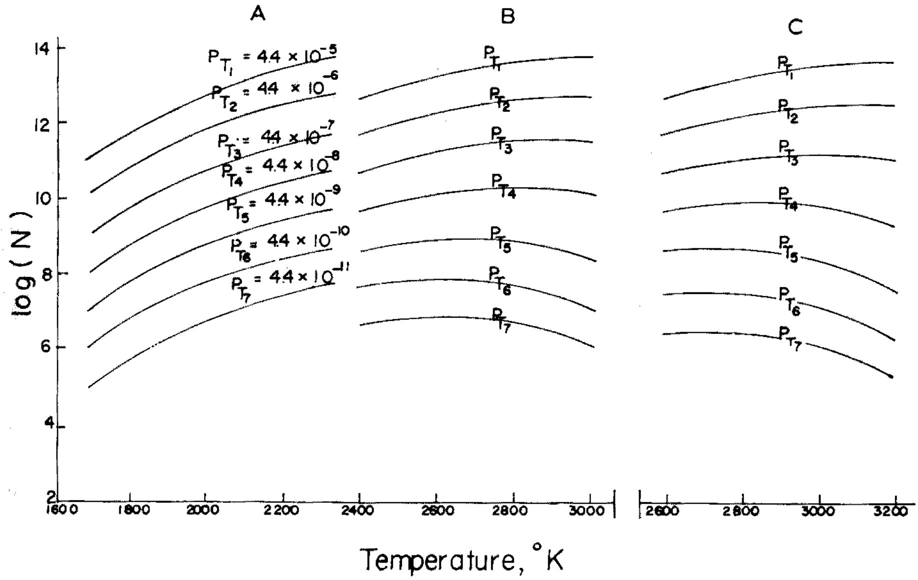


Fig. 1. Variation of atomic concentration, N, with flame temperature, T, and with total pressure of species of interest in all forms, P_T. P_e, $4 \cdot 10^{-9}$ atm. for A, B, C plots. (A) H_2/air; P_{OH}, 0.001 atm; (B) H_2/O_2; P_{OH}, 0.05 atm; (C) C_2H_2/O_2; P_{OH}, 0.2 atm.

In all the calculations whose results are shown in Fig. 1, the concentration of the compound NaCl was found to be completely negligible with respect to the concentration of NaOH in the flame. The results shown in Fig. 1 would be exactly the same if other salts, such as sodium nitrate and sodium perchlorate, with dissociation constants similar to sodium chloride, were chosen as the aspirated species.

Using N values from Fig. 1, it is possible for a given flame and flame temperature to calculate intensity as a function of P_T by eqn. (1) or (2). However, such calculations require knowledge of the intersection concentration, N_i, of the analytical curve. An expression has previously been given[7] which allows calculation of the approximate atomic concentration at which self-absorption becomes important

$$N_i = \frac{16\pi a \Delta\nu_D B(T)}{\sqrt{\ln 2}\, A_t L \lambda_0^2 g_u} \qquad (22)$$

For N values less than N_i, the intensity should be calculated from eqn. (1); for N values greater than N_i, the intensity should be calculated from eqn. (2).

Variation of solution flow rate and sample introduction efficiency

To obtain intensities as a function of solution concentration, it is only necessary to convert P_T to C by using eqn. (4). From eqn. (4), it may be seen that 2 other factors may have a small effect on the shape of analytical curves. If the sample introduction efficiency, ε, and the solution flow rate, ϕ, vary with concentration, they affect the proportionality between P_T and C, and hence ε and ϕ can affect the linearity of the analytical curve, although these effects are small compared to the effects mentioned in the previous sections.

Entrance optics and the effect of multiple lines

Generally in plotting analytical curves, intensity is not plotted but rather some measured quantity proportional to intensity, such as needle deflection on a meter. Hence, it is possible for instrumental factors to affect the shape of the analytical curve. WINEFORDNER AND VICKERS[8] have previously derived an expression relating emission intensity to the signal at the photodetector:

$$i = \kappa\gamma T_t IWH(A/F^2)n \tag{23}$$

where i is the photoanodic current in amperes for the photodetector, γ is the photosensitivity factor in amperes at the photoanode to watts of incident radiation at the photocathode, T_t is the transmission factor of the optical system including the monochromator and entrance optics, I is the integrated intensity (as given by eqn. (1) or (2)) in watts/cm^2 ster, W is the slit width in cm, H is the slit height in cm, A/F^2 is the number of steradians (no units) viewed by the monochromator, where A is the effective aperture of the monochromator in cm^2 and F is the focal length of the collimator (mirror or lens) in cm, n is the entrance optics factor (no units), and κ is the slit function parameter (no units).

Neglecting faults in the apparatus, such as stray light reaching the detector or saturation of the photodetector, only 2 factors in eqn. (23) can affect the shape of the analytical curve. The first is the entrance optics factor, n. This factor is the number of solid angles of value A/F^2 which are gathered into a single angle by means of a suitable arrangement of entrance optics. Almost all suggested systems[11] for increasing the intensity of radiation incident upon the spectrometric system require one or more passages of the radiation through the flame. For example, if a mirror is placed behind the flame in such a way as to focus an additional image of the flame on the entrance slit, then the incident intensity is increased by $n = 1 + R_t T_m$, where R_t is the reflectance of the mirror, and T_m is the transmittance of the flame for the spectral line of interest. As N increases, T_m decreases, and n decreases. Thus for this optical arrangement, and for all optical arrangements requiring one or more passages of the radiation through the flame before entering the spectrometric system, the proportionality between i and I and the shape of the analytical curve is affected by the variation of n with concentration.

The second factor in eqn. (23) which affects the shape of the experimental analytical curve is κ. This parameter accounts for the position of the spectral line with respect to the slit function distribution curve[12]. For equal entrance and exit slits the distribution curve is triangular, and the slit function parameter is given[12] by

$$\kappa = 1 - \frac{|\lambda - \lambda_0|}{s} \tag{24}$$

where λ is the wavelength setting of the monochromator, λ_0 is the wavelength of the line center, and s is the spectral band width of the monochromator. The units must be the same for λ, λ_0 and s. For monochromator wavelengths greater than λ_0+s and less than λ_0-s, κ is zero. If the monochromator has sufficient resolution to isolate a single, sharp spectral line, then the values of κ can be made equal to unity by adjusting the monochromator wavelength, λ, to the peak wavelength of the spectral line, λ_0. If more than one line lies within the spectral band width, then eqn. (23) must be altered to read

$$i = T_f WH(A/F^2)n\ \Sigma\, \kappa_j \gamma_j I_j \tag{25}$$

where the summation is over all spectral components passed by the monochromator. Because all components will not be passed centrally through the exit slit, κ_j, the slit function for each spectral component will be less than unity for each line.

The intensity of each of the spectral components in eqn. (25) is given by eqn. (1) or (2), depending on the concentration region. Generally speaking, the intensities of the components of a multiplet will differ only in the values of the statistical weights because ν_0, A_t, and E_u can be assumed to be the same for all closely spaced components of a multiplet. Also the photosensitivity factor, γ, can usually be assumed to be the same for all spectral components.

For 2 spectral components, such as one encounters with the Na 5890, 5896 Å doublet when using the Beckman DU, eqn. (25) becomes

$$i = \gamma T_f WH(A/F^2)n(\kappa_x I_x + \kappa_y I_y) \tag{26}$$

where x and y refer to the individual spectral components of the doublet. For low atomic concentrations, substituting for I_x and I_y from eqn. (1), the photo-anodic current is given by

$$i = \gamma T_f WH(A/F^2)n\ \frac{10^{-7} h\nu_0 N A_t L \exp(-E_u/kT)}{4\pi B(T)}\ (\kappa_x g_x + \kappa_y g_y) \tag{27}$$

where g_x and g_y are the statistical weights of the upper state of spectral components x and y. For high concentrations, substituting for I_x and I_y from eqn. (2), one obtains

$$i = \gamma T_f WH(A/F^2)n\ \frac{h\nu_0^2}{10^7 c}\ \exp(-E_u/kT) \left\{\frac{\Delta\nu_D a N A_t L}{\pi\sqrt{\ln 2}\ B(T)}\right\}^{\frac{1}{2}} [\kappa_x (g_x)^{\frac{1}{2}} + \kappa_y (g_y)^{\frac{1}{2}}] \tag{28}$$

From eqns. (27) and (28), it may be seen that since the κ and g terms do not vary with concentration, the slopes of the analytical curve in the high and low concentration regions are not affected by multiple lines being passed by the spectrometric system. However a special problem may occur if one or more of the spectral components lies near the extremes of the slit distribution curve. In this case, κ could vary with concentration if the line width of the spectral components varies with concentration. The shape of the measured analytical curve is then altered because the observed point at which self-absorption becomes important is different for multiple lines than for a single line passed by the monochromator[7]. The expression for the atomic concentration at which self-absorption just becomes important for multiple lines, analogous to eqn. (22), may be obtained by equating expressions (27) and (28) (at $N = N_i$) for the measured signal in the high and low concentration region. Upon solving for N_i, one obtains

$$N_i = \frac{16\pi B(T) \Delta\nu_D a [\kappa_x (g_x)^{\frac{1}{2}} + \kappa_y (g_y)^{\frac{1}{2}}]^2}{A_t L \lambda_0^2 \sqrt{\ln 2}\ (\kappa_x g_x + \kappa_y g_y)^2} \tag{29}$$

Thus, for 2 spectral components passed by a monochromator, for N values less than N_i as calculated from eqn. (29), the measured analytical curve is most accurately described by eqn. (27); for N values greater than N_i, the measured analytical curve is most accurately described by eqn. (28).

Comparison of experimental and theoretical analytical curves

In Fig. 2, experimental analytical curves are compared with curves calculated from the expressions derived in this paper. The experimental curves were obtained by recording the photodetector output signal for a wide range of solution concentrations of sodium chloride in water. The experimental curves were determined on a Beckman DU with the spectral energy recording attachment. Analytical curves were determined for 3 flames with conditions as noted on the curves. The analytical curves shown in Fig. 2 are average curves for quadruplicate measurements. The Beckman flame housing attachment was used throughout, but the mirror in the housing was blocked so that only radiation coming directly from the flame entered the spectrometric system.

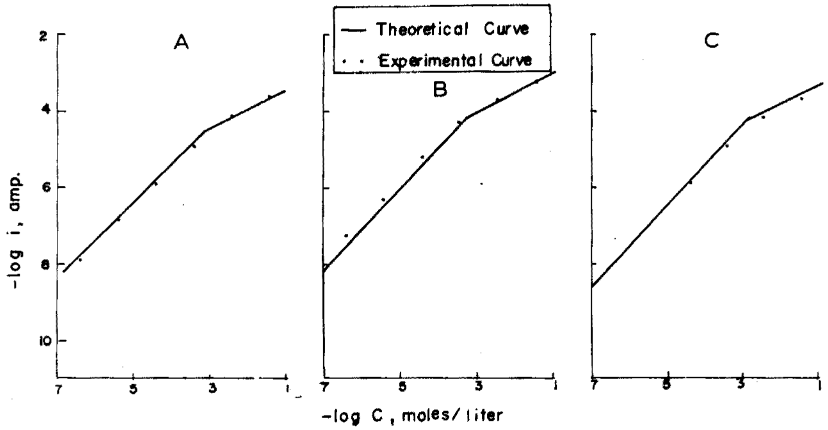


Fig. 2. Calculated and experimental analytical curves for Na-5890-6 Å doublet for NaCl introduced into 3 different flame types. ε, 0.5; L, 1 cm for A, B, C plots. (A) Φ_{H_2}, 9000 cm³/min; Φ_{air}, 4500 cm³/min; ϕ, 1.7 cm³/min; T, 2700°K. (B) Φ_{H_2}, 10000 cm³/min; Φ_{O_2}, 5860 cm³/min; ϕ, 2.0 cm³/min; T, 2500°K. (C) $\Phi_{C_2H_2}$, 1800 cm³/min; Φ_{O_2}, 4500 cm³/min; Φ = 1.7 cm³/min; T, 2700°K.

The theoretical curves were calculated using eqns. (27), (28), and (29). Choosing temperatures corresponding to the experimental flames, values of N as a function of P_T were read from Fig. 1. For N less than N_i (as calculated from eqn. (29)), i was calculated from eqn. (27); for N greater than N_i, i was calculated from eqn. (28). Values of κ were calculated using $\lambda = 5892$ Å and $s = R_d W$, where R_d is the reciprocal linear dispersion of the monochromator in mμ/cm ($R_d = 330$ mμ/cm at 5890 Å). The slit widths used were 0.045 cm for H_2/air, 0.017 cm for H_2/O_2, and 0.006 cm for C_2H_2/O_2. The P_T values, from Fig. 1, were converted to solution concentration, C, in moles/liter, using eqn. (4). Values of ϕ, Q, n_{298}, n_T, and ε used were those indicated by experimental conditions on the curves in Fig. 2.

After conversion of P_T values, the calculated analytical curves are in terms of signal in amperes at the photoanode of the photodetector as a function of solution concentration in moles per liter. The experimental analytical curves are in terms of peak heights in inches on the chart paper as a function of solution concentration in moles per liter. To compare directly the shapes of the measured and calculated curves, all the measured peak height values were multiplied by a constant factor to move the entire curves vertically and give the best fit of the two sets of curves. The same factor was used for all flame conditions. Agreement as to shape and slope of the theoretical and experimental curves for all three flames is quite good, as may be seen in Fig. 2.

Calculations and required data

The equilibrium constant for the dissociation of sodium chloride, K_1, as a function of temperature, was calculated from the expression given by MAVRODINEANU AND BOITEUX[13],

$$\log K_1 = -5040\,\frac{D_{\mathrm{NaCl}}}{T} + \frac{3}{2}\log T + \log\left(1 - 10^{-0.625\omega_e/T}\right) + i_{\mathrm{Na}} + i_{\mathrm{Cl}} - i_{\mathrm{NaCl}} \qquad (30)$$

where D_{NaCl} is the dissociation energy of NaCl in eV, ω_e is the vibrational constant[9] of the molecule in cm^{-1}, and i_{Na}, i_{Cl}, and i_{NaCl} are the chemical constants of Na, Cl, and NaCl, respectively. For a monatomic gas (either Na or Cl) the chemical constant is given[13] by

$$i_{\mathrm{M}} = -1.587 + \frac{3}{2}\log M_a + \log g_0 \qquad (31)$$

where M_a is the atomic mass of the species of interest and g_0 is the statistical weight of the ground state of the atom. For a diatomic gas, such as NaCl, the chemical constant is given[13] by

$$i_{\mathrm{NaCl}} = -1.738 + \frac{3}{2}\log M_{\mathrm{NaCl}} + \log g_0^* - \log B_e \qquad (32)$$

where M_{NaCl} is the molecular weight of NaCl, g_0^* is the statistical weight of the ground state of the molecule, and B_e is the rotational constant in cm^{-1} of the molecule. The equilibrium constant for the ionization reaction, K_2, as a function of temperature was also calculated from an expression given by MAVRODINEANU AND BOITEUX[13],

$$\log K_2 = -5040\ V/T + 5/2\log T + \log g_0' - \log g_0 - 6.1818 \qquad (33)$$

where V is the ionization energy of the atom in eV, g_0 is the statistical weight of the ground state of the neutral atom (no units), and g_0' is the statistical weight of the ground state of the ion (no units). The equilibrium constant for the dissociation of NaOH, K_3, as a function of temperature is obtained from the thermochemical data given in the JANAF tables[10]. The values found for K_1, K_2, and K_3 are summarized in Table I.

The partial pressure of flame electrons, p_e, was taken to be $4 \cdot 10^{-9}$ atm[14] in the outer cones of all 3 flames. The partial pressures of OH in the various flames were estimated from the information given by ZAER[15], and p_{OH} was assumed constant over the temperature range of the individual flames. In estimating the values of p_{OH}, it was necessary to take into account the solvent being aspirated into the flame because the solvent contributes a large portion of the flame gases. For the C_2H_2/O_2 flame, p_{OH} was estimated to be 0.2 atm. In the H_2/O_2 and H_2/air flames, p_{OH} was

TABLE I

VALUES OF K_1, K_2 AND K_3 AS A FUNCTION OF T

T(°K)	K_1 (atm)	K_2 (atm)	K_3 (atm)
1600	$4.4 \cdot 10^{-7}$	$2.5 \cdot 10^{-15}$	$1.3 \cdot 10^{-7}$
2000	$9.1 \cdot 10^{-5}$	$6.4 \cdot 10^{-12}$	$4.1 \cdot 10^{-5}$
2400	$3.2 \cdot 10^{-3}$	$1.5 \cdot 10^{-9}$	$2.0 \cdot 10^{-3}$
2800	$4.2 \cdot 10^{-2}$	$7.4 \cdot 10^{-8}$	$3.1 \cdot 10^{-2}$
3200	$1.4 \cdot 10^{-1}$	$1.6 \cdot 10^{-6}$	$2.5 \cdot 10^{-1}$

estimated to be, respectively, 0.05 atm and 0.001 atm. Atomization efficiencies and flame temperatures were estimated from work performed in this laboratory[16,17].

In calculating N_1 from eqn. (29), the value of a was taken from data given by HINNOV AND KOHN[18] and $B(T)$ was found to be equal to g_0, the statistical weight of the ground state of Na. Spectral data, such as E_u and g_0, were taken from the LANDOLT–BÖRNSTEIN tables[19]. Transition probabilities, A_t, were taken from data given by CORLISS AND BOZMAN[20]. The Doppler half-width, $\Delta\nu_D$, was calculated from the expression[21] below

$$\Delta\nu_D = \frac{2\sqrt{2R \ln 2}}{c}\, \nu_0 \left(\frac{T}{M_a}\right)^{\frac{1}{2}} \tag{34}$$

where R is the gas constant in ergs/mole °K, c is the speed of light in cm/sec, T is the absolute temperature in °K, and M_a is the atomic weight in atomic mass units of the species of interest.

The values used in the calculations were then taken as follows: $E_u = 2.10$ eV, $g_x = 4$, $g_y = 2$, $g_0 = 2$, $A_t = 0.45 \cdot 10^8$ sec^{-1}, $a = 0.86$, $\Delta\nu_D = 3.48 \cdot 10^9$ sec^{-1} at 2100°K, $\Delta\nu_D = 3.48 \cdot 10^9$ sec^{-1} at 2550°K, and $\Delta\nu_D = 3.95 \cdot 10^9$ sec^{-1} at 2700°K.

Conclusions

The equations for consideration of the effects of incomplete dissociation, compound formation, and ionization have been derived specifically for the case of Na introduced as an aqueous NaCl solution. However, the treatment and the derived equations are quite general in application, and Na was well chosen for purposes of illustration. The 3 sets of curves in Fig. 1 represent all the cases which will be encountered in flame spectrometry except the trivial case in which dissociation is complete in the flame and no ionization occurs. All elements will exhibit similar plots of log N *versus* T and P_T, but they will of course be shifted along the temperature axis as compared to the Na curves.

For the first and *most trivial case* in which dissociation is complete and no ionization occurs, it is obvious that eqn. (14) should be simply

$$P_T = p_M \tag{35}$$

where p_M is the partial pressure in atmospheres of the metal in the flame. Using the gas law to convert p_M to N

$$N = \frac{P_T}{kT} \tag{36}$$

It is obvious in this case that a plot of log N *versus* T and at various values of P_T would yield a set of curves in which log N varies only slightly with temperature, *i.e.*,

MONOGRAPH 1

THE CHEMISTRY OF BERYLLIUM

by D. A. EVEREST

The National Chemical Laboratory,
Teddington, Great Britain

Beryllium metal and its compounds are the object of lively interest, especially in view of their successful applications in the fields of atomic energy and space technology. Notwithstanding the considerable volume of work published about the metallurgical studies of beryllium metal and its compounds, there has been very little in the way of a recent accounting of the important features of beryllium chemistry as a whole. It is this deficiency which Dr. Everest answers in a critical, concise and essentially complete treatment of the subject.

This volume will be of interest to undergraduate and graduate students specializing in inorganic chemistry as well as scientists and engineers occupied with industrial applications of beryllium and its commercial extraction.

CONTENTS: 1. Introduction to Beryllium Chemistry. 2. Solution Chemistry of the Simple Be^{2+} Ion. 3. Simple Oxosalts of Beryllium. 4. The Beryllium Halides. 5. Complex Beryllium Compounds. 6. Simple Binary Compounds of Beryllium. 7. Organo-beryllium Compounds. 8. The Extractive Metallurgy of Beryllium. 9. The Analytical Chemistry of Beryllium. 10. The Beryllium Health Hazard and its Control. 11. Nuclear Properties and Reactions of Beryllium. Index.

5½ x 8½″ x + 151 pages 6 tables 5 illus. 1964
Price: 45s or Dfl. 22.50 or $8.00

MONOGRAPH 2

INORGANIC ION EXCHANGERS

by C. B. AMPHLETT

Chemistry Division, Atomic E
Research Establishment, Har
Great Britain

The first synthetic ion exchangers were of ganic origin but interest has long been centr organic resin exchangers. These, however, proven quite unstable toward solutions at temperature and massive doses of ionizing r tion. Attention has therefore been drawn again to the inorganic materials which are more stable under these conditions. Throug the book, Dr. Amphlett devotes attention t similarities and differences existing betwee different classes of inorganic exchangers, between the latter and their organic counterp Much of the impetus for this book has come the nuclear energy industry, where the possi of using these materials for chemical proces water disposal, and water treatment at high peratures is being actively studied. Rese workers in the fields of ion exchange, minera inorganic chemistry and nuclear energy will this volume a valuable reference work.

CONTENTS: 1. Introduction. 2. The Clay M rals. 3. The Zeolites. 4. Ion Exchange in He polyacid Salts. 5. Hydrous Oxides and Inso Salts.

5½ x 8½″ xi + 141 pages 32 tables 36 illus.
Price: 40s or Dfl. 20,— or $6.50

MONOGRAPH 3

INTRODUCTION TO THE ATOMIC NUCLEUS

by J. G. CUNINGHAME

Atomic Energy Establishment,
Harwell, Great Britain

A complete understanding of chemical problems relies to a certain extent upon a basic knowledge of nuclear physics. This is the first text to be written expressly for the non-nuclear physicist. It is a lucid, descriptive volume providing the physicist, biochemist, and chemist with the nuclear physics he is likely to need in the course of his work. It avoids the necessity of having to consult more ponderous works containing much extraneous information. In many cases, emphasis is placed on points which a specialist in the subject might well take for granted.

The need for a text of this nature has been felt for some years. The author's great experience of the problems involved will prove of great benefit to a wide spectrum of scientists, as well as research workers and teachers.

CONTENTS: 1. Historical Introduction. 2. General Definitions and Properties. 3. Nuclear Forces. 4. Stable Nuclides. 5. Radioactivity. 6. Nuclear Models. 7. Nuclear Reactions. 8. Fission. 9. Alpha-decay. 10. Beta-decay. 11. Gamma-emission. 12. Interaction of Particles and Rays with Matter. Appendix. Index.

5½ x 8½" xi + 220 pages 3 tables 58 illus. 1964
Price: 50s or Dfl. 25.— or $9.00
Paperback Edition 30s or Dfl. 15.— or $4.75

MONOGRAPH 4

CHEMISTRY OF THE RARE-EARTH ELEMENTS

by N. E. TOPP,

National Chemical Laboratory,
Teddington, Great Britain

Although practically all the rare-earth elements were isolated more than fifty years ago, it is only with the improved separation techniques developed during the past ten years that they have become readily available in any quantity. This volume comprises the most up-to-date systematic coverage of this important group of elements. The technical applications of these elements apply to a number of fields, including; electronics, glass manufacture, ceramics, metallurgy, nucleonics, phosphors, optical lasers and catalysts.

In addition to chemists, this work will prove valuable to metallurgists and solid-state physicists, as well as research students in these fields.

CONTENTS: 1. Introduction. 2. Extraction of the Rare-earth Elements from Minerals. 3. Modern Separation Techniques. 4. Salts of the Rare-earth Elements. 5. Solution Chemistry of the Rare-earth Elements. 6. Unusual Valancy States of the Lanthanide Elements. 7. Compounds with Elements from Group I, III, IV and V. 8. Rare-earth Oxides. 9. Sulphides, Selenides and Tellurides. 10. Analytical Methods. 11. The Rare-earth Metals. 12. Applications of the Rare-earth Metals.

5½ x 8½" viii + 164 pages 22 tables 21 illus. 1965
Price: 55s or Dfl. 27.50 or $10.00

MONOGRAPH 5

THE CHEMISTRY OF GALLIUM

by I. A. SHEKA, I. S. CHAUS and T. T. MITYUREVA

In recent years the importance of gallium and some of its compounds has grown considerably. This monograph describes the chemical and physical properties of the inorganic, organic, and complex compounds of gallium, the methods of their preparation, and the scope of their applications. The basic physico-chemical constants of the element and its compounds are included as an aid in research.

Engineers and technicians in the rare and non-ferrous metals industry will find this volume of particular interest, as will instructors, and graduate and undergraduate students in chemistry and chemical engineering.

CONTENTS: 1. Natural Occurrence, Properties and Applications. 2. Hydrogen Compounds. 3. Gallium Oxides and Hydroxides, and Gallates. 4. Gallium Halides and their Complex Compounds. 5. Compounds of Gallium with Sulphur, Selenium, Tellurium and their Acids. 6. Compounds of Gallium with Elements of Group V. 7. Reactions of Gallium with Carbon and its Compounds. 8. Interaction of Gallium with Metals. 9. Methods of Preparation of Gallium. 10. Coprecipitation of Gallium. 11. Catalytic Properties of Gallium Compounds. 12. Aspects of the Analytical Chemistry of Gallium. References. Subject Index.

5½ x 8½" viii + 310 pages 35 tables 51 illus. 1966
Price: £5.15.0 or Dfl. 57.50 or $21.00

This order may be returned to the publisher or to your regular bookseller.

I wish to order from the collection „Topics in Inorganic and General Chemistry":

copies of Monograph 1 copies of Monograph 5
copies of Monograph 2 copies of Monograph 6
copies of Monograph 3 copies of Monograph 7
copies of Monograph 4 copies of Monograph 8

I would also like to receive copies of:
which is still in preparation.

Name (please print):
Address:

Please detach this Order Form and forward in an envelope to your bookseller or the Elsevier Publishing Co.

To

MONOGRAPH 6

THE CHEMISTRY OF TECHNETIUM AND RHENIUM

by R. D. PEACOCK

Professor of Inorganic Chemistry,
University of Leicester,
Great Britain

Rhenium, the least abundant of the naturally occurring chemical elements, was also the last to be isolated by classical methods. In contrast, technetium was the first of the artificial elements. The chemistry of both has made rapid progress in the last decade, and this advance has been paralleled by the increasing market for rhenium and its derivatives. In this volume a cohesive picture is made of both the earlier work and recent developments. A selective summary of the analytical methods used to estimate the elements is also included.

Teachers in inorganic chemistry, chemists, in particular those working in transition metal chemistry in universities as well as in industry, and metallurgists who require a chemical background in their work, will find this monograph valuable, as will final year students at universities.

CONTENTS: 1. Discovery and Isolation of Rhenium and Technetium. 2. General and Elementary Properties. 3. Oxides. 4. Oxoacids and Oxosalts. 5. Halides and Oxide Halides. 6. Complex Halides, Complex Oxide Halides, and Complex Hydrides. 7. Chalcogenides and Compounds with Non-metals and Metalloids. Alloys. 8. Complex Cyanides and Related Compounds. 9. Carbonyls and Organometallic Derivatives. 10. Compounds with Group V and VI Ligands. 11. Analysis. Appendices. 1. Laboratory Handling of Technetium. 2. Bibliography. 3. Further References. Subject Index.

5½ x 8½″ ix + 137 pages 29 tables 14 illus. 1965
Price: 55s or Dfl. 27.50 or $10.00

MONOGRAPH 7

THE CHEMISTRY OF SELENIUM, TELLURIUM AND POLONIUM

by K. W. BAGNALL

Senior Principal Scientific Officer,
Chemistry Division, Atomic Energy
Research Establishment,
Harwell, Great Britain

Prior to the advent of the nuclear reactor, polonium was an unknown entity in the Periodic Table, separable only in microgram amounts. Its chemistry is now well established as a result of the availability of weighable amounts of polonium-210 synthesized by neutron irradiation of natural bismuth. This monograph covers existing knowledge of the chemistry of the group in as complete a fashion as possible. It includes a brief account of the very extensive literature on the organo compounds, a group which has not been reviewed in any detail for over a decade, as well as an account of the chemistry of the halides and complexes. Crystallographic data are included in tabular form.

Dr. Bagnall's work will certainly be interesting to university lecturers in inorganic chemistry and final year students, as well as radiochemists and research workers in the fields of sulphur, selenium and tellurium.

CONTENTS: 1. The Discovery and Uses of the Elements. 2. Separation, Purification and Determination. 3. The Elements, The Hydrides and other Derivatives. 4. Oxides, Oxo-acids, Sulphides and Sulphur-oxo-acids. 5. Halides. 6. Salts formed with Oxo-acids. 7. Carbon Compounds. Subject Index.

5½ x 8½″ viii + 200 pages 25 tables 11 illus. 1965
Price: 70s or Dfl. 35,— or $13.00

MONOGRAPH 8

INTERACTIONS IN ELECTROLYTE SOLUTIONS

by GEORGE H. NANCOLLAS,

Professor of Chemistry,
State University of New York at
Buffalo, N.Y., USA

The nature of the species present in solutions of electrolytes is a subject of great importance to the chemist. The major part of this volume is concerned with the free energy, enthalpy and entropy changes accompanying ion-pair and complex formation. A comparatively new development has been the determination of reliable calorimetric $\triangle H$ values and a feature of the book is the compilation of recent data. The application of new physical methods to the problem of electrolyte solution structure and the rate of formation of complexes are also discussed. Suggestions are included for the efficient use of electronic computers for calculations.

Undergraduate and graduate students in physical chemistry will find this work a valuable reference source, as will analytical chemists, inorganic chemists and electrochemists.

CONTENTS: List of Main Symbols. 1. Introduction. 2. Experimental Methods: Determination of Association Constants. 3. The Association Constant. 4. Relationships Involving the Association Constant. 5. Thermodynamic Properties. 6. Mechanism of Complex Formation and Structure of the Complex. Appendix. Author Index. Subject Index.

5½ x 8½″ x + 192 pages + indexes 18 tables 25 illus. 1966
Price: 80s or Dfl. 40.— or $14.50

N is related to T^{-1}. Therefore at constant T, if the instrumental factors discussed above are neglected, analytical curves of log I *versus* log C should, in the low concentration region, give a straight line of slope equal 1 and, in the high concentration region, give a straight line of slope equal $\frac{1}{2}$. In other words, as the temperature increases, the atomic concentration, N, decreases because of the expansion of the gases.

The *second case*, in which a stable molecular species exists in the flame, but ionization is not important, is represented by the low temperature portion of the H_2/air curves in Fig. 1. For this case eqn. (14) should read

$$P_T = p_M + p_{MY} \tag{37}$$

where p_{MY} is the partial pressure of the compound, MY, in the flame. If K_{MY} is the dissociation constant for the species MY, then

$$P_T = p_M + \frac{p_M p_Y}{K_{MY}} \tag{38}$$

and

$$p_M = \frac{K_{MY} P_T}{K_{MY} + p_Y} \tag{39}$$

It may be seen from eqn. (39) that for constant T and p_Y, p_M (and N) is proportional to P_T. Hence analytical curves in this case will be identical in shape with those obtained in the case of no compound formation and no ionization. Also, all the curves obtained by plotting log N *versus* T and P_T, as in Fig. 1, must be parallel, but their shape will be determined by the temperature dependence of K_{MY}.

The *third case*, in which a stable molecular species does not exist in the flame, but ionization occurs, is represented by the high temperature portion of the C_2H_2/O_2 curves in Fig. 1. In this case, eqn. (14) should read

$$P_T = p_M + p_{M^+} \tag{40}$$

where p_{M^+} is the partial pressure of the ion in the flame. No simple solution can be obtained by substituting for p_{M^+}. As may be seen from the C_2H_2/O_2 curves the percent ionization decreases as P_T increases leading to an analytical curve with slope greater than 1 in the low concentration region. However at very low concentrations the flame gas electrons may buffer ionization and flatten out this portion of the analytical curve.

The *fourth case*, in which compound formation and ionization are both important, is illustrated in the H_2/O_2 curves of Fig. 1. The shape of the analytical curve in this case is dependent on the relative contribution of each process.

From this discussion and the preceding discussion and derivation of equations, it should be clear that many factors affect the shape of analytical curves in atomic emission flame spectrometry. It should also be clear that of these factors the most important are self-absorption and the effects of incomplete dissociation, compound formation, and ionization, but other factors may also contribute to analytical curve bending if the experimental situation is not closely controlled. It is hoped that a clearer understanding of all these factors will have been gained by this treatment. It should be possible by the use of the derived equations to estimate the contributions of the various factors in any given experimental situation.

It should be noted that many of the results of this paper may be applied directly to atomic absorption and atomic fluorescence flame spectrometry. The two methods, like atomic emission flame spectrometry, depend on N, the atomic concentration of the species of interest in the flame. Thus the discussion of factors affecting N, *i.e.*, ionization dissociation, compound formation, and variations in solution flow rate, and atomization efficiency, pertains as well to atomic absorption and atomic fluorescence flame spectrometry.

APPENDIX

Effect of common atom on NaCl dissociation—Introduction of NaCl in an HCl solution into a flame

Consider the introduction of NaCl in the presence of HCl into a flame. The important equilibria are

$$\mathrm{NaCl} \rightleftarrows \mathrm{Na} + \mathrm{Cl} \qquad K_1 = \frac{p_{\mathrm{Na}} p_{\mathrm{Cl}}}{p_{\mathrm{NaCl}}} \tag{41}$$

$$\mathrm{HCl} \rightleftarrows \mathrm{H} + \mathrm{Cl} \qquad K_{\mathrm{H}} = \frac{p_{\mathrm{H}} p_{\mathrm{Cl}}}{p_{\mathrm{HCl}}} \tag{42}$$

$$\mathrm{NaOH} \rightleftarrows \mathrm{Na} + \mathrm{OH} \qquad K_3 = \frac{p_{\mathrm{Na}} p_{\mathrm{OH}}}{p_{\mathrm{NaOH}}} \tag{43}$$

To determine the effect of the common atom, Cl, the largest possible effect will be considered, *i.e.*, the case in which the HCl introduced into the flame is completely dissociated (actually the fraction of HCl dissociated is given by $K_{\mathrm{H}}/(K_{\mathrm{H}}+p_{\mathrm{H}})$ which will generally be greater than 0.9 for most analytical flames, and so the assumed case is actually a practical one). Thus $p_{\mathrm{Cl}} = P_{\mathrm{Cl}}$, where P_{Cl} is the partial pressure of Cl and HCl in the flame gases when NaCl in HCl is introduced into the flame. In order to obtain the full influence of the common atom effect, it will be assumed that the ionization of Na atoms is negligible at the flame temperature. Therefore,

$$P_{\mathrm{T}} = p_{\mathrm{Na}} + p_{\mathrm{NaCl}} + p_{\mathrm{NaOH}} \tag{44}$$

and

$$P_{\mathrm{T}} = p_{\mathrm{Na}} \left(1 + \frac{P_{\mathrm{Cl}}}{K_1} + \frac{p_{\mathrm{OH}}}{K_3}\right) \tag{45}$$

and so

$$p_{\mathrm{Na}} = \frac{P_{\mathrm{T}}}{1 + \dfrac{P_{\mathrm{Cl}}}{K_1} + \dfrac{p_{\mathrm{OH}}}{K_3}} \tag{46}$$

The influence of HCl on the value of p_{Na} can be considered significant when the condition below is met or exceeded, *i.e.*, the Cl from the HCl results in a 10% change in p_{Na}, and so

$$\frac{P_{\mathrm{Cl}}}{K_1} = 0.1 \left(1 + \frac{p_{\mathrm{OH}}}{K_3}\right) \tag{47}$$

and

$$P_{\mathrm{Cl}} = 0.1 K_1 \left(1 + \frac{p_{\mathrm{OH}}}{K_3}\right) \tag{48}$$

For a H_2/air flame at 2000°K, $K_1 = 9.1 \cdot 10^{-5}$, $K_3 = 4.1 \cdot 10^{-5}$ and $p_{OH} = 10^{-3}$ atm, and so P_{Cl} is $2.2 \cdot 10^{-4}$ atm. Using eqn. (4) and the aspirator conditions given in the text of the paper, it can be shown that this pressure of HCl corresponds to a solution concentration, C_{HCl}, of hydrochloric acid of 0.15 *M*. Similarly for a H_2/O_2 flame at 2600°K, $K_1 = 1.3 \cdot 10^{-2}$, $K_3 = 1.3 \cdot 10^{-2}$, $p_{OH} = 0.05$ atm, and so $P_{Cl} = 6.3 \cdot 10^{-3}$ atm and $C_{HCl} = 3.2$ *M*. For an C_2H_2/O_2 flame at 2700°K, $K_1 = 4.2 \cdot 10^{-2}$, $K_3 = 2.9 \cdot 10^{-2}$, $p_{OH} = 0.2$ atm, and so $p_{Cl} = 3.2 \cdot 10^{-2}$ atm and $C_{HCl} = 14$ *M* (an impossibly high solution concentration). Thus when using the H_2/air, H_2/O_2 and C_2H_2/O_2 flames, the concentration of hydrochloric acid in the NaCl solutions used for aspiration must exceed 0.15 *M*, respectively, before a 10% change in p_{Na} results. Because of the deleterious effects of acids on the aspiration characteristics, it is seldom necessary for the analyst to use mineral acids of any kind at concentrations greater than 0.1 *M*. At this concentration, even in the case of complete dissociation of the introduced HCl, the effect of the common atom is generally negligible.

This research was sponsored by AFOSR(SRC)-OAR, U.S.A.F. Grant No. AF-AFOSR-1033-66 with supplementary funds from Edgewood Arsenal, Md.

SUMMARY

Factors affecting the shape of analytical curves in atomic emission flame spectrometry are discussed. Equations are presented by which the effect on the analytical curve of self-absorption, ionization, compound formation, variation in solution flow rate and atomization efficiency, entrance optics, and multiple spectral lines can be considered quantitatively. Theoretical and experimental curves are compared for Na introduced as aqueous NaCl solution into H_2/air, H_2/O_2, and C_2H_2/O_2 flames. The portion dealing with the effect of ionization, compound formation, and variation in solution flow rate and atomization efficiency on the atomic concentration in the flame applies as well to atomic absorption and atomic fluorescence flame spectrometry.

RÉSUMÉ

Les auteurs ont examiné divers facteurs influençant les courbes analytiques en spectrométrie de flamme par émission atomique. On effectue une comparaison des courbes théoriques et expérimentales pour le sodium, introduit sous forme d'une solution aqueuse de NaCl, dans les flammes H_2/air, H_2/O_2 et C_2H_2/O_2. L'influence de l'ionisation, de la formation de composé, de la variation de vitesse du débit de la solution et du rendement d'atomisation, sur la concentration atomique dans la flamme s'applique aussi bien à la spectrométrie par absorption atomique qu'à la spectrométrie de flamme par fluorescence atomique.

ZUSAMMENFASSUNG

Faktoren, die die Gestalt analytischer Kurven bei der atomaren Emissionsflammenspektroskopie beeinflussen, werden diskutiert. Es werden Gleichungen angegeben, mit denen folgende Einflüsse sowohl für die atomare Absorption als auch für die atomare Fluoreszenzflammenspektroskopie quantitativ behandelt werden können:

Selbstabsorption, Ionisation, Verbindungsbildung, Variation der Lösungsmittelflussgeschwindigkeit und Atomisierungswirksamkeit, die Eintrittsoptik und vielfache Spektrallinien. Theoretische und experimentelle Kurven für Natrium, zugeführt als Natriumchloridlösung in H_2/Luft-, H_2/O_2- und C_2H_2/O_2-Flammen werden verglichen.

REFERENCES

1 I. RUBESKA AND V. SVOBODA, *Anal. Chim. Acta*, 32 (1965) 253.
2 M. SHIMAZU AND A. HASHIMOTO, *Sci. Light (Tokyo)*, 11 (1962) 131.
3 J. H. GIBSON, W. E. L. GROSSMAN AND W. D. COOKE, *Anal. Chem.*, 35 (1963) 266.
4 J. A. DEAN, in E. N. DAVIS, *Developments in Applied Spectroscopy*, Vol. 4, Plenum Press, New York, 1965, p. 443.
5 R. HERRMANN AND C. T. J. ALKEMADE, *Chemical Analysis by Flame Photometry*, translated by P. T. GILBERT, Wiley, New York, 1963.
6 J. D. WINEFORDNER, W. W. MCGEE, J. M. MANSFIELD, M. L. PARSONS AND K. E. ZACHA, *Anal. Chim. Acta*, 36 (1966) 25.
7 J. D. WINEFORDNER, T. J. VICKERS AND L. REMINGTON, *Anal. Chem.*, 37 (1965) 1216.
8 J. D. WINEFORDNER AND T. J. VICKERS, *Anal. Chem.*, 36 (1964) 1939.
9 C. G. JAMES AND T. M. SUGDEN, *Proc. Roy. Soc. (London)*, A248 (1958) 238.
10 *JANAF Interim Thermochemical Tables*, Dow Chemical Co., Midland, Mich., 1960.
11 P. T. GILBERT, JR., *Analytical Flame Photometry: New Developments*, Symposium on Spectroscopy, American Society for Testing Materials, Special Technical Publications No. 269, 1960.
12 S. BRODERSEN, *J. Opt. Soc. Am.*, 43 (1953) 877.
13 R. MAVRODINEANU AND H. BOITEUX, *Flame Spectroscopy*, John Wiley, New York, 1964.
14 A. G. GAYDON AND H. G. WOLFHARD, *Flames, their Structure, Radiation and Temperature*, Chapman and Hall, London, 1960.
15 A. R. ZAER, *Ph.D. Thesis*, Paris, 1935.
16 J. D. WINEFORDNER, C. T. MANSFIELD AND T. J. VICKERS, *Anal. Chem.*, 35 (1963) 1607.
17 J. D. WINEFORDNER, C. T. MANSFIELD AND T. J. VICKERS, *Anal. Chem.*, 35 (1963) 1611.
18 E. HINNOV AND H. KOHN, *J. Opt. Soc. Am.*, 47 (1957) 156.
19 LANDOLT-BÖRNSTEIN, *Atom- und Molekularphysik*, Vol. I, Part I, Springer-Verlag, Berlin, 1950.
20 C. H. CORLISS AND W. R. BOZMAN, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, National Bureau of Standards Monograph 53, 1962.
21 A. C. G. MITCHELL AND M. W. ZEMANSKY, *Resonance Radiation and Excited Atoms*, University Press, Cambridge, 1961.

THE DETERMINATION OF CALCIUM AND MAGNESIUM BY ATOMIC ABSORPTION SPECTROSCOPY

T. V. RAMAKRISHNA, J. W. ROBINSON AND PHILIP W. WEST
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)

(Received March 1st, 1966)

The importance of the determination of calcium and magnesium has been emphasized by the number of papers which have been published on this subject in recent years[1-13]. When atomic absorption techniques have been used, interferences have been noted from certain ions such as sulfate, phosphate, sodium and aluminum, but no systematic study has been made. Some of the interferences noted have been overcome by (*a*) addition of other salts which suppress the interference, (*b*) removing the interfering element, and (*c*) using standards similar to the composition of the sample. Since the determination of calcium and magnesium in the presence of diverse ions is of widespread interest, the application of atomic absorption spectroscopy to this problem has been investigated. Results indicate that severe chemical interferences may be encountered. Methods of eliminating these interferences are proposed.

EXPERIMENTAL

Apparatus

The apparatus used was the Perkin-Elmer Model 303 atomic absorption spectrophotometer fitted with a Beckman total consumption burner for sample atomization. Calcium and magnesium hollow cathode lamps (Ransley Glass Instruments, Melbourne, Australia) were used as radiation sources.

Reagents

Calcium stock solution (1000 p.p.m.). Oven-dried calcium carbonate was dissolved in a minimum quantity of hydrochloric acid and diluted to volume with water.

Magnesium stock solution (1000 p.p.m.). Pure magnesium turnings were dissolved in dilute hydrochloric acid and made up to volume with water.

Strontium chloride. 2% solution.

Ethylenediaminetetraacetic acid (EDTA) (disodium salt). 4%.

All other chemicals used were of reagent grade, and double-distilled water was used for dilution purposes.

Procedure

The following operating conditions were established with 10 p.p.m. and 1 p.p.m. of calcium and magnesium solutions, respectively.

	Calcium	*Magnesium*
Wavelength	4227 Å	2852 Å
Slit	13 Å	2 Å
Lamp current	18–20 mA	6 mA
Fuel: Oxygen flow rate	4.5 l/min	4.5 l/min
Hydrogen flow rate	25 l/min	25 l/min

Water was first sprayed through the flame followed by the calcium or magnesium solutions. This operation was repeated after each absorption measurement. Under these conditions, the sensitivity for calcium was 0.5 p.p.m., and for magnesium, 0.03 p.p.m. for 1% absorption.

INTERFERENCES STUDIES

Calcium

The effect of over 50 ions at the 100-p.p.m. level on the calcium and magnesium absorption was examined. The standard solutions used for comparison were $CaCl_2$ (10 p.p.m. of Ca^{2+}) and $MgCl_2$ (1 p.p.m. of Mg^{2+}).

Studies were made of the elimination of interferences by adding 10 ml of strontium chloride (final concentration, 0.2%) or EDTA (final concentration, 0.4%). The solutions were finally diluted to 100 ml with water. The anions were present as

TABLE I

EFFECT OF ANIONS ON CALCIUM ABSORPTION IN THE PRESENCE OF EDTA AND $SrCl_2$[a]

Interference (100 p.p.m.)	*Percentage absorption*			
	Ca^{2+} (10 p.p.m.)	*Ca^{2+} (10 p.p.m.) plus EDTA (10 ml)*	*Ca^{2+} (10 p.p.m.) plus $SrCl_2$ (10 ml)*	*Ca^{2+} (10 p.p.m.) plus EDTA and $SrCl_2$ (10 ml each)*
None	18.4	14.8	18.4	18.6
Br^-	8.8	14.7	18.4	18.6
I^-	10.5	14.8	18.6	18.6
F^-	3.9	5.6	5.3	7.6
SO_4^{2-}	3.7	12.0	15.8	18.4
SO_3^{2-}	4.1	12.0	15.6	18.6
NO_3^-	10.8	14.2	18.6	18.6
HPO_4^{2-}	2.2	4.9	16.8	17.5
SeO_3^{2-}	6.1	14.2	18.0	18.6
TeO_3^{2-}	8.3	14.8	18.3	18.6
WO_4^{2-}	3.2	6.9	18.5	18.6
MoO_4^{2-}	8.2	14.8	18.4	18.6
$B_4O_7^{2-}$	5.8	14.6	15.3	18.6
SiO_3^{2-}	0.04	2.3	12.0	15.6
CO_3^{2-}	1.5	9.1	12.2	18.0
$HAsO_4^{2-}$	8.7	14.3	16.9	18.6
VO_3^-	1.5	6.4	15.9	16.0
Oxalate	18.4	14.8	18.4	18.6
Tartrate	18.4	14.8	18.4	18.6
Citrate	18.0	14.8	18.4	18.6
Lactate	13.5	14.8	18.4	18.6

[a] In these investigations no correction was made for the effect of Na^+ ion on calcium absorption.

the sodium or potassium salt, and the cations were added mostly as chlorides or nitrates, and in certain instances, as sulfates. The results are shown in Table I.

It can be seen from Table I that, with the exception of fluoride, vanadate and silicate, the interferences from anions on calcium absorption were overcome by the addition of EDTA, $SrCl_2$, or both. The fluoride interference was subsequently overcome by the addition of hydrochloric acid (final concentration, 10%) or perchloric acid (final concentration, 5%). The addition of 10 ml each of hydrochloric and acetic acid showed no interference and a slight enhancement of sensitivity was noticed in the case of perchloric acid. The presence of a similar quantity of nitric or sulfuric acids, however, reduced the absorption value by about 30 and 60%, respectively.

Among the cations listed, Li^+, Na^+, K^+, Be^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Sb^{5+}, Cr^{3+}, Sn^{2+} and Fe^{3+} were found to suppress absorption of radiant energy by calcium. The suppressing effect of Li^+, Na^+, K^+, Fe^{3+} and Cr^{3+} was overcome by the addition of EDTA, while the interference from Sb^{5+} and Sn^{2+} was eliminated by the addition of strontium chloride. The interferences from Al^{3+}, Be^{2+}, Ti^{4+} and Zr^{4+} are perhaps due to the formation of anions such as the aluminate or titanate by the metal concerned. These anions may then combine with the calcium to form a salt such as calcium aluminate. Such salts possess low volatilities and high dissociation energies and thus impede the release of calcium atoms in the flame.

TABLE II

EFFECT OF CATIONS ON CALCIUM ABSORPTION

Interference (100 p.p.m.)	*% Absorption Ca^{2+} (10 p.p.m.)*	*Interference (100 p.p.m.)*	*% Absorption Ca^{2+} (10 p.p.m.)*
$CaCl_2$ standard			
None	18.3	Al^{3+} (50 p.p.m.)	7.6
Li^+	14.9	Ti^{4+} (50 p.p.m.)	0.0
Na^+	16.5	Zr^{4+} (50 p.p.m.)	12.8
K^+	17.5	Sn^{4+}	18.3
Rb^+	18.3	Sn^{2+}	10.0
Cs^+	18.2	Sb^{5+}	8.4
Cu^{2+}	18.2	Cr^{3+}	6.8
Be^{2+}	1.2	Mn^{2+}	18.4
Mg^{2+}	18.4	Fe^{3+}	10.9
Sr^{2+}	18.6	Co^{2+}	18.3
Ba^{2+}	18.0	Ni^{2+}	18.3
Zn^{2+}	18.4	Pd^{2+}	18.2
Cd^{2+}	18.4	La^{3+}	19.0
Hg^{2+}	18.4		
$Ca(NO_3)_2$ standard			
None	11.9	Pb^{2+}	12.0
Ag^+	11.4	Th^{4+}	11.8
$Hg_2{}^{2+}$	11.9	Bi^{3+}	11.2
Ce^{4+}	10.8		

To check this possibility, dual atomizers, as employed by ELWELL AND GIDLEY[14], were set up. One atomizer aspirated calcium solution and the other, the interference under investigation. Results showed no suppression of the calcium absorption. If, however, a solution containing both calcium and interfering ion was sprayed from the same atomizer and water through the second, serious interference occurred indicating that chemical interference takes place only when the calcium and the interfering metal are present in the same solution. The results supported the idea that the interferences were chemical in nature.

Attempts were then made to eliminate these interferences. It was found that both strontium chloride and EDTA were ineffective. As it was observed earlier that calcium can tolerate the presence of fluoride in hydrochloric or perchloric acid mediums, it was thought possible that these interferences could be eliminated by the addition of fluoride. Runs were made, therefore, in which 4 ml of a 2% solution of ammonium fluoride and 5 ml of 60% perchloric acid were added to the calcium solutions. Although considerable improvement was noted in calcium absorption, the interferences were not completely eliminated. It was subsequently found that the presence of 10 ml of 2% strontium chloride, in addition to fluoride and perchloric acid, completely eliminated the effect of all 4 metals. The results are shown in Table III. It seems that strontium serves to release calcium completely from the interference of Be, Al, Ti, or Zr. These refractory metals are subsequently complexed by fluoride with the result that the formation of a calcium salt from the oxy-acids concerned is completely prevented.

TABLE III

RECOVERY OF CALCIUM IN THE PRESENCE OF ALUMINUM, BERYLLIUM, TITANIUM AND ZIRCONIUM

Sample	*Percentage absorption*
$Ca^{2+} + HClO_4$	21.0
$Ca^{2+} + F^- + HClO_4$	21.2
$Ca^{2+} + Al^{3+} + F^- + HClO_4$	16.3
$Ca^{2+} + Al^{3+} + F^- + HClO_4 + SrCl_2$	21.0
$Ca^{2+} + Be^{2+} + F^- + HClO_4$	13.2
$Ca^{2+} + Be^{2+} + F^- + HClO_4$	21.4
$Ca^{2+} + Ti^{4+} + F^- + HClO_4$	8.9
$Ca^{2+} + Ti^{4+} + F^- + HClO_4 + SrCl_2$	21.0
$Ca^{2+} + Zr^{4+} + F^- + HClO_4$	16.5
$Ca^{2+} + Zr^{4+} + F^- + HClO_4 + SrCl_2$	21.0

Detergents. The detergents examined included Tide, Dreft, and Calgon. It was shown that they severely inhibited the calcium absorption. The use of EDTA or strontium chloride or both, which had been shown to control most of the other interferences, did not eliminate the effect of these detergents. If, however, 5 ml of diethylene glycol was also added in addition to strontium chloride, or strontium chloride and EDTA, the interference was completely eliminated. It was noted that diethylene glycol alone did not eliminate the interferences. The role of diethylene glycol was not evident, but it was effective in eliminating interferences when determining calcium in detergent-polluted waters. Table IV indicates the interference effects of Dreft and the effect of various compounds added to eliminate these effects.

Magnesium

Magnesium, like calcium, is subject to interference from several anions and cations, but to a lesser degree. The results obtained in the presence of various anions

TABLE IV

ABSORPTION OF CALCIUM IN THE PRESENCE OF DREFT AND OTHER COMPOUNDS

Sample composition			*Percentage absorption*
Ca^{2+} (p.p.m.) as $CaCl_2$	*Dreft (p.p.m.)*	*Other compounds*[a]	
10	—	—	18.6
10	10	—	16.1
10	100	—	3.1
10	1000	—	2.2
10	—	EDTA	14.8
10	1000	EDTA	6.3
10	—	$SrCl_2$	18.8
10	1000	$SrCl_2$	16.0
10	—	Diethylene glycol	19.1
10	1000	Diethylene glycol	7.5
10	—	EDTA + $SrCl_2$	18.6
10	1000	EDTA + $SrCl_2$	16.0
10	—	EDTA + diethylene glycol	18.8
10	1000	EDTA + diethylene glycol	9.5
10	—	$SrCl_2$ + diethylene glycol	20.0
10	1000	$SrCl_2$ + diethylene glycol	20.5
10	—	EDTA + $SrCl_2$ + diethylene glycol	19.5
10	1000	EDTA + $SrCl_2$ + diethylene glycol	19.4

[a] EDTA = 10 ml; $SrCl_2$ = 10 ml; diethylene glycol = 5 ml.

TABLE V

EFFECT OF ANIONS ON MAGNESIUM ABSORPTION IN THE PRESENCE OF EDTA, $SrCl_2$ AND ISOPROPANOL

Interference (100 p.p.m.)	*Percentage absorption*			
	Mg^{2+} (1 p.p.m.)	*Mg^{2+} (1 p.p.m.) plus EDTA (0.37%)*	*Mg^{2+} (1 p.p.m.) plus $SrCl_2$ (0.2%)*	*Mg^{2+} (1 p.p.m.) plus isopropanol (2%)*
None	30.7	29.0	31.4	31.7
Br^-	27.4	29.2	31.9	31.7
I^-	23.5	29.0	31.6	31.4
F^-	22.7	28.8	32.0	31.7
SO_4^{2-}	23.8	28.5	31.4	28.0
SO_3^{2-}	23.7	29.0	31.3	28.0
NO_3^-	26.7	29.0	31.6	31.5
HPO_4^{2-}	23.0	25.3	30.5	28.2
SeO_3^{2-}	24.3	29.2	30.2	31.5
TeO_3^{2-}	24.5	29.2	31.4	31.7
WO_4^{2-}	27.4	28.3	31.4	31.0
MoO_4^{2-}	30.7	29.0	31.4	31.7
$B_4O_7^{2-}$	25.6	29.0	30.9	31.4
SiO_3^{2-}	7.6	20.2	21.4	14.7
CO_3^{2-}	6.7	24.3	31.4	23.0
$HAsO_4^{2-}$	25.1	29.2	31.6	31.5
VO_3^-	25.0	28.8	26.3	27.2
Oxalate	30.5	29.0	31.4	31.7
Citrate	30.8	29.0	31.4	31.7
Lactate	30.7	29.0	31.4	31.7
Tartrate	30.8	29.0	31.4	31.7

are summarized in Table V. As in the case of calcium, most interferences are overcome by the addition of EDTA and strontium chloride, and the only two serious interferences are those from vanadate and silicate. Although the vanadate interference was overcome by the combined presence of EDTA and strontium chloride, the recovery of magnesium continued to be low in the presence of silicate. None of the acids interfered with the exception of sulfuric acid, in which case the absorption was reduced by about 10%.

From Table VI it is evident that only Li^+, Na^+, K^+, Rb^+, Fe^{3+}, Cr^{3+}, Sn^{2+}, Al^{3+}, Be^{2+}, Zr^{4+} and Ti^{4+} interfere in magnesium determinations. Experiments with dual atomizers showed that Al^{3+}, Be^{2+}, Zr^{4+} and Ti^{4+} interfere, as in the case of calcium, only when present in the same solution, and therefore must be considered as chemical interference. Strontium chloride eliminated all of the interferences except those due to Fe^{3+}, Cr^{3+} and Ti^{4+}. EDTA eliminated the effect of Fe^{3+} and Cr^{3+}, and therefore the only serious cationic interference is from titanium. Because titanium

TABLE VI

EFFECT OF CATIONS ON MAGNESIUM ABSORPTION

Interference (100 p.p.m.)	*% Absorption Mg^{2+} (1 p.p.m.)*	*Interference (100 p.p.m.)*	*% Absorption Mg^{2+} (1 p.p.m.)*
$MgCl_2$ standard			
None	31.0	Ce^{4+}	30.7
Li^+	28.0	Ti^{4+} (50 p.p.m.)	11.9
Na^+	29.4	Zr^{4+} (50 p.p.m.)	22.9
K^+	25.9	Sn^{4+}	31.0
Rb^+	27.8	Sn^{2+}	24.4
Cs^+	31.4	Pb^{2+}	30.6
Ag^+	30.8	Th^{4+}	31.6
Cu^{2+}	31.0	Sb^{5+}	30.5
Be^{2+}	21.6	Bi^{3+}	30.7
Ca^{2+}	32.0	Cr^{3+}	24.6
Sr^{2+}	32.0	Mn^{2+}	31.0
Ba^{2+}	31.3	Fe^{3+}	27.6
Zn^{2+}	31.0	Co^{2+}	30.8
Cd^{2+}	31.6	Ni^{2+}	31.6
Hg_2^{2+}	29.8	Pd^{2+}	32.0
Hg^{2+}	32.0	La^{3+}	33.5
Al^{3+} (50 p.p.m.)	18.5		

TABLE VII

PRECISION AND ACCURACY OF THE METHOD UNDER CONDITIONS DESCRIBED IN THE RECOMMENDED PROCEDURE

Metal	*Amount taken (p.p.m.)*	*Number of determinations*	*Error found at 95% confidence level (p.p.m.)*
Ca	10	10	±0.02
	5	10	±0.03
Mg	1	8	±0.03
	0.05	8	±0.07

is kept in solution only in strongly acidic media or as a complex, this interference is of little practical significance.

It is interesting to note that isopropanol overcame certain anionic interferences as evident from Table V. The addition of 2 ml of this solvent also overcame almost all cationic interferences with the exception of aluminum and titanium. Further studies on how isopropanol eliminates interferences are now being carried out in this laboratory. To date only isopropanol, of a number of solvents studied, has shown promise in eliminating these interferences.

As was found in the case of calcium, the presence of detergents markedly affected magnesium absorption. For example, the presence of 10 p.p.m. Dreft reduced the magnesium absorption by about 15%. However, the interference was readily eliminated, even in the presence of 100 p.p.m. of detergent, by the addition of 5 ml (2%) of strontium chloride.

CONCLUSION

The present investigation indicates that calcium and magnesium are subject to serious interference from a number of anions, cations and detergents. Many of these interferences can be eliminated by the addition of suitable reagents. No method was found to eliminate completely the vanadate and silicate interferences with calcium, and the silicate and titanium interferences with magnesium. Fortunately, vanadium and titanium would seldom be encountered in significant amounts in most samples being analyzed for calcium and magnesium, and there is no interference from up to 30 p.p.m. of silicate when the recommended procedure is employed. It is interesting to note that aluminum, beryllium, titanium and zirconium behaved similarly, both with calcium and magnesium, in that they all suppress the absorption when present in the same solution, but not when they are aspirated into the same flame through a different atomizer. With the exception of titanium, strontium chloride eliminated the interference of these metals with magnesium, and in conjunction with fluoride, their effect on calcium is removed. The ability of isopropanol to eliminate the interference effects of many ions on magnesium is also interesting. The process by which this takes place is not yet completely understood.

RECOMMENDED PROCEDURE

Calcium

Transfer a suitable aliquot (not exceeding 60–65 ml) of calcium solution to a 100-ml volumetric flask, add 10 ml each of 2% strontium chloride and 4% EDTA (disodium salt) and dilute to the mark with double-distilled water. The calcium content of the final solution should be 5–20 p.p.m. With the instrument set at optimum operating conditions as described under EXPERIMENTAL, prepare the appropriate working curve which can then be used to determine the calcium concentration of solutions of sample. Analyses must be performed under conditions which are identical to those used in calibrations.

If the presence of Al^{3+}, Ti^{4+}, or Be^{2+} is suspected, add 4 ml of a 2% solution of ammonium fluoride and 5 ml of 60% perchloric acid, and in the presence of detergents, add 5 ml of diethylene glycol before making up to volume.

Magnesium

To a solution of magnesium (not exceeding 75 ml) in a 100-ml volumetric flask, add 10 ml each of strontium chloride (2%) and EDTA (4%) and dilute to the mark with redistilled water. The concentration of magnesium in the final solution should not exceed 3 p.p.m. Determine the percentage absorption with the instrument set at optimum conditions as described under EXPERIMENTAL. Convert the percentage absorption into optical density and determine the concentration from a calibration graph prepared under identical conditions for 0–3 p.p.m. of magnesium.

The authors wish to express their gratitude for financial support supplied by U. S. Public Health Service Research Grant No. AP 00128.

SUMMARY

An examination of the atomic absorption spectroscopy of calcium and magnesium has been made and the results confirm that several anions and cations interfere. Simple and reliable means are suggested for overcoming these interferences. The possibility of the use of a 2% isopropanol medium for overcoming several interferences on magnesium is also presented.

RÉSUMÉ

Le dosage du calcium et du magnésium par spectroscopie par absorption atomique est perturbé par plusieurs anions et cations. On propose des moyens simples pour éviter ces interférences. Il y a possibilité d'utiliser un milieu isopropanol à 2% pour supprimer plusieurs interférences du magnésium.

ZUSAMMENFASSUNG

Es wurde eine Prüfung der Atomabsorptionsspektroskopie von Calcium und Magnesium durchgeführt. Die Ergebnisse bestätigen, dass einige Anionen und Kationen stören. Zur Vermeidung dieser Störung werden einfache und wirksame Mittel vorgeschlagen. Zur Verhinderung verschiedener Störungen auf Magnesium wird die Verwendung eines Mediums mit Isopropanol vorgeschlagen.

REFERENCES

1 D. J. DAVID, *Analyst*, 84 (1959) 536.
2 D. J. DAVID, *Analyst*, 85 (1960) 495.
3 J. B. WILLIS, *Spectrochim. Acta*, 16 (1960) 259.
4 J. B. WILLIS, *Nature*, 186 (1960) 249.
5 J. B. WILLIS, *Nature*, 184 (1959) 186.
6 J. B. WILLIS, *Anal. Chem.*, 33 (1961) 556.
7 E. NEWBURN, *Nature*, 192 (1961) 1182.
8 W. H. HINSON, *Spectrochim. Acta*, 18 (1962) 427.
9 J. E. ALLAN, *Analyst*, 83 (1958) 466.
10 D. J. DAVID, *Analyst*, 83 (1958) 655.
11 J. B. WILLIS, *Spectrochim. Acta*, 16 (1960) 273.
12 A. C. MENZIES, *Anal. Chem.*, 32 (1960) 898.
13 T. TEKEUCHI AND M. SUZUKI, *Talanta*, 11 (1964) 1391.
14 W. T. ELWELL AND J. A. F. GIDLEY, *Atomic Absorption Spectrophotometry*, Pergamon Press, Oxford, 1961.

USE OF A DIGITAL COMPUTER IN EQUILIBRIUM CALCULATIONS: THE EFFECTS OF DILUTION AND IONIC STRENGTH OF THE BUFFER INDEX AND SHARPNESS INDEX IN THE TITRATION OF A MONOPROTIC ACID WITH A STRONG BASE

JOHN BUTCHER AND QUINTUS FERNANDO
Department of Chemistry, University of Arizona, Tucson, Ariz. (U.S.A.)

(Received January 3rd, 1966)

The use of digital computers has, within the last 5 years, become almost a necessity for the experimental determination of closely spaced equilibrium constants[1-4]. Further, during the past year, several workers have shown that much of the tedium involved in many acid–base equilibrium calculations for systems containing polyprotic acids can be overcome with the aid of computers[5-8].

Equilibrium calculations that are far more rigorous than those that have been attempted heretofore in simple systems can easily be carried out with a digital computer. Valuable information can be obtained from such calculations even in systems containing a single conjugate acid–base pair. In the present report, the effects of 2 important, but almost always neglected, solution parameters (ionic strength and dilution) on the titration curve of a weak acid *versus* a strong base are considered.

CALCULATIONS

The thermodynamic dissociation constant for an uncharged, monoprotic weak acid HA is given by

$$K_A = \frac{[H^+][A^-]}{[HA]} \frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}} \tag{1}$$

where γ is the molar activity coefficient. Hereafter, it will be assumed that the activity coefficient of the undissociated acid, γ_{HA}, is unity. The thermodynamic ion product of water is

$$K_w = [H^+]\,[OH^-]\,\gamma_{H^+}\,\gamma_{OH^-} \tag{2}$$

The material balance and charge balance equations for a solution containing the acid HA and sodium hydroxide are

$$C_A = [HA] + [A^-] \tag{3}$$

$$[H^+] + [Na^+] = [OH^-] + [A^-] \tag{4}$$

Assuming that the titrant is sodium hydroxide, the fraction titrated, X, is defined by

$$X \equiv \frac{C_B}{C_A} = \frac{[Na^+]}{C_A} \tag{5}$$

where C_A and C_B are the analytical concentrations of acid and base, respectively, in the titration solution.

If a dilution coefficient, D, be defined by

$$D \equiv \frac{\text{initial titrand normality}}{\text{titrant normality}}$$

then the analytical concentration of acid at any time during the titration is given by

$$C_A = \frac{C_A{}^0}{1+XD} \tag{6}$$

where $C_A{}^0$ is the formality of the initial titrand solution.

Equations (4), (5), and (6) can be combined to give:

$$X = \frac{1+XD}{C_A{}^0}([\mathrm{OH}^-]+[\mathrm{A}^-]-[\mathrm{H}^+]) \tag{7}$$

Expressions for $[\mathrm{OH}^-]$ and $[\mathrm{A}^-]$ are readily obtained from eqn. (2) and eqns. (1) and (3), respectively.

$$[\mathrm{OH}^-] = \frac{K_w}{[\mathrm{H}^+]\,\gamma_{\mathrm{H}^+}\gamma_{\mathrm{OH}^-}} \tag{8}$$

$$[\mathrm{A}^-] = \frac{C_A{}^0 K_A}{(1+XD)(K_A+[\mathrm{H}^+]\gamma_{\mathrm{H}^+}\gamma_{\mathrm{A}^-})} \tag{9}$$

When these expressions are substituted into eqn. (7) the result is

$$X = \frac{1+XD}{C_A{}^0}\left(\frac{K_w}{[\mathrm{H}^+]\,\gamma_{\mathrm{H}^+}\gamma_{\mathrm{OH}^-}} + \frac{K_A C_A{}^0}{(1+XD)(K_A+[\mathrm{H}^+]\gamma_{\mathrm{H}^+}\gamma_{\mathrm{A}^-})} - [\mathrm{H}^+]\right) \tag{10}$$

Equation (10) can be solved to give an explicit expression for X

$$X = \frac{\dfrac{K_w}{[\mathrm{H}^+]\,\gamma_{\mathrm{H}^+}\gamma_{\mathrm{OH}^-}} + \dfrac{C_A{}^0 K_A}{K_A+[\mathrm{H}^+]\gamma_{\mathrm{H}^+}\gamma_{\mathrm{A}^-}} - [\mathrm{H}^+]}{C_A{}^0 + D[\mathrm{H}^+] - \dfrac{K_w D}{[\mathrm{H}^+]\,\gamma_{\mathrm{H}^+}\gamma_{\mathrm{OH}^-}}} \tag{11}$$

When all the activity coefficients are unity, eqn. (11) reduces to the expression used when ionic strength changes are not to be considered

$$X = \frac{\dfrac{K_w}{[\mathrm{H}^+]} + \dfrac{C_A{}^0 K_A}{(K_A+[\mathrm{H}^+])} - [\mathrm{H}^+]}{C_A{}^0 + D[\mathrm{H}^+] - \dfrac{K_w D}{[\mathrm{H}^+]}} \tag{12}$$

Several approaches may be taken to the solution of eqn. (11). Since this equation is cubic in $[\mathrm{H}^+]$, perhaps the simplest approach is to assign a value to $[\mathrm{H}^+]$ and then to calculate the corresponding value of X[7,9]. Of course, this calculation requires a knowledge of the activity coefficients. These, however, are dependent upon the ionic strength which, in turn, is a function of X as can be seen from the following. The ionic strength, μ, is given by

$$\mu = \frac{1}{2}([\mathrm{H}^+]+[\mathrm{Na}^+]+[\mathrm{OH}^-]+[\mathrm{A}^-]) \tag{13}$$

When combined with eqns. (4), (5) and (6), this reduces to

$$\mu = [\mathrm{H}^+]+[\mathrm{Na}^+] \tag{14a}$$

$$= [\mathrm{H}^+] + \frac{XC_{\mathrm{A}}{}^0}{(1+XD)} \tag{14b}$$

A simple, iterative procedure has been developed to calculate X. This procedure will be discussed with reference to the flow diagram (Fig. 1) for the computer program which actually performs the calculations. Table I lists the meanings of the symbols used in the flow chart and in the program itself.

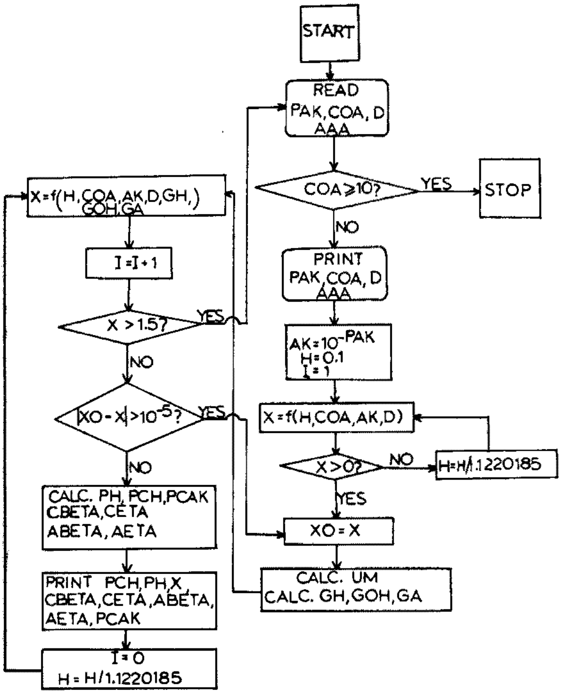


Fig. 1. Flow diagram for computer program listed in Fig. 2.

After the parameters PAK, COA, D, and AAA have been read in, COA is tested to see if it is greater than or equal to 10. No practical problem would involve such a large acid concentration. This is simply a test for the end of data and a data card with COA $\geqslant$ 10 causes termination of the run. If COA $<$ 10, the values of PAK, COA, D, and AAA are printed out along with a heading format before the calculations are begun.

The acid dissociation constant is then calculated from PAK, and the counting index, I, is initialized at 1. The initial value of H is taken to be 0.1 M (PCH = 1). This choice and the choice of antilog 0.05 as the factor by which H is changed considerably simplify the plotting of the results of the computations.

TABLE I

IDENTIFIERS USED IN THE PROGRAM AND FLOW DIAGRAM

AAA	a_{A^-}; Debye–Hückel ion size parameter for the acid anion (in Å)
ABETA	β_a; dC_B/dpa_H
AETA	η_a; dpa_H/dX
AK	K_A; thermodynamic dissociation constant for the acid HA
CBETA	β_c; $dC_B/dp[H^+]$
CETA	η_c; $dp[H^+]/dX$
COA	C_A^0; initial formal concentration of acid
D	Dilution coefficient; C_A^0/titrant normality
GA	γ_{A^-}; molar activity coefficient of the acid anion
GH	γ_{H^+}; molar activity coefficient of H^+
GOH	γ_{OH^-}; molar activity coefficient of OH^-
H	$[H^+]$
I	Counting index; number of times X has been calculated
PAK	pK_A; $-\log K_A$
PCAK	pK_c; $-\log (K_A/\gamma_{H^+}\gamma_{A^-})$; concentration dissociation constant for HA.
PCH	$p[H^+]$; $-\log [H^+]$
PH	pa_H; $-\log ([H^+]\gamma_{H^+})$
Q, RA, RH, ROH, S, T, U, V, W, Z:	Defined functions used to simplify the calculation of β and η
UM	$\sqrt{\mu}$; square root of the ionic strength
X	C_B/C_A; fraction of acid titrated
XO	Previous value of X

Using the initial value of H, X is calculated from eqn. (13). If this X is negative, H is decreased by a factor of 1.1220185 (*i.e.* PCH is increased by an increment of 0.05) and a new X is calculated. This process repeats until a positive X is obtained.

This value of X is then used to calculate the square root of the ionic strength, using eqn. (14). The hydrogen and hydroxyl ion and acid anion activity coefficients are then calculated from the DEBYE–HÜCKEL equation

$$\gamma_i = 10^{-\frac{AZ_i^2\mu^{\frac{1}{2}}}{1+Ba_i\mu^{\frac{1}{2}}}} \qquad (15)$$

Next, a new X is calculated from eqn. (9) and the index I is increased by 1. The new value of X is then tested: if it is greater than 1.5, the calculation is complete and a new set of data is read; if it is less than 1.5, the calculations are continued.

The new X is then compared to the previous X: if the difference is greater than 0.00001, the new X becomes the previous X and the calculation of yet another new X, beginning with the calculation of UM, is undertaken. This is repeated until the new X and previous X differ by less than 0.00001; then PCH, PH, CBETA, ABETA, CETA, and AETA are calculated and are printed out along with X.

The counting index is then reset to 0, the value of H is decreased by the factor of 1.1220185 and a new X is calculated. The values of the activity coefficients from the preceding H are still in the memory and are used in the initial calculation since they offer good approximations to the new values of activity coefficients.

The Van Slyke buffer index, β, is defined by

$$\beta \equiv \frac{\mathrm{d}C_\mathrm{B}}{\mathrm{dpH}} = -\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{dpH}} \tag{16}$$

There are two possible approaches to the calculation of β, depending upon the definition of pH which is employed. If the Sørensen definition of pH is used

$$\mathrm{p}[\mathrm{H}^+] = -\log[\mathrm{H}^+] \tag{17}$$

then β is given by

$$\beta = -2.303\,[\mathrm{H}^+]\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}[\mathrm{H}^+]} \tag{18}$$

An expression for the derivative in eqn. (18) is obtained as follows: differentiation of eqn. (4) gives

$$\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}[\mathrm{H}^+]} = \frac{\mathrm{d}[\mathrm{OH}^-]}{\mathrm{d}[\mathrm{H}^+]} + \frac{\mathrm{d}[\mathrm{A}^-]}{\mathrm{d}[\mathrm{H}^+]} - 1 \tag{19}$$

Expressions for $\mathrm{d}[\mathrm{OH}^-]/\mathrm{d}[\mathrm{H}^+]$ and $\mathrm{d}[\mathrm{A}^-]/\mathrm{d}[\mathrm{H}^+]$ can be obtained by differentiation of eqns. (8) and (9), respectively. These expressions will, in turn, contain terms in $\mathrm{d}X/\mathrm{d}[\mathrm{H}^+]$, $\mathrm{d}\gamma_i/\mathrm{d}[\mathrm{H}^+]$ and $\mathrm{d}\mu/\mathrm{d}[\mathrm{H}^+]$, so it is worthwhile to obtain expressions for these latter terms first.

If eqn. (6) is substituted into eqn. (5) and the result is differentiated with respect to $[\mathrm{H}^+]$, the result is

$$\frac{\mathrm{d}X}{\mathrm{d}[\mathrm{H}^+]} = \frac{(1+XD)^2}{C_\mathrm{A}^0}\,\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}[\mathrm{H}^+]} \tag{20}$$

Differentiation of eqn. (14a) gives

$$\frac{\mathrm{d}\mu}{\mathrm{d}[\mathrm{H}^+]} = 1 + \frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}[\mathrm{H}^+]} \tag{21}$$

An expression for $\mathrm{d}\gamma_i/\mathrm{d}[\mathrm{H}^+]$ is obtained by differentiation of eqn. (15) followed by substitution from eqn. (21) to give

$$\frac{\mathrm{d}\gamma_i}{\mathrm{d}[\mathrm{H}^+]} = R_i\left(1 + \frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}[\mathrm{H}^+]}\right) \tag{22}$$

where R_i is defined by

$$R_i \equiv \frac{-2.303\,A\,\gamma_i}{2\mu^{\frac{1}{2}}(1+Ba_1\mu^{\frac{1}{2}})^2} \tag{23}$$

The ion charge term, Z_i, has been omitted from this equation because all the ions considered are singly charged.

Differentiation of eqns. (8) and (9) with appropriate substitutions from eqns. (20), (21) and (22) then gives

$$\frac{\mathrm{d}[\mathrm{OH}^-]}{\mathrm{d}[\mathrm{H}^+]} = \frac{-K_\mathrm{w}}{[\mathrm{H}^+]^2{\gamma_{\mathrm{H}^+}}^2{\gamma_{\mathrm{OH}^-}}^2}\left(S + T\,\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}[\mathrm{H}^+]}\right) \tag{24}$$

$$\frac{\mathrm{d}[\mathrm{A}^-]}{\mathrm{d}[\mathrm{H}^+]} = \frac{-C_{\mathrm{A}}{}^0 K_{\mathrm{A}}}{UV^2}\left(W + Z\,\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}[\mathrm{H}^+]}\right) \tag{25}$$

where S, T, U, V, W, and Z are functions defined for convenience in manipulation as follows:

$$T \equiv [\mathrm{H}^+]\gamma_{\mathrm{H}^+} R_{\mathrm{OH}^-} + [\mathrm{H}^+]\gamma_{\mathrm{OH}^-} R_{\mathrm{H}^+} \tag{26}$$

$$S \equiv T + \gamma_{\mathrm{H}^+}\gamma_{\mathrm{OH}^-} \tag{27}$$

$$U \equiv 1 + XD \tag{28}$$

$$V \equiv K_{\mathrm{A}} + [\mathrm{H}^+]\gamma_{\mathrm{H}^+}\gamma_{\mathrm{A}^-} \tag{29}$$

$$W \equiv [\mathrm{H}^+]\gamma_{\mathrm{H}^+} R_{\mathrm{A}} + [\mathrm{H}^+]\gamma_{\mathrm{A}^-} R_{\mathrm{H}} + \gamma_{\mathrm{H}^+}\gamma_{\mathrm{A}^-} \tag{30}$$

$$Z \equiv [\mathrm{H}^+]\gamma_{\mathrm{H}^+} R_{\mathrm{A}} + [\mathrm{H}^+]\gamma_{\mathrm{A}^-} R_{\mathrm{H}} + \frac{DUV}{C_{\mathrm{A}}{}^0} \tag{31}$$

Upon substitution of eqns. (24) and (25) into eqn. (19) and collection of terms in $\mathrm{d}C_{\mathrm{B}}/\mathrm{d}[\mathrm{H}^+]$, an expression is obtained

$$\frac{-\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}[\mathrm{H}^+]} = \frac{\left(1 + \dfrac{WC_{\mathrm{A}}{}^0 K_{\mathrm{A}}}{UV^2} + \dfrac{SK_{\mathrm{w}}}{[\mathrm{H}^+]^2\gamma_{\mathrm{H}^+}{}^2\gamma_{\mathrm{OH}^-}{}^2}\right)}{\left(1 + \dfrac{ZC_{\mathrm{A}}{}^0 K_{\mathrm{A}}}{UV^2} + \dfrac{TK_{\mathrm{w}}}{[\mathrm{H}^+]^2\gamma_{\mathrm{H}^+}{}^2\gamma_{\mathrm{OH}^-}{}^2}\right)} \equiv \frac{1}{Q} \tag{32}$$

which, for convenience, is defined as $1/Q$. β is then given by

$$\beta_{\mathrm{c}} = \frac{2.303[\mathrm{H}^+]}{Q} \tag{33}$$

where the subscript c indicates that the concentration pH, p[H+], has been used.

On the other hand, the present day operational pH scale relates more closely to the hydrogen ion activity than to concentration. When β and pH are redefined in terms of activity,

$$\beta_{\mathrm{a}} \equiv \frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{dp}a_{\mathrm{H}}} \tag{34}$$

$$\mathrm{p}a_{\mathrm{H}} = -\log([\mathrm{H}^+]\gamma_{\mathrm{H}^+}) \tag{35}$$

Differentiation of eqn. (35) and substitution from eqns. (22) and (32) give an expression for β_{a}

$$\beta_{\mathrm{a}} = \frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{dp}a_{\mathrm{H}}} = \frac{2.303[\mathrm{H}^+]\gamma_{\mathrm{H}^+}}{Q[\mathrm{H}^+]R_{\mathrm{H}} + Q\gamma_{\mathrm{H}^+} - [\mathrm{H}^+]\mathrm{R}_{\mathrm{H}}} \tag{36}$$

The sharpness index, η, is defined by either

$$\eta_{\mathrm{c}} \equiv \frac{\mathrm{dp}[\mathrm{H}^+]}{\mathrm{d}X} = \frac{\mathrm{dp}[\mathrm{H}^+]}{\mathrm{d}C_{\mathrm{B}}} \cdot \frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}X} \tag{37}$$

$$\eta_{\mathrm{a}} \equiv \frac{\mathrm{dp}a_{\mathrm{H}}}{\mathrm{d}X} = \frac{\mathrm{dp}a_{\mathrm{H}}}{\mathrm{d}C_{\mathrm{B}}} \cdot \frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}X} \tag{38}$$

where the subscripts have the same significance as in β.

Upon substitution of eqns. (20) and (33) into eqn. (37) and of eqns. (20) and (36) into eqn. (35), expressions for the sharpness index are obtained:

$$\eta_c = \frac{C_A{}^0}{\beta_c(1+XD)^2} \tag{39}$$

$$\eta_a = \frac{C_A{}^0}{\beta_a(1+XD)^2} \tag{40}$$

For the case where ionic strength effects are ignored, differentiation of eqn. (12) followed by substitution from eqns. (12),(18) and (20) gives the expression for β

$$\beta = \frac{2.303[\mathrm{H}^+]C_A{}^0}{(1+XD)^2}\left[\frac{(1+XD)\left(1+\frac{K_w}{[\mathrm{H}^+]^2}\right)+\frac{C_A{}^0K_A}{([\mathrm{H}^+]+K_A{}^2)}}{C_A{}^0+D[\mathrm{H}^+]-\frac{K_wD}{[\mathrm{H}^+]}}\right] \tag{41}$$

Substitution of eqns. (20) and (37) into eqn. (41) then gives

$$\eta = \frac{C_A{}^0}{(1+XD)^2\beta} \tag{42}$$

The computer program used to perform most of the calculations for this study is presented in Fig. 2. The program is written in FORTRAN II for use with the FORT-PITT compiler and the IBM 7072. This program, *per se*, may give erroneous results with some other compilers due to the EXPF and LOGF functions. In the FORT-PITT compiler, these functions perform the exponentiation and logging operations, respectively, to base 10, while in some other compilers these operations are performed to base e. Should this program be used on such a compiler, it would be necessary to rewrite the arguments of the EXPF and LOGF functions to include the 2.3025851 factor for conversion to base 10.

Throughout these calculations, the following values of constants were used:

Thermodynamic ion product of water (25°): $10^{-14.00}$

Debye–Hückel A (25°): 0.5091

Debye–Hückel B (25°): $0.3286 \cdot 10^{-8}$

Debye–Hückel a for OH^-: 3.0 Å

Debye–Hückel a for H^+: 9.0 Å

If it were desired to study the effect of temperature changes, K_w, A and B could readily be defined as variables and read in with the other data.

The iterative loop for calculating X converges very quickly, requiring no more than 2 or 3 iterations except when X is greater than about 1.3.

The average processing time on the 7072 is about 20 sec per curve.

For the calculations with no dilution effect but with ionic strength effects considered, D is set to zero.

For the computations neglecting ionic strength effects, no iteration is required. A simple program, incorporating eqn. (12) and simplified equations for β and η, eqns. (41) and (42), was used to perform these calculations.

```
C    MONOPROTIC ACID  ACTIVITY AND DILUTION EFFECTS INCLUDED
 10  READ 100, PAK, COA, D, AAA
     IF (COA-10.0) 11,300,300
 11  PRINT 200, PAK, COA, D, AAA
 20  AK = EXPF(-PAK)
     H = 0.1
     I = 1
 30  X=(1.0E-14/H + COA*AK/(AK+H)-H) / COA
     IF (X) 31,40,40
 31   H = H / 1.1220185
     GO = TO 30
 40  XO = X
 41  UM = SQRTF(H + X*COA/(1.0+X*D))
     GH = EXPF((-0.5091*UM)/(1.0+2.957*UM))
     GOH = EXPF((-0.5091*UM)/(1.0+0.9858*UM))
     GA = EXPF((-0.5091*UM)/(1.0+0.3286*AAA*UM))
 500 X=((1.0E-14/(H*GH*GOH))+(COA*AK/(AK+H*GH*GA))-H)/
   1 (COA+D*(H-(1.0E-14/(H*GH*GOH))))
     I = I + 1
     IF (X-1.5) 60,10,10
 60  IF (ABSF(XO-X)-0.00001) 70,40,40
 70  PH = -LOGF(GH*H)
     PCH = -LOGF(H)
     RH = -GH*0.5861/(UM*((1.0+2.957*UM)**2.0))
     ROH= -GOH*0.5861/(UM*((1.0+0.9858*UM)**2.0))
     RA = -GA*0.5861/(UM*((1.0+0.3286*AAA*UM)**2.0))
     T  = H*GH*ROH + H*GOH*RH
     S  = T + GH*GOH
     U  = 1.0 + X*D
     V  = AK + H*GH*GA
     W = H*GH*RA + H*GA*RH + GH*GA
     Z  = H*GH*RA + H*GA*RH + D*U*V/COA
   0 Q = (1.0+Z*COA*AK/(U*V*V)+T*1.0E-14/(H*H*GH*GH*GOH*GOH)) /
   1 (1.0+W*COA*AK/(U*V*V) + S*1.0E-14/(H*H*GH*GH*GOH*GOH))
     CBETA = 2.30259*H / Q
     CETA = COA/(CBETA*(1.0+X*D)*(1.0+X*D))
     ABETA = 2.30259*H*GH/(Q*(GH+H*RH)-H*RH)
     AETA = COA/(ABETA*(1.0+X*D)*(1.0+X*D))
     PCAK= -LOGF(AK/(GH*GA))
     PRINT 201, PCH, PH, X, ABETA, AETA, CBETA, CETA, I, PCAK
     I = 0
     H = H / 1.1220185
     GO TO 50
100  FORMAT (4F10.5)
2000 FORMAT (1H1 34H WEAK ACID, STRONG BASE TITN. CALC /// 7H PKA =
   1 F6.3// 18H ACID FORMALITY =   F8.6 //19H DILUTION FACTOR =
   2      F4.2 // 35H DEBYE-HUCKEL ION SIZE PARAMETER =  F4.2  ///
   3 90H    PCH       PH              X          ABETA        AETA     CBETA
   4        CETA      I          CONC  K            )
2010 FORMAT(F7.3,4X,F6.3,4X,F8.5,2X,F8.6,2X,1PE11.4,2X, 0PF8.6,2X,
   1 1PE11.4, 2X, I2, 3X, 0PF8.4 )
300  STOP
     END
C    FOLLOWING IS A TYPICAL DATA CARD  PAK=5.0, COA=0.1, D=1.0, AAA=3
5.0           0.100    1.0          3.0
11.           11.00    11.          3.0
```

Fig. 2. Listing of FORTRAN II program for calculations when dilution and ionic strength effects are considered.

RESULTS

The results of calculations of β as a function of X in a typical case ($C_A{}^0 = 0.1$ F

$K_A = 10^{-5}$) are presented in Fig. 3. Curves C, F, and I were calculated from eqn. (41) which includes dilution but not activity effects. As indicated by these curves, increasing dilution has a considerable effect upon β; the value of X at which β is at a maximum is shifted from 0.5 when $D = 0$ (*e.g.* coulometrically generated titrant) to 0.33 when $D = 1$ and there is a concurrent decrease in β_{max} from 0.0576 to 0.0288.

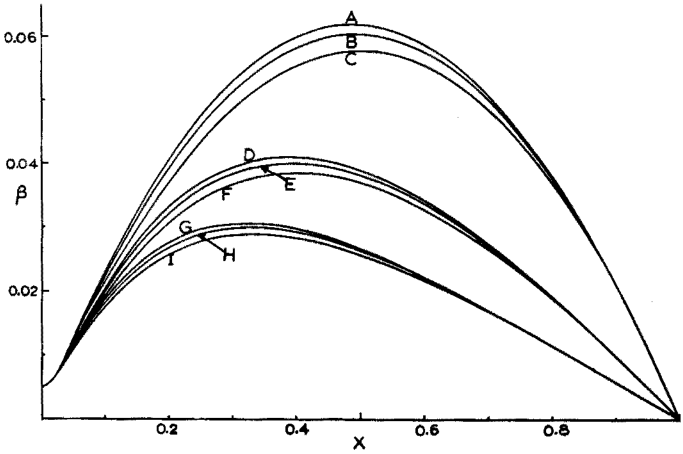


Fig. 3. Effect of dilution and ionic strength on β. pK_a = 5.000; $C_A{}^0$ = 0.1000. Curve A: β_c, D = 0.000; Curve B: β_a, D = 0.000; Curve C: β, D = 0.000; Curve D: β_c, D = 0.5000; Curve E: β_a, D = 0.5000; Curve F: β, D = 0.5000; Curve G: β_c, D = 1.000; Curve H: β_a, D = 1.000; Curve I: β, D = 1.000.

When the effects of ionic strength are included in the calculation of β for the above case, the remaining curves in Fig. 3 are obtained. It is noteworthy that both activity calculations predict shifts in the location of β_{max} and larger values of β_{max} than does the simple concentration calculation. The effect of increased dilution is qualitatively the same as when activity effects are not considered, increasing dilution resulting in decreasing values of β_{max} and increasing skewing of the β *vs.* X curves.

These unexpected effects of ionic strength upon the calculated location and magnitude of β_{max} cannot be predicted, even qualitatively from the usual expression for β

$$\beta = 2.303\left([H^+]+[OH^-] + \frac{C_A K_A[H^+]}{(K_A+[H^+])^2}\right) \tag{43}$$

The more rigorous equations contain cross terms, arising from the differentiation, whose magnitudes are quite significant and whose effects are not predicted by using an activity corrected concentration constant in eqn. (43). The effects of dilution can be predicted qualitatively by eqn. (43) if C_A is corrected for the dilution.

In general, these calculations have shown that, in the titration of a weak, monoprotic acid with a strong base:

(*1*) β_{max} does not often occur at the half-neutralization point ($X = 0.5$) or when pH = pK_A or pK_c.

(*2*) Increasing dilution decreases the value of β_{max} as well as the value of X at which β_{max} occurs.

(3) Ionic strength effects cause β_{max} to be significantly larger and to occur somewhat earlier in a titration than would be expected from a concentration-based calculation.

Since the activity coefficients γ_{H^+} and γ_{A^-} are calculated in the program, pK_c, the concentration dissociation constant for the acid, is readily obtainable. The variation of pK_c with X for various initial acid concentrations and for $pK_a = 5.0$ is shown in Fig. 4. As expected, pK_c changes more when the acid is more concentrated and increased dilution results in decreased changes in pK_c during the course of a titration.

The sharpness index (η_a or η_c) is equal to the slope of the titration curve (pa_H or $p[H^+]$ *vs.* X, respectively). The magnitude of η_{max} is a measure of the sharpness of an end-point and, unlike β_{max}, does not change appreciably when ionic strength effects are taken into account (Table II). In the vicinity of the equivalence point, the

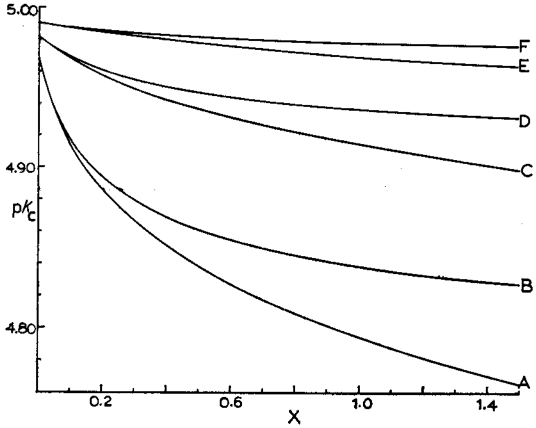


Fig. 4. Variation of pK_c during titrations. $pK_a = 5.000$; $a_{A^-} = 3.0$. Curve A: $C_A{}^0 = 0.1$, $D = 0.000$; Curve B: $C_A{}^0 = 0.1$, $D = 1.000$; Curve C: $C_A{}^0 = 0.01$, $D = 0.000$; Curve D: $C_A{}^0 = 0.01$, $D = 1.000$; Curve E: $C_A{}^0 = 0.001$, $D = 0.000$; Curve F: $C_A{}^0 = 0.001$, $D = 1.000$.

TABLE II

EFFECT OF DILUTION, pK_A, AND IONIC STRENGTH ON η_{max} ($C_A{}^0 = 0.1000$ F)

		No ionic strength effects		*Ionic strength effects included* $a_{A^-} = 3.0$		
D	pK_A	η_{max}	$p[H^+]$ *at* η_{max}	η_{max}	$p[H^+]$ *at* η_{max}	pa_H *at* η_{max}
0.0000	3.000	$2.16 \cdot 10^4$	8.00	$2.16 \cdot 10^4$	7.79	7.87
0.0000	5.000	$2.17 \cdot 10^3$	9.00	$2.17 \cdot 10^3$	8.79	8.87
0.0000	7.000	$2.17 \cdot 10^2$	10.00	$2.17 \cdot 10^2$	9.78	8.86
0.0000	9.000	$2.19 \cdot 10^1$	11.00	$2.19 \cdot 10^1$	10.77	10.85
0.5000	3.000	$1.76 \cdot 10^4$	7.92	$1.75 \cdot 10^4$	7.73	7.80
0.5000	5.000	$1.77 \cdot 10^3$	8.92	$1.77 \cdot 10^3$	8.73	8.81
0.5000	7.000	$1.78 \cdot 10^2$	9.91	$1.77 \cdot 10^2$	9.73	9.81
0.5000	9.000	$1.79 \cdot 10^1$	10.90	$1.79 \cdot 10^1$	10.72	10.80
1.000	3.000	$1.52 \cdot 10^4$	7.85	$1.52 \cdot 10^4$	7.69	7.76
1.000	5.000	$1.54 \cdot 10^3$	8.85	$1.53 \cdot 10^3$	8.68	8.75
1.000	7.000	$1.54 \cdot 10^2$	9.85	$1.54 \cdot 10^2$	9.68	9.75
1.000	9.000	$1.55 \cdot 10^1$	10.83	$1.55 \cdot 10^1$	10.67	10.74

activity coefficients of the solutes do not change appreciably with changes in pH and, as a result, $\eta_{a,max}$ and $\eta_{c,max}$ values differ by less than 0.1%. Thus the simplified calculations that have been used to obtain η_{max} values[10] are more than sufficiently valid if they are expanded to include the effects of dilution. The pH at which η_{max} occurs is dependent on ionic strength effects as well as on the dilution factor. For example, in the case considered in Table II, the pa_H at η_{max} is 10.80 (in the titration of a 0.1 *F* solution of a weak acid whose pK_A is 9.00 with 0.2 *F* sodium hydroxide ($D = 0.5$)), whereas the p[H$^+$] at η_{max} is 10.72 or 10.90 depending upon whether or not activity effects are considered. Figure 5 also illustrates these effects.

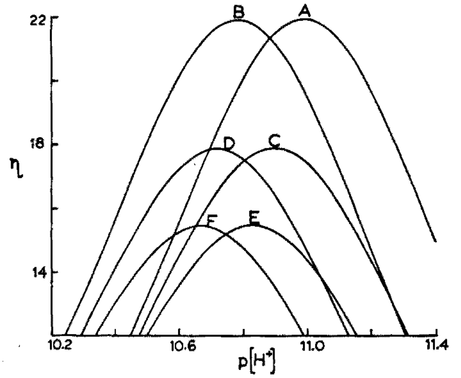


Fig. 5. Effect of dilution and ionic strength on η. $pK_a = 9.000$; $C_A{}^0 = 0.1000$. Curve A: $D = 0.000$, no ionic strength; Curve B: $D = 0.000$, $a_{A^-} = 3.0$; at η_{max}, $pa_H = p[H^+] + 0.083$; Curve C: $D = 0.5000$, no ionic strength; Curve D: $D = 0.5000$, $a_{A^-} = 3.0$; at η_{max}, $pa_H = p[H^+] + 0.075$; Curve E: $D = 1.000$, no ionic strength; Curve F: $D = 1.000$, $a_{A^-} = 3.0$; at η_{max}, $pa_H = p[H^+] + 0.069$.

It is of interest to note that the Debye–Hückel ion size parameter for the titrant cation does not appear in any of the expressions for X, β or η. Thus the titration curves and the β or η *vs.* X curves are not affected by change of the titrant, provided that the titrant is a uni-univalent strong base.

The shapes of the calculated titration curves, as would be expected from the foregoing, differ from the shapes of the idealized curves, which are commonly calculated, primarily in the buffer region and in the region well beyond the equivalence point. Also, the calculated pH at the equivalence point is affected strongly by the degree of sophistication of the calculation. In plots of the titration curves, these differences in shape do not appear to be large, but their significance and magnitude are clearly revealed by the β and η values.

CONCLUSIONS

The approximate equations that are usually used in the calculation of weak acid–strong base titration curves, are sufficient to show the general shape of these curves and the trends that occur with changes in concentration and pK_a. The more rigorous titration curve calculations performed in this work are principally useful for predicting more accurately the pH values obtained in the course of a titration.

The approximate equations for β and η, however, are often misleading. The introduction of the dilution effect into the calculations results in a large decrease in the values of β and η near their maxima; the locations of β_{max} and η_{max} are shifted significantly. The introduction of ionic strength effects into the calculations results in appreciable changes in the magnitude and location of β_{max} and the pH at the inflection point (*i.e.* at η_{max}) is shifted towards lower pH values; this shift becomes quite significant for moderately weak acids.

Calculations similar to those described above can be performed for titrations of weak bases and polyprotic acids. The location of the equivalence point with respect to the inflection point in these acid–base titrations is also of practical importance, for instance in the application of differential potentiometric method for the determination of pK_A values[11]. These aspects of acid–base equilibria are currently under study in this laboratory.

The authors are grateful to DAVID L. FRANKLIN of the Numerical Analysis Laboratory, University of Arizona, for helpful discussions and to the staff of the Numerical Analysis Laboratory for the use of the computer.

SUMMARY

The effects of dilution and ionic strength on weak acid–strong base titration curves and on the buffer index, β, and sharpness index, η, for these titrations have been calculated. It has been shown that the approximate equations generally used to calculate β and η are often misleading.

RÉSUMÉ

Les auteurs ont calculé les influences de la dilution et de la force ionique sur les courbes de titration acide faible–base forte, ainsi que sur l'indice tampon β et l'indice de netteté η.

ZUSAMMENFASSUNG

Die Einflüsse der Verdünnung und Ionenstärke auf die Titrationskurven, den Pufferindex β und den Schärfeindex η bei Titrationen einer schwachen Säure mit einer starken Base werden berechnet. Es wurde gezeigt, dass die Näherungsgleichungen, die allgemein zur Berechnung von β und η verwendet werden, oft irreführend sind.

REFERENCES

1 J. RYDBERG, J. C. SULLIVAN AND W. F. MILLER, *Acta Chem. Scand.*, 13 (1959) 2023 and 2057.
2 N. INGRI AND L. G. SILLEN, *Acta Chem. Scand.*, 16 (1962) 173.
3 W. P. SCHAEFER, *Inorg. Chem.*, 4 (1965) 642.
4 R. C. LANSBURY, V. E. PRICE AND A. G. SMEETH, *J. Chem. Soc.*, (1965) 1896.
5 A. J. BARD AND D. M. KING, *J. Chem. Educ.*, 42 (1965) 127.
6 A. R. EMERY, *J. Chem. Educ.*, 42 (1965) 131.
7 S. L. COOKE, JR., *J. Chem. Educ.*, 42 (1965) 620.
8 O. T. ZAJICEK, *J. Chem. Educ.*, 42 (1965) 622.
9 J. BUTCHER, *Ph.D. Thesis*, Georgia Institute of Technology, 1965.
10 S. BRUCKENSTEIN AND I. M. KOLTHOFF, in I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Chapter 12, Interscience, New York, 1959.
11 FR. L. HAHN AND R. KLOCKMAN, *Z. Physik. Chem.*, [A] 146 (1930) 373.

EXTRACTIONS WITH β-DIKETONES AS CHELATING SOLVENTS

GEO. K. SCHWEITZER AND WILLIAM VAN WILLIS
Department of Chemistry, The University of Tennessee, Knoxville, Tenn. 37916 (U.S.A.)
(Received February 1st, 1966)

The general situation in chelate solvent extraction is typified by a system consisting of an aqueous phase and an organic phase. The aqueous phase contains metal ion, a suitable reagent for maintenance of the ionic strength, acid or base for pH adjustment, and is usually presaturated with the organic solvent. The organic phase contains the chelating agent, and is usually presaturated with water adjusted to the appropriate ionic strength. Masking agents or adducting agents are sometimes present. Upon contacting the phases, interactions occur and various neutral species can distribute between the phases.

Such a system has several disadvantages. The concentration of many chelating agents in the organic phase is limited to $< 1\ M$ by their solubilities in most common organic solvents. The organic solvent can influence the distribution of metal chelate by solvate formation[1] and other solubility phenomena. These influences vary with solvent choice. Also, variations in extraction may be seen owing to chelating agent polymerization[2], or a change in chelating agent concentration in the organic phase can occur because of a pH change in the aqueous phase.

A compound which can act as a chelating agent and simultaneously as the bulk organic phase, which will be termed as a chelating solvent, possesses several advantages not found in the general situation described above. Larger concentrations of the chelating agent ($\sim 10\ M$ for acetylacetone) are possible in the organic phase; these facilitate macro extractions and allow extractions from more acidic aqueous media. Polymerization, or activity effects, may be maintained at a constant level over wider pH regions. Also, the similarity of the metal chelate and the chelating solvent might possibly lead to larger solubilities of the chelate in the chelating solvent. As long as the chelating solvent phase is present in contact with the aqueous phase, the former serves as a reservoir to replenish any chelating agent transferred to the latter, and the organic phase chelating agent concentration is held constant. This might possibly allow results to be obtained which more closely approximate the ideal theoretical situation than the general situation.

Chelating solvents do have the disadvantage that, since the organic phase chelating agent concentration is constant, it is no longer an experimental variable, and some definition in the system is lost. Also, the large amount of chelating agent present could make high pH values hard to obtain, since base would be consumed in converting the reagent to its anion, and might not be available to suppress the hydrogen ion concentration. This effect would quantitatively depend on the solubility of the chelating solvent in the aqueous phase and on its acid dissociation constant.

STEWARD[3] has investigated the properties of alkyl phosphoric acids as chelating solvents. Their high viscosities necessitate the use of diluents such as kerosene or other hydrocarbon mixtures, and therefore these compounds are not ordinarily used as chelating solvents.

SEGALL, ARIEL AND SHORR[4] have investigated the properties of 2,2′-thiodiethanethiol as a chelating agent in chloroform solvent. The material is a liquid (b.p. 138° at 13 mm Hg) which forms complexes with Co, Ni, Pd, and Cu but not with many other metal ions. Their results indicate that the reagent might have some utility as a chelating solvent, although no such studies have been reported.

STEINBACH[5] used acetylacetone (2,4-pentanedione) as a chelating solvent to study the extractions of the ions Cr(III), Co(III), Fe(III), Be, Cu, Al, Ga, In, V, Zr, and Zn as functions of pH, ionic strength, and temperature. Favorable solubilities of the metal acetylacetonates in the chelating solvent were reported; extractions from solutions of low pH were found feasible on micro and macro scales; extractions were enhanced kinetically by the high solubility of acetylacetone in water; quantitative separation procedures were obtained for most metals; and agreement between experimental data and a theoretical description was termed good.

KRISHEN[6] extended this work by investigating the acetylacetonates of Cu, Bi(III), Hf(IV), Fe(III), La, Pb, Pr, Zn, Zr, and uranyl ion. The masking agents EDTA, fluoride, tartrate, and ferron (8-hydroxy-7-iodo-5-quinoline sulfate) were studied also. Results and conclusions were obtained which were similar to those reported by STEINBACH. BROWN, STEINBACH AND WAGNER[7] studied the distribution of 8 lanthanides and yttrium using acetylacetone as a chelating solvent to determine the feasibility of quantitative separations. JASKOLSKA, WODKIEWICZ AND MINCZEWSKI[8] used acetylacetone as a chelating solvent for the determination of trace impurities in semiconductor materials.

This paper reports a study undertaken to synthesize and investigate a liquid compound whose chelating agent properties and low water solubility would enable it to act as a chelating solvent.

THEORETICAL CONSIDERATIONS

A theoretical approach to the solvent extraction of metal chelates has been presented by SCHWEITZER[9]. In this treatment the distribution coefficient D for the metal can be expressed as

$$D = \frac{K_{\mathrm{MRAH}} P_{\mathrm{MRAH}} [\mathrm{HR}]_{\mathrm{o}}^{\mathrm{R+A-r-a}} K_{\mathrm{w}}^{\mathrm{H-R}}}{C_{\mathrm{mrah}} K^{\mathrm{R-r}} P^{\mathrm{R+A-r-a}} [\mathrm{H}]^{\mathrm{R+H-r-h}}} \tag{1}$$

where K_{MRAH} is the formation constant for the partitioning species $\mathrm{M_M R_R (HR)_A (OH)_H}$, P_{MRAH} is its partition constant, $[\mathrm{HR}]_{\mathrm{o}}$ is the organic phase chelating agent concentration, K_{w} is the ion-product constant for water, C_{mrah} is the formation constant for the non-partitioning aqueous metal-containing species $\mathrm{M_m R_r (HR)_a (OH)_h}$, K is the acid association constant of the chelating agent, P is the partition constant of the chelating agent, and $[\mathrm{H}]$ is the hydrogen ion activity. Equation (1), or a similar equation containing a series of such terms will describe a large number of systems. Usually, $[\mathrm{H}]$ and $[\mathrm{HR}]_{\mathrm{o}}$ are the independent variables. However, if a chelating solvent is used, $[\mathrm{HR}]_{\mathrm{o}}$ is fixed, and it is no longer possible to uniquely determine the value of A from a log D

against $[HR]_o$ plot. Only appropriate combinations of R and H can be obtained from a log D against pH plot.

EXPERIMENTAL

Reagents

Indium-114, scandium-46, zinc-65, cobalt-60, and thallium-204 were obtained from Oak Ridge Isotopes Sales Division as the chlorides and converted to the nitrates by treatment with nitric acid. Lead-210 and promethium-147 from Atomic Accessories Inc. were treated similarly. Silver-110 and mercury-203, as the nitrates, were received from ORISD and treated once with nitric acid to oxidize any organic material present. Thorium-234 was extracted from uranyl nitrate using the procedure of BLEULER AND GOLDSMITH[10] and converted to the nitrate. Dilutions to appropriate concentrations were made with 0.1 M $NaNO_3$ for subsequent experimentation.

Ethyl acetate and 5-methyl-2-hexanone were condensed using sodium amide or sodium ethoxide as the condensing agent[11] to form 7-methyl-2,4-octanedione (MOD), which was isolated as the copper salt (m.p. 122–123°). The dione was recovered from the copper salt, dried, and distilled. The boiling point is 88° at 4 mm Hg; refractive index 1.4611; density 0.911 g/ml at 23.9°. Yields were 60–70% with sodium amide, and 40–65% with sodium ethoxide.

Ethyl trifluoroacetate and 5-methyl-2-hexanone were treated similarly to yield 1,1,1-trifluoro-7-methyl-2,4-octanedione (FMOD). The copper salt melts at 87–88°, and the dione distills at 50–55° under a pressure of 3 mm Hg. The refractive index is 1.4153, and the density is 1.130 g/ml at 21.2°. Overall yields were 5–10% with sodium amide, and 40–60% with sodium ethoxide.

The water used in the distribution studies was distilled from an alkaline permanganate solution through a packed glass column, stored in polyethylene jugs, and boiled just before use.

Methods

Equilibrations were carried out in 2-oz. glass bottles equipped with screw caps lined with Teflon gaskets which were placed in a water bath maintained at $25.0 \pm 0.5°$. Measurements of pH were made with a Beckman Model G pH meter using Leeds and Northrup #124138 miniature electrodes. Radioassay work was done using a Nuclear Instruments Model D-34 Geiger Detector or a Tracerlab Model P-20-D Scintillation Detector equipped with a 2-in. NaI(Tl) well crystal, both in conjunction with a Tracerlab Versamatic II Scaler. Spectrophotometric work was performed using a Bausch and Lomb Spectronic 20 and a Beckman DU Spectrophotometer. Gas chromatographic work was done with a Perkin Elmer Model 154 Vapor Fractometer using a one meter by 0.25 in. diameter column filled with dibenzyl ether on 40/60 mesh firebrick to determine water. The NMR measurements were made using a Varian Associates Model A60 instrument.

The values of the acid association constants of MOD and FMOD were determined by the two-phase technique of DYRSSEN[12] and by the method of ALBERT AND SARGENT[13]. Aliquots of 0.1 N base were added to 0.1 ml of the dione in 10 ml of 0.1 N $NaNO_3$, and the pH recorded after each addition. From the P value for the dione and the amount of base added, the $[HR]/[R]$ ratio, and hence the K value was determined.

The solubilities of the two chelating solvents in water were determined by several independent methods. RYDBERG's method[14] involved equilibration of the dione with 0.1 N $NaNO_3$, decomposition of the dione present in an aliquot of the aqueous phase with excess base, and titration of the unused base. Another method[15] used the absorbancy of a water solution of the dione at 259 mμ; a third method[16] used the absorbancy of the iron(III) chelate at 470 mμ.

The metal distribution coefficients were determined by radioassay of aliquots of each phase in the sample vessels at various pH values.

Experimental data

The acid association constant K was determined as its logarithm pK. The pK values were calculated for each pH and increment of standard base added, and these pK values were then averaged. The pK value for MOD was found to be 9.72, and for FMOD 7.14.

The solubility of each dione in 0.1 N sodium nitrate as being equal to the sum of the amounts of keto, enol, and enolate anion forms present, and expressed as moles per liter, is seen in Table I. The minimum solubility occurs at low pH where only small amounts of the enolate anion form are present. This minimum solubility is taken as $2.94 \cdot 10^{-4}$ moles/l for MOD and $2.15 \cdot 10^{-4}$ moles/l for FMOD.

TABLE I

SOLUBILITIES OF THE DIONES IN AQUEOUS 0.1 N SODIUM NITRATE

Dione—moles dione/l · 10^{-4} [a]*—(pH)—method*[b]
MOD: 10^{-4} m/l(pH)method, 3.01 (1.81)S, 3.01 (2.38)S, 2.98 (3.20)F, 3.30 (3.82)S, 3.40 (4.40)D, 2.89 (4.62)F, 3.12 (5.37)S, 3.85 (5.88)F, 3.34 (6.11)D, 3.07 (6.23)S, 3.06 (7.10)D, 2.91 (7.20)S
FMOD: 10^{-4} m/l(pH)method, 2.13 (1.70)S, 2.18 (2.43)D, 2.09 (2.51)S, 2.17 (3.84)S, 2.16 (4.18)D, 2.07 (4.69)S, 2.15 (5.10)S, 2.16 (5.50)D, 2.45 (6.30)S, 3.84 (6.98)S

[a] This includes the dione and its enolate anion.
[b] S = spectrophotometric determination at 2590 Å, D = decomposition with sodium hydroxide, F = spectrophotometric determination at 4700 Å.

TABLE II

EXPERIMENTAL EXTRACTION DATA

Metal ion—valence—metal ion concentration—chelating solvent—pH—(log D)
Th(IV), $1 \cdot 10^{-4}$ M, MOD: pH(log D), 0.70(−1.88), 0.91(−1.10), 1.11(−0.97), 1.14(−0.56), 1.41 (0.39), 1.75(1.48), 1.78(1.80), 2.04(1.75), 2.10(1.45), 2.40(2.07), 2.61(1.67), 3.20(2.15), 3.20(2.33), 4.55(2.47), 4.90(2.41), 5.39(2.33), 5.62(2.71), 5.64(2.65), 5.84(2.30), 6.50(2.30)
Th(IV), $1 \cdot 10^{-4}$ M, FMOD: pH(log D), 0.00(0.98), 0.20(2.75), 0.21(2.83), 0.21(3.00), 0.40(3.01), 0.47(2.30), 0.53(2.30), 0.62(3.35), 0.76(2.29), 0.92(3.73), 0.93(3.51), 1.45(3.55), 1.48(2.06), 1.73 (3.87), 1.80(2.50), 1.90(3.78), 2.46(3.31), 2.49(3.24), 2.56(3.88), 3.47(3.35), 3.88(4.35), 3.92(3.75), 4.60(3.21), 5.03(4.19), 5.09(3.90), 5.26(3.38), 5.37(3.89), 5.48(3.23), 5.51(3.05), 5.92(3.90), 5.95 (3.31), 6.03(3.52), 6.18(3.21), 6.40(3.84)
In(III), $6 \cdot 10^{-6}$ M, MOD: pH(log D), 1.19(−0.67), 1.28(−0.39), 1.36(−0.02), 1.55(0.48), 1.87 (1.41), 2.04(2.91), 2.06(2.08), 2.39(2.81), 2.95(3.25), 3.25(3.64), 4.01(3.47), 4.31(3.72), 4.50(4.17), 5.52(4.83), 5.52(4.75), 5.65(4.60), 5.69(4.66), 6.25(4.71), 6.25(4.80), 6.74(4.61), 6.86(4.31), 7.00 (4.35)

In(III), $6 \cdot 10^{-6}$ *M*, FMOD: pH(log *D*), 0.55(−0.38), 0.96(1.53), 1.40(2.96), 1.75(3.91), 2.02(3.97), 2.39(3.35), 2.91(4.43), 3.10(4.29), 4.34(4.64), 4.60(4.29), 5.06(4.44), 5.12(3.67), 5.85(5.63), 6.40(4.10)

Co(II), $3 \cdot 10^{-7}$ *M*, MOD: pH(log *D*), 1.18(−2.05), 2.04(−1.90), 2.24(−1.75), 2.77(−0.98), 3.74(0.55), 3.98(1.80), 4.55(2.34), 4.56(3.05), 5.00(2.91), 5.72(2.77), 6.08(2.85), 6.25(2.84), 6.32(3.00), 6.51(2.80)

Co(II), $3 \cdot 10^{-7}$ *M*, FMOD: pH(log *D*), 0.87(0.80), 1.13(1.01), 1.33(0.85), 1.35(0.83), 1.54(0.86), 1.61(1.06), 1.65(1.04), 1.68(0.93), 1.86(0.88), 1.88(0.90), 1.93(3.05), 2.16(1.04), 2.39(1.04), 2.72(0.99), 3.02(3.05), 3.19(1.35), 3.47(2.82), 3.60(1.59), 4.04(2.08), 4.12(2.54), 4.55(2.87), 4.97(3.35), 5.88(2.37), 5.90(3.37), 5.98(2.85), 6.08(2.60), 6.14(3.63), 6.18(3.22), 6.41(2.42), 6.49(3.42), 6.89(3.50)

Pm(III), $1 \cdot 10^{-8}$ *M*, MOD: pH(log *D*), 1.40(−1.30), 1.96(−1.10), 2.41(−1.24), 2.61(−1.44), 2.80(−1.14), 2.84(−1.84), 2.92(−0.30), 2.95(−1.26), 3.36(−0.59), 3.54(−0.78), 3.60(−0.97), 3.74(−0.55), 4.07(−0.78), 4.14(−0.10), 4.40(−0.66), 4.41(−0.33), 4.60(−0.66), 4.62(−0.68), 4.92(−0.12), 5.11(−0.17), 5.43(0.98), 5.49(0.18), 5.52(0.58), 5.58(0.73), 5.78(1.23), 5.80(3.40), 5.84(2.30), 6.21(1.97), 6.35(2.64), 6.51(2.30), 6.89(2.60)

Pm(III), $1 \cdot 10^{-8}$ *M*, FMOD: pH(log *D*), 0.68(1.30), 0.84(−1.39), 0.90(0.90), 1.11(−1.22), 1.58(−1.08), 1.83(0.25), 2.13(−0.07), 2.68(0.92), 3.10(0.77), 3.38(1.03), 3.46(2.98), 3.69(1.69), 4.19(1.04), 4.38(0.88), 4.62(0.85), 5.12(2.38), 5.35(1.49), 5.60(3.04), 5.96(2.21), 6.10(3.05), 6.35(2.79)

Zn(II), $5 \cdot 10^{-6}$ *M*, MOD: pH(log *D*), 2.78(−3.81), 2.81(−3.11), 3.05(−1.77), 3.23(−3.64), 4.01(−1.67), 4.24(−0.94), 4.32(0.14), 4.34(−1.22), 4.40(−1.33), 4.44(−1.16), 5.33(−0.09), 5.49(0.64), 5.51(0.87), 5.81(1.91), 5.82(1.61), 5.84(1.61), 5.90(0.17), 6.09(2.09), 6.24(2.37), 6.24(2.37), 6.97(3.36), 6.98(3.43), 7.09(3.35), 7.15(3.48), 7.29(3.54), 7.30(3.57), 7.32(3.44), 7.38(3.74), 7.54(3.48), 7.62(3.35), 7.88(3.62), 7.96(3.53), 8.01(3.33), 8.14(4.77), 8.34(3.71)

Zn(II), $5 \cdot 10^{-6}$ *M*, FMOD: pH(log *D*), 0.26(0.48), 0.64(0.54), 1.34(0.37), 1.62(−0.36), 1.91(0.24), 2.25(−0.47), 2.31(−0.37), 2.86(0.31), 3.22(0.38), 3.39(0.57), 3.71(0.94), 4.42(2.05), 5.13(3.03), 5.45(3.43), 5.71(3.60), 6.05(2.97), 6.20(3.72), 6.48(2.22), 6.54(3.66), 6.68(3.66), 6.71(3.83)

Sc(III), $1 \cdot 10^{-6}$ *M*, MOD: pH(log *D*), 0.57(−1.17), 0.90(−0.95), 1.15(−0.15), 1.42(0.73), 1.51(1.09), 1.51(1.12), 1.70(1.19), 1.70(1.27), 1.95(1.80), 2.20(2.41), 2.25(2.02), 2.42(2.46), 2.59(2.97), 2.93(2.23), 2.96(2.88), 3.71(2.75), 4.62(2.64), 4.92(2.24), 5.38(3.30), 5.93(2.69), 6.34(2.91)

Sc(III), $1 \cdot 10^{-6}$ *M*, FMOD: pH(log *D*), 0.24(0.20), 0.59(1.42), 0.64(1.80), 0.85(2.67), 1.10(3.93), 1.42(3.37), 2.08(3.57), 2.60(3.92), 3.43(3.93), 4.10(3.76), 4.45(3.51), 4.96(3.89), 5.65(4.16), 6.92(4.09), 7.28(4.28)

Ag(I), $2 \cdot 10^{-6}$ *M*, MOD: pH(log *D*), 0.38(−0.11), 0.70(−0.37), 1.08(−0.38), 1.19(−0.36), 1.56(−0.34), 1.65(−0.38), 2.10(−0.34), 2.41(−0.47), 2.58(−0.53), 3.18(−0.08), 3.50(−0.59), 3.65(−0.17), 4.01(−0.51), 4.56(0.49), 4.60(0.39), 5.02(0.06), 5.19(0.17), 5.21(0.42), 5.58(0.29), 5.80(0.17), 5.89(0.62), 5.93(0.00), 6.60(−0.07)

Ag(I), $2 \cdot 10^{-6}$ *M*, FMOD: pH(log *D*), 0.07(0.17), 0.10(−0.33), 0.36(0.11), 0.40(−0.01), 0.46(0.10), 0.64(0.43), 1.00(−0.11), 1.66(−0.09), 2.02(−0.71), 2.60(−0.73), 3.01(−0.68), 4.13(−0.51), 4.46(−0.09), 5.01(0.96), 5.40(1.41), 5.49(1.32), 5.84(1.32), 6.10(1.43), 6.25(2.02), 6.60(2.01), 6.90(2.06)

Hg(II), $1 \cdot 10^{-8}$ *M*, MOD: pH(log *D*), 0.92(0.16), 1.43(0.08), 1.45(0.38), 1.90(−0.02), 2.67(−0.61), 2.75(−0.32), 2.80(−0.60), 2.88(−0.23), 2.89(−0.41), 3.05(−0.51), 3.08(−0.66), 3.20(−0.61), 3.25(−0.70), 3.30(−0.65), 3.40(−0.52), 3.70(−0.42), 4.20(−0.52), 4.20(−0.22), 4.50(−0.56), 4.76(−0.37), 4.91(−0.32), 4.92(−0.28), 5.20(−0.43), 5.55(−0.43), 6.18(−0.12), 7.40(0.04), 7.46(0.07), 7.75(0.26), 8.09(1.30), 8.66(0.57), 8.70(0.39), 8.90(0.37), 9.43(0.53), 9.50(0.44)

Hg(II), $1 \cdot 10^{-8}$ *M*, FMOD: pH(log *D*), 0.09(0.49), 0.11(0.21), 0.99(0.09), 1.39(0.40), 1.51(0.91), 1.72(0.65), 1.86(0.33), 2.00(−0.06), 2.40(0.46), 3.26(0.30), 3.75(0.51), 4.12(0.30), 4.19(1.04), 4.84(0.41), 5.38(0.59), 5.69(0.80), 6.00(0.71), 6.40(1.25), 6.48(0.26), 6.97(0.31)

Tl(I), $1 \cdot 10^{-6}$ *M* MOD: No extraction observed in the pH range 1 to 7

Tl(I), $1 \cdot 10^{-6}$ *M*, FMOD: pH(log *D*), 0.41(−2.00), 0.86(−1.98), 1.08(−1.59), 1.31(−2.11), 1.71(−1.81), 2.09(−1.66), 2.54(−1.48), 3.00(−2.10), 3.40(−1.64), 4.00(−1.54), 4.39(−0.98), 4.64(−0.90), 4.85(−0.68), 5.49(−0.11), 5.90(0.25), 6.42(0.58), 6.78(0.58)

The solubilities of water in the respective diones were determined by a gas chromatographic method to be $4.7 \cdot 10^{-4}$ moles/l in MOD and $8.9 \cdot 10^{-3}$ moles/l in FMOD.

Table II presents the logarithms of the distribution coefficients and the corresponding pH values for the metals used in this study, and the metal ion concentrations employed.

DATA ANALYSIS

A comparison of the acid association constants listed in Table III shows that substitution of fluorine for hydrogen on a methyl group adjacent to a carbonyl group increases the acidity by a factor of roughly 100. This is also true for 7-methyl-2,4-octanedione and its fluorinated analog reported in this work. One would anticipate such a result based on the well-known large inductive effect of the trifluoromethyl group.

TABLE III

SELECTED ACID ASSOCIATION CONSTANTS

Dione	*Log K*	*Ref.*
3-Ethyl-2,4-pentanedione	11.34	23
3-Methyl-2,4-pentanedione	10.87	23
5,5-Dimethyl-2,4-hexanedione	10.01	23
7-Methyl-2,4-octanedione	9.72	This work
5-Methyl-2,4-hexanedione	9.43	23
1,3-Diphenyl-1,3-propanedione (dibenzoylmethane)	9.35	18
2,4-Pentanedione (acetylacetone)	9.03, 8.95, 8.82	22,19,5
1-Phenyl-1,3-butanedione (benzoylacetone)	8.73	20
1,1,1-Trifluoro-7-methyl-2,4-octanedione	7.14	This work
1,1,1-Trifluoro-2,4-pentanedione (trifluoroacetylacetone)	6.6, 6.3	21,22
1,1,1-Trifluoro-6-methyl-2,4-heptanedione	6.5	23
1,1,1-Trifluoro-4-phenyl-2,4-butanedione	6.3	23
4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (thenoyltrifluoroacetone)	6.2	24

The addition of alkyl groups of various sizes to the 5 position of the β-diketone system causes only minor variations in the acidity, as seen in Table III. The addition of large organophilic moieties might cause an apparent reduction in the acidity by decreasing the water solubility of the β-diketone rather than by electronic effects, but again the effect is small in the compounds shown herein.

The integral NMR spectra of both β-diketones used in this work showed only one methylene hydrogen in the 3 position, indicating that both compounds are highly enolized in the pure liquid. No attempt was made to determine the extent of this enolization, but other workers have shown for several similar β-diketones that the enol form constitutes 90% or more of the material[16,17].

The distribution d of an acidic compound HR between an organic phase and water is given by

$$d = \frac{[\mathrm{HR}]_o}{[\mathrm{HR}] + [\mathrm{R}]} \qquad (2)$$

The value of $[HR]_o$ can be determined from the density of the pure compound and the solubility of water in the compound for the case of interest here, namely that wherein the compound is also the bulk organic phase. The sum of [HR] and [R] was determined as previously described and presented in Table I.

The constant *d* values at low pH indicate that [R] is negligible with respect to $[HR]_o$. The equation for *d* then reduces to

$$d = \frac{[HR]_o}{[HR]} \tag{3}$$

which is the defined value of *P* in eqn.(1). This number is a constant characteristic of the system. As long as a bulk organic phase consisting of the β-diketone is present, any HR which is converted to the enolate anion R in the aqueous phase is replaced, and [HR] remains constant. The decrease in *d* is then due to an increase in [R], and not a decrease in [HR].

The value of *P* chosen to fit best the experimental data in Table I for 7-methyl-2,4-octanedione is $1.93 \cdot 10^4$, and for 1,1,1-trifluoro-7-methyl-2,4-octanedione is $2.52 \cdot 10^4$. Agreement between the theoretical and calculated values is better for the trifluorinated compound than for the analogous non-fluorinated β-diketone. This might be attributed to the more acidic nature of the 1,1,1-trifluoro-7-methyl-2,4-octanedione. Presumably, this enhanced acidity would favor a more complete reaction with base or metal ion.

Although nitrate ion often tends to complex with various metal ions, nitric acid and sodium nitrate were used in this study in preference to the corresponding perchlorates which have considerably smaller complexing tendencies. The work of STEINBACH[5] has shown that acetylacetone has abnormally high solubilities in perchlorate media below a pH of 3. Since the β-ketones used in this study were similar to 2,4-pentanedione, nitrate was used to attempt to anticipate any such anomalous effects which might occur.

STARY[18] has found for acetylacetone and some 30 metals in benzene, that complexes of the type $MR_R(HR)_A$ are not usually found, and the dominant organic phase species is MR_R. The single exception was the uranyl ion, which forms UO_2R_2HR. On this basis in a chelating solvent, the general species $MR_R(HR)_AS_S$ becomes simply $MR_R(HR)_A$, since HR and S are the same. Thus the term for HR in the general theoretical equation can be incorporated in the extraction constant without any loss of definition to the system.

Extraction studies were not generally extended beyond pH 7 since base decomposes 2,4-diones to an acid anion and ketone[19]. This decomposition cannot be neglected over a period of hours, not so much for its diminution of the amount of dione present as for the introduction of compounds whose effects on the extraction are not known. The degradation products of FMOD and MOD are known to complex with metal ions.

Four to six hours of continuous stirring was sufficient to establish reproducible *D* values. The one exception was the cobalt extraction.

Thorium(IV)

A plot of log *D* against pH for MOD has a curve shape represented by the *cd* portion of the idealized plot in Fig. 1, with an ascending slope of 4. This is congruent with a dominant organic phase species of ThR_4 and a dominant aqueous phase species of the simple metal ion Th (charges are omitted for simplicity). The curve lays over in a regular fashion as the aqueous phase dominance probably shifts rapidly from Th to ThR, ThR_2, ThR_3, and finally ThR_4. The FMOD curve can be similarly explained, and shows a smaller $pH_{\frac{1}{2}}$ (the pH at which $D=0$; see Table IV). WAGNER[21] has studied the acetylacetonates of yttrium and 8 lanthanides, and identifies the species present as $MR_3(HR)_n$, where n is non-zero, in solutions where the [HR]/[M] ratio is 3 or larger. If a species such as $MR_R(HR)_A$ is dominant in the organic phase, then, since HR is also the solvent and A is not uniquely determined, the HR dependence can be included in the $P_{MRAH}K_{MRAH}$ product. This does not detract from the definition of the system, and therefore this and all subsequent dominant organic phase species for the various metals investigated will be discussed in terms of MR_R and not $MR_R(HR)_A$.

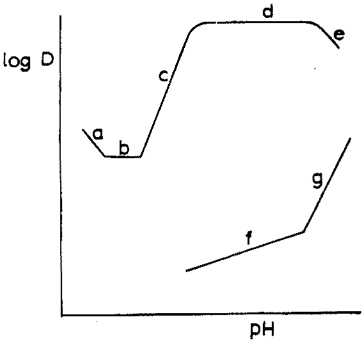


Fig. 1. Idealized extraction curves.

TABLE IV

THE $pH_{\frac{1}{2}}$[a] VALUES AND MAXIMUM LOG VALUES FOR THREE CHELATING SOLVENTS

Metal	*7-Methyl-2,4-octanedione*		*1,1,1-Trifluoro-7-methyl-2,4-octanedione*		*2,4-Pentanedione*[b]	
	$pH_{\frac{1}{2}}$	$Log\ D_{max}$	$pH_{\frac{1}{2}}$	$Log\ D_{max}$	$pH_{\frac{1}{2}}$	$Log\ D_{max}$
Th(IV)	1.4	2.5	< 0	3.8	2.4	$> 1.7^c$
In(III)	1.5	4.5	0.6	4.5	1.8	$> 1.8^c$
Co(II)	3.4	3.0	—[h]	3.0	—[g]	—[g]
Pm(III)	5.2	—[e]	2.3	—[e]	3.3^c	—[e]
Zn(II)	4.8	3.5	3.1^c	3.7	5.1	0.3
Sc(III)	1.1	2.8	0.1	4.0	—[g]	—[g]
Ag(I)	4.3	0.3	4.4	2.0	—[g]	—[g]
Hg(II)	7.3^d	—[e]	—[h]	0.5	—[g]	—[g]
Tl(I)	—[f]	—[f]	5.5	—[e]	—[g]	—[g]

[a] The pH at which $\log D = 0$. [b] See references 5 and 6. [c] Estimated. [d] Interpreted as due to ion-pair extraction. [e] Plateau not found. [f] No extraction observed. [g] No data available. [h] $\log D = 0$ not seen.

KRISHEN[6] has studied the extraction of thorium with pure acetylacetone. A $\log D$ against pH plot constructed from his work shows a curve of shape c (see Fig. 1) with broad transitions from *b* to *c* and *c* to *d* indicated. The maximum instantaneous slope is 3, and the plateau is not described. Where comparable, both MOD and FMOD show lower $pH_{\frac{1}{2}}$ values (see Table IV) and higher log *D* values than acetylacetone.

Indium(III)

Indium(III) shows a curve shape similar to the *cd* region for both chelating solvents studied herein (see Fig. 1). The ascendant region slope for both curves is 3, which suggests that InR_3 is the extracting species and In dominates the aqueous phase.

STEINBACH[5] has studied indium and pure acetylacetone, and one slope region, 3, is seen, with 1.8 being the largest log *D* value shown. Again, Table IV indicates that both MOD and FMOD have more acidic $pH_{\frac{1}{2}}$ values and show larger *D* values for a given pH than their parent homolog acetylacetone.

Cobalt(II)

Cobalt shows log *D* against pH curves of the type *bcd* (see Fig. 1) for both chelating solvents. When MOD is the chelating solvent, region *c* has a slope of 3 and equilibration times are at least 72 h, suggesting that Co(III) is being extracted (CoR_3 predominating in the organic phase). A slope of 2 is seen for the *c* region on the FMOD curve (CoR_2 dominating the organic phase), and much shorter (24 h at most) equilibration times are seen. The initial region *b* of slope zero might be attributed to some type of ion-pair phenomena. No study of cobalt has been reported using pure acetylacetone.

Promethium(III)

The log *D* against pH curve for Pm(III) and MOD follows the form of curve *fg* in Fig. 1. The portion corresponding to *f* has a slope of 0.4, and to *g*, 2. Possibly species involving both nitrate ion and the enolate anion R such as PmR_2NO_3 may be involved. Rare earth nitrates are known to extract as ion pairs[22] into solvents containing an oxygen moiety.

The analogous curve for FMOD shows only one slope region, 0.8. Again, one might assume the involvement of ion-pair phenomena.

KRISHEN[6] has studied Ce(III) with pure acetylacetone, and sees a slope of 1 on the rising portion and a $pH_{\frac{1}{2}}$ of 3.2, with a general curve shape of the type *cd*. BROWN *et al.*[7] have studied 8 lanthanides and Y(III) with acetylacetone. All exhibit a rising slope of 1, and have curves similar to *cd* in Fig. 1. Erbium(III) has a $pH_{\frac{1}{2}}$ of 5.0, and Yb(III) one of 4.5. Region *d* is not well-defined for any metal studied, but seems to lie below a value of log $D=0$ in all instances.

Zinc(II)

The log *D* against pH curve for MOD and zinc shows the shape *cd* with a rising slope of 2, which suggests ZnR_2 in the organic phase and Zn in the aqueous phase. The curve for FMOD has the shape *bcd*, with region *c* showing a slope of 2. The *b* region might involve extraction of a mixed species such as $ZnRNO_3$, since Zn and nitrate do not complex[23]. The mixed species $ZnRClO_4$ has been reported in benzene where R is β-isopropyltropolone[24].

Zinc has been extracted using acetylacetone as a chelating solvent (Table IV), and its log *D* against pH curve has the *cd* shape. Both MOD and FMOD show lower $pH_{\frac{1}{2}}$ values and higher plateaux than acetylacetone.

Scandium(III)

Both chelating solvents give curves of the *cd* shape, with slopes of 3 on the ascendant portion. The MOD curve seems to pass through two distinct slope regions, 3 and 2, before laying over. If ScR_3 dominates the organic phase, then the dominance could shift from Sc to ScR in the aqueous phase to give this result.

Extractions of scandium with pure acetylacetone have not been reported.

Silver(I)

Ion-pair extraction phenomena are indicated by the trends in the log D against pH curves. For MOD, the curve type is *abcde*, and for FMOD, it is *abcd*, with a longer discernible *c* region of slope 1. This suggests AgR in the organic phase and Ag in the aqueous. The initial region *a* of negative slope seen with both chelating solvents indicates that ion-pair extraction becomes increasingly important below pH 3. No work with silver and acetylacetone as the chelating solvent has been reported.

Mercury(II)

The chelating solvent FMOD gives a log D against pH curve of slope zero only, and MOD gives a curve of the type *abc*.

This suggests involvement of ion-pair phenomena in the extraction rather than chelate formation. The Hg(II)–MOD system was the one example in which D values were obtained in the basic region. The pH values greater than 8 were obtained with difficulty, and no attempt was made to detect decomposition of the MOD.

Mercury has not been studied with pure acetylacetone.

Thallium(I)

No transfer of Tl(I) to the chelating solvent was observed with MOD, and the sensitivity of the radioassay places the minimum detectable log D value as -4. When FMOD is the chelating solvent, a curve of the type *fg* in Fig. 1 is seen, with respective slopes of 0.3 and 1. Presumably TlR is being extracted in the latter region, and possibly $TlNO_3$ is forming in the aqueous layer in region *f*, and preventing extraction by tying up the metal, much as a masking agent functions. Thallium has not been studied with acetylacetone.

DISCUSSION

If a direct comparison between chelating solvents is to be made, perhaps the best basis for such an evaluation is the value of the product $P_{MRAH}K_{MRAH}$ for each metal with each chelating solvent. A knowledge of P and K for each reagent is needed. The value of P for the neat chelating solvent and water is available for 2,4-pentanedione. Most other β-diketones which have been extensively studied are solids and therefore excluded from consideration here.

Table V was prepared using P, K, $\text{pH}_{\frac{1}{2}}$ and $[HR]_o$ values for each of the β-diketones and assuming the metal is present as the neutral chelate MR_R in the organic phase and as the simple metal ion M in the aqueous phase. By using the $\text{pH}_{\frac{1}{2}}$ values, the value of D used is set at 1. Operating with eqn. (1), it can be shown that $\log P_{MRAH}K_{MRAH} = R \log ([H][HR]_o PK)$ where R is the valence of the metal, and hence the number of attaching R groups. A comparison of these results shows that 7-methyl-

2,4-octanedione is a somewhat better chelating solvent than its 1,1,1-trifluoro derivative for Th(IV), In(III), Zn(II), and Sc(III), and that the reverse is true for Pm(III) and Tl(I). In all cases, both reagents performed better than did 2,4-pentanedione. The latter has a much larger concentration (9.8 *M*) in the pure liquid which should enhance extractions, but this is quite insufficient to offset its low *P* value.

TABLE V

A COMPARISON OF THE LOG $P_{\mathrm{1ROO}}K_{\mathrm{1ROO}}$ VALUES

Metal	*MOD*[a]	*FMOD*[b]	*ACAC*[c]
Th(IV)	53.6	>48	33.6
In(III)	39.9	34.8	27.0
Co(II)	22.8	—	—
Pm(III)	28.8	29.7	22.5
Zn(II)	20.0	18.2	11.4
Sc(III)	41.1	36.3	—
Ag(I)	—	—	—
Hg(II)	—	—	—
Tl(I)	—	6.7	—

[a] log PK = 14.0, log $[\mathrm{HR}]_o$ = 0.8, MOD = 7-methyl-2,4-octanedione. [b] log PK = 11.5, log $[\mathrm{HR}]_o$ = 0.7, FMOD = 1,1,1-trifluoro-7-methyl-2,4-octanedione. [c] log PK = 9.8, log $[\mathrm{HR}]_o$ = 1.0, ACAC = 2,4-pentanedione.

TABLE VI

A COMPARISON OF $\mathrm{pH}_{\frac{1}{2}}$ VALUES FOR 6 β-DIKETONES[a]

	MOD[b]	*DBM*[b]	*ACAC*[b]	*BA*[b]	*FMOD*[b]	*TTA*[b]
Log *K*	9.72	9.35	9.03	8.73	7.14	6.2
Th(IV)	2.1	1.6	3.4	1.9	—	−0.2
In(III)	2.2	2.6	2.8	3.1	1.4	1.5
Co(II)	4.3	5.4	—	5.6	—	3.7
Pm(III)	6.0	6.4[c]	4.3[d]	6.9[c]	2.0	2.6
Zn(II)	5.1	5.4	6.1	5.5	3.8	4.7
Sc(III)	2.0	2.1	2.0	1.1	0.9	0.3
Ag(I)	5.1	8.9	—	7.9	5.1	—
Hg(II)	8.0	—	—	—	—	—
Tl(I)	—	—	—	—	6.2	—

[a] All reagents are 1 *M* in benzene, except MOD and FMOD. [b] MOD, 7-methyl-2,4-octanedione; DBM, 1,3-diphenyl-1,3-propanedione; ACAC, 2,4-pentanedione; BA, 1-phenyl-1,3-butanedione; FMOD, 1,1,1-trifluoro-7-methyl-2,4-octanedione; TTA, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione. [c] Based on value in ref. 16 for lanthanum. [d] Based on value in ref. 6 for cerium.

Another basis commonly used to compare the efficiency of extraction by various chelating agents is the $\mathrm{pH}_{\frac{1}{2}}$ for the extraction of the metal of interest. This number reflects the ability of the reagent to compete with other potential ligands in the system (such as nitrate, hydroxide, or solvent water) and form a neutral, extractable species. In terms of eqn. (1), the $P_{\mathrm{MRAH}}K_{\mathrm{MRAH}}/P^{\mathrm{R}}K^{\mathrm{R}}$ ratio reflects this efficiency. A large value of this ratio gives a low $\mathrm{pH}_{\frac{1}{2}}$, but without additional information the controlling factors in this ratio cannot be ascertained.

Table VI presents a comparison of the $\text{pH}_{\frac{1}{2}}$ values for 6 β-diketones. Equation (1) indicates that a 10-fold increase in $[\text{HR}]_0$ must be accompanied by a 10-fold decrease in [H] in order to maintain a constant D value. This assumes that the dominant species in each phase does not change. For example, if a particular chelating agent–solvent combination shows a $\text{pH}_{\frac{1}{2}}$ of 2 at $[\text{HR}]_0 = 0.1\ M$, then $\text{pH}_{\frac{1}{2}}$ would be 1 at $[\text{HR}]_0 = 1.0\ M$. This type of argument was used to prepare Table VI from published results using benzene as the organic solvent. The data for 2,4-pentanedione, 7-methyl-2,4-octanedione, and 1,1,1-trifluoro-7-methyl-2,4-octanedione were obtained by scaling down from the reagent concentration in the pure organic liquid to $[\text{HR}]_0 = 1$, and assuming that the metal-chelating solvent systems would behave similarly at both concentrations. Several $\text{pH}_{\frac{1}{2}}$ values for 2,4-pentanedione obtained by scaling up from 0.1 M in benzene and down from 9.8 M in the pure β-diketone give an indication of the validity of this procedure: Th(IV), 3.1 pure, 3.4 benzene and In(III), 2.4 pure, 2.8 benzene. Since the Table is given in order to show general trends in $\text{pH}_{\frac{1}{2}}$ values rather than absolute comparisons, this seems to be reasonable agreement.

In most instances, low $\text{pH}_{\frac{1}{2}}$ values (hence more efficient extractions) are favored by the more acidic β-diketones. Exceptions are noted in that the $\text{pH}_{\frac{1}{2}}$ order does not always follow the specific order of increasing acidity of the β-diketone, but in general 1,1,1-trifluoro-7-methyl-2,4-octanedione (FMOD) and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) are the best extracting agents on a basis of $\text{pH}_{\frac{1}{2}}$ comparisons.

SUMMARY

This study was undertaken to prepare a liquid compound with low water solubility which would form metal chelates readily and also act in the dual role of organic solvent in the solvent extractions of metal chelates. The compounds 7-methyl-2,4-octanedione and 1,1,1-trifluoro-7-methyl-2,4-octanedione were prepared and their P and K values determined. Radiotracer distribution studies with 9 metals indicate that the stated goal was reached. The observed distribution coefficients for the majority of the metals were much larger than those obtained with another pure β-diketone, acetylacetone. Also, extractions occur at lower pH values. Ion-pair phenomena are indicated in several cases. The principal general difference between the fluorinated and non-fluorinated β-diketones is a shift in the distribution curves towards the acid region for the fluorinated compounds.

RÉSUMÉ

Cette étude a été entreprise pour préparer un composé liquide, peu soluble dans l'eau, pouvant former facilement des chélates métalliques et agir ainsi comme solvant organique lors des extractions de chélates métalliques. On a préparé la méthyl-7-octanedione-2,4 et la trifluoro-1,1,1-méthyl-7-octanedione-2,4, et déterminé leurs valeurs P et K. Les coefficients de distribution observés pour la plupart des métaux étaient beaucoup plus élevés que ceux obtenus avec la β-dicétone ou l'acétylacétone. Les extractions se font à des pH plus bas. La principale différence générale entre β-dicétones fluorées et non fluorées est un changement dans les courbes de distribution vers la région acide des composés fluorés.

ZUSAMMENFASSUNG

Es wurde versucht, eine flüssige Verbindung mit geringer Wasserlöslichkeit zu finden, die leicht Metallchelate bildet und gleichzeitig wie ein organisches Lösungsmittel bei Flüssigextraktionen von Metallchelaten wirksam ist. Es eigneten sich die Verbindungen 7-Methyl-2,4-octandion und 1,1,1-Trifluoro-7-methyl-2,4-octandion. Die mit radioaktiven Tracern von 9 Metallen beobachteten Verteilungskoeffizienten der Mehrheit der Metalle waren erheblich grösser als die mit Acetylaceton. Die Verteilungskurven für die fluorierten β-Diketone liegen mehr im sauren Bereich.

REFERENCES

1 G. K. Schweitzer, R. B. Neel and F. R. Clifford, *Anal. Chim. Acta*, 33 (1965) 514.
2 D. Dyrssen, *15th International Congress of Pure and Applied Chemistry*, Actas Do Congresso, Vol. II, VI-10, Lisbon, Portugal, 1958.
3 D. C. Stewart, *Alkylphosphoric Acids as Extraction Agents for Uranium*, University of California Radiation Laboratory, Publication UCRL-585, 1950.
4 J. Segall, M. Ariel and L. M. Shorr, *Analyst*, 88 (1963) 314.
5 J. F. Steinbach, *Acetylacetone as an Analytical Extraction Agent*, Master's Thesis, University of Pittsburg, Pittsburg, Penn., 1953.
6 A. Krishen, *A Systematic Study of Solvent Extraction with Acetylacetone*, Doctoral Dissertation, University of Pittsburg, Pittsburg, Penn., 1957.
7 W. B. Brown, J. F. Steinbach and W. F. Wagner, *J. Inorg & Nucl. Chem.*, 13 (1960) 119.
8 H. Jaskolska, L. Wodkiewicz and J. Minczewski, *Chem. Anal. (Warsaw)*, 9 (1964) 453; *Nucl. Sci. Abstr.*, 18, 31389.
9 G. K. Schweitzer, *Anal. Chim. Acta*, 30 (1964) 68.
10 E. Bleuler and G. J. Goldsmith, *Experimental Nucleonics*, Rinehart and Co., New York, 1952, p. 198.
11 C. R. Hauser, F. W. Swamer and J. T. Adams, in R. Adams, *Organic Reactions*, Vol. 8, John Wiley, New York, 1954, p. 89.
12 D. Dyrssen, *Svensk Kem. Tidskr.*, 64 (1952) 213.
13 A. Albert and E. P. Sargent, *Ionization Constants of Acids and Bases*, John Wiley, New York, 1962, p. 28.
14 J. Rydberg, *Svensk Kem. Tidskr.*, 9 (1950) 179.
15 J. Rydberg, *Svensk Kem. Tidskr.*, 65 (1953) 37.
16 G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, 27 (1944) 1044.
17 W. G. Scribner, unpublished results.
18 J. Stary and E. Hladky, *Anal. Chim. Acta*, 28 (1963) 227.
19 A. Combes, *Ann. Chim. (Paris)*, (6), 12 (1887) 213.
20 R. M. Diamond and D. G. Tuck, Extraction of Inorganic Compounds into Organic Solvents, in F. A. Cotton, *Progress in Inorganic Chemistry*, Vol. II, Interscience, New York, 1960.
21 W. F. Wagner, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, 23 (1962) 1955.
22 W. Fischer, G. Braune, W. Dietz, O. Juberman, G. Krause, K. Niemann and G. Siekmeir, *Angew. Chem.*, 66 (1954) 317.
23 J. Bjerrum, G. Schwarzenbach and L. G. Sillen, *Stability Constants*, Vol. I, The Chemical Society, London, 1957.
24 D. Dyrssen, *Kungl. Tekniska Hogsk. Handl.*, 188 (1962) 1.

THE EXTRACTION OF CAESIUM WITH NITROBENZENE IN THE PRESENCE OF PHOSPHOMOLYBDIC ACID

J. RAIS, S. PODEŠVA AND M. KYRŠ
The Nuclear Research Institute, Czechoslovak Academy of Sciences, Řež near Prague (Czechoslovakia)

(Received January 11th, 1966)

Several methods for solvent extraction of caesium have been published in recent years[1-4], but the choice of a suitable extraction method for analytical purposes is more restricted than for most metals. Particularly limited are the possibilities for extraction from an acidic aqueous phase, which might be required to prevent precipitation of some cations or excessive adsorption of trace caesium on the walls of the vessels. Only the polyiodide[5,6], polybromide[7] and iodobismuthite[8] systems have so far been proposed. However, all the above-mentioned methods give trouble, if cations such as Ag^+, Hg^+, Pb^{2+}, or strong oxidizing agents are present.

The extraction procedure suggested in this paper can be considered superior in special cases such as those mentioned above. The method offers the advantage of an easily prepared extracting solution and the distribution ratios are higher than with iodobismuthite.

The choice of heteropolyacids as reagents suitable for the extraction of caesium from acidic solutions into nitrobenzene is based on the following reasoning: (*i*) any reagent capable of forming a relatively high concentration of anions in a nitrobenzene phase in contact with an aqueous phase can be expected[1] to be an effective extractant for caesium, (*ii*) heteropolyacids can be easily extracted[9] into a number of organic solvents, (*iii*) heteropolyacids are rather strong acids in water and could be expected to behave similarly in nitrobenzene (*e.g.* forming anions).

The present study consists of an investigation of the main factors controlling the distribution of caesium in the system in question, an evaluation of the selectivity of the extraction and an examination of its potential use in analytical chemistry.

EXPERIMENTAL

Reagents

All substances used were of reagent-grade purity. The stock solution of phosphomolybdic acid, $H_7P(Mo_2O_7)_6 \cdot 24.8\ H_2O$ (Lachema) (abbreviation HPMo), was prepared by dissolving it in dry nitrobenzene. The amount of water in the HPMo sample was determined by heating it at 164° to constant weight[10]. Nitrobenzene was not further purified because the caesium distribution ratios (q_{Cs}) obtained with samples after an additional purification and with the commercial product were the same within the experimental error. ^{137}Cs, ^{85}Sr, ^{106}Ru, ^{95}Zr, ^{90}Y and ^{144}Ce (all carrier-free of Soviet origin) were used as tracers. ^{86}Rb was prepared by neutron irradiation of rubidium chloride (ZfK, Dresden, Germany). The radiochemical purity of these isotopes was checked by their γ-spectra or by the respective maximum energies of β-particles.

Apparatus

The β-radioactivity was counted with an G.M. tube fed to a commercial decade scaler. A 200-channel γ-spectrometer (Intertechnique) was used for taking the γ-spectra. The relative conductances of the organic phases were measured by a resistance conductometer (Konduktoskop, Laboratorní přístroje, ČSSR) at $25 \pm 0.1°$.

Procedures

Before extraction, the aqueous phase contained caesium or other metals and nitric acid. A volume ratio of 1 : 1 for the aqueous and organic phases and a shaking time of 24 h were used unless otherwise stated. (The difference between the distribution ratios q_{Cs} obtained after 3 min and 30 h of shaking was found to be negligible.) If after the equilibration the organic phase was not perfectly clear, centrifugation (4000 rev./min) was used. Aliquots (0.5 ml) of both phases were evaporated on aluminium dishes for counting the β-activity. When caesium was separated from the mixture of fission products, the samples were shaken for 30 min. For the separation of caesium and rubidium, stock solutions of both phases (barren) were prepared beforehand by equilibrating 50 ml of 1 *M* nitric acid with 50 ml of HPMo (5.6 g/l) in nitrobenzene for 20 h. The solution containing rubidium and caesium was evaporated to dryness and taken up with 3 ml of the aqueous phase for the first equilibration. The separation was carried out by extraction repeated 10 times, the aqueous phase (3 ml) being stationary (as in the simplest procedure in a Craig apparatus). In each step 3 min of equilibration were allowed with no centrifugation. The distribution ratio of phosphomolybdic acid, q_{HPMo}, was found from the conductance measurements of the organic phase after extraction (maximum values of q_{HPMo} amounted to about 1).

Calibration curves of conductance against concentration of HPMo for extracts obtained with aqueous phases of varying acidity and for solutions prepared by dissolving HPMo in wet nitrobenzene were in agreement. An independent method for checking the q_{HPMo} values was developed using the "concentration-dependent distribution principle"[11]. The ^{137}Cs-containing organic phase after extraction was diluted with nitrobenzene and shaken with an equal volume of 0.1 *M* nitric acid. The total amount of HPMo present in the second extraction was found from the q_{Cs} values obtained from the calibration curve. The q_{HPMo} values given by the two methods were in good agreement.

RESULTS AND DISCUSSION

The choice of diluent and reagent

The distribution of caesium in the presence of HPMo for various solvents is shown in Table I. Nitrobenzene ensures the highest q_{Cs} value. The general trend towards lower q_{Cs} values for solvents of lower dielectric constant as shown in the Table can be explained theoretically[12]. Binary mixtures of nitrobenzene (90–20%) with furfural, diethylether, tri-*n*-butyl phosphate, cyclohexanone, benzene and chloroform were also tested. In no case could q_{Cs} values higher than with pure nitrobenzene be obtained. This solvent was used for all further experiments. In a comparison of the extraction of caesium in the presence of commercial HPMo, phosphotungstic acid (HPW) and tungstosilicic acid (HWSi) it was shown that HPW could also be used for the extraction of caesium (q_{Cs} values very close to those obtained with HPMo were found) whereas q_{Cs} values about one order of magnitude lower were observed for HPSi. This result corresponds to the reported[9] much lower extractability of HPSi. HPMo (easily obtainable in sufficient purity) was chosen for further work.

TABLE I

THE EXTRACTION OF CAESIUM WITH VARIOUS SOLVENTS

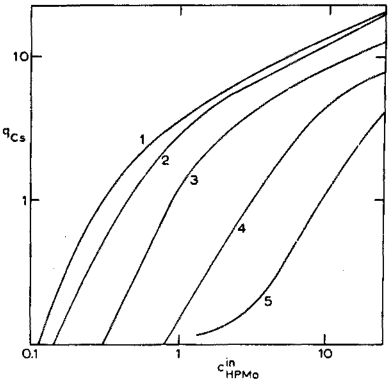
(1 g/l HPMo, ^{137}Cs carrier-free, initial pH of water phase *ca.* 7)

Solvent	q_{Cs}	*Dielectric constant*	*Solvent*	q_{Cs}	*Dielectric constant*
Nitrobenzene	9.1	34.8	Cyclohexanone	0.07	18.2
Nitrotoluene	3.7		Isoamyl alcohol	0.06	
Ethylacetoacetate	1.2	15.9	Chloroform	0.03	4.8
Ethylacetate	1.13	6.4	Diethyl ether	0.004	4.3
Methyl cyclohexanone	0.54	12–14	Xylene	0.001	
Methyl-isobutyl-ketone	0.16	13.1	*n*-Hexane	0.0005	4.0
Amyl alcohol	0.07	15.8			

The influence of the concentration of reagent, caesium and nitric acid

It was found that in the range of 0.1–2 *M* [H$^+$] the same q_{Cs} values were obtained for the same acidity regardless of which of the following acids were used: HNO_3, HCl, H_2SO_4 or $HClO_4$. Further experiments were carried out only with nitric acid, in the presence of which most cations were not precipitated.

The dependence of q_{Cs} on the concentration of nitric acid and the extractant is shown in Fig. 1. At higher concentrations of HPMo a decrease in q_{Cs} appears. This



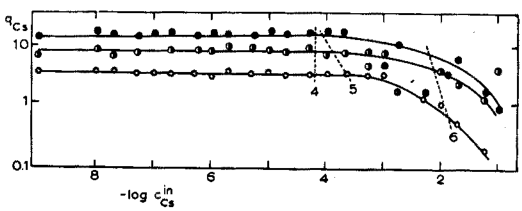


Fig. 1. The extraction of caesium as a function of the acidity and of the concentration of HPMo. c^{in}_{HPMo}, the initial concentration of HPMo (g of $H_7P(Mo_2O_7)_6 \cdot 25.5\ H_2O$ for 1 litre of nitrobenzene); volume ratio of solvents 1 : 1. (*1*) 0.1 *M* HNO_3 in the aqueous phase; (*2*) 0.2 *M*; (*3*) 0.4 *M*; (*4*) 1 *M*; (*5*) 2 *M*.

Fig. 2. The influence of concentration of caesium on its distribution. 0.5 *M* HNO_3, c^{in}_{Cs}, the initial concentration of caesium (mole per litre). (*1*) 5 g of HPMo per litre; (*2*) 20 g of HPMo per litre; (*3*) 40 g of HPMo per litre; (*4*) turbidity of the aqueous phase starts; (*5*) loss of caesium on glass-walls starts; (*6*) turbidity of the organic phase starts.

region of higher reagent concentration was therefore not investigated. For the region $[H^+] < 0.1\ M$, the q_{Cs} values were practically independent of the acidity. At pH $\cong$ 11 a sharp decrease in q_{Cs} was found (due to the decomposition of HPMo in alkaline medium).

The dependence of q_{Cs} values upon the original concentration of caesium in the aqueous phase is given in Fig. 2. The independence of q_{Cs} from the caesium concentration indicates an absence of polymerization of the caesium-containing species in the organic phase. At a concentration of caesium $> 5 \cdot 10^{-5}\ M$, precipitation of caesium phosphomolybdate occurs with a concomitant "loss" of radioactivity on the walls. In radiochemical separations, however, the concentration level of $10^{-5}\ M$ is only rarely met.

The influence of various substances on the extraction

The distribution of caesium in the presence of several cations is shown in Fig. 3. It is clear that caesium can easily be separated from large amounts of natrium, lithium and calcium. The drop in the q_{Cs} values in the presence of small amounts of zirconium and iron cannot be ascribed to any competition of these metals with caesium for the reagent in organic phase, because the metals remain almost entirely in the aqueous phase. The most probable explanation is the formation of a complex compound between HPMo and iron or zirconium in the aqueous phase[13,14] with a consequent decrease in the reagent concentration in the organic phase. The influence of some oxidizing and reducing agents was also studied. Hydrogen peroxide (0.1 M), sulphites (0.1 M) and hydroxylamine (0.05 M) did not decrease the q_{Cs} values to any measurable extent. Tin(II) chloride ($> 5 \cdot 10^{-4}\ M$) in 0.5 M nitric acid after 2.5 h of shaking produced the well-known blue colouration with a decrease in q_{Cs}. The blue product in the aqueous phase did not undergo the partition. If sufficient time (24 h) was allowed in the extraction experiments, tin(II) chloride was oxidized by nitric

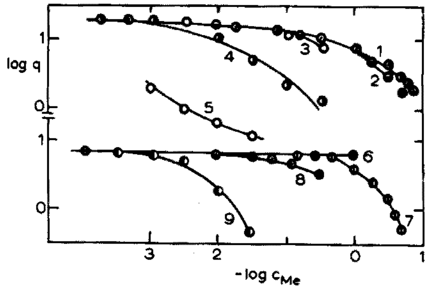


Fig. 3. The influence of cations on the extraction of caesium. 20 g of HPMo per litre; c_{Me}, the initial concentration of the respective cation (as nitrate) in mole per litre. (*1*) 0.1 M HNO_3, Na^+; (*2*) 0.1 M HNO_3, Ca^{2+}; (*3*) 0.1 M HNO_3, Al^{3+}; (*4*) 0.1 M HNO_3, Fe^{3+}; (*5*) 0.5 M HNO_3, Th^{4+}; (*6*) 1.0 M HNO_3, Li^+; (*7*) 1.0 M HNO_3, Ca^{2+}; (*8*) 1.0 M HNO_3, Fe^{3+}; (*9*) 1.0 M HNO_3, Zr^{4+}.

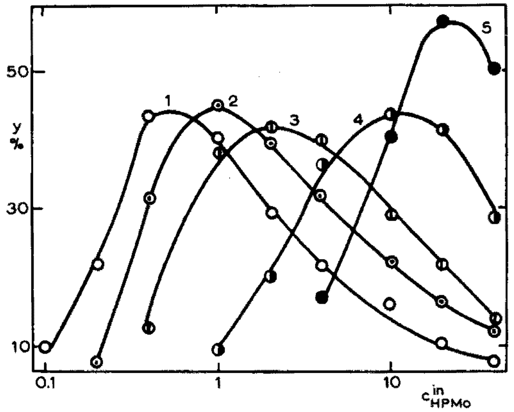


Fig. 4. The partition of HPMo between the aqueous and organic phases (for the legend see Fig. 1).

acid and so did not influence the caesium distribution at the above-mentioned concentration level.

The selectivity of caesium extraction

The relevant results are listed in Table II. A good separation of caesium from most of the substances tested is evident. Elementary iodine and cerium(IV) might contaminate the organic phase primarily. This can be avoided by a previous reduction. The separation of caesium from rubidium was considered to be of special interest.

TABLE II

THE SELECTIVITY OF EXTRACTION (20 g/l HPMo)

Element (Me)	*Me concn.*	*Aqueous HNO_3 (mol/l)*	q_{Me}	*Method for finding q_{Me}*
Sr^{2+}	Traces	0.1	$7.5 \cdot 10^{-2}$	R
Sr^{2+}	Traces	1	$6.9 \cdot 10^{-2}$	R
Zr^{4+}	Traces	0.1	$3.8 \cdot 10^{-1}$	R
Zr^{4+}	Traces	1	$3.7 \cdot 10^{-3}$	R
Zr^{4+}	10^{-3} *M*	0.5	$4 \cdot 10^{-3}$	R
Y^{3+}	Traces	0.1	$7.5 \cdot 10^{-3}$	R
Y^{3+}	Traces	1	$1.6 \cdot 10^{-3}$	R
Ce^{3+}	Traces	0.5	$< 10^{-3}$	R
Na^{+}	1 *M*	1	$\sim 10^{-2}$	G
Li^{+}	1 *M*	1	$\sim 10^{-2}$	G
Ca^{2+}	1 *M*	1	$\sim 10^{-2}$	G
Fe^{3+}	0.02 *M*	1	$\sim 10^{-3}$	G
Al^{3+}	0.3 *M*	1	$\sim 10^{-3}$	C
Rb^{+}	Traces, 10^{-5} *M*	1, 0.5	$q_{Rb} \doteq 1/5\ q_{Cs}$	R
I_2	Traces	1	1.0	R
I^{-}	Traces	0.5 *M* HCl	0.07	R

[a] R = radiometric; G = gravimetric; C = colorimetric.

As the possibility of enhancing the separation of the 2 elements by dilution of nitrobenzene with a nonpolar solvent has been suggested[15], the influence of diluting nitrobenzene with several solvents (the same as those mentioned above) upon the ratio of $q_{Cs}/q_{Rb} = \alpha$ was investigated systematically. For most binary mixtures the α value was lower than for pure nitrobenzene ($\alpha°$). Only 3 mixtures (60 and 75% (v/v) of diethyl ether, 15% (v/v) of tributylphosphate) exhibited somewhat higher α values ($\log \alpha \pm 0.1 = 0.76$; 0.88; and 0.80 respectively compared with $\alpha° = 0.66$). However, the q_{Cs} values given were too low to warrant recommendation of the above-mentioned mixtures for the separation of both elements in practice.

The back-extraction of caesium

The most convenient method of back-extraction for analytical purposes involves equilibrating the extract with an acidic aqueous solution (*ca.* 1.0 *M* of $[H^+]$) after diluting it (1 : 1) with diethyl ether or any other solvent, thus lowering the q_{Cs} value and enhancing q_{HPMo} (see Table III). If the extractant is to be recovered, caesium can be back-extracted by mineral acids of higher concentration (>5 *M* of

[H+]). In special cases, any of the mentioned substances which lower the q_{Cs} values can be added to the aqueous phase for back-extraction.

For repeated extractions a knowledge of the distribution of HPMo is of great importance. Such information on conditions useful for practice can be obtained from Fig. 4. A rather complex form of the q_{HPMo} curves is evident. Only a qualitative interpretation of the distribution data is available at present[16].

TABLE III

THE BACK-EXTRACTION OF CAESIUM q_{Cs} BY 1 M NITRIC ACID

Solvent used for dilution	*Diethyl ether*	*Isoamyl alcohol*	*Methyl isobutyl ketone*	*Chloroform*
dilution:				
2×	$4 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
3×	$4 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$4 \cdot 10^{-3}$
4×	$4 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$4 \cdot 10^{-3}$

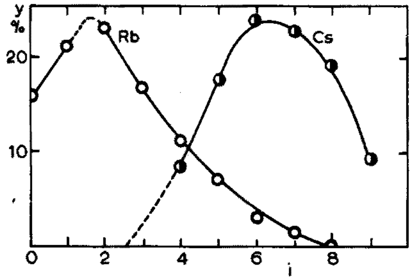


Fig. 5. The separation of ^{86}Rb and ^{134}Cs. i, the serial number of the test tube; y, the percentage content of the element in the respective test tube (relative to the total amount in all test tubes).

Practical examples of the separation of caesium

(*A*) A mixture of long-lived fission products (^{144}Ce, ^{85}Sr instead of ^{90}Sr, which does not emit γ-rays, ^{106}Ru, ^{137}Cs and ^{95}Zr—all carrier-free) in 0.5 M nitric acid was prepared. The photopeaks of all nuclides were of approximately the same height. After a single extraction step (20 g HPMo/l) the γ-spectrum of the organic phase (90% of Cs) corresponded to that of pure ^{137}Cs. Consequently, the extraction procedure can be used for an efficient and rapid separation of ^{137}Cs from long-lived fission products.

(*B*) About 5 mg of a rubidium salt containing ^{86}Rb had to be purified from ^{134}Cs formed during neutron irradiation from the nearly inevitable impurity of inactive caesium in the target rubidium salt. The distribution of both elements (as found by γ-spectrometry) in 11 test tubes is shown in Fig. 5. One can see that 60% of rubidium containing less than 1% of caesium could be isolated in a volume of 9 ml.

The mechanism of the extraction of caesium in this system will be described elsewhere. Essentially, HPMo exists in the organic phase almost entirely in the anionic form; the distribution ratio is controlled by the reaction $Cs_{aq}^{+} + H_{org}^{+} \rightleftharpoons H_{aq}^{+} + Cs_{org}^{+}$ with the corresponding equilibrium constant $\log K = 3.05 \pm 0.2$ (25°, $\mu_{aq} = 0$–0.5; HNO_3).

SUMMARY

The main factors controlling the distribution of caesium between the aqueous phase and a nitrobenzene phase in presence of phosphomolybdic acid were investigated. Data on the distribution of the heteropolyacid are given. The selectivity of caesium extraction was evaluated. The possibility of separating caesium by this method for analytical purposes was demonstrated in isolating caesium from a mixture of long-lived fission products and in isolating caesium from rubidium by repeated extraction.

RÉSUMÉ

On a examiné les principaux facteurs contrôlant le partage du césium entre la phase aqueuse et la phase nitrobenzène, en présence d'acide phosphomolybdique. La sélectivité de l'extraction du césium est évaluée. On a isolé le césium d'un mélange de produits de fission et séparé d'avec le rubidium pour montrer la possibilité d'utiliser ce procédé pour l'analyse du césium.

ZUSAMMENFASSUNG

Die Hauptfaktoren, die die Verteilung von Cäsium zwischen einer wässrigen Phase und Nitrobenzol in Gegenwart von Phosphormolybdänsäure bestimmen, wurden untersucht. Daten für die Verteilung der Heteropolysäure werden angegeben. Die Selektivität der Cäsiumextraktion wurde abgeschätzt. Es wurde die Möglichkeit der Trennung des Cäsiums durch diese Methode für analytische Zwecke demonstriert, indem Cäsium aus einer Mischung von langlebigen Spaltprodukten und Rubidium durch wiederholte Extraktion abgetrennt wurde.

REFERENCES

1 M. Kyrš, *Collection Czech. Chem. Commun.*, 27 (1962) 2380.
2 L. A. Bray and F. P. Roberts, *Report HW-76222*, 1963.
3 G. L. Richardson, *Report HW-81091*, 1964.
4 V. M. Vdovenko and L. S. Bulyanitsa, *Radiokhimiya*, 7 (1965) 104.
5 M. Kyrš and S. Podešva, *Zh. Neorgan. Khim.*, 8 (1963) 499.
6 L. M. Slater, *Nucl. Sci. Eng.*, 17 (1963) 576.
7 J. H. Moss, *British Patent 949483*, 1964; *Nucl. Sci. Abstr.*, 18 (1964) 12276.
8 M. Kyrš and S. Podešva, *Anal. Chim. Acta*, 27 (1962) 183.
9 I. P. Alimarin, F. P. Sudakov and V. I. Klitina, *Usp. Khim.*, 34 (1965) 834.
10 E. A. Nikitina, *Heteropolyacids*, Gosud. izd. chim. lit., Moscow, 1962, p. 196.
11 M. Kyrš, *Anal. Chim. Acta*, 33 (1965) 245.
12 R. M. Diamond and D. G. Tuck, *Extraction of Inorganic Compounds into Organic Solvents*, Interscience, New York, 1960, Chapter 5.
13 M. Jean, *Anal. Chim. Acta*, 31 (1964) 24.
14 Yu. F. Shkaravskiy, *Ukr. Khim. Zh.*, 30 (1964) 241.
15 R. Bock and T. Hoppe, *Anal. Chim. Acta*, 16 (1957) 407.
16 M. Kyrš and J. Rais, *Proc. Radiochemical Conference, Starý Smokovec, 11.X.1965*, Institute of Nuclear Research, Řež.

AN ION-EXCHANGE METHOD FOR THE DETECTION OF AMIDES, IMIDES AND ANILIDES

PHILIP W. WEST
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)
MOHSIN QURESHI AND SAIDUL ZAFAR QURESHI
Chemical Laboratories, Aligarh Muslim University, Aligarh (India)
(Received January 15th, 1966)

A number of tests are available for the detection of amides and imides. Amides have been detected by the hydroxamic acid test in the presence of nitriles, esters, acid anhydrides, acid chlorides or trichloromethyl grouping[1-3] and in the presence of nitriles alone by the soda lime–methanolic copper sulphate test[4]. The mercury(II) chloride–bromothymol blue test[4] is useful for the differentiation between nitriles and amides, but it is unreliable in the presence of crotonaldehyde, acetone, cyclopentanone, 2,4-pentadione, diethyl malonate, ethylacetoacetate, vinyl acetate, phenol, some carboxylic acids and alkynes. The presence of olefinic or acetylenic multiple bonds or α-hydrogen atoms also invalidates the test.

The simplest approach to the problem appears to be to hydrolyze the compound and to detect the presence of the ammonium ions or aniline so produced, by the specific tests available for them. FEIGL[5] developed such a procedure for amides and imides. The substance is heated to dryness with concentrated hydrochloric acid and the ammonium ions formed by hydrolysis are detected by Nessler's reagent. Ammonium salts in the original sample, however, interfere. To overcome this difficulty another test is made for the carboxylic acid and the presence of amide is confirmed if positive tests are obtained both for ammonium ions and for the carboxylic acid. Even then the fatty acids should be absent. FEIGL[5] developed a similar test for anilides. The anilides are heated with guanidine carbonate which pyrolyzes the anilide to give aniline. Aniline is detected by its color reaction with *p*-dimethylaminobenzaldehyde. In this test the reactions are carried out under drastic conditions and the reagent, guanidine carbonate, is not easily available. There is still need for simple tests for amides, imides and anilides, and such tests are now proposed based on the use of the resin spot test technique.

Ion-exchange resins are efficient catalysts. They can bring about hydrolysis under relatively mild conditions without the introduction of any new ions. They should therefore prove advantageous in all those reactions where hydrolysis is performed prior to detection. Thus, it was found that they can be used successfully for the detection of esters[6]. An investigation of the use of ion-exchange resins for the detection of amides, imides and anilides has also been made and it was found that their use simplifies the procedure significantly and eliminates many possible interferences. The resin beads serve to insure efficient hydrolysis and they also serve as excellent media for final test reactions. FUJIMOTO proposed the use of a resin spot test technique for studying metal ions[7]. Although few studies have been made of the detection of organic substances using resin spot tests, we have found that this method holds promise of providing a flexible, simple and efficient means of studying certain organic substances.

EXPERIMENTAL

Reagents

All chemicals used were of reagent grade.

Test solutions. (*1*) Solutions of common amides and imides containing 1 mg/ml were prepared in water, free from ammonium ions. (*2*) Saturated aqueous solutions containing approximately 0.4 mg/ml of oxamide and phthalimide were prepared and used as such.

Resin. Dowex 50W-X8 (20–50 mesh) in either the H^+ or Na^+ form was regenerated and used as such in the test for anilides. For amide or imide tests, the resin beads in H^+ form were regenerated and washed until they no longer gave pink color with Nessler's reagent[8].

p-*Dimethylaminobenzaldehyde.* A 1% solution was prepared in water saturated with benzene.

Test for amides and imides

Procedure. Place about 10 ion-exchange beads in H^+ form in a micro casserole and add one drop (0.05 ml) of the test solution. Heat the contents just to boiling using a low flame and then wash the resin beads with 3 or 4 ml of water. Transfer the washed beads to a spot plate and remove any adhering water by blotting with a qualitative filter paper (quantitative filter paper contains ammonium ions). Add a drop of Nessler's reagent. A reddish pink color is developed at once on the bead surface if the test drop contained an amide or imide. The sensitivity of the test may be improved by using freshly regenerated resin in wet form. To detect very small amounts, it is preferable to wait for 2–3 min so that the color may develop fully.

Modified test for amides and imides in presence of ammonium salts. One milliliter of the test solution is shaken or slightly warmed with approximately 0.5 g of resin in Na^+ form. The contents are filtered through a glass wool plug and one drop of the filtrate is tested for NH_4^+ with Nessler's reagent. If a positive test is obtained the process is repeated. The amide test is performed on the NH_4^+-free filtrate as described earlier.

Test for anilides

Procedure. A few milligrams of the test substance are added to about 10 resin beads in H^+ form in a micro test tube. One drop of water and a few drops of *p*-dimethylaminobenzaldehyde solution are added. The contents are heated for 1–2 min on a low flame. In the case of an anilide, a pale yellow color develops on the bead surfaces.

RESULTS

Detection of amides and imides

The following N-unsubstituted amides and imides gave a positive test by the resin bead method: acetamide, benzamide, *n*-butyramide, chloralformamide, chloroacetamide, nicotinamide, oxamide, propionamide, phthalimide and guanidine hydrochloride.

A negative test was given by the following: palmitic amide, urea, cyanoguanidine, sulphanilamide, toluene *p*-sulphonamide and saccharin.

Behaviour of miscellaneous compounds. A number of typical organic compounds were tested to the recommended procedure and were found not to interfere. Those studied include the following.

Hydrocarbons and their derivatives: benzene, bromobenzene and nitrobenzene, carbon tetrachloride, chloroform, cyclohexane and toluene.

Amines: methylamine, dimethylamine and trimethylamine, monoethanolamine, diethanolamine and triethanolamine, ethylenediamine, aniline, diphenylamine and diethylaniline.

Alcohols: methanol, ethanol, *n*-propanol, *n*-butanol, isobutanol, isopropanol, glycerol and ethylene glycol.

Acids: acetic, benzoic, formic, propionic, oxalic, sulphanilic and tartaric.

Aldehydes: formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde and chloral hydrate.

Ketones: acetone, cyclohexanone, methyl ethyl ketone, di-isobutyl ketone and methyl isobutyl ketone.

Ethers: anisole, dioxane and ether.

Esters: ethyl acetate, methyl benzoate, *n*-tributyl phosphate, ethyl acetoacetate and diethyl malonate.

Carbohydrates: fructose, raffinose and sucrose.

Nitriles: acetonitrile, chloroacetonitrile, benzonitrile and cyanoacetic acid.

Phenols: *m*-cresol and phenol.

Anilides: acetanilide, *p*-bromoacetanilide, carbanilide, oxanilide, phenyl urea.

Heterocyclic bases: pyridine and piperidine.

Limit of identification. The limit of identification for a number of amides and imides was determined. The results are summarized in Table I.

Detection of amide and imide in presence of foreign substances. The detection of

TABLE I

LIMIT OF IDENTIFICATION OF AMIDES AND IMIDES

Amide/imide	*Amount detected (μg)*	*Limiting proportion*	*Amide/imide*	*Amount detected (μg)*	*Limiting proportion*
Formamide	0.05	$1:2\cdot10^5$	Propionamide	0.32	$1:1.2\cdot10^4$
Chloral formamide	0.40	$1:1\cdot10^4$	Oxamide	1.6	$1:1.2\cdot10^4$
Acetamide	0.30	$1:6.6\cdot10^4$	Nicotinamide	2	$1:5\cdot10^3$
Chloroacetamide	0.10	$1:1\cdot10^5$	Phthalimide	4	$1:2.5\cdot10^3$
Benzamide	2	$1:5\cdot10^3$	Guanidine hydrochloride	5	$1:1\cdot10^3$
n-Butyramide	0.30	$1:3.3\cdot10^4$			

amide and imide in the presence of a large amount of foreign substances was studied. Formamide and phthalimide were taken as the representative compounds. The results are summarized in Tables II and III.

Detection of anilides

The following anilides gave positive tests with the recommended procedure:

TABLE II

DETECTION OF FORMAMIDE IN THE PRESENCE OF FOREIGN SUBSTANCES

Foreign substances	*Amount added (μg)*	*Amide detected (μg)*	*Color of resin phase*[a]	*Limiting proportion*
Acetic acid	150	0.10	L.P.	$1:1 \cdot 10^5$
Acetaldehyde	250	0.05	L.P.	$1:2 \cdot 10^5$
Acetone	450	1	L.P.	$1:1 \cdot 10^4$
Acetanilide	100	1.5	P	$1:1 \cdot 10^4$
Aniline	50	0.50	P	$1:1 \cdot 10^4$
Anisole	300	0.2	P	$1:5 \cdot 10^4$
Benzene	400	0.30	R	$1:5 \cdot 10^4$
Carbon tetrachloride	600	0.05	L.P.	$1:2 \cdot 10^5$
Glycerol	800	3	P	$1:1 \cdot 10^3$
Methanol	150	0.05	L.P.	$1:2 \cdot 10^5$
Methyl acetate	100	5	P	$1:1 \cdot 10^3$
Methyl amine	100	5	P	$1:1 \cdot 10^3$
Nitrobenzene	200	0.4	P	$1:5 \cdot 10^4$
Phenol	50	0.5	P	$1:1 \cdot 10^4$
Pyridine	50	0.5	L.P.	$1:1 \cdot 10^4$
Sucrose	550	0.05	P	$1:1 \cdot 10^5$

[a] P = pink; L.P. = light pink; R = red.

TABLE III

DETECTION OF PHTHALIMIDE IN THE PRESENCE OF FOREIGN SUBSTANCES

Foreign substances	*Amount added (μg)*	*Imide detected (μg)*	*Color of resin phase*[a]	*Limiting proportion*
Acetic acid	150	4	P	$1:2.5 \cdot 10^3$
Acetaldehyde	120	4	L.P.	$1:2.5 \cdot 10^3$
Acetone	200	6	P	$1:2.5 \cdot 10^3$
Acetanilide	500	4	P	$1:2.5 \cdot 10^3$
Aniline	50	8	L.P.	$1:2.5 \cdot 10^3$
Anisole	110	4	L.P.	$1:2.5 \cdot 10^3$
Benzene	100	6	L.P.	$1:2.5 \cdot 10^3$
Glycerol	100	4	L.P.	$1:2.5 \cdot 10^3$
Methanol	200	4	P	$1:2.5 \cdot 10^3$
Methyl acetate	400	4	P	$1:2.5 \cdot 10^3$
Methyl amine	100	6	L.P.	$1:2.5 \cdot 10^3$
Phenol	200	4	L.P.	$1:2.5 \cdot 10^3$
Pyridine	50	6	P	$1:2.5 \cdot 10^3$
Sucrose	500	4	P	$1:2.5 \cdot 10^3$

[a] P = pink; L.P. = light pink.

acetanilide, *p*-bromoacetanilide, carbanilide and phenylurea. Oxanilide failed to give the test. Likewise, aliphatic amines (except for dimethylamine), methylaniline and diethylaniline gave no color. Other representative compounds such as hydrocarbons, alcohols, ketones, acids, etc., were tested (as described in the case of amides and imides) and failed to give the test.

The following aromatic amines gave a positive test in the cold. The color developed in the resin beads is indicated in parentheses: Aniline (pale yellow), *o*- and *m*-nitroaniline (pale yellow), *p*-nitroaniline (orange), diphenylamine (pale yellow), benzidine (red), *p*-toluidine (pale yellow), 1-naphthylamine (yellow), 2-naphthylamine (yellow), and *o*-phenylenediamine (red).

TABLE IV

LIMIT OF IDENTIFICATION OF ANILIDES

Anilides	*Amount detected (μg)*	*Anilides*	*Amount detected (μg)*
Carbanilide	8	*p*-Bromoacetanilide	8
Phenylurea	10	Acetanilide	1

TABLE V

DETECTION OF ACETANILIDE IN THE PRESENCE OF FOREIGN SUBSTANCES

Foreign substances	*Amount added (μg)*	*Acetanilide detected (μg)*	*Color of resin phase*	*Limiting proportion ($\cdot 10^4$)*
Acetic acid	700	2	Pale yellow	1:1
Acetaldehyde	250	1.5	Pale yellow	1:1
Acetone	300	1	Pale yellow	1:1
Anisole	150	2	Pale yellow	1:1
Benzene	200	2	Pale yellow	1:1
Carbon tetrachloride	350	1	Pale yellow	1:1
Formamide	100	2	Pale yellow	1:1
Methanol	500	1	Pale yellow	1:1
Methyl acetate	200	2	Pale yellow	1:1
Methylamine	200	1	Pale yellow	1:1
Nitrobenzene	150	2.5	Pale yellow	1:1
Pyridine	250	1	Pale yellow	1:1
Phthalimide	300	1	Pale yellow	1:1
Phenol	400	1.5	Pale yellow	1:1
Sucrose	1000	1	Pale yellow	1:1

Limit of identification. The limit of identification of available anilides—except acetanilide which was soluble in water—was determined by thoroughly mixing them with sucrose in a finely powdered form in the ratio 1:100 and weighing them accurately. The results are summarized in Table IV.

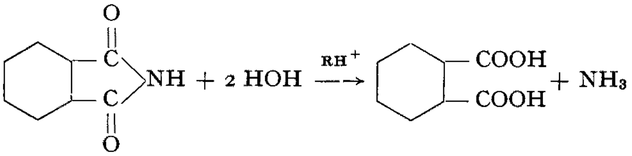
Detection of anilide in presence of foreign substances. The microgram detection of acetanilide was found to be possible in a large amount of foreign substances. The results are summarized in Table V.

DISCUSSION

When aqueous solutions of amides, imides or anilides are heated with cation-exchange resin in H^+ form, the latter catalyzes the acid hydrolysis of the substance in question and either ammonia or aniline is produced.

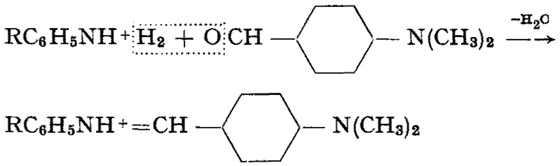
$$\phi CONH_2 + HOH \xrightarrow{RH^+} \phi COOH + NH_3$$

(ϕ = alkyl or aryl group)



$$\phi CONHC_6H_5 + HOH \xrightarrow{RH^+} \phi COOH + C_6H_5NH_2$$

$$C_6H_5\,NH_2 + RH^+ \rightarrow RC_6H_5NH_3^+$$



Pale yellow resin beads

Ammonia and aniline react with proton from the acids produced or from the resin in the hydrogen form and are thus converted to NH_4^+ and $C_6H_5NH_3^+$. These ions easily replace H^+ from the resin and are detected on the bead surface by means of Nessler's reagent or *p*-dimethylaminobenzaldehyde.

The amide test is negative for urea since on hydrolysis it gives carbon dioxide and ammonia. The carbonic acid is too weak to donate a proton and ammonia probably escapes as a gas. Palmitic amide also gives a negative test by the ion-exchange method since both palmitic acid and palmitic amide are insoluble in water and ammonium ions are not produced. Amides and imides of sulphonic acid are not hydrolyzed by the ion-exchange resin and therefore give a negative test.

The anilide test could not be tried with N-monosubstituted amides ($-CONHR$, R = alkyl group) as they were not available; but on hydrolysis they would yield an acid and an aliphatic primary amine. The latter should not give a color with *p*-dimethylaminobenzaldehyde in the resin phase. Oxanilide gives a negative test as it is not hydrolyzed, being insoluble in water. The ion-exchange test for amide and imide is simple, selective and sensitive. The interference due to ammonium ions is easily removed by shaking with a little resin in the Na^+ form. In this manner it was possible to detect 1 μg formamide in presence of 10 μg of ammonium chloride. Fatty acids also do not interfere (see Tables II, III). The ion-exchange test for anilides also is simpler than previous methods. In both cases the ion-exchange method is faster and more selective. The test is very compact since the hydrolysis as well as detection is performed using only a few resin beads. It is therefore interesting to compare the relative merits of the ion-exchange method with soda lime–methanolic copper sulphate and mercuric chloride–bromothymol blue tests[4]. This is done in Table VI.

TABLE VI

COMPARISON OF THE VARIOUS TESTS FOR AMIDES, IMIDES AND ANILIDES

Substances	*Ion-exchange test for amides and imides*	*Ion-exchange test for anilides*	*Soda lime test*	*Mercuric chloride test*
Nitriles	Negative	Negative	Positive	Negative
N-Unsubstituted amide	Positive[a]	Negative	Positive	Positive
N-Monosubstituted amide (anilides also)	Negative	Positive[b]	Positive	Positive
N,N-disubstituted amide	—	—	Positive	Negative
Interferences				
Amines	Negative	Dimethyl-amine	Positive	Positive
Acetone, diethyl malonate, ethyl acetoacetate and phenol	Negative	Negative	—	Positive
Alkynes, acetylene multiple bond and hydrogen atom	—	—	—	Positive

Palmitic amide, urea and amides of sulphonic acid gave negative tests.
Oxanilide gave negative test.

The authors are grateful to Professor A. R. KIDWAI, Head of the Department of Chemistry, for his interest in this work. Thanks are due to the Government of India for awarding Research Training Scholarship to one of us (S.Z.Q.)

SUMMARY

Ion-exchange resins are efficient catalysts for the acid hydrolysis of amides, imides and anilides; the ammonium ion or aniline so formed can be detected by the well-known specific tests for these species. In general, the proposed tests are simpler, faster and more selective than those already available. The amounts that can be detected are of the order of 0.05–5 μg depending on the compound.

RÉSUMÉ

On propose une méthode avec échangeur d'ions pour la détection des amides, des imides et des anilides; elle est basée sur l'effet catalytique de résines sur l'hydrolyse de ces composés. Les tests proposés sont plus simples, plus rapides et plus sélectifs que ceux généralement effectués. Les quantités décelables sont de l'ordre de 0.05 à 5 μg suivant le composé.

ZUSAMMENFASSUNG

Ionenaustauscherharze sind wirksame Katalysatoren für die Säurehydrolyse von Amiden, Imiden und Aniliden. Die so gebildeten Ammoniumionen oder das gebildete Anilin können durch gut bekannte, spezifische Reaktionen dieser Verbindungen nachgewiesen werden. Im allgemeinen sind die vorgeschlagenen Nachweise einfacher, schneller und selektiver als die bereits verfügbaren. Die nachweisbaren Beträge liegen je nach Verbindung in der Grössenordnung von 0 05 bis 5 μg

REFERENCES

1 R. E. BUCKLES AND C. J. THELEN, *Anal. Chem.*, 22 (1950) 676.
2 R. L. SHRINER, R. C. FUSON AND D. Y. CURTIN, *Systematic Identification of Organic Compounds*, 4th Edn., Wiley, New York, 1956.
3 S. SOLOWAY AND A. LIPSCHITZ, *Anal. Chem.*, 24 (1952) 898.
4 S. TROFIMENKO AND T. J. SEASE, *Anal. Chem.*, 30 (1958) 1432.
5 F. FEIGL, *Spot Tests in Organic Analysis*, 7th Edn., Elsevier, Amsterdam, 1966, pp. 256, 260.
6 M. QURESHI AND S. Z. QURESHI, *Anal. Chim. Acta*, 34 (1966) 108.
7 M. FUJIMOTO, *Chemist–Analyst*, 49 (1960) 4.
8 A. I. VOGEL, *Micro and Semimicro Qualitative Inorganic Analysis*, 4th Edn., Longmans, Green and Co., London, 1954, p. 319.

Anal. Chim. Acta, 36 (1966) 97–104

STEPWISE PHOTOMETRIC TITRATIONS

BENGT SKRIFVARS AND ANDERS RINGBOM
Department of Analytical and Inorganic Chemistry, Åbo Akademi, Åbo (Finland)
(Received March 28th, 1966)

The introduction of new complexing agents and indicators has greatly increased the scope of photometric titrations based upon complexation reactions. When the stability constants of the compounds formed are known, it is usually possible to compare various methods critically and thus avoid time-consuming work based on the principle of "trial and error". Sensitive photometers are able to record colour changes not detected by the human eye, and hence indicators can be used in quite a new way to detect the end-points of compleximetric titrations. Two metals may form with an indicator compounds that are nearly identical in colour, but the absorption spectra may show differences that can be utilized for a stepwise titration of the 2 metals.

If a metal M_I is titrated with a complexing agent Y (say, the EDTA anion) in the presence of an indicator forming the complex $M_I I$, all the indicator is bound to the metal at the beginning of the titration, and the colour changes as a result of the reaction

$$M_I I + Y = M_I Y + I \tag{1}$$

The charges of the ions are omitted here and in the following for clarity. Since $M_I I$ and I differ in colour, it is easy to follow the course of the reaction photometrically. When a second metal ion, M_{II}, that forms a less stable complex with Y is present, the condition for a successful detection of the first equivalence point is that the conditional constant of the complex $M_I Y$ is sufficiently high in value. If the metal ions are not involved in any side reactions, the conditional constant is computed from the equation

$$\log K_{M_I Y'} = \Delta \log K + pM_{II} \tag{2}$$

$\Delta \log K$ is the difference $\log K_{M_I Y} - \log K_{M_{II} Y}$, and pM_{II} is the negative logarithm of the concentration of the interfering metal M_{II}. This conditional constant does not change with pH as long as $\alpha_{Y(M)} > \alpha_{Y(H)}$ (see note 1 below).

Note 1. The concept of conditional constant introduced by RINGBOM[1] is used in this paper. For the sake of clarity, some comments on this concept are given below.

A conditional constant takes into account all side reactions interfering with the main reaction to which it refers. If M_I and Y are involved in side reactions with other species, the stability constant $K_{M_I Y}$ is replaced by the conditional constant $K_{M_I' Y'}$ defined by

$$\frac{[MY]}{[M_I'][Y']} = K_{M_I' Y'} \tag{3}$$

where $[M_I']$ and $[Y']$ denote the total concentrations of M_I and Y that have *not* reacted to form the complex M_IY according to the main reaction. The concentration sum $[Y']$ thus includes, in addition to the concentration of the anion Y, not only the concentration of all acid ions, HY, H_2Y, etc., but also the concentration of the formed $M_{II}Y$. Equation (2) is valid if $M_{II}Y$ predominates over the hydrogen complexes of Y. The sum $[M_I']$ includes the concentrations of all formed hydroxo complexes (M_IOH, $M_I(OH)_2$, . . .) of the metal as well as the concentrations of complexes formed with any other complexing agent present (*e.g.*, $M_I(NH_3)$, $M_I(NH_3)_2$, . . ., if ammonia is present). The conditional constant is calculated from the equation

$$K_{M_I'Y'} = \frac{K_{M_IY}}{\alpha_{M_I}\alpha_Y} \tag{4}$$

where the coefficients α_{M_I} and α_Y are defined by

$$\alpha_{M_I} = \frac{[M_I']}{[M_I]} \quad \text{and} \quad \alpha_Y = \frac{[Y']}{[Y]} \tag{5}$$

The values of the α coefficients can be readily computed from the equilibrium constants or taken from Tables[1]. If several side reactions occur, an overall α coefficient approximately equal to the sum of the individual α coefficients should be used.

Possible side reactions of M_IY lead to a third coefficient α_{M_IY} which is introduced into the numerator and thus increases the value of the conditional constant:

$$K_{M_I'Y'(M_IY)'} = \frac{\alpha_{M_IY}}{\alpha_{M_I}\alpha_Y} K_{M_IY} \tag{6}$$

When 2 metals, M_I and M_{II}, are titrated in the presence of the indicator anion I, the complexing agent will first react with M_II according to eqn. (1) and the liberated indicator will then combine with M_{II} to form $M_{II}I$. The colour change thus results from the transformation of M_II into $M_{II}I$. The equilibria between the reacting components are defined by the equations

$$K_{M_II} = \frac{[M_II]}{[M_I][I]} \quad \text{and} \quad K_{M_{II}I} = \frac{[M_{II}I]}{[M_{II}][I]} \tag{7}$$

Division of these two equations gives

$$\frac{[M_II]}{[M_{II}I]} = \frac{K_{M_II}[M_I]}{K_{M_{II}I}[M_{II}]} \tag{8}$$

This expression gives the distribution of the indicator in the solution. It is not necessary that $K_{M_II} > K_{M_{II}I}$ — although the colour change will then be sharper — but, as a rule, at least 5–10 % of the indicator must be present as M_II at the beginning of the titration. However, when a very sensitive photometer is used or when the difference between the absorptivities of M_II and $M_{II}I$ is large, the detection of the end-point may be possible even if a smaller fraction of the indicator is present as M_II.

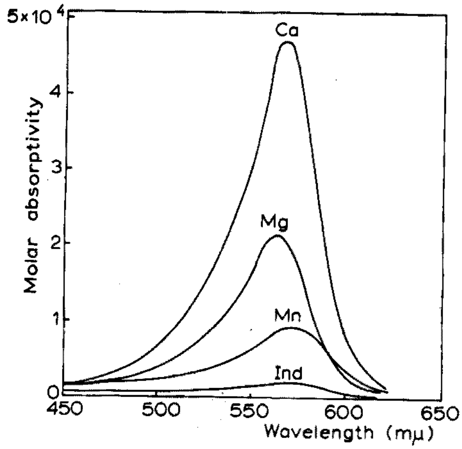
When very dilute solutions are to be titrated, not only M_II and $M_{II}I$, but also free I ions present have to be considered.

The second equivalence point of the titration coincides with the completion of the reaction $M_{II}I + Y = M_{II}Y + I$. The complex M_IY present does not interfere with this reaction.

Note 2. The theoretical treatment of photometric titrations in this paper follows the approach suggested in the monograph by RINGBOM[1] where the titration curves are divided into 3 groups: low sensitivity break-point curves ($pM_{trans} < pM_{eq}$), medium sensitivity rounded curves ($pM_{trans} = pM_{eq}$) and high sensitivity break-point curves ($pM_{trans} > pM_{eq}$). If very dilute solutions are titrated, an indicator correction may be necessary in the last 2 cases, but low sensitivity curves do not require the application of a correction.

The theory of photometric titrations with indicators was recently discussed on this basis in a paper by STILL AND RINGBOM[2], where particular attention was paid to the significance of the inflection point and the errors arising when the inflection point is taken to be the end-point.

In the following, the use of the indicator metalphthalein (phthaleincomplexone) for various stepwise photometric titrations will be discussed. This indicator, introduced by ANDEREGG *et al.*[3], is a hexabasic acid that forms red complexes with various metal ions. The absorption curves of its calcium, magnesium and manganese complexes are presented in Fig. 1. All the metal complexes have absorption maxima at about the same wavelength, but the molar absorptivities differ considerably. Consequently, it should be possible to detect end-points in stepwise titrations of metals photometrically in the presence of metalphthalein if a suitable complexing agent is available. Unfortunately, the equilibrium conditions are not quite simple since 3 different compounds, MI, MHI, and M_2I, may be formed. A diagram showing the



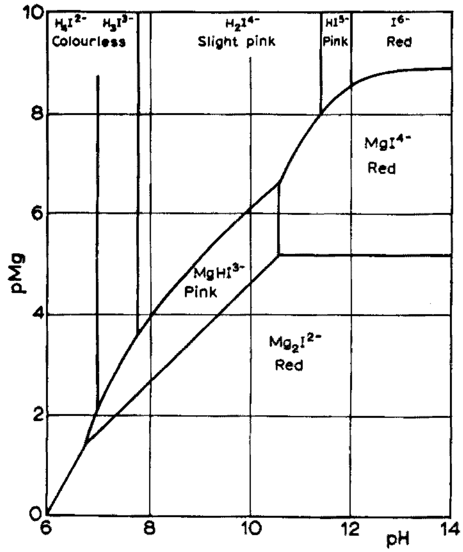


Fig. 1. Molar absorptivities of metalphthalein and its metal complexes: free indicator at pH 9.25; calcium complex at pH 10.0; magnesium complex at pH 9.2; manganese complex at pH 9.1.

Fig. 2. The variation of the colour of the indicator metalphthalein with magnesium and hydrogen concentrations as calculated from constants given by ANDEREGG *et al.*[3].

relative concentrations of the various magnesium–metalphthalein complexes at various pH values is presented in Fig. 2. A similar diagram illustrating the behaviour of metalphthalein as an indicator for calcium is given in ref. 1. The values of the stability constants of the manganese complexes are not known.

Titration of manganese and calcium with metalphthalein as indicator

The manganese complexes of polyaminocarboxylic acids are, as a rule, more stable than the corresponding calcium complexes. A study of the numerical values[1] reveals that the difference between the stability constants of the DTPA (diethylenetriaminepentaacetic acid = H_5X) complexes of manganese and calcium is particularly large: $\Delta \log K = \log K_{MnX} - K_{CaX} = 15.5 - 10.6 = 4.9$.

According to eqn. (2), the conditional constant $K_{MnX'}$ when manganese is titrated with DTPA in a solution containing calcium in 10^{-3} M concentration is $4.9 + 3 = 7.9$, a value sufficiently high for a satisfactory stepwise titration. Assuming a total concentration of manganese, C_{Mn}, of 10^{-3} M, it follows that at the equivalence point $pMn_{eq} = \frac{1}{2}(\log K_{MnX'} + pC_{Mn}) = \frac{1}{2}(7.9 + 3) \approx 5.5$.

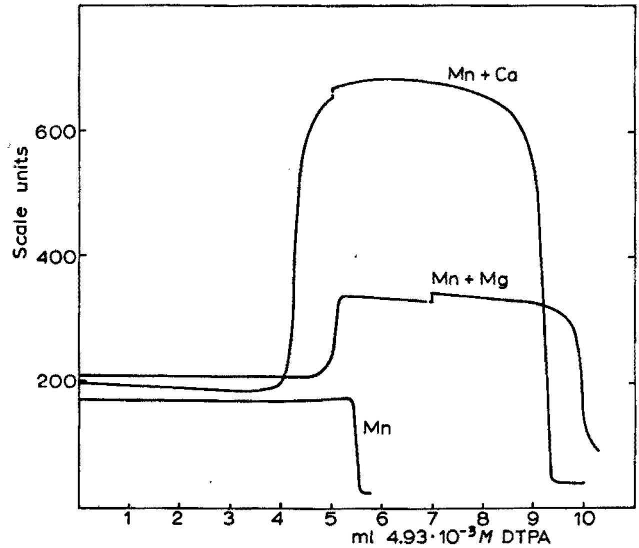


Fig. 3. (a) Titration of manganese with $4.93 \cdot 10^{-3}$ M DTPA at pH 9.3; eq. point at 5.50 ml. (b) Titration of manganese at pH 9.3 and calcium at pH 10 with $4.93 \cdot 10^{-3}$ M DTPA; eq. points at 4.28 ml and 9.34 ml. (c) Titration of manganese at pH 9.3 and magnesium at pH 9.6 with $4.93 \cdot 10^{-3}$ M DTPA; eq. points at 5.10 ml and 9.93 ml. Indicator: metalphthalein, $3 \cdot 10^{-6}$ M. The final volume of the titrated solutions was about 70 ml. The discontinuities in curves (b) and (c) indicate pH shifts. Lange colorimeter, green filter.

If manganese is titrated without any calcium present, pMn_{eq} will depend on pH. At pH 9 we have

$$\log K_{MnX'} = \log K_{MnX} - \alpha_{X(H)} = 15.5 - 1.8 \approx 13.7$$

a very high value, and the corresponding $pMn_{eq} = \frac{1}{2}(13.7 + 3) \approx 8.4$.

Figure 3 illustrates a number of titrations performed. When no calcium is present, a low sensitivity curve characterized by a sharp break-point arises. Therefore, pMn_{trans} is considerably smaller (probably about 2 pMn units) than $pMn_{eq} = 8.4$. If calcium is present, the curve has a very peculiar shape. The initial small slope is due to a dilution effect; the following steep rise relates to the conversion of the manganese complex into the more strongly coloured calcium complex; and the steep fall before the end of the curve relates to the conversion of the calcium complex into the free indicator.

The rising part of the curve does not start with a sharp break-point. The curve is a little rounded and points to a medium sensitivity indicator, *i.e.*, pMn_{trans} is not far from $pMn_{eq} = 5.5$, probably between 5 and 6. It should be noted, however, that in this titration pMn_{trans} corresponds to the transition of the manganese–indicator complex into the calcium–indicator complex, and will be smaller than the conventionally defined pMn_{trans} relating to the transformation of the manganese complex into the free indicator. Values of pMn_{trans} based on $\alpha_{I(Ca)}$ (or $\alpha_{I'(Ca)}$) coefficients can be calculated from the stability constants. If only MnI complexes were formed, this calculation would be a simple task. However, the present case is somewhat more involved owing to the probable occurrence of the complexes MnHI and Mn_2I, and, as mentioned above, the equilibrium constants of the manganese–indicator complexes are not known. To avoid precipitation of manganese hydroxide, manganese titrations were usually performed at pH 9.

After the titration of manganese, the pH of the solution was usually raised to 10. The steep fall of the curve resulting in a break-point (possibly with a very small rounded part) is in accordance with theory, as can be shown by calculating pCa_{eq} and pCa_{trans}. Since $\log K_{CaX'} = \log K_{CaX} - \log \alpha_{Y(H)} = 10.6 - 0.7 = 9.9$, it follows that $pCa_{eq} = \frac{1}{2}(9.9 + 3) \approx 6.5$. For pCa_{trans} a value of 4.5 can be taken[1]. pCa_{eq} and pCa_{trans} thus differ by 2 units and a break-point of the low sensitivity type will arise.

Procedure. The pH of the solution containing manganese and calcium is adjusted to about 9 with an ammonia buffer, and metalphthalein is added to give a concentration of about $3 \cdot 10^{-6}$ *M*. To avoid oxidation of manganese, the solution should contain some ascorbic acid. The titration is performed with about 0.005 *M* DTPA using light with a wavelength of 560–580 mμ or, when a filter photometer is used, a green filter. The inflection point of the rising curve is taken as the first equivalence point. The break-point (possibly extrapolated, if the curve is slightly rounded) at the end of the curve corresponds to the second equivalence point (Fig. 3).

Since the manganese–indicator complex is more stable than the corresponding calcium complex, the ratio $[Mn]_{total} : [Ca]_{total}$ is not critical.

Note 3. In a rigorous theoretical treatment there is a difference between pM_{eq} and pM_{infl} (and between pM_{eq} and pM_{break}). The error due to this difference can be calculated[2] from the equation

$$\Delta\, pM = pM_{infl} - pM_{eq} = 1/3\,(pM_{trans} - pM_{eq}) \tag{9}$$

and the corresponding relative error determined from Δ pM and the conditional constant by means of a diagram given in ref. 1. Since the above equation is based on the assumption that MI is the only metal–indicator complex formed, this treatment is not quite exact for titrations with metalphthalein. Moreover, if a sufficiently low indicator concentration is not used, the inflection point of the photocurrent curve (*i.e.*, the transmittance curve) can differ slightly from the inflection point of the absorbance curve (*cf.* ref. 2). However, for the titrations reported in this paper, Δ pM, calculated as above, was always less than one unit, and the corresponding error seldom more than a few tenths of a percent. Furthermore, the discussed errors can be largely eliminated if, when standardizing the titrant, the end-point is detected in the same way (from the inflection point or from the break-point) as when analysing the sample solution.

If very dilute solutions are titrated, an indicator correction may be necessary. The amount of metal bound to the indicator at the inflection point is then computed, and this amount is added to the result[1]. Titrations leading to low sensitivity break-points need no indicator correction.

Titration of manganese and magnesium with metalphthalein as indicator

The shape of the titration curve can easily be predicted from the absorption curves of Fig. 1 and from the known stability constants. A curve similar to the Mn–Ca curve will be obtained but the maximum will be lower because the colour of the magnesium complex is less intense than that of the calcium complex. The important pM values can be calculated in exactly the same way as in the preceding case. The following values were obtained for the titration of a solution in which the initial manganese and magnesium concentrations were both 10^{-3} *M*. A pH value of 9 was assumed for the titration of manganese and a pH value of 10 for the titration of magnesium.

$$\log K_{\mathrm{MnX'}} = \Delta \log K + \mathrm{pMg} = 6.2 + 3 = 9.2$$

$$\log K_{\mathrm{MgX'}} = \log K_{\mathrm{MgX}} - \log \alpha_{\mathrm{X(H)}} = (9.3 - 0.7) = 8.6$$

$$\mathrm{pMn_{eq}} = \tfrac{1}{2}(9.2 + 3) = 6.1; \quad \mathrm{pMg_{eq}} = \tfrac{1}{2}(8.6 + 3) = 5.8$$

$$\mathrm{pMg_{trans}} \approx 4.7 \quad \text{(Fig. 2)}$$

Considerations analogous to those for the titration of manganese in the presence of calcium point to a value of $\mathrm{pMn_{trans}}'$ of about 5–6.

Also in this case the inflection point of the rising curve can be taken as the first equivalence point.

The difference (= 1.1) between $\mathrm{pMg_{eq}}$ and $\mathrm{pMg_{trans}}$ is considerably smaller than the corresponding difference (= 2.4) when calcium is titrated. A rounding of the curve at the second equivalence point can thus be expected and was also observed as the curve in Fig. 3 shows.

A procedure analogous to that used when manganese and calcium are titrated can be followed.

Titration of calcium and magnesium with metalphthalein as indicator

The problem of determining calcium and magnesium by a stepwise titration or 2 separate photometric titrations has been discussed in the literature. An appropriate reagent for the titration of calcium is EGTA (ethyleneglycol-bis(2-aminoethylether)-tetraacetic acid) since the difference between the stability constants of its calcium and magnesium complexes is unusually large: $\log K_{\mathrm{CaZ}} - \log K_{\mathrm{MgZ}} = 11.0 - 5.2 = 5.8$. Hence, if $C_{\mathrm{Mg}} = 10^{-3}$ *M*, the conditional constant for the calcium complex is log $K_{CaZ'} = 5.8 + 3 = 8.8$ (eqn. (2)). A visual (and, of course, also photometric) titration of calcium is possible if the blue zinc–zincon[4] or zinc–PAN[5] is used as an indirectly functioning indicator.

FLASCHKA AND GANCHOFF[6] proposed a photometric titration of calcium in the presence of a hundred-fold amount of magnesium with EGTA using murexide as indicator. After the end-point is reached, magnesium is titrated in the same solution with EDTA using eriochrome black T as indicator. In a later paper FLASCHKA AND SAWYER[7] described a stepwise titration of calcium and magnesium with EDTA in which the indicator calmagite is added in excess of the amount of magnesium. LACY[8] used eriochrome black T in a similar titration. In the last 2 methods the excess of indicator is needed to mask the magnesium. In this way the conditional constant of the calcium–EDTA complex is increased by about one logarithmic unit. However, a drawback of these 2 methods is that the concentration of magnesium must be low compared to the concentration of calcium, or the excess of indicator must be large, for otherwise a sharp end-point will not be obtained.

Several methods for the stepwise titration of calcium and magnesium are thus available. In addition, it should be mentioned that a stepwise titration can also be performed with metalphthalein as indicator. This method is possible in spite of the fact that $pCa_{trans} = 4.5$ is a little lower than $pMg_{trans} = 4.7$ (at pH 10). However, the method is somewhat less accurate than the methods given in the preceding sections of this paper, and a photometer of rather high sensitivity is needed since at the beginning of the titration only a small fraction of the indicator is present as its calcium complex.

Owing to the influence of the formed magnesium–indicator complex, pCa_{trans} will be smaller than when a solution containing only calcium is titrated ($pCa_{trans} = 4.5$) and, of course, much smaller than $pCa_{eq} = \frac{1}{2}(8.8 + 3) = 5.9$. It follows that a low sensitivity curve will arise; the fall before the end-point will be almost linear. Because of the small change in colour intensity, the angle at the end-point—being the intersection point of two lines—will not be very acute.

After the titration of calcium with EGTA, the titration can be continued with EDTA—or better with DTPA—for the determination of magnesium.

The excess of EGTA added before calcium is titrated should not be too large, for otherwise the accuracy of the magnesium titration will decrease.

The ratio of magnesium to calcium should not exceed unity.

Titration of manganese, calcium and magnesium with metalphthalein as indicator

The methods described above can be used to analyse a solution containing manganese, calcium and magnesium. Various procedures can be followed. One way is to titrate stepwise manganese (with DTPA), calcium (with EGTA) and magnesium (with DTPA). However, an excess of EGTA can be avoided if manganese and the sum of calcium and magnesium are first titrated stepwise with DTPA and then the sum of manganese and calcium in a separate sample with EGTA.

Titration of zinc and magnesium with erio T as indicator

As a further example, the titration of 2 metals successively using only one complexing agent and one indicator is described. The results presented relate to the titration of zinc and magnesium with eriochrome black T (erio T, HI) as indicator.

The absorptivities of I′, ZnI and MgI are presented in Fig. 4. At a wavelength of 520 mμ the absorptivities of the 3 species differ considerably. The equilibria of the erio T complexes are less involved than those of the metalphthalein complexes. As the values of all constants are known, a more exact theoretical treatment is possible. The conditional stability constants and pM values needed are calculated below for the titration of a solution containing zinc and magnesium, each in 10^{-3} M concentration, with EDTA at pH 9.7. An ammonia-ammonium buffer is used and $[NH_3'] = [NH_3] + [NH_4]$ is assumed to be 0.1 M.

The values of the constants used are taken from ref. 1.

$$\log K_{\mathrm{Zn'Y'}} = \log K_{\mathrm{ZnY}} - \log \alpha_{\mathrm{Zn(NH_3)}} - \log \alpha_{\mathrm{Y(Mg)}} = 16.5 - 4.2 - 5.7 = 6.6$$

$$\log K_{\mathrm{Zn'I'}} = \log K_{\mathrm{ZnI}} - \log \alpha_{\mathrm{Zn(NH_3)}} - \log \alpha_{\mathrm{I(Mg)}} = 12.9 - 4.2 - 4.0 = 4.7$$

$$\log K_{\mathrm{MgY'}} = \log K_{\mathrm{MgY}} - \log \alpha_{\mathrm{Y(H)}} = 8.7 - 0.7 = 8.0$$

$$\log K_{\mathrm{MgI'}} = \log K_{\mathrm{MgI}} - \log \alpha_{\mathrm{I(H)}} = 7.0 - 1.9 = 5.1$$

$$\mathrm{pZn_{eq}}' = \tfrac{1}{2}(\log K_{\mathrm{Zn'Y'}} + \mathrm{p}C_{\mathrm{Zn}}) = \tfrac{1}{2}(6.6 + 3) = 4.8$$

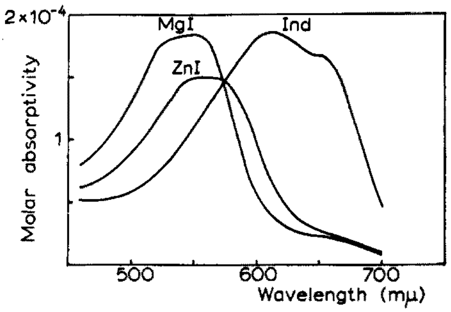
$$\mathrm{pZn_{trans}}' = \log K_{\mathrm{Zn'I'}} = 4.7$$

$$\mathrm{pMg_{eq}} = \tfrac{1}{2}(\log K_{\mathrm{MgY'}} + \mathrm{p}C_{\mathrm{Mg}}) = \tfrac{1}{2}(8.0 + 3) = 5.5$$

$$\mathrm{pMg_{trans}} = \log K_{\mathrm{MgI'}} = 5.1$$

Since no free indicator is present at the first equivalence point where ZnI is transformed into MgI, the formation of ZnI_2 complexes can be neglected.

It can be seen that $\mathrm{pZn_{eq}}'$ and $\mathrm{pZn_{trans}}'$ almost coincide; also $\mathrm{pMg_{eq}}$ and $\mathrm{pMg_{trans}}$



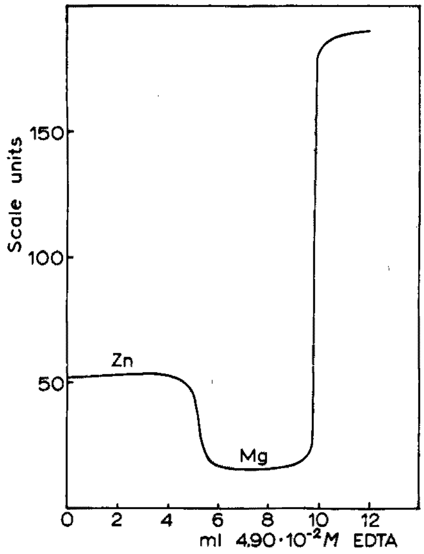


Fig. 4. Molar absorptivities of eriochrome black T and its metal complexes at pH 9.8: free indicator; magnesium complex, MgI; zinc complex, ZnI.

Fig. 5. Titration of zinc and magnesium with $4.90 \cdot 10^{-2}$ M EDTA at pH 9.7 (ammonia buffer, $[NH_3'] \approx 0.1$). Eq. points at 5.28 and 9.87 ml. Indicator eriochrome black T. Final volume about 190 ml. Beckman B spectrophotometer, 520 mμ.

are nearly equal. Rounded medium sensitivity curves can thus be expected.

Figure 5 illustrates one titration. A curve symmetrically rounded at the ends of the jumps is obtained. The midpoints of the two jumps will almost coincide with the equivalence points. However, if very accurate results are needed, the following approximately valid equation (*cf.* ref. 1, p. 110) should be used:

$$n_{\mathrm{eq}} \approx \frac{n_{\mathrm{I}}^{\max} + n_{\mathrm{MI}}^{\max}\,[\mathrm{M}']_{\mathrm{eq}}\,K_{\mathrm{M'I'}}}{1 + [\mathrm{M}']_{\mathrm{eq}}\,K_{\mathrm{M'I'}}}$$

where n's denote the scale unit readings of the galvanometer. This equation gives $n_{\mathrm{eq}} = 33$ and $n_{\mathrm{eq}} = 140$, respectively, at the 2 equivalence points; the corresponding volumes agree with the theoretical ones (Fig. 5).

EXPERIMENTAL

The instrumentation needed for the described photometric titrations can be simple, and most commercial photometers can be adapted for photometric titrations by minor alterations. In some experiments a Beckman B spectrophotometer with a modified cell compartment or a Metrohm Spectrocolorimeter E 1009 connected with a Metrohm Potentiograph E 336 for automatic recording of titration curves was used. When a high sensitivity was desired (*e.g.* in the titrations of calcium and magnesium with metalphthalein as indicator) a Lange colorimeter (filter photometer) was used. The instrument has 2 barrier layer cells connected in opposition and by using shutters the galvanometer zero reading can be shifted to any arbitrary point on the scale. When green filters and a Radiometer Model GVM 23 spotlight galvanometer were used, the maximum sensitivity was 15–25 scale units per 1% transmittance depending on the lamp used.

If necessary an indicator correction should be applied.

TABLE I

STEPWISE TITRATIONS OF MANGANESE, CALCIUM, MAGNESIUM AND ZINC[a]

(Mn and Mg titrated with 0.00493 *M* DTPA, Ca with 0.00494 *M* EGTA. Final volumes about 70 ml. Zn and Mg titrated with 0.0490 *M* EDTA. Final volume 190 ml)

Manganese		*Calcium*		*Magnesium*		*Zinc*	
Taken (mg)	*Found (mg)*	*Taken (mg)*	*Found (mg)*	*Taken (mg)*	*Found (mg)*	*Taken (mg)*	*Found (mg)*
—	—	0.601	0.605	0.258	0.255	—	—
—	—	1.04	1.04	0.515	0.515	—	—
1.28	1.28	—	—	0.569	0.574	—	—
1.39	1.38	0.921	0.914	0.362	0.360	—	—
1.16	1.16	0.881	0.885	0.284	0.282	—	—
—	—	—	—	5.46	5.46	16.87	16.84

[a] Titrations of larger amounts with a more concentrated titrant will increase the accuracy.

The results of a series of various analyses are given in Table I. These results are seen to be satisfactory.

This investigation has been supported by grants from Statens Teknologiska Kommission, Finland, and from Svensk-Österbottniska samfundet, Vasa, Finland.

SUMMARY

Stepwise titrations of several metals with photometric end-point detection are described. The equivalence points when 2 metal ions are titrated compleximetrically can be detected if the conditional stability constants are sufficiently high in value even if there are only slight differences between the colours of the different species of the indicator compounds.

The following systems were analysed by stepwise photometric titration using either metalphthalein or eriochrome black T as indicator: manganese–calcium; manganese–magnesium; calcium–magnesium; manganese–calcium–magnesium; zinc–magnesium. EDTA, DTPA and EGTA were used as titrants. A satisfactory accuracy was attained in each case. The results agreed with conclusions drawn from the theory of stepwise photometric titrations based on equilibrium calculations and absorbance values.

RÉSUMÉ

Les auteurs décrivent des titrages simultanés de plusieurs métaux avec détection photométrique du point final. On peut ainsi titrer compleximétriquement 2 métaux lorsque les constantes de stabilité sont suffisamment élevées, même s'il n'y a que peu de différence entre les couleurs des complexes métal–indicateur et la couleur de l'indicateur libre. Les analyses suivantes ont été effectuées: manganèse–calcium; manganèse–magnésium; calcium–magnésium; manganèse–calcium–magnésium, et zinc–magnésium, en présence de métalphtaléine ou de noir ériochrome T comme indicateurs et à l'aide d'EDTA, de DTPA et d'EGTA.

ZUSAMMENFASSUNG

Es wird die Titration verschiedener Metalle mit photometrischer Endpunktsanzeige beschrieben. Wenn 2 Metallionen komplexometrisch titriert werden, können die Äquivalenzpunkte angezeigt werden falls die Stabilitätskonstanten ausreichend hohe Werte besitzen, sogar dann, wenn nur geringe Unterschiede zwischen der Farbe der zwei Metall–indikatorkomplexe und der Farbe des freien Indikators vorliegen. Die folgenden Systeme wurden durch stufenweise photometrische Titration analysiert unter Verwendung von Metallphthalein oder Eriochromschwarz T als Indikator: Mangan–Calcium, Mangan–Magnesium, Calcium–Magnesium, Mangan–Calcium–Magnesium, Zink–Magnesium. EDTA, DTPA und EGTA wurden als Titrationsmittel benutzt. Die Genauigkeit war in jedem Falle ausreichend. Die Ergebnisse stimmen gut mit den Zusammenhängen überein, die aus der Theorie der stufenweisen photometrischen Titrationen abgeleitet werden.

REFERENCES

1 A. Ringbom, *Complexation in Analytical Chemistry*, Wiley–Interscience, New York, 1963.
2 E. Still and A. Ringbom, *Anal. Chim. Acta*, 33 (1965) 50.
3 G. Anderegg, H. Flaschka, R. Sallman and G. Schwarzenbach, *Helv. Chim. Acta*, 37 (1954) 113.
4 A. Ringbom, E. Wänninen and G. Pensar, *Anal. Chim. Acta*, 19 (1958) 525.
5 G. Nakagawa, H. Wada and M. Tanaka, *Talanta*, 10 (1963) 325.
6 H. Flaschka and J. Ganchoff, *Talanta*, 8 (1961) 720.
7 H. Flaschka and P. Sawyer, *Talanta*, 9 (1962) 249.
8 J. Lacy, *Talanta*, 10 (1963) 1031.

ANALYTICA CH

AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATION OF IRON AND/OR ALUMINUM WITH EDTA

C. VASSILIADIS, C. TH. KAWASSIADES, T. P. HADJIIOANNOU AND G. COLOVOS
Laboratories of Analytical and Inorganic Chemistry, University of Thessaloniki, Thessaloniki (Greece)

(Received November 25th, 1965)

Several methods have been proposed for the compleximetric determination of iron and aluminum. The published data on the possibility of titrating iron in the presence of aluminum with EDTA are contradictory[1]. Positive errors due to partial cotitration of aluminum with iron have been reported[2-5]. In some methods the effect of aluminum has been eliminated by pH[6] or temperature[7] adjustment or by appropriate masking[8,9] and use of other complexing agents.

Direct titration of aluminum or of the sum of iron and aluminum is not very satisfactory, because the formation of the aluminum–EDTA complex is very slow. The methods more generally used involve addition of a measured excess of EDTA, followed by back-titration with a suitable cation[1,8-11].

One difficulty often encountered with EDTA titrations is the visual end-point detection. In the present paper, a method is described which permits the automatic titration of iron and/or aluminum. The iron in an aliquot of sample is automatically titrated with EDTA and 3,5-dinitrosalicylic acid (DNS) as indicator. To another aliquot of the sample an excess of standard EDTA solution is added and back-titrated automatically with copper solution and calcein W as indicator. The second derivative technique is used for the automatic termination at the end-point[12]. Aluminum is determined by difference.

The method makes possible a very rapid determination of iron and/or aluminum within a very large range of their concentration ratios. The automatic end-points are reproducible and accurate within 0.02 ml of titrant.

GENERAL TITRATION CONSIDERATIONS

The stability constants for the iron(III)–DNS and iron(III)–EDTA complexes are $10^{5.47}$ and $10^{25.1}$, respectively. This large difference is advantageous for the automatic derivative spectrophotometric titration of iron, because the color change at the end-point is sharp, thus providing a large signal for operation of the derivative control unit. The reactions are rapid and the automatic end-point is very close to the equivalence point. Blank corrections of 0.05 ml and 0.04 ml ± 0.01 ml were obtained at flow rates of 4 ml/min when the EDTA titrant was 0.01 and 0.1 M respectively. In the titration of excess EDTA blank corrections of 0.06 ml and 0.08 ml were obtained when the copper titrant was 0.01 and 0.04 M respectively. Since the blank depends on many experimental conditions (flow rate, strength of titrant, position of delivery tip relative to the stirrer, size of the beaker, etc), it should be determined for each experimental set-up by titrating various aliquots of standard solutions.

The sharpness of the color change at the end-point during the titration of iron depends on the pH of the solution. As the titration proceeds, the pH decreases because of the release of hydrogen ions. The solution should be strongly buffered prior to titration, so that the pH at the end-point will be in the range 1.8–3.0.

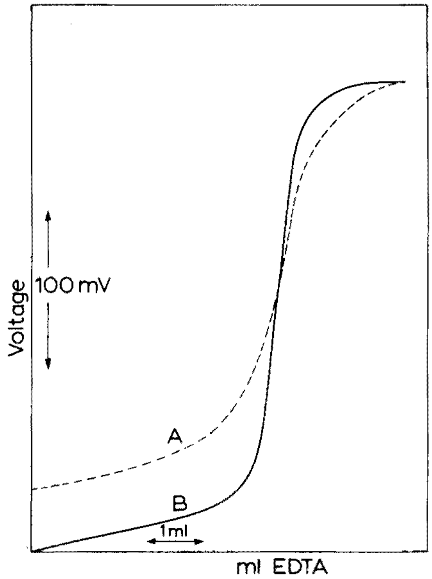
The volume of the solution in the 100-ml beaker should be kept within the range 50 to 75 ml to ensure efficient stirring without formation of vortices.

The regular output voltage *versus* volume curve for the titration of iron with EDTA titrant and DNS indicator is shown in Fig. 1(B). Curve A shows the titration curve of iron in the presence of aluminum. It can be seen that the sharpness and the magnitude of the signal at the end-point decrease in the presence of aluminum. Actually, in the presence of very large amounts of aluminum, the sharpness and the magnitude of the signal are not sufficient for operation of the derivative control unit. This change of the signal in the presence of aluminum is due to reaction (1)

$$\underset{\text{colored}}{\mathrm{FeDNS^{+}}} + \mathrm{Al^{3+}} = \mathrm{Fe^{3+}} + \underset{\text{colorless}}{\mathrm{AlDNS^{+}}} \qquad (1)$$

which takes place simultaneously with the reaction between iron and EDTA. A similar decolorization was observed[13] when an aluminum salt was added to a solution containing the colored iron–salicylate complex.

Figure 2 shows the change in voltage from the output of the detector circuit



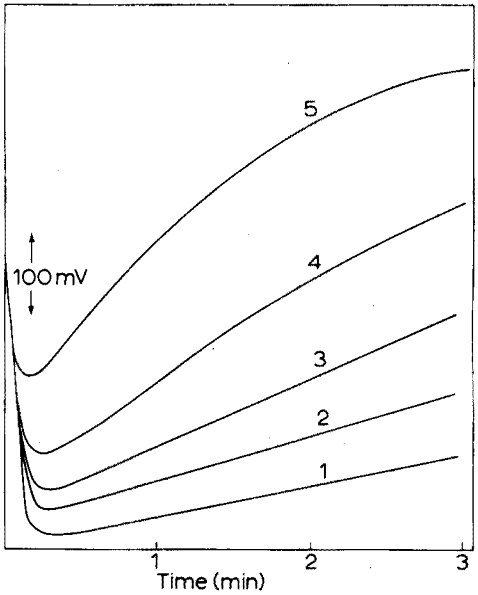


Fig. 1. Recorded curves from output of detector circuit for the automatic titration of iron with EDTA. (A) In the presence of aluminum. (B) In the absence of aluminum.

Fig. 2. Recorded curves from output of detector circuit for the reaction between the iron(III)–DNS complex and aluminum. The molar ratio of aluminum to iron is 300, 450, 500, 750 and 1000 for the curves 1, 2, 3, 4 and 5 respectively.

which is due to reaction (1). At first, the formation of the iron–DNS complex prevails and therefore the absorbance of the solution increases and the output voltage decreases. Then, as reaction (1) proceeds the absorbance decreases and the output voltage increases, because the iron–DNS complex absorbs strongly at 470 mμ whereas the aluminum–DNS complex does not absorb at this wavelength. Therefore, when iron is determined in the presence of aluminum the titration should be started immediately after the addition of the DNS indicator.

In the determination of aluminum, the back-titration of excess EDTA is carried out in a buffered weakly acidic medium. In this way the interference of the alkaline earth metals and magnesium is eliminated because at pH values of about 4 their EDTA complexes are practically completely dissociated. Aluminum can therefore be determined in silicates, rocks, glass, without prior separation of calcium and magnesium.

EXPERIMENTAL

Apparatus

The Sargent-Malmstadt "Spectro-Electro" titrator was used[14]. Since 2 different titrants are required for the titrations, a buret valve and suitable buret for each titrant were mounted on each of the 2 support rods. A titrant selector can also be used[15].

Two 5-ml burets, graduated in 0.01-ml divisions and equipped with delivery and refill stopcocks and titrant reservoir were used for the EDTA and copper titrants respectively. An appropriate aliquot of the sample was taken for the titration of iron and the volume of excess EDTA for the determination of the sum of iron and aluminum was adjusted so that less than 5 ml of titrant was used. If larger volumes of titrant are to be used, the buret stopcock can be closed and the buret refilled without deactivating the control unit of the titrator.

Reagents

All reagents used were of reagent grade.

Buffer solution, pH 2.2. Mix 1 *M* glycine (in 1 *M* sodium chloride) solution with 1 *N* hydrochloric acid in a ratio 3 : 2.

Buffer solution, pH 3.4. Dissolve 17 g of glycine and 13.1 g of sodium chloride in about 200 ml of water, adjust the pH to 3.4 with 1 *N* hydrochloric acid (using a pH meter) and dilute to the mark in a 250-ml volumetric flask.

Buffer solution, pH 4.4. Mix 638 ml of 2 *N* acetic acid with 362 ml of 2 *N* sodium acetate.

Preparation of automatic titrator

Switch the "Spectro-Electro" titrator to the "Spectro" position; set the pegs in the base to position the 100-ml beakers; connect stirrer No. A, delivery tips and burets for EDTA and copper titrants and set the titrant delivery at about 4 ml/min. For the titration of iron and the standardization of EDTA solution, throw the polarity switch to position 1, turn the filter wheel to the blank position and place a 470-mμ interference filter in the auxiliary filter holder in the titration compartment. For the titration of excess EDTA, throw the polarity switch to position 2 and turn the filter wheel to the 500-mμ position (the 470-mμ interference filter is *not* in the light path).

Standardization of EDTA solution

Procedure A (for 0.01 *M* EDTA solution). Pipet a 2-ml aliquot of standard 0.01 *M* iron solution into a 100-ml beaker, dilute to about 55 ml with distilled water and add 2 ml of buffer solution pH 2.2 and 4 drops of aqueous 0.02 *M* DNS indicator solution. Insert the beaker into the titrator, push the start button to start stirring and delivery of EDTA reagent and read the buret after automatic termination at the end-point. Repeat the same procedure with a 4-ml aliquot of standard 0.01 *M* iron solution.

Procedure B (for 0.1 *M* EDTA solution). Procedure B is similar to procedure A, except that 1 ml of buffer solution pH 3.4 is added and a standard 0.1 *M* iron solution is used.

Titration of iron

Procedure A′ (for amounts of iron up to 5 mg) and *Procedure B′* (for 5–35 mg of iron). Transfer an aliquot of the slightly acidic sample solution to a 100-ml beaker. On a separate aliquot determine, while stirring vigorously, the amount of 10% sodium hydroxide required to bring the pH of the solution to about 2.0. Add the predetermined amount of 10% sodium hydroxide and continue as in procedures A and B respectively.

Titration of total iron and aluminum

Procedure A″ (for the range 0.01 to 0.1 meq of iron and aluminum). Transfer an aliquot of the slightly acidic sample solution to a 100-ml beaker and add the predetermined amount of 10% sodium hydroxide to bring the pH to about 2.0. Dilute to about 35 ml with distilled water, buffer strongly with buffer solution pH 4.4, add 4 drops of a 0.1% solution of calcein W indicator in 0.001 *N* sodium hydroxide and insert the beaker into the titrator. Start the stirrer and add 0.01 *M* EDTA solution until the appearance of the green fluorescence of the free indicator. Add an additional 2 ml of EDTA solution, adjust the volume to about 60 ml with distilled water, push the start button to start the delivery of 0.01 *M* copper solution and read the buret after automatic termination at the end-point.

Procedure B″ (for samples containing more than 0.1 meq of iron and aluminum). Transfer an aliquot of the slightly acidic sample solution to a 100-ml beaker and add the predetermined amount of 10% sodium hydroxide to bring the pH to about 2.0. Dilute to about 35 ml with distilled water, buffer strongly with buffer solution pH 4.4, add 2 drops of calcein W indicator solution and insert the beaker into the titrator. Start the stirrer and add 0.1 *M* EDTA solution until the appearance of the green fluorescence of the free indicator. Add an additional 1 ml of 0.1 *M* EDTA solution, remove the beaker and boil the solution for 2 min. Add 3 drops of calcein W indicator solution, adjust the volume to about 60 ml with distilled water, insert the beaker into the titrator, push the start button to start the delivery of 0.04 *M* copper solution and read the buret after automatic termination at the end-point.

Aluminum

Aluminum is calculated from the volume of EDTA obtained by subtracting the volume of EDTA equivalent to the amount of iron from the volume of EDTA equivalent to the sum of iron and aluminum.

CALCULATIONS

If V and V' are the volumes of EDTA titrant used for the titration of 2 and 4 ml of standard iron solution respectively, the blank, B, of the titration and the molarity M_T of the EDTA titrant are calculated as follows: $B = 2V - V'$, and $M_T = 2M_{Fe}/(V - B)$.

The amounts of iron and aluminum are then calculated from: $(A - B)C = \text{mg}$ Fe, and $[D - (A - B)]\,E = \text{mg Al}$, where A = ml of EDTA used with DNS as indicator; C = mg of iron per ml of EDTA solution; D = ml of EDTA equivalent to Fe + Al, making full and proper correction for blank values; and E = mg of aluminum per ml of EDTA solution.

When procedure A′ is employed (0.01 M EDTA titrant) no cotitration of aluminum with iron takes place. When procedure B′ is employed (0.1 M EDTA titrant) aluminum is cotitrated with iron to the extent of about 0.4%. Therefore the amount of aluminum calculated above should be multiplied by the factor 1.004 and the amount of iron calculated should be reduced by an amount equivalent to 0.4% of the aluminum found.

RESULTS AND DISCUSSION

Analysis of solutions containing known concentrations of iron and aluminum in different amounts and ratios gave the results shown in Tables I and II. The average error in the determination of iron and/or aluminum was equivalent to about 0.01 ml of titrant. No positive error was found in the determination of iron when procedure A′

TABLE I

ANALYSIS OF MIXTURES OF IRON AND ALUMINUM (SYNTHETIC SOLUTIONS)

(Buffers pH 2.2 and pH 4.4; 0.01 M EDTA; 0.01 M Cu^{2+}; procedures A′ and A″)

Taken (mg)		*Found (mg)*		*Difference (mg)*	
Fe	*Al*	*Fe*	*Al*	*Fe*	*Al*
—	1.349	—	1.346	—	−0.003
—	1.349	—	1.346	—	−0.003
—	2.698	—	2.698	—	±0.000
—	2.698	—	2.691	—	−0.007
0.558	—	0.564	—	+0.006	
0.558	0.809	0.564	0.799	+0.006	−0.010
0.558	2.698	0.558	2.692	±0.000	−0.006
1.675	—	1.667	—	−0.008	
1.675	2.698	1.686	2.694	+0.011	−0.004
1.675	5.396	1.664	5.405	−0.011	+0.009
2.792	—	2.792	—	±0.000	
2.792	0.809	2.786	0.809	−0.006	±0.000
5.585	—	5.602	—	+0.017	

was employed and the amount of aluminum was less than 5 mg. When larger amounts of aluminum were present (procedure B′) the aluminum was cotitrated with iron to the extent of about 0.4% and therefore appropriate corrections were applied.

When the amount of aluminum was less than 5 mg a small excess of EDTA was sufficient to bind the aluminum quantitatively in the cold. When larger amounts of aluminum were present boiling for 2 min was necessary to ensure quantitative binding.

TABLE II

ANALYSIS OF MIXTURES OF IRON AND ALUMINUM (SYNTHETIC SOLUTIONS)

(Buffers pH 3.4 and pH 4.4; 0.1 *M* EDTA; 0.04 *M* Cu^{2+}; procedures B′ and B″)

Taken (mg)		*Found (mg)*		*Difference (mg)*	
Fe	*Al*	*Fe*	*Al*	*Fe*	*Al*
—	16.19	—	16.22		+0.03
—	26.98	—	26.93		−0.05
5.58	—	5.61	—	+0.03	
11.17	—	11.14	—	−0.03	
11.17	8.09	11.22	8.11	+0.05	+0.02
11.17	26.98	11.14	27.06	−0.03	+0.08
16.75	—	16.75	—	±0.00	
22.34	—	22.34	—	±0.00	
22.34	8.09	22.40	8.09	+0.06	±0.00
22.34	26.98	22.25	27.00	−0.09	+0.02
22.34	53.96	22.20	53.94	−0.14	−0.02
33.51	—	33.56	—	+0.05	
33.51	8.09	33.55	8.09	+0.04	±0.00
33.51	26.98	33.42	26.99	−0.09	+0.01

It is possible to use iron as titrant and DNS as indicator for the titration of excess EDTA; however, in this case the blank is very large and the results less reproducible than when copper is used as titrant with calcein W as indicator. Calcein W has the additional advantage of both fluorescing and absorbing in the visible region thus making possible the detection and the titration of excess EDTA.

The authors are indebted to V. ARGYRAKIS for his valuable assistance in experimental work.

SUMMARY

Automatic derivative spectrophotometric EDTA titration procedures for the determination of iron and/or aluminum are described. Iron is automatically titrated in the presence of aluminum at pH 1.8–3.0 using 3,5-dinitrosalicylic acid as indicator. Total iron and aluminum, or aluminum alone, are determined by adding a small excess of standard EDTA, as visually indicated by the fluorescence of calcein W, with subsequent automatic titration of excess EDTA. The intense color of the iron–EDTA complex causes no difficulty in the automatic method, and macro as well as micro quantities of iron and/or aluminum can be determined with relative errors of 0.3% or less, even when the amount of aluminum is 4 times that of iron.

RÉSUMÉ

On décrit une méthode de titrage spectrophotométrique automatique pour le dosage du fer et de l'aluminium. Le fer est titré automatiquement en présence d'aluminium au pH 1.8–3.0, au moyen de l'acide dinitro-3,5-salicylique. Fer + aluminium ou aluminium seul sont dosés par addition d'un léger excès d'EDTA étalon, en présence de calcéine W, et titrage de l'excès d'EDTA. La coloration intense du complexe Fe/EDTA ne gène pas.

ZUSAMMENFASSUNG

Es werden automatische, abgewandelte spektralphotometrische AEDTE-Titrationsverfahren zur Bestimmung von Eisen und/oder Aluminium beschrieben. Eisen wird automatisch in Gegenwart von Aluminium beim pH 1.8–3.0 titriert, unter Verwendung von 3,5-Dinitrosalicylsäure als Indikator. Das Gesamteisen und Aluminium oder das Aluminium allein werden durch Zugabe eines kleinen Überschusses von AEDTE bestimmt, visuell angezeigt durch die Fluoreszenz von Calcein W, und anschliessend der Überschuss an AEDTE automatisch titriert. Die intensive Farbe des Eisen–AEDTE-Komplexes verursacht bei der automatischen Methode keine Schwierigkeiten und es können Makro- ebseno gut wie Mikromengen von Eisen und/oder Aluminium mit einem relativen Fehler von 0.3% oder weniger bestimmt werden, sogar, wenn der Anteil des Aluminiums 4 Mal so gross ist wie der des Eisens.

REFERENCES

1 H. FLASCHKA, A. J. BARNARD, JR. AND W. C. BROAD, *Chemist Analyst*, 47 (1958) 22, 52.
2 C. S. PANDE AND T. S. SRIVASTAVA, *Z. Anal. Chem.*, 172 (1960) 356.
3 C. VASSILIADIS, G. COLOVOS AND P. KARAYIANNIDIS, *Chim. Chronika (Athens, Greece)*, 29A (1964) 327.
4 T. DANZUKA AND K. UENO, *Japan Analyst*, 8 (1959) 126.
5 P. B. SWEETSER AND C. E. BRICKER, *Anal. Chem.*, 25 (1953) 253.
6 D. G. DAVIS AND W. R. JACOBSEN, *Anal. Chem.*, 32 (1960) 215.
7 H. KRISTIANSEN, *Anal. Chim. Acta*, 25 (1961) 513.
8 R. PŘIBIL AND V. VESELY, *Talanta*, 9 (1962) 23.
9 R. PŘIBIL AND V. VESELY, *Talanta*, 10 (1963) 383.
10 G. W. F. BRANDY AND J. R. GWILT, *J. Appl. Chem.*, 12 (1962) 75.
11 F. J. WELCHER, *Analytical Uses of Ethylenediaminetetraacetic acid*, Van Nostrand, New York, 1958, p. 165 et seq.
12 H. V. MALMSTADT AND T. P. HADJIIOANNOU, *Anal. Chim. Acta*, 23 (1960) 288.
13 A. BABKO AND R. RYCHKOVA, *Zh. Obshch. Khim.*, 17 (1947) 1259.
14 E. H. Sargent Co., *Scientific Apparatus and Methods*, 10 (1958) No. 2, 1.
15 H. V. MALMSTADT AND T. P. HADJIIOANNOU, *Anal. Chim. Acta*, 21 (1959) 41.

Anal. Chim. Acta, 36 (1966) 115–121

NEW SPECTROPHOTOMETRIC THIOCYANATE DETERMINATION OF IRON IN METALS, ALLOYS, ACIDS AND SALTS

C. L. LUKE
Bell Telephone Laboratories, Incorporated, Murray Hill, N. J. (U.S.A.)

(Received January 11th, 1966)

In spectrophotometric analyses it is often desirable to isolate the metal to be determined from interfering metals by a suitable solvent extraction separation before proceeding to the analysis. If the extracted metal is obtained as a colored chelate or salt in the immiscible organic solvent it is often possible to make a direct spectrophotometric analysis. When the extract is colorless or only slightly colored, it is usually necessary to recover the metal from the solvent before attempting the analysis. However, it is sometimes possible to add to the organic extract, a suitable reagent that will react with the metal to form a soluble, colored compound, capable of being measured spectrophotometrically. In recent work along these lines in these laboratories several of the well known, relatively specific, solvent extraction separations of metals have been investigated. The first results from this work have been reported[1]. The present paper is concerned with the analysis of iron. DOLL AND SPECKER[2] have shown that traces of iron(III) can be quantitatively extracted from 7 N lithium chloride solution or 7 N hydrochloric acid with methyl isobutyl ketone (MIBK). Not too many metals accompany iron in this separation. Hence, it appeared that, if it were possible to form the iron(III) thiocyanate color directly in the MIBK extract, this should provide a convenient and fairly specific determination of iron in a wide variety of materials. Experiments have shown that this is indeed possible and as a result an excellent new spectrophotometric method for iron has been developed. A welcome feature of the new procedure is that the iron thiocyanate color produced is very stable. The method has been successfully applied to the analysis of a large number of acids, salts and metals and to several NBS standard alloys of known iron content.

EXPERIMENTAL

Reagents

Methyl isobutyl ketone. Twice extract about 250 ml of reagent-grade MIBK (b.p. 114–116°) for 30 sec with 100-ml portions of water and discard the water.

Lithium chloride solution (7 N). Dissolve 150 g of reagent-grade lithium chloride in about 300 ml of water by warming. If necessary, filter to remove suspended material. Add 10 ml of (1+3) hydrochloric acid, cool, dilute to 500 ml and mix. Twice extract about 250 ml of the solution for 30 sec with 20 ml of MIBK and discard the ketone extracts.

Hydrochloric acid (7 N). Mix 600 ml of hydrochloric acid with 350 ml of water

Cool and dilute to 1 liter. Extract about 250 ml of the solution with 50 ml of MIBK and discard the ketone extract. If, in time, the extracted solution turns brown as a result of decomposition of the MIBK therein, discard and extract a fresh portion of the 7 *N* acid solution.

Preparation of calibration graph

Transfer 0, 0.25, 0.50, 0.75 and 1.00 ml of standard iron(III) chloride solution (20 μg Fe/ml) to a 75-ml separatory funnel containing 25 ml of 7 *N* lithium chloride solution. Extract for 30 sec with 10.0 ml of MIBK. Remove the aqueous layer and pour most of the MIBK extract into a clean dry 50-ml conical flask containing about 0.5 g of ammonium thiocyanate. Swirl until the red color of the iron(III) thiocyanate appears and then for an additional 15 sec. Filter through a dry 7-cm close-texture paper into a clean, dry 50-ml conical flask. Measure the solution spectrophotometrically in a covered 1-cm absorption cell at 490 mμ using water as the reference liquid. Prepare a calibration graph.

Analysis of sample

Metals and alloys. Dissolve up to 0.500 g of the sample in a suitable oxidizing acid or acid mixture. Then, if more than a few drops of nitric acid was used or if hydrofluoric acid was added to dissolve silicon-containing samples, remove these acids by evaporation to fumes with sulfuric or perchloric acid; or, if the sample has been dissolved in nitric acid alone, remove most of this acid by twice evaporating to moist dryness with hydrochloric acid. Finally evaporate the sample solution or a suitable aliquot, to about 0.25 ml. Add 25 ml of 7 *N* lithium chloride solution or 7 *N* hydrochloric acid, whichever is appropriate for the sample being analyzed. Then warm to dissolve salts, cool and pour into a 75-ml separatory funnel.

Acids and salts. Transfer up to 0.500 g of acid or 1.000 g of salt to a 100-ml beaker. If the sample is not too soluble in 7 *N* chloride solution, add 2 ml of water and heat to dissolve the sample as completely as possible. Then add 25 ml of the appropriate 7 *N* chloride solution and heat until dissolution of the sample is complete. If there is any danger that the iron in the sample is in the iron(II) state add 1 drop of 3% hydrogen peroxide. Cool and pour into a 75-ml separatory funnel.

Extraction of the iron. Extract with 10.0 ml of MIBK and proceed as directed in *Preparation of calibration graph.* Make a suitable reagent blank correction. Determine the amount of iron present in the sample with the aid of the calibration graph.

DISCUSSION AND RESULTS

Choice of complexing medium

In the MIBK extraction of iron(III) the chloride concentration must be about 7 *N*. When large samples of soluble metal chlorides are to be analyzed for iron it is sometimes possible to use a 7 *N* solution of the metal chloride itself as the complexing medium. In most cases, however, it will be necessary to use 7 *N* lithium chloride or 7 *N* hydrochloric acid as the complexing medium. Hydrochloric acid must be used in the analysis of certain metals and especially in the analysis of most salts of ammonia, sodium and potassium. However, lithium chloride should be used in the analysis of most metals and metal salts because the co-extraction by MIBK of interfering metals is less the lower the acidity. Moreover, when lithium chloride is used, moderate amounts of such oxidizing materials as nitric acid and perchloric acid can be tolerated. The lithium chloride solution used must be slightly acid in order to prevent hydrolysis of iron and to ensure complete color development in the MIBK extract. After color development the solution must be filtered to remove the excess ammonium thiocyanate and decomposition products and insoluble salts of the same. The iron(III) thiocyanate color in the MIBK extract is stable for at least 1 h. Calibration graphs obtained with iron samples that have been extracted from 7 *N* lithium chloride solution or 7 *N* hydrochloric acid are identical and Beer's law is followed.

Interfering metals

DOLL AND SPECKER[2] have shown that the extraction of several metals can be completely suppressed and that of several others can be materially decreased by using neutral 7 *N* lithium chloride in place of 7 *N* hydrochloric acid as the complexing medium in the MIBK extraction. By using the mildly acidified lithium chloride recommended in the present method the suppression of the co-extraction of metals is not as pronounced as it would be if neutral lithium chloride were used. Thus, when a 0.5-mg portion of each of 56 of the common metals[3], in the form of a 1-ml aliquot of a standard solution, was treated as directed in *Preparation of calibration graph*, all or part of each of the metals Cr^{6+}, Mo^{6+}, V^{5+}, Co, Cu, Os, Au, In, Ga, As^{3+}, Sb^{3+}, Sn^{4+}, Te, Tl^{3+}, and U^{6+} was extracted by MIBK. The first 7 metals yield a colored MIBK extract and the last 8 metals produce a milky cloudiness in the extract on shaking with thiocyanate. Fortunately, when no more than 0.5 mg of these metals is present, only 2 of the 15 interfere seriously in the iron determination. The yellow color of the extracted chromium(VI) or the brown color of the molybdenum(V)–thiocyanate complex causes positive interference in the iron analysis. Apparently some of the molybdenum(VI) in the MIBK extract is reduced to molybdenum(V) by the MIBK itself. Because of the interference described, it is necessary, when more than about 50 μg of Cr^{6+} or Mo^{6+} is present in the sample to be analyzed, to modify the proposed method for iron. The extraction of these interfering metals by MIBK can be prevented by reducing Cr^{6+} to Cr^{3+} by boiling with hydrochloric acid or by complexing Mo^{6+} with tartrate.

Analysis of metals

Tests on the analysis of 0.05–0.5-g samples of several common metals by the proposed thiocyanate method were made. In most of this work a 1-g sample of the commercially available, normal chloride of the metal in question was dissolved in 25 ml of 7 *N* lithium chloride solution and then extracted with MIBK to remove contaminating iron. Then 1 ml of standard iron solution (20 μg Fe/ml) was added and the mixture was analyzed for iron as directed in *Preparation of calibration graph*. No difficulty was encountered in the analysis of 1-g portions of the normal chlorides of Ni, Zn, Cd, Mn, Be, Al, Cr^{3+}, Pb, Bi, Hg^{2+}, Mg, Sr, Ca and Th. On the other hand, in the analysis of the remaining common metals, the proposed method had to be modified.

Copper, cobalt and uranium. The filtered MIBK extracts from iron-free solutions of copper, cobalt or uranium chloride are all quite colored, especially when 7 *N* hydrochloric acid is used as the complexing medium. As expected, the extracted metals cause appreciable positive interference in the iron determination. In the case of cobalt the interference is caused by the colored cobalt–thiocyanate complex. Fortunately, when extraction is made from 7 *N* lithium chloride solution, the interfering metal can be removed from the MIBK extract, before the addition of thiocyanate, by a single 30-sec wash-extraction, in the case of cobalt and uranium, or a double wash-extraction, in the case of copper, with fresh 25-ml portions of 7 *N* lithium chloride solution. When this is done recoveries of added iron are satisfactory.

Zirconium and titanium. The analysis of zirconium chloride is successful when extraction is made from 7 *N* lithium chloride solution but fails when 7 *N* hydrochloric acid is used because a copious precipitate forms during the MIBK extraction. On the other hand, in the analysis of titanium, 7 *N* hydrochloric acid must be used as the complexing medium since it is difficult to prevent hydrolysis of large amounts of titanium tetrachloride when 7 *N* lithium chloride is used.

Molybdenum. Molybdate, tungstate, vanadate and chromate are not extracted from neutral 7 *N* lithium chloride solution with MIBK[2]. However, it is not possible to separate iron from these potentially interfering materials by MIBK extraction from neutral solution since the iron tends to hydrolyze. Because of this it is necessary to make the MIBK extraction from acidic solution. However, in the analysis of molybdenum metal, when the extraction is made from 7 *N* hydrochloric acid solution, most of the molybdenum accompanies the iron and prevents it from reacting with the thiocyanate. When mildly acidified 7 *N* lithium chloride is used, the extraction of molybdenum is considerably less. The red iron(III) thiocyanate is formed but high results for iron are obtained due to the formation of considerable amounts of brown molybdenum(V)–thiocyanate complex in the MIBK. However, it was found that extraction of molybdenum from the 7 *N* lithium chloride solution can be prevented by the addition of tartrate. Successful analysis of molybdenum metal was obtained by the following method.

Dissolve 0.050 g of metal in a covered 125-ml conical flask in a mixture of 3 ml of hydrochloric acid plus 0.5 ml of nitric acid plus 0.25 ml of perchloric acid by heating gently. Remove the cover and heat on a flame until the molybdenum precipitates and all of the perchloric acid has been removed. Cool, add 5 ml of hydrochloric acid down the inside wall of the flask and evaporate on a flame to 1 ml. Add 1 ml of water, 25 ml of 7 *N* lithium chloride solution and 1 g of neutral ammonium tartrate (pH 6–7). Heat to boiling to dissolve the tartrate. Cool and make the MIBK extraction. Do not add the tartrate to the sample before adding the lithium chloride solution otherwise some reduction of the molybdenum may occur. Discard the sample if a blue color is noted in the solution.

Tungsten. Successful analysis of tungsten metal was obtained by the following method.

Dissolve 0.050 g of the metal in a smooth surfaced platinum crucible in a mixture of 0.5 ml of hydrofluoric acid plus 2 drops of nitric acid plus 2 drops of perchloric acid. Evaporate to complete dryness on a sand bath, add 0.5 ml of 10% (w/v) sodium hydroxide solution and warm to dissolve the tungstic oxide. Add 5 ml of hydrochloric acid and heat and stir to dissolve the precipitated tungstic acid as much as possible. When only a small flocculent white precipitate remains, pour and wash, with policing, into a 125-ml conical flask and then evaporate on a flame to 1 ml. Add 1 ml of water plus 1 g of ammonium tartrate and heat on a flame until all or most of the tungstic oxide is dissolved. Add 25 ml of 7 *N* lithium chloride solution and heat to gentle boiling to dissolve the remaining tartrate. Cool and make the MIBK extraction.

Vanadium. Appreciable amounts of vanadium accompany the iron in the MIBK extraction from lithium chloride or hydrochloric acid solution. The extraction of vanadium(V) appears to be considerably greater than that of vanadium(IV). The extracted vanadium causes interference in the iron determination. However, it has been found that most of the vanadium can be removed from the MIBK extract by extraction with 7 *N* lithium chloride solution containing tartaric acid. When this is done correct results for iron are obtained. The following method is recommended for the analysis of vanadium metal.

Dissolve 0.1 g of metal in 5 ml of nitric acid (1 + 1) by heating gently. Evaporate to moist dryness. Twice evaporate to moist dryness with 5 ml of hydrochloric acid to remove most of the nitric acid. Add 25 ml of 7 *N* hydrochloric acid and heat to boiling to dissolve salts and to allow the vanadium(V) to be reduced to vanadium(IV) by the MIBK in the acid solution. When all of the vanadium has been converted to the blue vanadyl state, cool and extract for 30 sec with 10.0 ml of MIBK. Discard the aqueous layer and add to the extract 1 g of tartaric acid dissolved in 25 ml of 7 *N* lithium chloride solution. Wash-extract for 30 sec and then continue in the usual manner.

Tantalum and niobium. The following method is recommended for the analysis of these metals.

Dissolve 0.050 g of the metal in 1 ml of hydrofluoric acid plus 3 drops of nitric acid in a smooth surfaced platinum crucible by heating gently. Evaporate the tantalum sample to complete dryness or evaporate the niobium sample to moist dryness on a sand bath. Add 2 drops of hydrofluoric acid to the tantalum sample or one drop to the niobium sample and swirl and warm to dissolve the precipitate. Add 25 ml of 7 *N* lithium chloride solution and 5 ml of 5% (w/v) boric acid solution and make the MIBK extraction. Since the hydrofluoric acid tends to complex the iron slightly, recoveries of this metal are about 10% low. This loss can be compensated for by using a calibration graph prepared from mixtures of aliquots of standard iron solution plus 2 drops of hydrofluoric acid and 5 ml of 5% boric acid solution.

Gallium and indium. On adding thiocyanate to the MIBK extract of iron from 1 g of gallium chloride in 7 *N* lithium chloride solution or 7 *N* hydrochloric acid, little or no red iron(III) thiocyanate color is produced. Apparently the large amount of gallium present in the MIBK extract pre-empts the available thiocyanate. Indium behaves similarly. When analyzing 1 g of indium chloride, only about 25% of the iron color is obtained. However, it would appear that as much as about 25 mg of gallium or indium can be analyzed, provided that hydrochloric acid is used as the complexing medium in the analysis of gallium or lithium chloride in the analysis of indium. Perhaps it would be possible to separate iron from most of the gallium by carbamate extraction or from most of the indium by cupferron extraction before attempting the MIBK extraction.

Germanium. Most of the germanium must be removed by distillation as chloride from perchloric acid solution[3] before the iron analysis is attempted.

Arsenic, antimony, tin and tellurium. These metals tend to accompany the iron in the MIBK extraction and prevent complete reaction of the iron with the thiocyanate. For this reason the first 3 metals (plus selenium if it is present) should be removed by distillation as bromide from sulfuric or perchloric acid solution; or the tellurium should be removed as metal, before attempting the MIBK extraction.

Analysis of alloys

In order to show that the proposed method for iron yields quantitative results in the analysis of alloys, several NBS standard alloys of known iron content were analyzed using appropriate sample sizes or aliquots and suitable methods of dissolution of the sample. In most of the analyses the sample was dissolved as completely as possible in hydrochloric acid. Then a few drops of 30% hydrogen peroxide was added to ensure complete dissolution of the sample and oxidation of the iron. Finally the excess of peroxide was destroyed by boiling down to a small volume. In all cases, 7 *N* lithium chloride solution was used as the complexing medium. In the analysis of Ounce Metal 124-b and Tin Base Alloy 54-d most of the arsenic, antimony and tin was removed from the sample aliquot by a single or a double fuming with hydrobromic acid from perchloric acid solution[4] and the solution was evaporated to about 0.25 ml to expel excess perchloric acid. One wash-extraction of the MIBK extract with 7 *N* lithium chloride solution was made to remove copper in the analysis of Samples 124-b, 54-d and 157. In the analysis of Magnesium Base Alloy 171, after dissolution of 0.5 g of the sample in hydrochloric acid and hydrogen peroxide, the solution was evaporated to a small volume to destroy excess peroxide and the salts were dissolved in 5 ml of water to make a solution that was about 7 *N* with respect to chloride ion. Then 20 ml of 7 *N* lithium chloride solution was added and the iron extraction was made. In the analysis of Titanium Base Alloys 173 and 174, 0.2-g samples were dissolved in 10 ml of (1+1) hydrochloric acid plus a few drops of hydrofluoric acid. Boric acid was added to neutralize the complexing action of hydrofluoric acid. A little sulfuric acid plus enough hydrogen peroxide was added to an aliquot containing 10 mg of titanium to oxidize the titanium(III). The solutions were then evaporated almost to the evolution of white fumes. Then 25 ml of 7 *N* lithium chloride was added, the solution was heated to dissolve salts and the MIBK extraction was made. In the analysis of Electrical Heating Alloy 169, a 0.300-g sample was dissolved in 10 ml of (4+1) hydrochloric acid–nitric acid mixture plus about 10 drops of hydrofluoric acid. The solution was evaporated to moist dryness,

TABLE I

ANALYSIS OF ALLOYS FOR IRON

Material analyzed	*Iron present (%)*	*Iron found (%)*
Ounce Metal 124-b	0.26	0.27, 0.25
Tin Base 54-d	0.030	0.030, 0.029
Zinc Base 94-b	0.018	0.018, 0.018
Magnesium Base 171	0.0018	0.0018
Aluminum Base 85-a	0.21	0.21
Titanium Base 173	0.16	0.15, 0.15
Titanium Base 174	0.18	0.19, 0.18
Electrical Heating 169	0.54	0.53
Nickel Silver 157	0.053	0.054, 0.054
Nickel Oxide 672	0.079	0.080

10 ml of a 5% solution of boric acid was added and the solu[illegible] 500 ml. A 5-ml aliquot was evaporated to 0.25 ml and analyzed for iro[illegible]ined in the analysis of the NBS samples are shown in Table I.

Analysis of acids and salts

Tests showed that it is possible to determine iron in most of the [illegible] inorganic acids and in boric, acetic, tartaric and citric acids by the proposed method. Hydrofluoric, oxalic, hydriodic and sulfurous acids cannot be analyzed. The first 2 complex the iron and the last 2 reduce the iron. Most acids can be analyzed with either lithium chloride or hydrochloric acid as the complexing medium. However, lithium chloride must be used when analyzing such oxidizing materials as nitric or perchloric acids and hydrochloric acid must be used when analyzing phosphoric or citric acid. If lithium chloride is used for the analysis of the latter 2 acids, recoveries of iron tend to be low due to the complexing action of the acids on the iron. If hydrochloric acid is used in the analysis of nitric or perchloric acid the recoveries of iron are low, presumably owing to excessive oxidation of the thiocyanate.

Tests also showed that 1-g portions of most of the common organic and inorganic salts of ammonia, sodium and potassium can be analyzed for traces of iron by the proposed method. With the exception of nitrates and perchlorates it is usually necessary to make the extraction from hydrochloric acid rather than from lithium chloride solution. Some of the salts are not completely soluble in lithium chloride solution. Moreover, low recoveries of iron are obtained in the analysis of 1-g portions of alkali phosphates, citrates, tartrates, arsenates and borates when extraction is made from 7 *N* lithium chloride solution. In these analyses the pH of the solutions is so high that the iron is either hydrolyzed or complexed.

In the analysis of thiocyanate it was noted that iron is extracted as the thiocyanate when 7 *N* lithium chloride solution is used and as the chloride when 7 *N* hydrochloric acid is used.

For various reasons, iodide, fluoride, sulfite, bromate, permanganate, and oxalate cannot be analyzed using either chloride medium. In addition, it is necessary to resort to modifications in the proposed method for the analysis of chromate, molybdate, tungstate and vanadate. Chromate must be reduced to chromium(III) before the analysis is attempted. To analyze molybdate or tungstate, dissolve 1 g of the salt plus 1 g of tartaric acid in 2 ml of water; add 25 ml of 7 *N* lithium chloride solution and make the MIBK extraction. To analyze vanadate, dissolve 1 g of the salt as completely as possible in 2 ml of water. Then add 25 ml of 7 *N* hydrochloric acid, boil to reduce the vanadium and proceed as directed above for the analysis of vanadium metal.

SUMMARY

A rapid, sensitive and fairly selective spectrophotometric thiocyanate method for the determination of traces of iron in metals, alloys, acids and salts is described. The iron is isolated from the bulk of the sample by solvent extraction with methyl isobutyl ketone from 7 *N* lithium chloride solution or 7 *N* hydrochloric acid. The iron(III) thiocyanate color is developed directly in the ketone extract and then measured spectrophotometrically.

RÉSUMÉ

Une méthode rapide, sensible et sélective est proposée pour le dosage spectrophotométrique de traces de fer, au moyen de thiocyanate, dans des métaux, alliages, acides et sels. Le fer est séparé par extraction dans un solvant, la méthylisobutylcétone, à partir de solutions de chlorure de lithium ou d'acide chlorhydrique 7 *N*.

ZUSAMMENFASSUNG

Es wird eine schnelle, empfindliche und leidlich selektive spektralphotometrische Thiocyanatmethode für die Bestimmung von Spuren Eisen in Metallen, Legierungen, Säuren und Salzen beschrieben. Das Eisen wird durch Extraktion mit Methylisobutylketon aus 7 *N* Lithiumchloridlösung oder 7 *N* Salzsäure von der Menge der Probe isoliert. Die Eisen(III)-thiocyanatfarbe wird direkt im Ketonextrakt entwickelt und spektralphotometrisch gemessen.

REFERENCES

1 C. L. Luke, *Anal. Chim. Acta*, 32 (1965) 286.
2 W. Doll and H. Specker, *Z. Anal. Chem.*, 161 (1958) 354.
3 C. L. Luke and M. E. Campbell, *Anal. Chem.*, 25 (1953) 1588.
4 ASTM, *Methods of Chemical Analysis of Metals*, Philadelphia, 1960, p. 593.

SHORT COMMUNICATIONS

An attempt to determine the boron natural abundance [illegible] $^{11}B/^{10}B$, by atomic absorption spectrophotometry*

Since water-cooled hollow-cathode discharge tubes have been successfully used to determine lithium[1] and uranium isotopes[2,3] by atomic absorption techniques, an attempt was made to determine the natural abundance ratio of the boron isotopes, $^{11}B/^{10}B$, by similar techniques. A schematic diagram depicting the apparatus used for the determination of the boron isotopes is shown in Fig. 1.

Experimental and results

The 2 boron lines that were investigated for this work were the 2496 and 2497 Å lines. These lines appear suitable for atomic absorption work because they are the strong resonance lines. MROZOWSKI[4], employing liq[illegible]r tubes, reports that the isotopic displacement for these lines is about 168 [illegible] Thus, if the half-widths of the boron lines, obtained with water-cooled tubes, [illegible] smaller than the isotopic displacements, the determination of the natural abundance ratio, $^{11}B/^{10}B$, might be possible employing standards. To test the degree [illegible] overlapping of the lines of the 2 isotopes, the following experiment was performed: [illegible] of amorphous boron,

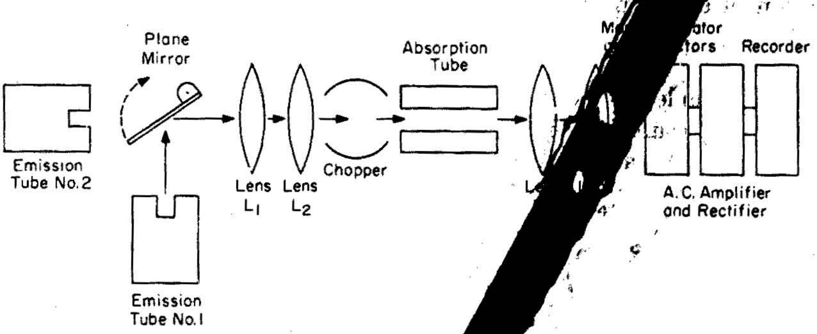


Fig. 1. Diagram depicting the apparatus [illegible]ination of the boron isotopes.

essentially boron-10, was placed in o[illegible]te[illegible]d Schüler–Gollnow emission tube, and 15 mg of amorphous boron, essentially boron-11, was placed in the other water-cooled Schüler–Gollnow emission [illegible] The water-cooled absorption tube[3], designed at this laboratory, contained a [illegible] normal amorphous boron in the form of a cylinder that was 1.5 in. long [illegible] an inside diameter of 0.5 in. The emission tubes were operated at 25 mA [illegible] at a pressure of 1 mm of mercury. The absorption tube was operated [illegible] xenon at a pressure of 0.5 mm of mercury. To increase the sign[illegible] this experiment, the simultaneous intensities of the 2 strong boron [illegible] and 2497 Å, were measured instead of one. This was

---

* Based on wor[illegible]der the auspices of the U.S. Atomic Energy Commission.

d[illegible] employing a 300-μ slit on the monochromator. When boron-10 and boron-11 lig[illegible]pectively was passed through the active absorption tube a number of times, ab[illegible] same average amount, 70%, of boron-10 and boron-11 light was absorbed. Fr[illegible]nce, it appears that the determination of the natural abundance ra[illegible]B, by atomic absorption spectrophotometry, employing the previously des[illegible]paratus, is not possible. The reason for this is that the percentage of boron[illegible]d boron-11 light absorbed was the same even though the sample in the absorp[illegible]tube contained approximately 4 times more boron-11 than boron-10. It is th[illegible]t that the percent absorption values for boron-10 and boron-11 were essential[illegible]e same because the half-widths of the spectral lines employed were greater t[illegible]he isotopic displacements. Therefore, it is expected that essentially the same p[illegible]ntage of light will be absorbed from the 2 emission tubes irrespective of the isoto[illegible] composition of the boron cylinder in the absorption tube. This reasoning appea[illegible]lid, because the test just described was repeated using a boron cylinder made[illegible]t amorphous boron-10 in the absorption tube. The results observed agree with the [illegible]t test. That is, about the same amount, 70%, of boron-10 and boron-11 light was ab[illegible]bed.

The fact t[illegible]t an appreciable amount of boron light was absorbed when amorphous boron was [illegible]ttered in the absorption tube should be of interest to workers in the field of at[illegible]i[illegible]bsorption. In the past, very little analytical work for boron has been attemp[illegible]ing conventional atomic absorption techniques, probably because boron co[illegible]s are not readily dissociated in conventional flames to produce atoms in th[illegible]nd state. However, by sputtering boron in a discharge tube, a large number [illegible]n atoms can be obtained in the ground state to absorb incident light.

The author is ind[illegible]to Dr. Howard H. Claassen, of our Chemistry Division, for helpful consul[illegible]ons regarding the experiment described herein, and to Joseph Dusek of our Meta[illegible] Division, for the fabrication of the boron inserts.

Argonne National Laboratory,
9700 South Cass Avenue,
Argonne, Ill. 60439 (U.S.A.)

Joseph A. Goleb

1 J. A. Goleb and Yu. Yokoyama, *An*[illegible]*a*, 30 (1964) 213.
2 J. A. Goleb, *J. Anal. Chem.*, 35 (196[illegible]
3 J. A. Goleb, *Anal. Chim. Acta*, 34 (19[illegible]
4 S. Mrozowski, *Z. Physik*, 112 (1939) 2[illegible]

(Received February 24th, 1966)

Some experimental observations on inter-element effects in atomic fluorescence spectrometry

WINEFORDNER *et al.*[1-4] have described the theory and application [illegible] trace analysis of atomic fluorescence spectrometry using a spray-in-flame source as the fluorescing medium, and have demonstrated the outstanding sensitivity of the method with such elements as zinc, cadmium and thallium. They have suggested that in general inter-element effects should be negligible, the exceptions being those normally encountered in a flame due to the formation of stable molecules and to changes in atomisation rate at high concentrations of dissolved solids.

During work in this laboratory on the applications of atomic fluorescence spectrometry in analysis, some inter-element effects have been studied and are described in this note.

Experimental

In principle, the apparatus followed that described by WINEFORDNER. The excitation sources used were Philips "Spectral" lamps and an experimental type of microwave discharge tube powered by a 2450 Mc/sec magnetron unit coupled to a tuned cavity. Two types of flame source were used (*i*) a premixed acetylene/air burner with settling chamber[5] and (*ii*) a Beckman burner Type 4020 burning an air/H_2 fuel gas mixture. A Hilger "Medium" Spectrograph fitted with [illegible] H720 photomultiplier head (containing an R.C.A. IP28 tube) was used with the amplified signal displayed on a 0–10 mV chart recorder. At low wavelengths amplification was by means of the Hilger D.C. unit FA7 while at high wavelengths (>300 [illegible]) an A.C. amplifier was used tuned to a mechanical chopper placed between [illegible] excitation source and the flame.

TABLE I

EFFECT OF SODIUM ON ZINC DETERMINATION

Na (μg/ml)	*Zn added (μg/ml)*	*Zn "found" (μg/ml) 1000 μ/1000 μ slit*	[illegible] *"found" (μg/ml) [illegible]/250 μ slit*
80	20	20.4	—
200	20	20.1	—
800	20	21.5	—
2000	20	22	19
2000	Nil	1.7	*ca.* 0.3

In Table I the effect in an acetylene flame of increasing additions of sodium on zinc at 20 μg/ml is shown. The fluorescence measurements were made on the Zn 2138 Å line using D.C. amplification with exit and entrance slit widths initially of 1.0 mm. At levels of 80 and 200 μg/ml there was no significant difference but at higher levels there was an apparent increase. By using a glass filter to remove the zinc radiation, the increase was shown [illegible] be due to scattered light from Na 5890/5896 Å falling on the zinc exit slit at 2[illegible]. Since the ratio of signal to scattered light is increased by a decrease in slit width the fluorescence measurements of the two solutions of 2000 μg Na/ml with [illegible] without zinc additions were repeated with exit and entrance slit widths both reduced to 250 μ. The zinc values decreased to 19 and *ca.* 0.3 μg/ml respectively, which agree well with the values of 18.8 and < 0.5 μg/ml obtained on the same solutions in the same flame by atomic absorption. The apparent decrease from 20 to *ca.* 18.7 μg Zn/ml in the presence of 2000 μg Na/ml (≡0.5% w/v NaCl) could be entirely accounted for by reduced atomisation in the presence of relatively high concentrations of dissolved solids.

The influence of 1000 μg/ml each of Al, Cu, Li and Sn on 10 μg Cd/ml is shown in Table II; a Beckman burner with two different air/H_2 mixtures was used. In one case the hydrogen concentration was below the stoichiometric value ("lean" flame) while in the other the concentration was higher than the stoichiometric value ("rich" flame). Provided that the hydrogen concentration is on the rich side then there is little apparent interference from Al, Cu and Li, although tin appears to suppress by about 10%. It is possible that some compound formation is responsible, although this is difficult to reconcile with the fact that aluminium, well known for its ability to form stable molecules in the flame, has no such effect.

TABLE II

EFFECT OF OTHER ELEMENTS ON CADMIUM DETERMINATION

Added element (μg/ml)	*Cd added (μg/ml)*	*Cd "found" (μg/ml)*		*Added element (μg/ml)*	*Cd added (μg/ml)*	*Cd "found" (μg/ml)*	
		Lean flame	*Rich flame*			*Lean flame*	*Rich flame*
1000 Al	10	8.9	9.6	1000 Li	10	9.1	10.3
1000 Al	Nil	< 0.2	< 0.2	1000 Li	Nil	< 0.2	< 0.2
1000 Cu	10	9.4	9.8	1000 Sn	10	7.1	9.0
1000 Cu	Nil	< 0.2	< 0.2	1000 Sn	Nil	< 0.2	< 0.2

TABLE III

EFFECT OF POTASSIUM ON COPPER DETERMINATION

K (μg/ml)	*Cu added (μg/ml)*	*Cu "found" (μg/ml)*	*K (μg/ml)*	*Cu added (μg/ml)*	*Cu "found" (μg/ml)*
200	5	5.0	2000	5	4.4
700	5	5.1	2000	Nil	0.2

The behaviour of copper in an air/H_2 flame in the presence of varying quantities of potassium is shown in Table III. It was necessary to use A.C. amplification to eliminate a strong background radiation from potassium in the region of copper fluorescence at 3247 Å. There was virtually no alteration in fluorescence intensity in the presence of potassium except at the highest concentration of 2000 μg/ml when there was some depression, probably because of changes in atomisation rates.

If multi-element determinations were attempted by this technique, another form of interference might arise with interactions between atoms of different elements fluorescing in the flame at the same time. This possibility was examined by spraying mixed solutions of Cd, In, Tl and Zn into a flame which was being irradiated by light from an array of appropriate "Spectral" lamps placed on either side of the optical axis. The results in Table IV with an air/H_2 Beckman burner indicate that at the concentration ratios shown there is no interaction between the fluorescing atoms of different elements. Although the values of cadmium and zinc at the two highest levels suggest some suppression, these are not significant because the calibration curves are not linear at these concentrations (due to self-reversal) and as a result introduce larger errors in the estimation of concentrations.

TABLE IV

INTER-ELEMENT EFFECTS

Ga (µg/ml)		*Zn (µg/ml)*		*Cd (µg/ml)*		*Tl (µg/ml)*	
Added	*Found*	*Added*	*Found*	*Added*	*Found*	*Added*	*Found*
2	< 5	20	18.8	2	1.9	20	19.5
5	5.4	10	10.2	5	5.1	10	10.0
10	10.0	5	5.0	10	9.1	5	5.2
20	20.5	2	1.8	20	18.5	2	2.3

The lack of interference can be attributed to the high dilution of the elements in the flame gases virtually eliminating any possibility of energy interaction by collision.

Conclusions

Without exhaustive testing of every combination of elements, it is impossible to say that no interference of the "excitation" type occurs, but the above results suggest that the technique can be as free from inter-element effects as atomic absorption spectrometry. The lack of interference in the presence of alkali metals is particularly noteworthy since the low excitation potentials of these elements often cause considerable suppression of normal atomic emission spectra. At the higher levels of dissolved solids the effect on atomisation becomes noticeable, but this is frequently observed with flame sources, the extent depending upon the type of atomiser and burner that is used.

The author wishes to acknowledge helpful discussions with Mr. R. C. H. MacCormac during the course of this work and in the preparation of this note. Thanks are also due to Mr. R. H. Rippon for assistance in the experimental work.

Atomic Weapons Research Establishment,
Aldermaston,
Berkshire (Great Britain)

G. I. Goodfellow

1 J. D. Winefordner and T. J. Vickers, *Anal Chem.*, 36 (1964) 161.
2 J. D. Winefordner and R. A. Staab, *Anal. Chem.*, 36 (1964) 165.
3 J. D. Winefordner and R. A. Staab, *Anal Chem.*, 36 (1964) 1369.
4 J. D. Winefordner, J. M. Mansfield and C. Veillon, *Anal. Chem.*, 37 (1965) 1049.
5 W. A. Bettison, H. E. R. Hartley and R. C. H. MacCormac, *A.W.R.E. Report 0-14/58.*

(Received March 9th, 1966)

Spectrophotometric determination of chromium with thioglycollic acid

Thioglycollic acid (TGA) forms stable complexes with several metals. Some of the complexes are coloured and consequently TGA has been recommended as spectrophotometric reagent for iron[1], molybdenum[2], cobalt[3], uranium[4], vanadium[5], and palladium[6]. Chromium(III) does not react with TGA at room temperature, but a violet chromium–TGA complex is formed on heating in acidic solution and a green complex[7] is formed above pH 6. The green colour reaction has been used for the detection of chromium in the presence of titanium[8], but no spectrophotometric determination of chromium based on these reactions has so far been reported.

Recently a detailed investigation was made of the complex formation between chromium(III) and TGA[9]. The red colour obtained in acidic medium was found to be due to a mixture of various complexes and the absorption maxima as well as the extinctions measured were highly dependent on the excess of reagent and on pH. In alkaline solutions only one complex with the formula $Cr(SCH_2COO)_3^{3-}$ was formed on heating the reactants. The colour intensity of this blue-green complex appeared to be independent of the excess TGA and of pH[9].

The present work was carried out in order to investigate the application of this green complex for quantitative determination of chromium(III) in the presence of other metals.

Reagents and apparatus

Thioglycollic acid (80% in water) was obtained from E. Merck AG., Germany. The acid was purified and standardized as described previously[9]. Stock solution of chromium was prepared from reagent-grade chromium(III) perchlorate (G. F. Smith Chem. Co.) and standardized by oxidation with persulphate followed by iodimetric titration. The remaining chemicals were of analytical grade and used without further purification. Extinction measurements were carried out with a Beckman DB recording spectrophotometer with 1.000-cm glass cells. The pH of the solutions was measured with a Beckman Zeromatic pH meter.

Results

The green $Cr(SCH_2COO)_3^{3-}$ complex is easily formed upon heating an alkaline solution of the reactants on a boiling water bath; the complex is stable for several days provided that an excess of TGA is present. The absorption curve exhibits maxima at 476 and 632 nm, and the extinctions were found to be independent of the excess of TGA and of pH in the range 7–10.

Preliminary experiments showed that some metals, particularly iron, cobalt and nickel, form coloured complexes with TGA and attempts were made to find a suitable masking agent. Citrate, fluoride and triethanolamine interfered in the chromium–TGA complex formation, but cyanide appeared to be useful. Upon heating an alkaline mixture of TGA and cyanide a yellow colour is formed which contributes to the extinction even at 632 nm. In the following experiments the extinctions were therefore measured against a blank containing the same amount of TGA, cyanide and ammonia.

For the verification of Beer's law the purified TGA was used as reagent. The solutions were prepared and the extinctions measured as in the *Recommended procedure* given below. The system was found to obey Beer's law in the concentration range

20–150 µg chromium per ml. The molar extinction coefficient of the complex was found to be 202.

Further experiments showed that exactly the same calibration curve was obtained using the unpurified commercial product as reagent and this was used in the following experiments. A precipitate of chromium hydroxide was formed upon addition of ammonia, but dissolved during heating on the water bath. The precipitate could be avoided by heating the acidic medium, adjusting the pH to 7–10, and heating again to complete the complex formation, but exactly the same extinction was obtained. Chromium(VI) is rapidly reduced by TGA and the extinction measured was independent of the oxidation state of chromium in the original solution.

Recommended procedure

To the sample solution containing 0.5–5 mg chromium add 5 ml of 1 *M* potassium cyanide and 1 ml of a 1:1 mixture of commercial 80% TGA and concentrated ammonia. Heat the solution on a water bath for 5 min and dilute to 25 ml with distilled water after cooling to room temperature. Measure the extinction at 632 nm against a blank containing the same amounts of all reagents and which has been heated in the same way as the sample solution.

Interferences

The results obtained by the above procedure were not affected by the presence of perchlorate, chloride, nitrate, sulphate, acetate or tartrate in amounts 100 times by weight greater than that of chromium. The same amount of phosphate, fluoride and citrate caused, however, low results. The presence of a 50-fold amount of sodium, potassium, calcium, barium, cadmium or zinc and a 20-fold amount of nickel, aluminium, molybdenum or tungsten did not cause any interference. The error was less than ±2% also in the presence of a five-fold excess of copper, manganese and cobalt. Manganese forms a coloured complex with TGA, but the colour fades rapidly on standing. Aluminium must be kept in solution by adding excess tartrate.

Iron forms an intensively coloured complex even in the TGA–cyanide mixture and causes significant interference when present in amounts greater than half that of chromium. Vanadium and uranium also contribute to the colour intensity and should be removed before the analysis.

Discussion

The present method is simple and rapid and gives satisfactory accuracy in the determination of chromium(III). The interference from iron, the toxicity of cyanide and the unpleasant smell of TGA make, however, the method rather unattractive for practical analysis. A brief comparison of the reagents so far tested may be useful. A literature survey showed that EDTA[10,11], NTA[11], and DCTA[12,13], sodium azide[14], chrome azurol S[15], and pyridine-2,6-dicarboxylic acid[16,17] have recently been recommended as reagents for chromium(III).

The sodium azide method[18] appears to be of no practical importance.

The presence of iron, copper and aluminium causes serious interference in the chrome azurol S method[15] which is also more time-consuming than the present TGA method. Chrome azurol S is, however, by far the most sensitive available reagent for chromium(III), being used for 0.04 to 0.4 µg chromium per ml.

When EDTA or NTA is used as reagent for chromium, careful control of pH and a 30-min heating period are needed, which makes these methods less suitable than the DCTA, pyridine dicarboxylic acid and the present TGA method.

Several common metals interfere in the DCTA and EDTA method. The combined presence of copper, nickel, cobalt and iron causes no interference when NTA is used as reagent[11], but this method is less sensitive than the TGA method. The pyridine-2,6-dicarboxylic acid appears to be the most selective reagent for chromium(III) and it is probably the most useful reagent so far tested.

The TGA method is, however, the only method which is applicable for the determination of chromium both in the tri- and hexavalent state.

Department of Chemistry A,
University of Oslo,
Blindern (Norway)

EINAR JACOBSEN
WALTER LUND

1 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1959, p. 542.
2 A. I. BUSEV AND CHANG FANG, *Zh. Analit. Khim.*, 16 (1961) 39; *J. Anal. Chem. USSR*, 16 (1961) 38.
3 V. D. ANAND, G. S. DESHMUKH AND C. M. PANDEY, *Anal. Chem.*, 33 (1961) 1933.
4 W. H. DAVENPORT AND P. F. THOMASON, *Anal. Chem.*, 21 (1949) 1093.
5 M. ZIEGLER AND W. RITTNER, *Z. Anal. Chem.*, 164 (1958) 310.
6 V. WIDTMAN, *Chem. Listy*, 58 (1964) 211.
7 V. M. BHUCHAR, *Nature*, 191 (1961) 489.
8 V. M. BHUCHAR AND M. R. VERMA, *Mikrochim. Acta*, (1958) 342.
9 E. JACOBSEN AND W. LUND, *Acta Chem. Scand.*, 19 (1965) 2379.
10 G. DEN BOEF, W. J. DE JONG, G. C. KRIJN AND H. POPPE, *Anal. Chim. Acta*, 23 (1960) 557.
11 G. DEN BOEF AND B. C. POEDER, *Anal. Chim. Acta*, 30 (1964) 261.
12 A. R. SELMER-OLSEN, *Anal. Chim. Acta*, 26 (1962) 482.
13 H. KHALIFA, J. E. ROBERTS AND M. M. KHATER, *Z. Anal. Chem.*, 188 (1962) 428.
14 F. G. SHERIF, W. M. ORABY AND H. SADEK, *J. Inorg. & Nucl. Chem.*, 24 (1962) 1373.
15 M. MALÁT AND M. HRACHOVCOVÁ, *Collection Czech. Chem. Commun.*, 29 (1964) 2484.
16 H. HARTKAMP, *Z. Anal. Chem.*, 187 (1962) 16.
17 G. DEN BOEF AND B. C. POEDER, *Z. Anal. Chem.*, 199 (1964) 348.

(Received February 14th, 1966)

Inorganic chromatography on impregnated ion-exchange papers

Extensive use has been made of paper impregnated with various extractive and gravimetric reagents and so-called liquid ion exchangers to achieve separations by reversed-phase paper partition chromatography[1]. One of the earliest examples involved the separation of a number of cations on paper impregnated with 8-quinolinols[2]. Very recently, a striking separation of rare earths has been reported on paper impregnated with organic phosphorus compounds[3]. In almost every case, the reagent is fixed on standard filter paper, such as Whatman no. 1. Under these conditions, the properties of the support are unimportant compared with those of the organic reagent[1]. It is shown below that if a reagent such as phenylbenzohydroxamic acid (PBHA) is instead combined with commercial ion-exchange paper containing polystyrene resins, separations of certain ions may be achieved which are better than those obtained on either stationary phase alone. PBHA has been found to be a selective reagent for the paper chromatographic separation of metal ions by development with perchloric or hydrochloric acids[4]. No reported procedures have been noted involving the impregnation of ion-exchange papers with such reagents.

Experimental

The following 26 ions were studied by descending development in commercial apparatus using standard techniques previously described[5]: Ag, Al, As^{3+}, Au^{3+}, Ba, Bi, Cd, Ce^{3+}, Ce^{4+}, Co, Cr^{3+}, Cu, Fe^{3+}, Hg^{+}, Hg^{2+}, Mg, Mn^{2+}, Ni, Pb, Pt^{4+}, Sb^{3+}, Sn^{4+}, Tl^{+}, U^{6+}, V^{5+} and Zn. The composition of the test solutions[6] and detection methods[5,7] were also reported earlier.

The migration behavior of 10–25 μl of a 0.050 *M* solution of each ion was tested individually in each chromatographic system. For comparison, each ion was also tested in systems including the same developers with unimpregnated ion-exchange paper and Whatman no. 1 paper impregnated with reagent. Synthetic binary, ternary and more complex (up to 8 ions) representative mixtures were also studied in each case to prove the reliability of separations predicted by individual migrations. There was no significant difference between the migration behavior of any ion when alone and when included as part of a mixture.

Amberlite SA-2 strong-acid cation-exchange paper (lot 7802) or SB-2 strong-base anion-exchange paper (lot A-10297) (H. Reeve Angel and Co., Clifton, N. J.) was used throughout. The ionic form of the paper was changed when necessary by the procedure of LEDERER AND RALLO[8]. Sheets were impregnated by dipping into a 2% solution of reagent in absolute ethanol in a glass tray. The excess solution was allowed to drip back into the tray, and the sheets were air-dried for at least 1 h at room temperature before use. The solvent front was allowed to migrate at least 30 cm in each run, which required 1.5–2 h with impregnated and unimpregnated ion-exchange paper and up to 4 h with impregnated Whatman no. 1.

Results

The ion-exchange systems chosen for study were some which had earlier proven to be highly selective for the separation of certain cations from complex mixtures[5-7,12]. The R_F values given below are for the front and rear boundaries of the developed zones. In most cases, the values are the average of at least 2 runs and often many more. In all cases, the reproducibility of R_F for replicate determinations was excellent. A typical result was a range of 0.06 units for 15 migrations of cadmium (alone and in mixtures) in the first system described.

When all 26 ions were developed with 0.50 *M* hydrochloric acid on SA-2 paper in the hydrogen form[6], arsenic (R_F 0.94, 0.88) was separated from all other ions, and cadmium (R_F 0.46, 0.25) was separated from all except vanadium (R_F 0.25, 0.08), tin (R_F 0.45, 0.35), antimony (R_F 0.39, 0.11) and mercury(II) (R_F 0.45, 0.35). Everything else remained at the origin or migrated with $R_F < 0.15$. When all ions were developed on SA-2 paper impregnated with PBHA, cadmium (R_F 0.42, 0.25) was separated from every other ion. Most were retained at or near the origin by the ion-exchange properties of the paper as before. Tin, antimony and vanadium were strongly complexed by PBHA and had $R_F < 0.10$. Even mercury(II) which was not strongly complexed by PBHA[4] had $R_F < 0.20$ and was separated from cadmium. Arsenic (R_F 0.94, 0.87) was uncomplexed and remained separated from everything. The beneficial effect of this reagent could be predicted from extraction studies which had shown that cadmium was poorly extracted by PBHA[9] but that tin[10], antimony[10] and vanadium[11] were well extracted by this reagent. On Whatman no. 1 paper impregnated with PBHA, cadmium was uncomplexed (R_F 1.0, 0.91) and was not separated from most other ions including mercury (R_F 1.0, 0.91) and vanadium which was mostly at the origin but gave a faint comet to R_F 0.98. So although cadmium was not separated from 4 ions on ion-exchange paper and from many other ions including 2 of the same 4 on PBHA, when the 2 stationary phases were combined cadmium was separated from all ions.

When all 26 ions were developed with 0.050 *M* potassium cyanide and 0.075 *M* ammonium oxalate in 0.20 *M* ammonia on SB-2 paper in the chloride form[5], thallium (R_F 0.80, 0.46) was separated from all ions except magnesium (R_F 0.97, 0.72) and arsenic (R_F 0.86, 0.78). No other ions left the origin. When all ions were developed with the same solution on SB-2 paper impregnated with 8-hydroxyquinoline (8-quinolinol), Tl (R_F 0.32, 0.18) was separated from all other ions except tin (R_F 0.43, 0.17). Magnesium was complexed by the reagent and remained at the origin, and arsenic (R_F 0.88, 0.80) was again near the solvent front and was now separated from everything. Even though tin and thallium were not separated, it was possible to differentiate them by the color of the qualitative detection test. Tin forms a bright yellow spot and thallium a brown spot with hydrogen sulphide. On Whatman paper impregnated with the reagent, arsenic was not sorbed, thallium and tin were moderately sorbed and magnesium was at the origin. Although thallium was separated from magnesium on the reagent alone, it was not separated from many other ions. Impregnation of the ion-exchange paper in this case increased the sorption of 2 ions (Mg and Tl) but caused another (Sn) to be less sorbed. By use of both ion-exchange systems, thallium can be separated from all other ions.

When all 26 ions were developed with 0.10 *M* ammonium thiosulphate and 0.10 *M* ammonia on SB-2 paper in the thiosulphate form[12], magnesium (R_F 1.0, 0.63) was separated from every ion except nickel (R_F 0.98, 0.72), arsenic (R_F 0.81, 0.0), barium (R_F 0.80, 0.0), cobalt (R_F 0.94, 0.0) and manganese (R_F 0.76, 0.0). All other ions were at or near the origin. When all ions were developed with the same solution on SB-2 paper impregnated with dimethylglyoxime (DMG), Mg (R_F 1.0, 0.81) was separated from everything except arsenic (R_F 0.92, 0.0) and iron (R_F 0.93, 0.0). These two ions cometed from the origin. In the case of iron, the comet was very faint and most of the sample was at the origin. These three unseparated ions were again easily differentiated by the qualitative detection tests employed. Nickel was complexed by DMG in a characteristic red zone which was sorbed at the origin. Cobalt (R_F 0.07, 0.0) and barium (R_F 0.13, 0.0) were in rather compact zones at the origin, and although manganese still streaked from the origin (R_F 0.61, 0.0), it was apparently separated from magnesium. Impregnation of the ion-exchange paper in this system greatly increased the sorption of 3 interfering ions (Ba, Co and Ni), decreased the sorption of one ion (Fe) and left 2 interferences virtually unchanged (As and Mn). Magnesium itself formed a slightly less diffuse zone on the impregnated paper. The increased sorption of nickel was of course expected because of the selectivity of DMG for this ion. The increased sorption of cobalt and barium was unexpected because these ions were sorbed only slightly on Whatman no. 1 paper impregnated with DMG. Iron behaved identically on impregnated Whatman and impregnated ion-exchange paper. On unimpregnated ion-exchange paper, iron hardly moved. These results (and those for tin in the system directly above) indicate the very complex nature of the chromatographic systems involved in these separations.

Discussion

These few examples demonstrate that it can be advantageous to use ion-exchange paper rather than conventional chromatography paper as the support in paper extraction chromatography. When the effect of a stationary complexing reagent is added to the effect of a stationary phase capable of ion exchange, chromatographic systems with greater or altered selectivity may result.

In the thiosulphate systems described above, some of the interfering ions yielded elongated and cometed zones. This indicates that for these ions, the best chromatographic conditions did not obtain and that R_F values should probably not even be given in these cases. Although non-equilibrium conditions always apply in paper chromatography[13], an approach to equilibrium is indicated only when reasonably compact zones are obtained. However, the separations which are described in these systems do work and are reproducible, and most of the 26 ions do yield quite compact zones.

The addition of a hydrophobic organic reagent to the stationary phase alters and complicates the nature of the chromatographic systems. The ions of the mixture can interact with the complexing agent in the mobile phase. The mixture can also interact with the cellulose, resin, binder or reagent in the stationary phase. The interactions with the resin can be of many different kinds: actual ion exchange, sorption on the organic network, complex formation with the reactive groups or partition[8]. In addition, the interactions between the stationary and mobile phases must be considered. As aqueous wash liquids pass through fairly dry filter paper, water is removed from the solvent to form the "water–cellulose complex"[14]. Water is also removed in order to hydrate the functional groups of the resin. Impregnated ion-exchange paper may remove less water from the developer, which would effectively change the composition of the mobile phase. The complexing agents in the wash liquids can also interact with the stationary phase by the mechanisms suggested above.

PBHA could not be used in systems including ammonia-containing or other basic wash liquids. The reagent was stripped from both Whatman and ion-exchange paper, so that after development very little was left near the origin while progressively more remained toward the solvent front.

Department of Chemistry,
Lafayette College,
Easton, Pa. 18042 (U.S.A.)

JOSEPH SHERMA

1 E. CERRAI, in K. MACEK AND I. M. HAIS, *Stationary Phase in Paper and Thin-Layer Chromatography*, Elsevier, Amsterdam, 1965, pp. 180–198.
2 Q. FERNANDO AND J. P. PHILLIPS, *Anal. Chem.*, 25 (1953) 819.
3 J. W. O'LAUGHLIN, J. W. FERGUSON, G. J. KAMIN AND C. V. BANKS, *Abstracts of Papers, American Chemical Society 150th National Meeting, Atlantic City, N. J., September, 1965.*
4 J. SHERMA AND J. S. FRITZ, *J. Chromatog.*, in press.
5 J. SHERMA, *Talanta*, 9 (1962) 775.
6 J. SHERMA, *Anal. Chem.*, 36 (1964) 690.
7 J. SHERMA AND C. W. CLINE, *Talanta*, 10 (1963) 787.
8 M. LEDERER AND R. RALLO, *J. Chromatog.*, 7 (1962) 552.
9 G. K. SCHWEITZER AND D. R. RANDOLPH, *Anal. Chim. Acta*, 26 (1962) 567.
10 E. E. RAKOVSKII AND G. M. PETRYKHIN, *Zh. Analit. Khim.*, 18 (1963) 539; *C.A.*, 59 (1963) 2142f.
11 CHE-MING NI, CHUNG-FEN CHU AND SHU-CH'UAN LIANG, *Hua Kung Hsueh Pao*, 29 (1963) 249; *C.A.*, 59 (1963) 14,644f.
12 J. SHERMA, *Talanta*, 11 (1964) 1373.
13 R. CONSDEN, in K. MACEK AND I. M. HAIS, *Stationary Phase in Paper and Thin-Layer Chromatography*, Elsevier, Amsterdam, 1965, p. 163.
14 C. S. HANES AND F. A. ISHERWOOD, *Nature*, 164 (1949) 1107.

(Received February 24th, 1966)

A selective spot test for silver with arsenic trisulfide*

Recently it was reported[1] that solid arsenic trisulfide reacts with an acid or neutral solution of mercury(II) cyanide to form a black mixture of metallic mercury and mercury(II) sulfide. A new test for this cyanide could be based on this effect as well as a differentiation between arsenic trisulfide and arsenic pentasulfide because the latter does not react with mercuric cyanide. It was stated that filter paper impregnated with arsenic trisulfide is suitable for detection of mercury(II) cyanide; if this stable yellow paper is spotted with a drop of an acid or neutral mercury(II) cyanide solution a black stain or ring is formed immediately. As this is not the case with mercury(II) chloride, nitrate or acetate it was assumed that mercury(II) itself, in contrast to mercury(II) cyanide, does not react with arsenic trisulfide. This assumption must be modified as will be shown in this paper.

In order to examine the selectivity of the new test for mercury(II) cyanide, the behaviour of other metal salts was studied. Acidic 1% salt solutions were prepared and a drop containing 500 μg of the salt was placed on arsenic trisulfide paper. The results were as follows:

---

* Research work carried out at the Laboratório da Produção Mineral, Rio de Janeiro, Brazil.

Solution produces no black stain

Mercury(II) nitrate (chloride)
Copper(II) nitrate
Lead nitrate
Cadmium nitrate
Antimony trichloride
Tin(IV) chloride
Iron(III) nitrate
Zinc sulfate
Manganese(II) sulfate
Cobalt nitrate
Nickel nitrate
Ammonium molybdate
Thallium(I) sulfate
Bismuth nitrate
Platinum chloride
Uranyl sulfate

Solution produces black or brown stain

Silver nitrate
Palladium chloride
Gold(III) chloride

It is assumed that, in the case of silver salt, silver sulfide is formed:

$$As_2S_3 + 6\ Ag^+ \rightleftharpoons 3\ Ag_2S + 2\ As^{3+} \tag{1a}$$

or

$$As_2S_3 + 6\ Ag^+ + 6\ H_2O \rightleftharpoons 3\ Ag_2S + 2\ AsO_3^{3-} + 12\ H^+ \tag{1b}$$

It was found that in accordance with these reversible reactions an acidic silver nitrate solution containing AsO_3^{3-} ions does not react with arsenic trisulfide. Furthermore, it was found that, if this sulfide is suspended in a nitric acid solution of silver nitrate, black silver sulfide is produced and after filtration a solution is obtained in which yellow silver arsenite can be precipitated by addition of excess sodium acetate.

In view of the fact that drops of mercury salt solutions (with the exception of the cyanide) placed on arsenic trisulfide paper do not form black mercury(II) sulfide it was expected that the formation of silver sulfide should permit the detection of silver(I) in the presence of mercury(II). Surprisingly this is only true if the ratio Ag:Hg is not lower than 1:3. In this case the picture of the spot test is somewhat different. Instead of a black-brown circular stain, a black-brown ring is formed. If a greater excess of mercury(II) is present, then the formation of silver sulfide fails completely. It was also observed that if arsenic sulfide paper is spotted with silver nitrate, the brown-black stain produced is completely removed when further spotted with a mercury(II) nitrate solution. The reason for these effects can be explained. Obviously, mercury(II) reacts with arsenic trisulfide without formation of black mercury(II) sulfide in its proper phase. Instead the mercury(II) sulfide first formed on the surface of the arsenic trisulfide particle reacts with mercury(II) to form sulfosalts such as $x\mathrm{HgS} \cdot y\mathrm{Hg(NO_3)_2}$ which are white or yellow. Evidence for this assumption was found when arsenic trisulfide was treated with mercury(II) nitrate in the same manner as described before with silver nitrate; no black sulfide was formed but a solution was obtained which contained arsenic(III) or arsenite. The pertinent reactions in which mercury(II) ions are acting may be:

$$As_2S_3 + 3\ Hg^{2+} = 3\ HgS + 2\ As^{3+} \tag{2}$$

$$HgS + Hg(NO_3)_2 = HgS{\cdot}Hg(NO_3)_2 \qquad (3)$$

According to eqn. (2), arsenic(III) is formed which, as reported before, hinders the reversible reaction of silver nitrate with arsenic sulfide. Therefore no positive response to the spot test for silver(I) on arsenic trisulfide paper is obtained if the ratio Ag:Hg is lower than 1:5 or if an excess of arsenic(III) is present.

It is noteworthy that the stain formed by spotting arsenic trisulfide paper with silver nitrate is not black like silver sulfide but brown. Probably, the black silver sulfide formed on the surface of arsenic trisulfide protects the latter from further rapid reaction with silver(I). Another explanation may be that instead of black silver sulfide a dark brown double sulfide such as $Ag_2S \cdot As_2S_3$ is formed.

The reaction with arsenic trisulfide can be recommended for the spot detection of small amounts of silver(I) provided that Hg^{2+}, As^{3+}, Pd^{2+} and Au^{3+} ions are absent. In addition, procedures have been developed which permit the detection of metallic silver or silver in alloys and the detection of silver in highly diluted solutions.

Spot test for silver

A drop of the acid test solution is placed on arsenic trisulfide paper. Depending on the amount of silver, a black-brown stain or ring is formed immediately or within a few minutes; warming is recommended.

Limit of identification: 1 μg silver

Preparation of arsenic trisulfide paper. Weigh 3 g of arsenic trisulfide and dissolve it in 100 ml of concentrated ammonium hydroxide:

$$As_2S_3 + 6\ NH_4OH = (NH_4)_3AsSO_2 + (NH_4)_3AsS_2O + 3\ H_2O$$

Impregnate filter paper S & S No. 589 with a few ml of the ammoniacal solution in a culture dish; drain off excess liquid and hang on a hook to dry.

Detection of metallic silver

Place a drop of nitric acid (1:4) on the arsenic trisulfide paper and rub it with the solid sample; the silver nitrate thus produced reacts with arsenic trisulfide to form black silver sulfide. (It was found that some silver alloys do not give satisfactory results. A general procedure consists of previous dissolution of the sample by warming a minute quantity in a drop of nitric acid in the depression of a spot plate, followed by partial evaporation. After addition of some drops of water proceed as described for the straightforward silver(I) test.)

Detection of silver in highly diluted solution

If a drop of a dilute ammoniacal solution of arsenic trisulfide is added to a diluted acid, arsenic trisulfide is precipitated:

$$(NH_4)_3AsSO_2 + (NH_4)_3AsS_2O + 6\ H^+ = As_2S_3 + 3\ H_2O + 6\ NH_4^+$$

In the presence of silver ions the finely divided yellow arsenic trisulfide produces and collects silver sulfide. When compared with a blank the formation of silver sulfide is easily detected because of the difference in the color of the precipitate.

To 3 ml of a dilute silver nitrate solution which has been acidified with nitric acid, add one drop of an ammoniacal solution of arsenic trisulfide. Compare with a blank prepared in the same manner but in the absence of silver ions.

In this way it was possible to detect silver at a dilution of $1:3 \cdot 10^6$.

The support of this study by the Conselho Nacional de Pesquisas and the Aerospace Research Laboratories is gratefully acknowledged.

Laboratório da Produção Mineral,
Ministério das Minas e Energia,
Rio de Janeiro (Brazil) FRITZ FEIGL
Aerospace Research Laboratories,
Wright-Patterson Air Force Base,
Dayton, Ohio (U.S.A.) FRANK L. CHAN

1 F. FEIGL AND A. CALDAS, *Chemist-Analyst*, in press.

(Received March 25th, 1966)

BOOK REVIEWS

M. R. F. ASHWORTH, *Titrimetic Organic Analysis. Part II. Indirect Methods*, Chemical Analysis Series, Vol. 15, Interscience Publishers – J. Wiley and Sons, Inc., New York, 1965, xix + 1023 pp., price 245 s.

Part I of this work on titrimetric organic analysis, which dealt with direct methods, was reviewed last year in this journal (*Anal. Chim. Acta*, 32 (1965) 599). Part II, dealing with indirect methods, is arranged in the same fashion and is just over twice the size. Of course, far more reactions of organic compounds with inorganic or organic reagents can be utilized indirectly than directly, though one had scarcely realized the extent to which this is true until faced with this large volume.

Section I of this volume (28 pp.) contains general information on indirect methods of three types: (*1*) the common back-titration of an excess of reagent, (*2*) the determination of a product of some reaction of the required compound, and (*3*) the determination of secondary components in a mixture after the total of the components had been determined and the required component has been rendered inactive. Section III consists of indexes to the functional groups, compound classes and individual compounds which appear in Section II, the main part of the text. In this Section, each reagent which can be utilized in indirect procedures is considered in turn; after concise and useful general remarks, the available methods are listed chronologically with information on the materials titrated, the reagent and reaction conditions, the subsequent treatment and final titration, and the literature reference; the literature is covered into 1964.

This volume possesses all the virtues and vices of its predecessor on direct methods. The amount of material summarized is such that there can be nothing but praise for the courage and tenacity of the author in carrying out the enormous task of compilation. The whole work should certainly be made available in libraries, for it provides a very valuable, if rather daunting, guide to the literature.

A. M. G. MACDONALD (Birmingham)

G. KORTÜM, *Treatise on Electrochemistry*, 2nd Ed. (completely revised), Elsevier Publishing Company, Amsterdam, 1965, xxii + 637 pp., price Dfl. 85.—.

It is good to be able to welcome a new edition of this textbook after an interval of 15 years. The present edition is a translation with revision of the 3rd German edition of 1962. However, although the citations of textbooks extend into 1962 and in one instance 1963, the literature citations of more recent vintage than 1955 are sparse, and 1957 (one reference) appears to be the limit on a quick inspection. This rather invalidates the claim that the book is up to date to August 1965. However, it is primarily intended as a comprehensive textbook for advanced students with emphasis on the understanding of fundamentals and on established research developments, and so coverage of very recent work is less important than a sound treatment of theoretical principles. On the whole, for a one-volume treatise on so large a subject, coverage and treatment are good. Readers of this Journal will wish to know more particularly about the treatment of analytical methods. This is limited to a 20-page summary of the more classical methods, the most recent citation being 10 years old. However, this field is excellently served by other well-known specialist textbooks at least as up-to-date. Processes and phenomena of analytical interest are, of course, dealt with in the body of the text in general terms. The usefulness of this book to the analytical fraternity is therefore as a reference source of fundamental electrochemistry, and as such it can be recommended.

E. BISHOP (Exeter)

G. SCHWARZENBACH UND H. FLASCHKA, *Die komplexometrische Titration*, 5. völlig neu verfasste Auflage (Die chemische Analyse, Bd. 45), Ferdinand Enke Verlag, Stuttgart, 1965, xvi + 339 S., Geheftet DM 48.—, Ganzleinen DM 53.—.

This entirely revised edition of Professor SCHWARZENBACH's classic text on compleximetric titrations celebrates the twentieth anniversary of the first papers on this type of analysis. The utility of these titrations needs no stressing; the vitality of the research conducted into them is shown by the literature: the first edition of this book (1955) contained less than 300 references whereas this fifth edition (with references to the end of 1963) contains over 1400, although the many references which contain nothing basically new have not been included.

The book is divided into 2 parts. In the first, the theoretical bases of the titrations are discussed and authoritative information is given on visual indicator systems, instrumental methods of end-point detection, general titration methods (*e.g.* substitution titrations) and selectivity. In the second part, the literature on the determination of the many titratable ions is surveyed and wherever possible reliable titration procedures are given.

One would naturally expect a book written by these protagonists in the development of compleximetric titrations to be indispensably excellent; for once, expectation is in no way confounded by reality. It is to be hoped that the English edition will soon be forthcoming.

A. M. G. MACDONALD (Birmingham)

P. G. JEFFERY AND P. J. KIPPING, *Gas Analysis by Gas Chromatography*, International Series of Monographs on Analytical Chemistry, Vol. 17, Pergamon Press, Oxford, 1964, xi + 213 pp., price 70 s.

Conventional chemical methods of gas analysis are inadequate for many of the complicated gas mixtures which are now presented for analysis; and the analysis of mixtures of closely related gases can be extremely laborious by classical techniques. For those problems, as well as many others, gas chromatography offers a solution which has a speed, accuracy and elegance undreamt of only 15 years ago.

The book under review deals with analysis for hydrogen, noble gases, nitrogen, oxygen, carbon oxides, gaseous hydrocarbons, nitrogen oxides, sulphur- and halogen-containing gases and various more unusual gases; determination of omnipresent water vapour is also discussed. In the preliminary chapters, the general techniques and apparatus for gas chromatography are excellently described. Part II of this essentially practical text contains much valuable information on the determination of individual gases. In Part III, methods of analysis for materials such as coal gas, mine air, sludge digestion gas are described; and the determination of gases in solids and liquids is discussed. Finally, there is a brief chapter on gas sampling.

The collation of this material, and particularly the large quantity of tabulated data for the various gases in Part II, illumined as it is by the authors' own experiences, must be of great value to all concerned with gas analysis.

A. M. G. MACDONALD (Birmingham)

K. ABRESCH AND I. CLAASSEN, *Coulometric Analysis*, translated by L. L. LEVESON, Chapman and Hall, Ltd., London, 1965, xii + 275 pp., price 36 s.

This book is the authorized translation of a German text that was completed in 1960; it therefore contains none of the developments that have been made since 1959 in a field of analytical chemistry that has become increasingly popular in the last few years.

The first part of the book describes the electrochemical basis of the various coulometric techniques and discusses end-point detection and the interpretation of current–voltage curves. The descriptions of apparatus contained in this part are rather dated. The second section deals with the wide applications of coulometry, particularly coulometric titrations, and includes numerous practical examples. The extensive tables (51 pp.) summarizing the experimental conditions and literature sources for methods of analysing a host of inorganic and organic compounds are especially valuable.

To those who do not find a knowledge of recent developments essential, this monograph will provide a suitable introduction to the principles and application of coulometry at a very reasonable cost.

A. TOWNSHEND (Birmingham)

J. A. BARNARD AND R. CHAYEN, *Modern Methods of Chemical Analysis*, McGraw–Hill Publishing Company, London, 1965, xiii + 273 pp., price 42 s. 6 d.

The enormous changes in analytical chemistry during recent years can bewilder even established analytical chemists, let alone students and the inexperienced members of staff to whom the teaching of analytical chemistry is unhappily all too often left in British Universities and Colleges. Accordingly, the present text, which has been written to provide an introduction to many of the newer techniques and instrumental methods, should find a large readership.

The book begins with a description of EDTA, potentiometric and non-aqueous titrations. Polarographic and amperometric methods are discussed adequately but, surprisingly, there is no mention of coulometric titrations, which can provide elegant and quite economical teaching exercises. The treatment of spectroscopic analysis is much better than that of electrochemical analysis; the sections on infrared, visible and ultraviolet spectrophotometry are good, as is the section on flame photometry, whereas atomic absorption spectroscopy and spectrofluorimetry are merely outlined. The discussions of mass spectrometry and radiochemical techniques are very useful, though here, understandably, no experimental work is provided.

The final and longest chapter in the book deals with separation techniques; various types of chromatography—adsorption, partition, gas, paper, thin layer—are excellently described, as are ion exchange, gel filtration and zone electrophoresis.

Full details are given for 56 set experiments, 17 of which deal with titrimetric methods, 15 with spectrophotometric and flame photometric analysis, and 18 with separations.

The level of the discussions appears to be entirely appropriate to the level of advanced undergraduates for whom the book is primarily intended. One could argue with the choice of experiments but on the whole the presentation of the widely diverse techniques is excellent. The book must be welcomed by all teachers of analytical chemistry, particularly as its price makes it suitable as a class-text.

A. M. G. MACDONALD (Birmingham)

ANNOUNCEMENTS

A. A. BENEDETTI-PICHLER MEMORIAL AWARD

The American Microchemical Society has created a fund to commemorate the work of the late Dr. A. A. BENEDETTI-PICHLER. The award will be made to an individual who has made outstanding contributions to the practice or teaching of microtechniques. The award will be given at regular intervals with the understanding that the recipient will give a lecture at a gathering of analytical chemists covering the field for which the award has been designed.

Nominations are now being solicited and must be in the hands of the committee by April 1, 1967. A letter of 300 words or less, giving the name and address of the nominee and citing, in general, his work may be sent to the chairman of the 1966 committee, Mr. DAVID B. SABINE, U.S. Vitamin and Pharmaceutical Corporation, Yonkers, N.Y.

The Fund is not closed and gifts payable to the A. A. Benedetti-Pichler Memorial Fund may be sent to the Chairman.

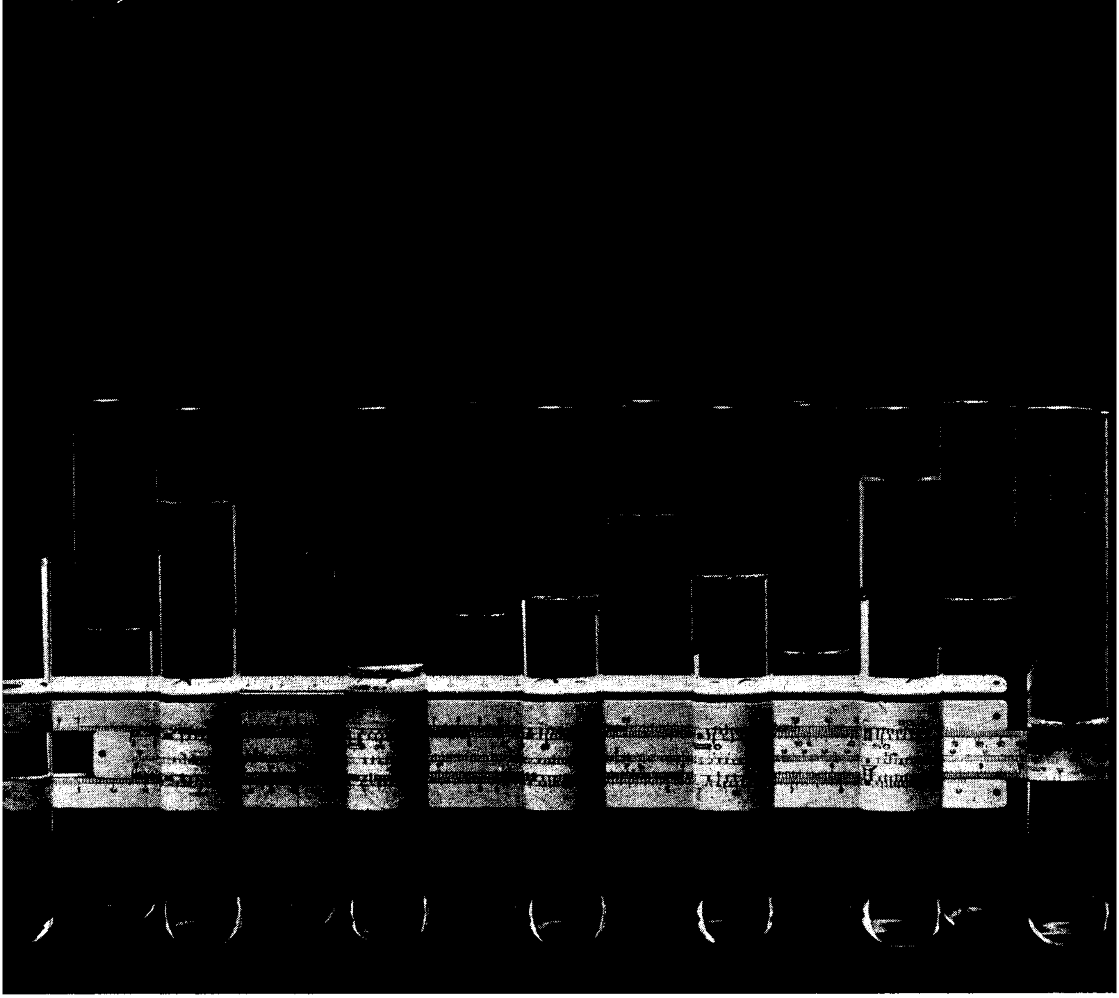
Anal. Chim. Acta, 36 (1966) 148

MEETING ON THE GAS CHROMATOGRAPHIC DETERMINATION OF HORMONAL STEROIDS, ROME 22nd–23rd SEPTEMBER 1966

The Second International Endocrinological Symposium will be held in Rome, Accademia Nazionale dei Lincei, via delle Lungara 230, 22nd–23rd September 1966. Chairmen of this Meeting are: Prof. L. CALIFANO, President of the Biological Committee, and Prof. M. LEDERER, Director of the Chromatographic Laboratory of the Italian National Research Council, Rome.

The Meeting will consist of a series of 12 plenary lectures and 3 Round Tables. The Meeting will have three official languages: Italian, English and French; simultaneous translation is planned.

Anal. Chim. Acta, 36 (1966) 148



CHEMICAL GEOLOGY

An International Journal

During the last few decades chemistry has played an increasingly large part in solving problems of a geological nature and it is expected that this cooperation will continue to intensify in the future. This trend has been encouraged by a shift in the geo-sciences from descriptive and theoretical work to empirical and practical studies demanded by the progress in related sciences and developments in the industrial sphere. Chemical techniques and methods of investigation are already finding a wide application in various branches of the earth sciences.

As the genesis, nature and occurrence of mineral deposits cannot be fully understood without a thorough knowledge of chemistry, the formation of minerals has attracted considerable research by geochemists. Much work is being done on geochemical mineral exploration. The vast mineral potential of the oceans will also require extensive study in the near future. Organic geochemistry has gained in importance during the last few years, and so have studies in the field of „isotope geology", involving both stable and radioactive nuclides, which contribute to the solutions of many geological problems.

CHEMICAL GEOLOGY aims to fill the need for a journal in this multi-disciplinary area of investigation by publishing research results, details of methods and apparatuses used, reviews and short notes. Supervision by an Editorial Board consisting of 27 members from 14 countries will ensure the international character of the journal.

Publication Publication started early in 1966 and initially the yearly volume will comprise four issues. The size of the journal is 6½ x 9½" (16 x 24 cm), with a printed page area of 5 x 7½" (12.7 x 19.2 cm).

Subscription Subscription prices: £5.8.0 or US $15.00 or Dfl. 54.00 per volume (plus postage). Additional charges for copies by air mail available on request. Subscriptions can be placed with Elsevier Publishing Company, P. O. Box 211, Amsterdam (The Netherlands).

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

New Elsevier teaching texts

FUNDAMENTAL PRINCIPLES OF CHEMICAL ANALYSIS

by W. F. Pickering, Professor of Chemistry, University of Newcastle, N.S.W., Australia

5½ x 8½", ix + 270 pages, 3 tables, 64 illus., 149 lit. refs., 1966, Dfl. 30.00, 60s., $10.00

CONTENTS: 1. Introduction. 2. Determinations based on phase separations. 3. Electrical transformations. 4. Ionic equilibria in solution. 5. Energy transitions. 6. Physical properties of matter. 7. Statistics, sampling and solution of samples. 8. Selective chemical reactions. 9. Heterogeneous equilibrium reactions. 10. Chromatographic separations. 11. Selection of analytical methods. 12. Tutorial problems. Index.

PRINCIPLES OF MODERN CHEMISTRY A guide to advanced study

A series of monographs

edited by W. F. Forbes, Professor of Chemistry, University of Waterloo, Ontario, Canada; and

W. J. Orville-Thomas, Professor of Chemistry, Royal College of Advanced Technology, Salford, Great Britain

Monograph 1

THE STRUCTURE OF SMALL MOLECULES

by W. J. Orville-Thomas

5½ x 8½", ix + 189 pages, 31 tables, 55 illus., 1966, Dfl. 26.00, 52s., $9.50

Paperback edition: Dfl. 15.00, 30s., $5.00

CONTENTS: Preface. 1. Introductory survey. 2. The formation of chemical bonds. 3. Characteristics of chemical bonds. 4. Quantum theory. 5. The stereochemistry of valence bonds. 6. The structure of individual molecules. Subject index.

Monograph 2

PHYSICAL ORGANIC CHEMISTRY

by Owen H. Wheeler, Department of Chemistry and Puerto Rico Nuclear Center, University of Puerto Rico at Mayaguez

in preparation, 1966

TEXTBOOK OF COLLOID CHEMISTRY

by A. Sheludko, Professor at the Institute of Physical Chemistry, Sofia, Bulgaria

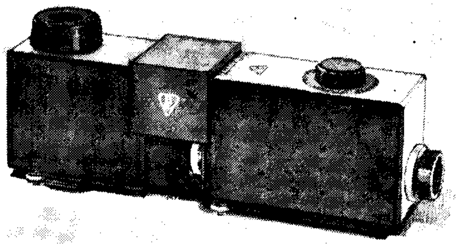
6 x 9" x + 280 pages, 11 tables, 70 illus., 288 lit. refs., Dfl. 40.00, £4.0.0., $14.50

CONTENTS: Foreword. 1. Preparation and purification of lyophobic colloidal systems. 2. The optical properties of colloids. 3. The molecular kinetic properties of colloidal solutions. 4. Physical chemistry of surfaces. 5. Electrokinetic phenomena. 6. Thin layers. 7. Stability of lyophobic sols. 8. Foams and emulsions. Index.

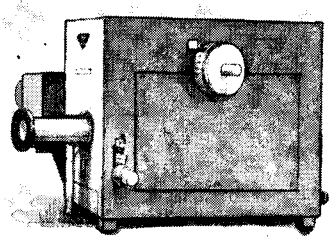
ELSEVIER PUBLISHING COMPANY

AMSTERDAM LONDON NEW YORK

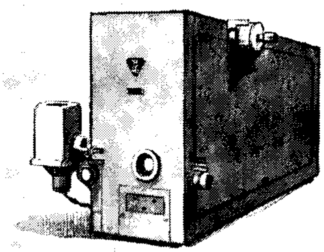
283 E



HIGH INTENSITY MONOCHROMATOR



250mm MONOCHROMATOR



500mm MONOCHROMATOR

VOL. 36 NO. 1 ANALYTICA CHIMICA ACTA SEPTEMBER 1966

CONTENTS

Short communications

PRINTED IN THE NETHERLANDS

SUBMICRO METHODS OF ORGANIC ANALYSIS

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

6 × 9″, ix + 173 pages, 12 tables, 35 illus., 186 lit. refs., 1966, Dfl.27.50, 55s., $10.00

Contents: 1. Introduction. 2. The balance. 3. General apparatus. 4. The determination of nitrogen. 5. Carbon and hydrogen. 6. Chlorine. 7. Bromine and iodine. 8. Fluorine. 9. Sulphur. 10. Phosphorus and arsenic. 11. Carboxyl groups. 12. Organic bases in non-aqueous media. 13. Alkoxyl and N-methyl groups. 14. Acetyl groups. 15. The carbonyl group. 16. Olefinic unsaturation. 17. Oxidation with periodate. 18. The determination of nitro and nitroso groups. 19. Thiol groups. 20. The cryoscopic determination of molecular weight. Index.

TECHNIQUES OF OSCILLOGRAPHIC POLAROGRAPHY

Second Edition, completely revised and enlarged
by R. Kalvoda
Institute of Polarography, Czechoslovak Academy of
Sciences, Prague, Czechoslovakia
with a preface by Professor J. Heyrovský

6 × 9″, 213 pages, 3 tables, 90 illus., 263 lit. refs., 1965, Dfl. 30.00, 60s., $11.00

Contents: Preface (J. Heyrovský); Author's Preface; 1. Introduction. 2. Examples of application of the oscillopolarographic method. 3. Practical oscillopolarographic exercises. 4. Maintenance of apparatus and construction of auxiliary electrical circuits. Index.

TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

by J. H. Beynon, R. A. Saunders and A. E. Williams
Research Department, Imperial Chemical Industries Ltd.,
Manchester, Great Britain

9½ × 6½″, xix + 392 pages, 1965, Dfl. 45.00, 90s., $16.50

These tables are intended to make it easy to determine the ionic reaction which gives rise to any meta-stable peak in a mass spectrometer, and will prove indispensable to any laboratory possessing this equipment. The introduction is given in English, German, French and Russian, to make the tables more generally useful.

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Second International Symposium organized by the Chromatography
Group of the Czechoslovak Chemical Society, at Liblice
by K. Macek and I.M.Hais

7 × 10″, 358 pages, 69 tables, 135 illus., 494 lit. refs., 3 coloured plates, 1965, Dfl. 42.50, 85s., $16.00

Contents: List of participants in the discussion. Introduction. Opening speech. I. Chromatography papers. II. Thin-layer materials. III. Stationary liquids and adsorbents in paper chromatography. IV. Stationary liquids and impregnations for thin layers. V. General problems of the stationary phase. Discussion. Closing remarks. Author index. Subject index.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK