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Vibrational Spectra and Structure

A SERIES OF ADVANCES, VOL. 4

edited by **JAMES R. DURIG,** Department of Chemistry, University of South Carolina, Columbia, South Carolina

1975. 316 pages. US $31.25/Dfl. 75.00. ISBN 0-444-41380-4

One of the greatest needs of science today is for competent people to critically review the recent literature in conveniently small areas and to evaluate the real progress that has been made, as well as to suggest fruitful avenues for future work. The current volume, number 4 in a series now published by Elsevier Scientific Publishing Company, attempts to fulfill these goals. Chapter 1 reports on the complementary infrared and Raman matrix isolation studies of similar chemical systems, and the usefulness of the newer laser-Raman technique is demonstrated relative to the well-established infrared matrix methods. Recent studies on the vibrational spectra and structure of plastic crystals are reviewed in Chapter 2, while Chapter 3 describes methods and applications of intramolecular force field calculations. Chapter 4 continues the theme of Chapter 1 with an example of the valuable use of infrared and Raman matrix isolation techniques. This section reviews the characterization of the products of metal atom-molecule cocondensation reactions studied by these methods. The techniques described should provide the inorganic and organometallic chemist with new chemical pathways for the synthesis and stabilization of chemical species which would have been difficult if not impossible to prepare and study by conventional chemical procedures. Physical chemists, spectroscopists, physicists, and other research scientists who use vibrational spectroscopy in their work should find this volume of immense value.

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1741E

FLAVINS AND FLAVOPROTEINS

Proceedings of the Fifth International Symposium

edited by THOMAS. P. SINGER, Molecular Biology Division, Veterans Administration Hospital, San Francisco, California, U.S.A.

1976 xvi+816 pag. US $99.50/Dfl. 258.00 ISBN 0-444-41458-4

This treatise presents the most comprehensive and up-to-date survey of established knowledge in the chemistry, biochemistry and biophysics of flavins and flavoproteins and of the applications of this knowledge to a host of related topics in the biological and physical sciences. Comprising the proceedings of the Fifth International Symposium on Flavins and Flavoproteins, this volume covers many exciting new developments in this particular branch of biochemistry, such as the functional and structural roles of new flavins, the elucidation of novel reaction mechanisms, the transport and biosynthesis of flavoproteins and the hormonal control of flavoprotein metabolism. The 89 papers cover all major advances in the field in recent years as well as review the current status of many problems under active investigation and focus attention on the frontiers yet to be explored. This book should become the primary reference work in flavin chemistry and flavoprotein biochemistry, and will be of prime interest to organic chemists, biophysicists, protein chemists, enzymologists, nutritionists, endocrinologists and microbiologists.

CONTENTS: Parts I. Introduction. II. Oxygen Activation by Reduced Flavins and Flavoproteins. III. Luciferase. IV. Oxygenases. V. Mechanisms of Proton Abstraction. VI. Covalently Bound Flavins and New Flavins. VII. Deazaflavin and Other Model Flavins. VIII. Flavodoxin. IX. Lipoyl Dehydrogenase and Glutathione Reductase. X. Complex Flavoproteins. XI. Adrenodoxin, Ferredoxin, and Cytochrome Reductases and Electron Transferring Flavoprotein. XII. Structure and Function of Flavoprotein Oxidases. XIII. Biosynthesis, Metabolism, and Transport of Riboflavin. XIV. Special Topics.

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1922 E

PREPARATION OF CATALYSTS

Scientific Bases for the Preparation of Heterogenéous Catalysts

Proceedings of the International Symposium held at the Solvay Research Centre, Brussels, October 14-17, 1975.

edited by B. DELMON, P.A. JACOBS *and* G. PONCELET.

1976. xvi+706 pages
Price: US $61.50/Dfl. 160.00
ISBN 0-444-41428-2

This book contains the proceedings of the first international symposium devoted to the processes involved in the preparation of industrial heterogeneous catalysts. The subjects covered include the preparation of phases associating two or more metallic elements in the form of alloys or mixed oxides; the preparation of "complex catalists" by impregnation, coprecipitation, mixing or other novel methods; the activation stage, with particular reference to decomposition, reduction, influence of the carrier, promotion or inhibition of crystallite growth and of compound formation with the carrier. This book is practically oriented and will be of particular value to those involved in the fabrication of catalysts in manufacturing plants and industrial research laboratories. It will also interest academic workers in the field.

CATALYSIS: HETEROGENEOUS AND HOMOGENEOUS

Proceedings of the International Symposium on the Relations between Heterogeneous and Homogeneous Catalytic Phenomena, Brussels, 23-25 October, 1974.

edited by B. DELMON *and* G. JANNES

1975. xxvi+550 pages
Price: US $42.50/Dfl. 110.00
ISBN 0-444-41346-4

These proceedings comprise twenty-eight contributed papers and ten invited lectures or reviews. The main topics are: similitude of active species or elementary steps: heterogenization of homogeneous catalysts; interpretation of heterogeneous phenomena through approaches pertaining to homogeneous catalysis; metallic clusters in solution.

1903 E

REACTION KINETICS IN HETEROGENEOUS CHEMICAL SYSTEMS

Proceedings of the 25th International Meeting of the Société de Chimie Physique, Dijon, 8-12 July, 1974.

edited by P. BARRET

1975. xvi+788 pages
Price: US $61.50/Dfl. 160.00
ISBN 0-444-41351-0

This volume contains the complete text of 16 plenary and special lectures, and 42 communications together with discussions. The papers describe the current state of knowledge concerning corrosion of metals and alloys, and solid-solid and gas-solid reactions involving inorganic compounds. Fundamental ideas of chemical kinetics and thermodynamics of irreversible processes are covered in relation to these subjects.

REACTION KINETICS AND CATALYSIS LETTERS

edited by G.K. BORESKOV *and* F. NAGY

1976. Volumes 4 and 5 (in 8 issues)
Subscription price: US $103.95/Dfl. 260.00
in 1976 including postage.

This journal, established by the USSR and Hungarian Academies of Science, aims to assist scientists of all countries by ensuring the rapid publication of original work in the fields of kinetics and catalysis. Of special interest is the inclusion of much new work from the USSR.

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Analytica Chimica Acta, 84 (1976) 231–257

STANDARDIZATION OF METHODS FOR THE DETERMINATION OF TRACES OF MERCURY
PART II. DETERMINATION OF TOTAL MERCURY IN MATERIALS CONTAINING ORGANIC MATTER

A REPORT PREPARED BY THE MERCURY ANALYSIS WORKING PARTY OF THE BUREAU INTERNATIONAL TECHNIQUE DU CHLORE*

BITC, 250 Avenue Louise, B-1050, Bruxelles 4 (Belgium)

(Received 12th December 1975)

SUMMARY

Three procedures are given for the destruction of organic materials as a pretreatment in the determination of total mercury by flameless atomic absorption spectrometry. These procedures were accepted as reference methods by the member companies of the Bureau International Technique du Chlore. The procedures are applicable to a great variety of sample types; they will not always be the fastest for every type of sample, but are considered as reference methods in checking other methods. Results for interlaboratory trials involving 25 industrial laboratories are presented. For a fish meal sample a mercury content of 308 μg kg^{-1} was found with a repeatability of 3.9 % and a reproducibility of 13.6 %.

The European chlorine manufacturers cooperating in the Bureau International Technique du Chlore (BITC) have a number of Working Groups considering various aspects of the problem of mercury in the environment, one of which is responsible for the development of reliable methods for measuring mercury levels both in products and process intermediates and also in the environment. This Working Group has already published [1] a paper giving details of procedures for the determination of mercury in process intermediates and products together with the results obtained in interlaboratory trials for both synthetic and industrial samples. The present paper deals with the second aspect of the problem, the measurement of mercury in the immediate environment of mercury cell plants.

The main object of this paper is to specify procedures which can be used reliably to convert a wide variety of naturally occurring materials to a form in which their mercury content can be measured by the well established

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*The members of the Working Party responsible for the preparation of this report were R. Ankersmit, J. Barjhoux, F. Cappellina, W. T. Carter, W. Dürr, Ch. Killens, J. Lutz, P. Mélard, Sven. A. Norberg, F. Nouyrigat, M. Olivier, P. Reiners and H. Romeis. This report has been approved by the General Technical Committee of the BITC, which also authorized its publication.

tin(II) chloride reduction—u.v. absorption procedure*. However, it proved to be extremely difficult to write down the procedures in such a way that they are applicable in detail and without slight deviations to the great variety in environmental samples. It was also found that one may need some experience with the methods before reliable results can be obtained. Since completely erroneous results can be obtained if care is not used in sample collection, detailed advice on sampling is also included.

CHOICE OF OXIDATION PROCEDURE

The basic principle adopted is to destroy the sample as completely as possible by oxidation to produce a solution containing mercury in the ionic form which can be readily measured by the tin(II) chloride—u.v. absorption procedure [1].

The published literature on mercury determinations is vast [1, 2]. Many of the procedures are reliable, some of them less so, and no one procedure is capable of dealing with all types of sample. The philosophy adopted here has been to select three procedures, all of which are reliable under the specified conditions of use. The three methods chosen have complementary areas of application and it is hoped that between them they are capable of dealing with any type of sample. It is not claimed that they are the only reliable methods, only that they have been evaluated in the laboratories of BITC members. Nor is it claimed that they are the most rapid; indeed for certain samples much faster procedures exist, e.g. for urine [3—5] and for fish tissue [6]. However, in general these rapid procedures are intended for use with only one type of sample, whereas the aim of the present paper is to cater for as wide a range of samples as possible. It is not suggested that other methods should not be used but that in cases of doubt or dispute one of the three methods described below should be used as appropriate to provide a reliable cross-check. The three selected methods are as follows.

1. Wet oxidation under reflux with nitric—sulphuric acids [7]

This is a long established method based on inexpensive apparatus. The thermometer prescribed [7] is omitted because of the risk of mercury contamination; an air lock is provided to prevent loss of mercury. With sufficient apparatus one operator can carry out 8 determinations per day but difficulty is experienced in destroying fatty matter, and acid-insoluble residues sometimes retain mercury tenaciously, particularly atmospheric grit. More drastic oxidation could be achieved with perchloric acid [8] but the use of this reagent has been avoided because of the danger of explosions with samples of unknown composition.

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*For technical reasons, the text of the original method has been modified and shortened in certain places; those interested in the original text can obtain it in French, German or English on application to the BITC.

2. Bomb digestion with nitric acid [9]

This method is particularly suitable for use when only limited quantities of sample are available, but the use of small samples may lead to sampling problems. Other advantages are the relatively low apparatus cost, and if digestion can be allowed to proceed overnight, a short manipulation time. However, care must be taken to avoid applying the technique to substances such as methanol which form explosive compounds with nitric acid; the method is not applicable to chlorinated hydrocarbons.

3. Combustion in a Wickbold burner [10]

This is the most widely applicable of the three techniques but has the highest equipment cost. It is necessary to avoid samples containing salts of alkali metals and phosphorus compounds, which may damage the quartz burner. This could be avoided by using a stainless steel burner, but chloride corrosion may then become a problem.

Table 1 provides guidance on the method to be used for each type of sample.

SAMPLING AND SAMPLE PRETREATMENT

Shellfish

These can be valuable indicators of trends in mercury pollution in a marine environment since specimens, particularly mussels, are often easy to obtain. When collected the shells contain approximately 50 % of water which does not contain significant quantities of mercury. If, however, the specimens are deep-frozen, cell disruption occurs on thawing and the liquid which exudes may contain mercury. For these reasons the following sampling procedure is recommended.

TABLE 1

Recommended procedures for different types of sample[a]

Sample	Wet oxidation	Bomb	Wickbold combustion
Animal matter	XX	XX	XX
Vegetable matter	XX	XX	XX
Hair	XX	XX	XX
Soil, mud and atmospheric dust	X	XX	XX
Urine and waste water	XX	XX	X
Blood	X	XX	X
Volatile organic material	—	—	XX
Chlorinated hydrocarbons	—	—	XX
Materials containing highly volatile Hg compounds such as $(CH_3)_2Hg$	—	XX	XX

[a] XX Method is acceptable; X method has limitations; — method is not recommended.

Prise open the shells of several specimens and sever the muscular tissue which secures the animal to the shell. Remove the animal tissue, discarding the fluid, and pass through a mincer. Thoroughly mix the product and store in a polythene bag until required for analysis.

Samples which have been deep-frozen in the shells are best left in the deep-freeze until required for analysis. Select sufficient specimens to give approximately 10 g of tissue and allow to thaw out; retain all the fluid which drains out. Remove the animal tissue from the shells and allow it to drain, retaining all the fluid. Weigh the fluid and the solid, and for the wet digestion method, recombine and analyse the whole sample. For the bomb and Wickbold methods, analyse representative quantities of the solid and the fluid separately.

Mobile fish

The internationally adopted practice has been to carry out analysis on the edible portions of fish on a wet basis. Various fish organs such as liver, brain, etc., may contain elevated concentrations of mercury but this is not normally relevant unless the fish are eaten whole or it is desired to carry out investigations into the effect of mercury on the metabolism of fish. In large fish there is some evidence that mercury concentration gradients occur with higher concentrations near the backbone and for this reason the following sample procedure is recommended: fillet the fish, retaining only the portions regarded as edible, and remove the skin. Pass the fillets through a mincer, mix the product thoroughly, and store in a polythene bag at —10 °C until required for analysis.

Grass and vegetation

Care is necessary in sampling vegetation since the mercury content may vary with the rate of growth and different results may be obtained at different times of the year. The water content of vegetation is also high and variable and trace metal analysis is normally carried out on material dried at 80 °C. However, there is evidence that mercury losses may occur at this temperature with some species of plants and it is advisable to analyse the undried specimens and then correct the results to a dry basis after measuring the loss on drying of another sample. The following sampling procedure is recommended: chop up the vegetation into short pieces 1—2 cm long immediately on collection, mix thoroughly and take a representative sample of approximately 200 g. Store in a refrigerator in a polythene bag until required for analysis.

Atmospheric dust deposits

Collect deposits by exposing 2-l narrow-necked bottles with 20-cm diameter funnels in the necks. To avoid losses of mercury during collection add to each container 200 ml of water containing 20 ml of concentrated nitric acid and 10 ml of potassium permanganate solution (40 g l^{-1}). Expose for one month or until the containers are almost full of rain water.

Immediately before analysis, decolourize the sample in the original container by the dropwise addition of hydroxyammonium chloride solution (100 g l^{-1}) and allow to stand for a short while in order to solubilize manganese compounds. Filter the contents of the container through a 47-mm cellulose acetate membrane filter, pore diameter 5 μm, into a 2-l standard flask, dilute to volume with water and mix. Carry out an oxidation of this membrane filter, preferably by Wickbold combustion, but if apparatus for this is not available, by either of the other two methods, and determine the mercury content of the filtrate by the method given under Photometric Measurement.

Soil and river mud

Soil samples should be taken as small cores 10 cm diameter and 10 cm deep. Split each one into 3 sections each 3 cm thick and store separately. Mud samples vary widely both in depth and liquidity and it may not be possible to sample in this way. The sampling technique adopted should depend on the circumstances and will vary from coring as above to merely scraping up sufficient mud to provide a sample.

Thoroughly mix each sample and determine the loss on drying at 105 °C. Discard this sample weight and use a second one for mercury analysis. Express the results as mg Hg kg^{-1} on a dry basis.

WET OXIDATION UNDER REFLUX WITH NITRIC AND SULPHURIC ACIDS

Scope and field of application

This method is suitable for the determination of total mercury in materials containing organic matter (see Table 1). The lower limit of detection based on the three-fold overall standard deviation of the blank on the reagents is approximately 0.08 μg Hg/sample weight. The latter is a maximum of 10 g in the case of solids or of 50 ml in the case of aqueous liquids giving lower limits of detection of 8 μg Hg kg^{-1} for solids and 2 μg Hg l^{-1} for liquids. With eight sets of apparatus it should be possible with most types of sample for one operator to complete eight analyses in a working day.

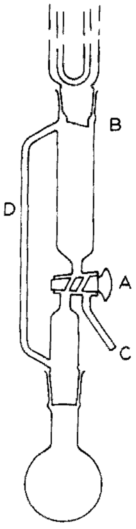
Principle

The sample weight, prepared as described, is digested under reflux with sulphuric and nitric acids in an apparatus which has a condensate reservoir provided with a tap by means of which condensate can be returned to the digestion flask or removed from the apparatus. This allows water to be removed from the system, thus subjecting the sample to digestion at increasing temperatures, and at a later stage permits high temperature oxidation of the residue by dropping nitric acid on to it from the reservoir at the temperature of fuming sulphuric acid. The residue and the condensate are then combined and the mercury content determined by flameless atomic absorption.

The method will not readily decompose oils and fats, particularly if they are volatile at the digestion temperature employed, but undecomposed oils can often be separated off without loss of mercury. Difficulty may also be experienced in completely extracting mercury from acid-insoluble material. This may be detected by submitting residual insoluble matter to a second digestion. Finally, low results may be obtained if very volatile mercury compounds such as dimethylmercury are present, probably owing to losses through the condenser. In all three cases cross-checks by the Wickbold method are advisable.

Apparatus and reagents

An atomic absorption spectrophotometer and accessories, and reagents as described previously [1] are required. The reflux apparatus is of borosilicate glass, with a double surface condenser, as shown in Figs. 1 and 2. (The thermometer mentioned in ref. 7 is omitted because of the risk of mercury contamination, although it can be of use for checking the temperature reached during digestion.) The apparatus should be erected in a fume chamber with the flask supported on a tripod and gauze and held upright by one clamp on the condenser so that the apparatus can be swirled if necessary. The digestion flask is heated by means of a bunsen burner. All the apparatus should be carefully cleaned with concentrated nitric acid before use and if it is used for a sample with a high mercury content it should be cleaned and a satisfactory blank obtained on it before re-use.



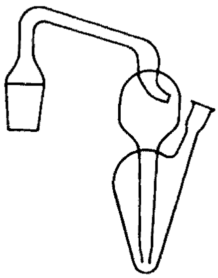


Fig. 1. Apparatus for the wet decomposition of organic matter.

Fig. 2. Trap with ground-glass joint, to fit the top of the reflux condenser.

Digestion procedure

Weigh out or measure out the sample (up to 10 g of solids weighed to 0.01 g and up to 50 ml of liquids measured to 0.5 ml) and transfer to the digestion flask. Add several glass beads and if the sample contains no water, 5 ml of water. Attach the flask to the condensate reservoir with tap A closed and place 10 ml of concentrated sulphuric acid (ca. 18 M) and 20 ml of concentrated nitric acid (ca. 14 M) into the condensate receiver (see Note 4). Turn on the condenser cooling water and attach the condenser. To the top of the condenser attach the air lock containing 5 ml of nitric acid (ca. 14 M). The lock should be of such a volume that it is sealed by 5 ml of nitric acid. Carefully operate tap A so that the mixed sulphuric—nitric acids run on the sample, momentarily closing the tap if the reaction becomes violent. The remainder of the digestion procedure contains four separate phases which are used as required depending on the nature of the sample.

Initial reaction. The object is to complete this stage as rapidly as possible without causing violent emission of oxides of nitrogen from the condenser or allowing froth from the digestion flask to enter the condenser. With particularly reactive or frothy samples, it is advisable to start the digestions in the late afternoon and allow them to stand in the cold in contact with the mixed acids overnight. Unreactive samples such as soil may be heated immediately. However this phase is achieved, it is complete when froth is no longer being formed and the sample is refluxing vigorously with the condensate being returned to the flask via tap A.

Initial digestion. In this continuation of the first stage, reflux is continued with the condensate returning to the flask, so that all residual froth on the walls of the condensate receiver is washed back into the flask and that the volatile oils are oxidized as much as possible at the relatively low temperature which can be achieved here.

Water removal. In this stage, as much water as possible is collected in the condensate receiver but sufficient nitric acid is left in the apparatus to complete the final oxidation. Close tap A and collect condensate roughly equal in volume to the water present; then run off through side arm C into a 100-ml standard flask by manipulating tap A.

Final oxidation. During this stage material of low volatility is oxidized. Close tap A. Heat the contents of the digestion flask so that nitric acid distils and condenses in reservoir B. When a slight darkening of the digest occurs, admit small amounts of condensate via tap A in order to continue the oxidation and remove the darkening. Continue heating with tap A closed until the darkening re-occurs and repeat the addition of small amounts of condensate so that the darkening is again removed. Repeat these operations until darkening no longer occurs and the residual sulphuric acid is boiling.

Stop heating, allow the apparatus to cool, run the condensate into the 250-ml flask and also add the contents of the air lock. Rinse the air lock and the condenser with small quantities of water, collecting the rinsings in the flask. Stop the cooling water and disconnect the condenser. Add to reservoir B (with tap A open) the distillate collected in the 100-ml standard flask and water rinsings followed by 10 ml of potassium permanganate solution (40 g l^{-1}) and 5 ml of sodium chloride solution (300 g l^{-1}), mixing between each addition. Rinse the reservoir, including tube D, with small amounts of water into the flask and disconnect the reservoir. Heat the contents of the flask to boiling, and boil gently for 10 min. (The solution should be completely decolourized.) After cooling return the mineralized solution quantitatively to the original 100-ml standard flask. Just before the mercury measurement add 2 drops of hydroxyammonium chloride solution (100 g l^{-1}), dilute to volume and mix.

Prepare a blank by introducing into a 250-ml flask several glass beads, ca. 30 ml of water, 10 ml of sulphuric acid (ca. 18 M), 25 ml of nitric acid (ca. 14 M), 10 ml of potassium permanganate solution (40 g l^{-1}) and 5 ml of sodium chloride solution (300 g l^{-1}). Heat and boil for 10 min. Cool and transfer quantitatively to a 100-ml standard flask. Just before the mercury measurement add 2 drops of hydroxyammonium chloride solution (100 g l^{-1}), dilute to volume with water and mix.

Remarks. A digestion should not normally take longer than 90 min (apart from overnight digestion in the cold if utilized). If more than 10 ml of potassium permanganate solution (40 g l^{-1}) is required in the digestion procedure, the presence of excessive quantities of oxides of nitrogen or an incomplete digestion should be suspected. In this case the quantity of potassium permanganate solution added can be increased to a total volume of 20 ml. Another indication of incomplete mineralization is excessive frothing during the aeration procedure. If the addition of 20 ml of potassium permanganate solution does not give a colour indicating the presence of an excess, or if excessive frothing occurs during the aeration, another method such as the Wickbold technique should be used.

When large amounts of organic matter are present during the final oxidation additional water is formed. It is then advisable to return the whole of the condensate to the digestion flask and repeat the operations of water removal and final oxidation.

Some samples of animal matter may leave an unoxidized oily residue. With fish tissue it has been established that this oil contains no mercury and may be ignored. In cases of doubt the oil should be separated off and subjected to a second digestion when it will usually dissolve. Alternatively, checks should be made with a Wickbold burner.

Some samples which contain large quantities of acid-insoluble matter may retain mercury in the insoluble residue left on digestion. This may be detected by filtering off the residue on an acid-resistant filter paper

(Whatman No. 541 or its equivalent) and carrying out a second digestion. If significant quantities of mercury are found, the samples should be analyzed by the Wickbold method.

Photometric measurement; calibration of photometer

Establish a calibration curve in the range 0—1 μg Hg as follows. Prepare 300 ml of a blank solution as described at the end of Digestion procedure. Introduce 50 ml of this solution into the aeration flask. Dilute to 60 ml with water, add 2 ml of tin(II) chloride solution (100 g l^{-1}), attach the aerator to the apparatus, swirl to mix and elute the mercury 30 s after the addition of the tin(II) chloride. Repeat this procedure with the addition of 0.2, 0.4, 0.6, 0.8 and 1.0 ml of standard mercury solution (1 mg Hg l^{-1}), selecting the recorder sensitivity to give an adequate peak height for the highest mercury standard. Convert the readings to absorbance (if necessary). Deduct the absorbance of the blank measurement from the other absorbances, and plot a calibration graph of absorbance against μg of mercury present. Between each aeration, empty and carefully rinse out the aeration flask. At the same time purge the gas circuit of the photometer, using a second aeration flask containing 5 ml of concentrated nitric acid and 55 ml of water.

Photometric measurement; examination of mineralized solution

Pipette an aliquot of the mineralized solution containing not more than 1 μg Hg and not exceeding 50 ml in volume into the aeration flask. Dilute to 60 ml with water, add 2 ml of tin(II) chloride solution (100 g l^{-1}), attach the aerator to the apparatus, swirl to mix and elute the mercury 30 s after the addition of the tin(II) chloride.

In recording the mercury elution peak, choose the recorder sensitivity to give an adequate peak height. Calculate the height of the peak which would have been obtained for the sensitivity used for the calibration and convert the result to absorbance (if necessary). Read off from the calibration curve the quantity of mercury present in the sample solution aliquot (see Note 2). Repeat the procedure on an aliquot of the blank solution of equal volume.

Remarks. The rate of elution of mercury from a mineralized solution after the addition of tin(II) chloride is practically always lower than that observed when additions are made to a blank solution. This is particularly true for solutions obtained from the treatment of large quantities of organic material. It is therefore always necessary to use standard additions. To achieve this, a new calibration is carried out as described above but using the mineralized solution instead of the blank solution.

The following factors must be considered when aliquots of the mineralized solution are taken: (a) the concentration of mercury in the liquid in the aeration flask must be in the range for which the instrument response is linear; (b) depending on the importance attached to the result, one or several additions can be made.

A 50-ml aliquot taken from a 100-ml dilution of all the reagents in the quantities used in a determination plus 2 ml of tin(II) chloride solution, should not yield an absorption equivalent to more than 0.1 μg of mercury.

Calculation from a calibration graph

$$\text{Hg (mg kg}^{-1}\text{)} = \frac{(C - C_0)V_2}{WV_1} \quad \text{or} \quad \text{Hg (mg l}^{-1}\text{)} = \frac{(C - C_0)V_2}{V_3 V_1}$$

where C = μg Hg in sample solution aliquot; C_0 = μg Hg in blank solution aliquot; V_1 = volume of sample/blank solution aliquot (ml); V_2 = volume of standard flask used (ml); V_3 = volume of liquid sample (ml); and W = weight of solid sample (g).

Calculation by the method of standard additions

$$\text{Hg (mg kg}^{-1}\text{)} = \left[\left(\frac{A_1 C_1}{A_2 - A_1}\right) - C_0\right] \frac{V_2}{WV_1} \quad \text{or} \quad \text{Hg (mg l}^{-1}\text{)} = \left[\left(\frac{A_1 C_1}{A_2 - A_1}\right) - C_0\right] \frac{V_2}{V_3 V}$$

where C_1 = μg Hg in the addition; C_0 = μg Hg in blank solution aliquot; A_1 = absorbance of mineralized solution without addition; A_2 = absorbance of mineralized solution with addition; V_1 = volume of sample/blank solution aliquot (ml); V_2 = volume of standard flask used (ml); V_3 = volume of liquid sample (ml); and W = weight of solid sample (g).

MINERALIZATION WITH NITRIC ACID IN A BOMB

Scope and field of application

This method is suitable for the determination of total mercury in materials containing organic matter (see Table 1). The lower limit of detection, based on the three-fold overall standard deviation of the blank on the reagents, is approximately 0.005 μg Hg/sample weight. The latter is a maximum of 0.5 g for solids and liquid organic materials and 1.0 ml for aqueous liquids. With such sample weights the lower limits of detection are 10 μg Hg kg^{-1} for the former materials and 5 μg Hg l^{-1} for the latter. In order to reduce all contamination to a minimum during measurement, the whole of the mineralized solution is subjected to photometry. This necessitates limiting the sample weight so that the amount of mercury measurable by photometry is not exceeded.

If six bombs are available and the mineralizations are all done together, 6 determinations can be carried out in 4 operator hours. This working time is that necessary for weighing out the samples, adding the reagent, calibrating the photometer, measuring the 6 solutions, calculating the results, and preparing the bombs for a further series of determinations.

Principle

The sample weight, prepared as described, is treated with nitric acid and maintained at a temperature of 140 °C in a bomb with PTFE inserts for a period of at least 15 h. After cooling, the whole of the mineralized solution is transferred to the aeration flask for examination by flameless atomic absorption.

Apparatus and reagents

An atomic absorption spectrophotometer and accessories and reagents as described previously [1] are required.

Steel bombs provided with PTFE inserts of approximately 20-ml volume, e.g. the bombs supplied by Uni-seal Decomposition Vessels Ltd (Israel), are used. After the decomposition, if no carbonaceous deposits are present, rinse the PTFE inserts with water, cover them with filter papers, dry in an oven at 125 °C and store in an empty desiccator. If deposits form, they can easily be removed by means of filter paper moistened with dilute nitric acid. The bombs are heated in an oven fitted with a thermostat adjusted to 140 °C and provided with a safety cut-out to turn off the electricity supply if the temperature exceeds 150 °C.

Safety precautions. The use of bombs presents certain hazards. It is therefore necessary to adhere strictly to the instructions in the procedure, particularly to those concerning the volume of the bomb, the temperature of use, the sample type and sample weight and the volume of nitric acid added. The bombs should only be handled at room temperature. It is recommended that the oven in which the bombs are heated is installed in an isolated room not used for any other purpose.

Mineralization of sample

Into the PTFE insert of the bomb place the sample containing no more than the maximum amount of mercury which can be measured by photometry. Use up to 0.5 g (weighed to 0.001 g) of solids or liquid organic materials, and up to 1 ml (measured to 0.02 ml) of aqueous liquids. Place the PTFE insert in the metallic case of the bomb. Add 5 ml of concentrated nitric acid (ca. 14 M), (see Note 4). Place the PTFE cover on the rim of the insert. Screw on the metal cover and place the closed bomb into the oven previously heated to 140 °C. Allow the digestion to proceed at this temperature for at least 15 h. Switch off the oven. Remove the bomb when the temperature is low enough (about 40 °C) and then allow to cool completely. In the same way prepare a blank by heating 5 ml of nitric acid (ca. 14 M) in the bomb.

Remarks. It is advisable to load the bombs during the afternoon and leave them in the oven overnight; these samples can then be examined by photometry the following morning.

The mineralization period required will vary with the nature of the sample. The 15-h period recommended will suffice in most cases.

Photometric measurement; calibration of photometer

Establish two calibration curves. The first corresponds to 0—0.2 μg Hg/ total liquid content of the aeration flask, and the second to 0—1.0 μg Hg. For each curve, choose the recorder sensitivity which gives the maximum peak height for the standard containing the highest quantity of mercury. Proceed as follows. Into the aeration flask introduce 5 ml of concentrated nitric acid (ca. 14 M) and then dilute to 60 ml with water. Swirl the aeration flask to mix the liquid. Remove the slight mist formed by the dilution of the concentrated acid by introducing the air delivery tube and holding it 1 cm above the surface of the liquid for about 30 s. Remove the air delivery tube, turn off the air, introduce 2 ml of tin(II) chloride solution (100 g l^{-1}) into the aeration flask, attach the aerator to the apparatus and swirl to mix the liquid. Elute the mercury 30 s after the addition of the tin(II) chloride. This measurement serves as a blank. Determine the other points of the calibration curve by introducing the following into the aeration flask in the order given: 5 ml of nitric acid (ca. 14 M); x ml of standard mercury solution (1 mg Hg l^{-1}) where x = 0.04, 0.08, 0.12, 0.16 and 0.2 ml for the first calibration curve and x = 0.2, 0.4, 0.6, 0.8 and 1.0 ml for the second; and water to a volume of 60 ml. For each mixture, proceed as described above, starting at "Swirl the aeration flask............".

Convert the peak height readings to absorbance (if necessary), deduct the absorbance of the measurement of the blank solution from all the other readings and construct calibration graphs of absorbance vs. μg of mercury present.

Between each elution empty and carefully rinse out the aeration flask. At the same time purge the gas circuit of the photometer using a second aeration flask containing 5 ml of concentrated nitric acid (ca. 14 M) and 55 ml of water.

Photometric measurement; examination of mineralized solution

After cooling the bomb completely, open it and blow gently over the solution with gentle agitation in order to remove dissolved oxides of nitrogen. The solution must be pale yellow to colourless, clear and free from charred matter.

Transfer the mineralized solution together with any insoluble matter present quantitatively to the aeration flask. Rinse the PTFE bomb insert and its cover with water into the aeration flask and dilute to 60 ml with water. Follow the procedure described under "Calibration of photometer", starting with "Swirl the aeration flask............". In recording the mercury peak, choose the recorder sensitivity to give an adequate peak height. Calculate the height of the peak which would have been obtained for one or the other of the two sensitivities used for the calibration and convert the reading to absorbance (if necessary). Read from the corresponding calibration curve the quantity of mercury present in the sample solution (see Note 2).

Remarks. Any leakage of the bomb will lead to low results. It is therefore advisable to carry out the determinations in duplicate.

All the reagents used in the proportions of 5 ml of nitric acid + 55 ml of distilled water + 2 ml of tin(II) chloride solution should not produce an absorption equivalent to more than 0.005 μg of mercury.

Calculation

$$\text{Hg (mg kg}^{-1}) = \frac{(C - C_0)}{W} \quad \text{or} \quad \text{Hg (mg l}^{-1}) = \frac{(C - C_0)}{V}$$

where C = μg Hg in sample solution; C_0 = μg Hg in blank solution; V = volume of sample (ml); and W = weight of sample (g).

COMBUSTION IN THE OXY—HYDROGEN FLAME (WICKBOLD COMBUSTION)

Scope and field of application

The method is suitable for the determination of total mercury in materials containing organic matter (see Table 1). The lower limit of detection based on the three-fold overall standard deviation of the blank on the reagents and gases is 0.08 μg Hg/sample weight. With a 10-g sample for solids and a 50-ml sample for liquids, the limits of detection are 8 μg Hg kg^{-1} and 2 μg Hg l^{-1}, respectively.

The combustion step requires 10—20 min depending on the type of sample. This means that the total operator time per sample allowing for instrument calibration and analysis of the sample solutions but excluding the time necessary for carrying out blanks, is 35—45 min.

Principle

The samples, prepared as described, are burned in the Wickbold apparatus with either a solids burner or a liquids burner. Some flammable liquids may be burned undiluted but viscous, non-flammable and aqueous liquids are diluted with an equal volume of acetone or methanol. Carbon tetrachloride is also added if the sample contains no chlorine. Solid samples are burned in a quartz boat in a specially modified solids burner in which the decomposition is started in an atmosphere of nitrogen which is gradually replaced by oxygen to oxidize the residue. In order to ensure the presence of chlorine throughout the combustion the gas entering the chamber of the solids burner is passed through a small saturator containing carbon tetrachloride. The mercury is absorbed in potassium permanganate—sulphuric acid solution and determined by flameless atomic absorption.

Apparatus and reagents

An atomic absorption spectrophotometer and accessories and reagents are used as described previously [1]. In addition to normal laboratory glassware several 150-ml standard volumetric flasks are needed. The Wickbold apparatus is supplied by Heraeus in three basic versions but numerous minor modifications exist. The equipment used for much of the work quoted here is basically a Heraeus High Capacity burner (Type 2) with modifications as detailed below. The Heraeus standard burner (Type 1) or the continuous burner (Type 3) could be used, but combustion rates, sample weights and gas flows would need to be modified.

Apparatus for the combustion of liquids. The following quartz or borosilicate glass components are required:

(1) Heraeus High Capacity suction burner SB2.

(2) Heraeus High Capacity combustion chamber with condenser C2; for convenience, the cone and socket joint on the exit of this is replaced with a ball and socket joint.

(3) Heraeus absorption vessel D2; to cut down liquid dead volume the three-necked flask in the Heraeus version is removed, and the absorber inlet fitted with a three-way tap of the type used on the Heraeus standard absorption vessel D1 and a ball and socket joint to fit the exit from the combustion chamber.

(4) Splash trap; to prevent liquid hold-up, the drain hole in the gas inlet must coincide with the bottom of the inner surface of the bulb (see Fig. 5).

Apparatus for the combustion of solids (see Fig. 3). This includes the same components as described for liquids, except for the following parts:

(1) Heraeus High Capacity solids burner AB modified [11] to accommodate a larger sample boat fitted with a quartz perforated disc between sample boat and burner, and with two inlets for oxygen 1; in this arrangement, oxygen 1 can either be guided over the sample or by-passed to the flame (see Fig. 4).

(2) Quartz boat 150 mm long, 15 mm deep and 20 mm wide.

Gas supplies and controls. Cylinders of hydrogen, oxygen and nitrogen, fitted with pressure regulators in the range 0—20 kg cm^{-2}, are required with flow-meters fitted with needle valves as follows: hydrogen, 80—800 l h^{-1}; oxygen 1, 200—2000 l h^{-1} (for enriching the sample with oxygen); oxygen 2, 80—800 l h^{-1} (for oxy-hydrogen flame); nitrogen, 25—250 l h^{-1}.

A 100-ml glass flask containing carbon tetrachloride is arranged so that the nitrogen entering the gasification chamber passes over (not through) the carbon tetrachloride.

The high-capacity water ejector, made of plastic, has an extraction rate of ca. 3000 l h^{-1}. A Model F2 ejector (Weineck & Co., Volmerswerther Strasse 26-30, Düsseldorf) is suitable. The vacuum gauge is a +50 to −4000-mm

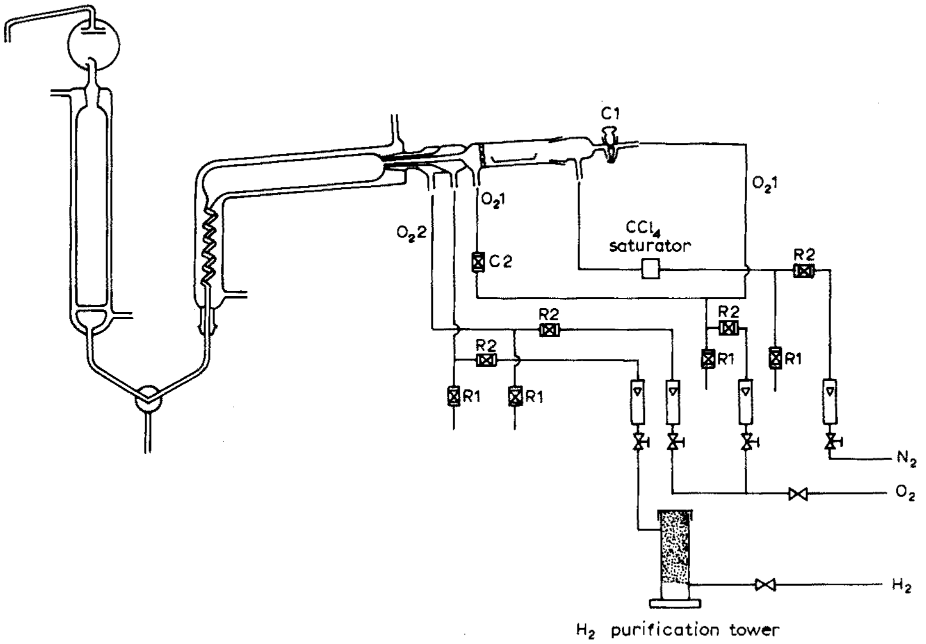


Fig. 3. Circuit for the combustion of solid samples with the Wickbold burner.

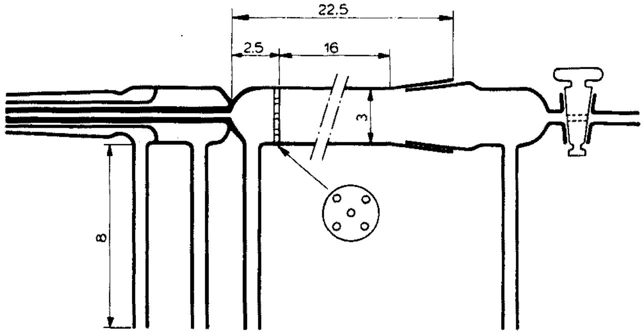


Fig. 4. Modified Heraeus AB solids burner (dimensions in cm).

water gauge fitted with a stainless steel needle valve.

The packing of the hydrogen purification tower (design pressure 20 kg cm^{-2}) is iodized charcoal (preferably 1/8-in pellets) kept in place by a layer of cotton wool on a perforated steel plate at the bottom and a perforated steel plate covered by glass beads and tightly packed cotton wool at the top. It is important to locate this purifier between the pressure regulator and needle valve. (This type of purifier must never be fitted on oxygen lines because of violent reaction between compressed oxygen and carbon.)

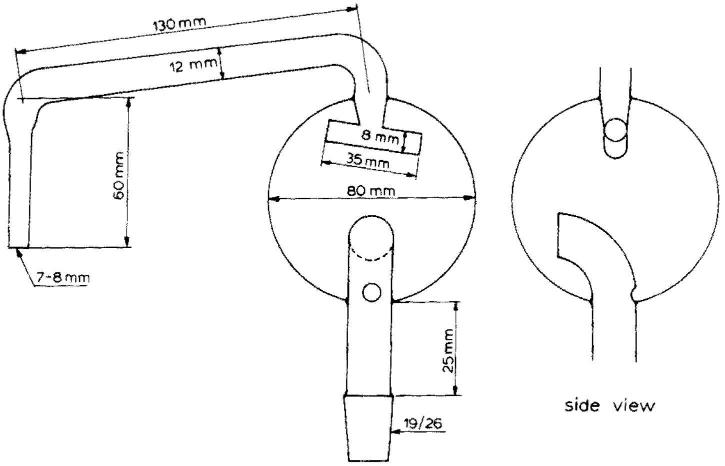


Fig. 5. Modified splash head.

All the gas lines are fitted with one-way valves R2 and pressure-release valves R1. The former are intended to prevent cross-contamination of the gas supplies in the event of a blockage, and the latter to prevent over-pressurizing the glassware (it is possible that joints will also blow). Suitable R2 valves are supplied by Heraeus; alternatively Nupro Check Valves Type 4C (Techmation) in brass with Buna N seats (opening pressure 1 p.s.i.) may be used. Suitable R1 valves are Nupro Check Valves Type 4C (Techmation) in brass with Buna N seats (opening pressure 10 p.s.i.). The hydrogen valve R1 must be vented to a safe location; it is convenient to fit small bubblers to all the pressure relief valves to indicate when venting occurs.

Two gas burners are provided under the solids burner gasification tube on a horizontal sliding bracket the same length as the tube.

All flexible gas and water connections should be made with silicone rubber tubing. Closure C2 on the oxygen 1 line is a screw clip on the silicone rubber tubing.

All the glass and quartz components and the flow-meters should be surrounded by a transparent plastic safety screen. An additional removable blue screen may be hung on in front of the burner to prevent eye damage from the light emission of the flame.

Safety precautions. The use of mixtures of hydrogen and oxygen presents certain hazards. It is essential therefore to use the plexiglass screen provided with the apparatus and to adhere strictly to the instructions on the order of operation of the gas valves when lighting and extinguishing the flame.

Combustion of solid samples

Set up the apparatus with the hydrogen burner and the splash trap disconnected. Weigh the sample to the nearest 0.01 g and transfer to the quartz boat.

Into the absorption vessel place 5 ml of potassium permanganate solution (40 g l^{-1}), 1 ml of (1 + 4) sulphuric acid and 5 ml of water (see Note 4).

Attach the splash trap and the vacuum line, turn on the water ejector and adjust the vacuum gauge reading to −1800 mm water with the needle valve. Turn on the cooling water. With all the needle valves on the flow-meters closed, open the gas cylinder valves and adjust the pressure regulators to 5 kg cm^{-2}. Set the gas flows at the following rates by means of the needle valves: oxygen 1, 600 l h^{-1}; oxygen 2, 300 l h^{-1}; hydrogen, 400 l h^{-1}.

Ignite the hydrogen burner and insert it into the combustion chamber with the gas inlet tubes inclined at an angle of approximately 45° to the vertical to allow room for the gas burners behind them. Oxygen 1 is by-passed to the flame. Insert the sample boat into the gasification chamber, attach the ground-glass joint and turn on the nitrogen supply to 250 l h^{-1}. The vacuum reading should now be between −3000 and −4000 mm water on the gauge. If necessary, adjust its value by adjusting the oxygen 1 flow. Attach the gas burners, one fixed to heat the gasification chamber downstream of the disc, in order to prevent blockage of the burner jet, and the other on the sliding bracket at the end of the sample boat farthest away from the disc. Light both burners and move the one under the sample boat slowly along the bracket so that the sample is charred. Return the burner to the end of the sample boat away from the disc and slowly start passing some oxygen 1 into the gasification chamber. Continue moving the gas burner back and forth along the bracket, by-passing oxygen 1 momentarily if the combustion becomes too violent. Finally pass all oxygen 1 via the gasification chamber, turn off the nitrogen flow at the needle valve, and complete the combustion in an atmosphere of pure oxygen. Turn off the gas burners, disconnect the burner from the apparatus, turn off the hydrogen supply and then the oxygen supply, unless further samples are to be analyzed. Remove the ground joint from the gasification chamber, tip the sample boat on to an asbestos sheet and allow to cool.

Rinse out the combustion chamber with a small amount of water and then disconnect the vacuum line. Remove the splash trap and rinse it with a small amount of water into the absorption vessel. Place a 150-ml volumetric flask under the run-off from the absorber and operate the bottom tap to run the absorber contents into it. (Passage of the liquid through the sinter may be assisted by applying slight air pressure to the top of the absorber.) Rinse the walls of the absorber with 5 ml of hydroxyammonium chloride solution (100 g l^{-1}) and allow to stand for a few minutes to solubilize manganese dioxide. Blow into the flask as before, rinse the absorber with a small amount of water and blow into the flask. Dilute the contents of the flask to volume with water and mix.

Note the time required for combustion and carry out a blank determination using the same gas flows for the same period.

Combustion of liquid samples

Set up the apparatus with the hydrogen burner and the splash trap disconnected.

Prepare the sample as follows. For flammable liquids of low viscosity, add 3 ml of carbon tetrachloride to 100 ml of sample. For flammable liquids of high viscosity and for aqueous liquids, dilute 50 ml of sample with 50 ml of methanol or acetone and add 3 ml of carbon tetrachloride. For chlorinated hydrocarbons, dilute 50 ml of sample with 50 ml of methanol or acetone. Place the sample in a 150-ml conical flask.

Charge the absorption vessel, and make the initial settings on the apparatus in the same way as described above for the combustion of solid samples, but set the gas flows at the following rates: oxygen 1, 600 l h^{-1}; oxygen 2, 400 l h^{-1}; hydrogen, 400 l h^{-1}.

Ignite the hydrogen burner and insert it into the combustion chamber with the aspirator tap closed. The vacuum reading should now be between —3000 and —4000 mm water on the gauge. If necessary, correct its value by adjusting the oxygen 1 flow.

Place the sample container under the suction burner and slowly open the tap so that sample is drawn into the burner. The exact adjustment of the tap requires some experience; if the flame is sooty the sampling rate is too high. The correct rate is 5—7 ml min^{-1}, giving a flame approximately three quarters the length of the combustion chamber. When the sample has almost gone, tilt the flask so that the last traces are drawn up. Rinse the flask with a small amount of acetone or methanol and aspirate this into the burner.

Disconnect the burner and turn off the hydrogen supply and then the oxygen supply, unless further samples are to be analysed. Rinse the combustion chamber with a small amount of water and then disconnect the vacuum line and the splash trap. Rinse the splash trap with a small amount of water into the absorption vessel. Place a 150-ml volumetric flask under the run-off from the absorber and then proceed as described for the combustion of solid samples.

Note the time required for combustion and carry out a blank determination using the same gas flows for the same period together with the same volumes of carbon tetrachloride and acetone or methanol added to the sample.

Photometric measurement; calibration of photometer

Establish a calibration curve in the range 0—1 μg Hg as follows. Prepare 300 ml of a stock solution containing 10 ml of potassium permanganate solution (40 g l^{-1}), 2 ml of (1 + 4) sulphuric acid and 10 ml of hydroxyammonium chloride solution (100 g l^{-1}). Dilute to volume with water and mix. Pipette 50 ml of this solution into the aeration flask, dilute to 60 ml with water, add 2 ml of tin(II) chloride solution (100 g l^{-1}), attach the aerator to the apparatus, swirl to mix and elute the mercury 30 s after the addition of the tin(II) chloride. Repeat this procedure with the addition of 0.2, 0.4, 0.6, 0.8 and 1.0 ml of standard mercury solution (1 mg Hg l^{-1}), selecting the recorder sensitivity to give an adequate peak height for the highest mercury standard. Convert the readings to absorbance (if necessary) and deduct the absorbance of the blank measurement from the other absorbances before plotting the calibration graph.

Between each aeration, empty and carefully rinse out the aeration flask. At the same time purge the gas circuit of the photometer using a second aeration flask containing 5 ml of concentrated nitric acid and 55 ml of water.

Photometric measurement; examination of mineralized solution

Pipette an aliquot of the solution containing no more than 1 μg Hg and not exceeding 50 ml into the aeration flask. Dilute to 60 ml with water, add 2 ml of tin(II) chloride solution (100 g l^{-1}). Immediately attach the aerator to the apparatus, swirl to mix and elute the mercury 30 s after the addition of the tin(II) chloride. In recording the mercury elution peak choose the recorder sensitivity to give an adequate peak height. Calculate the height of the peak which would have been obtained for the sensitivity used for the calibration and convert the reading to absorbance (if necessary). Use the calibration curve to establish the quantity of mercury present in the sample aliquot (see Note 2).

Repeat the procedure on an aliquot of the blank solution of equal volume.

Remarks. All the reagents used, including the compressed gases, should not produce an absorption greater than that equivalent to 0.1 μg Hg for a combustion time equivalent to that necessary for burning a 10-g sample, when a 50-ml aliquot of the absorption solution is taken. It is recommended that an average blank should be obtained by carrying out 10 blank runs in succession and thereafter a daily blank carried out. If the daily blank is within the range of twice the standard deviation of the average blank, the latter should be used; if it is not, a new average blank should be derived from a further series of 10 blank runs.

If the apparatus is new, or if it has not been used for some time, very high amounts of mercury may be found in the first determination. To avoid this, it is advisable to clean the apparatus with nitric acid, and to check a blank determination with the analysis gas flows and time.

Calculation

$$\text{Hg (mg kg}^{-1}) = \frac{(C - C_0)\,V_2}{W V_1} \quad \text{or} \quad \text{Hg (mg l}^{-1}) = \frac{(C - C_0)\,V_2}{V_3 V_1}$$

where C = μg Hg in sample solution aliquot; C_0 = μg Hg in blank solution aliquot; V_1 = volume of sample/blank solution aliquot (ml); V_2 = volume of standard flask used (ml); V_3 = volume of liquid sample (ml); W = weight of solid sample (g).

Notes to the three methods given

These notes are in addition to notes 1, 3 and 5 given previously [1].

1. *Reduction solution.* Add 1—2 g of metallic tin after preparation of the tin(II) chloride solution. Remove traces of mercury from this solution by aeration with nitrogen for 30 min. Tin(II) ions are oxidized by air to tin(IV), and so the reduction solution is useless after it has become turbid.

2. *Matrix effects.* The presence in the solution of ions which form complexes or compounds of low solubility with mercury(II) or (I) diminishes the absorbance of the mercury elution peaks, all other things being equal. The presence of chloride above a concentration of 2.5 g/60 ml in the aeration flask therefore causes low results. In the presence of bromide and iodide, this effect appears at even lower concentrations, particularly in the case of iodide, which forms very stable complexes with mercury.

These ions also cause a major decrease in the speed of reduction of mercury by tin(II) chloride. Accordingly, it is advisable when their presence in significant concentrations is suspected, to prolong the delay between the introduction of the tin(II) chloride and the aeration, in order to obtain reproducible signals. In such cases the calibration curve is invalid and it is necessary to resort to the method of additions given below.

Control tests for matrix effects. Interferences from matrix effects in the sample solution can be detected by making standard additions. This is done by repeating the calibration procedure with aliquots of the sample solution instead of the stock solution as described in "Photometric measurement; calibration of photometer". The sample solution aliquots should be of an equal volume to that used in "Photometric measurement; examination of mineralized solution" and depending on the importance of the sample the whole calibration graph or just one point may be measured. It is important in carrying out this procedure to ensure that the mercury in the sample aliquot plus the addition does not exceed the amount for which the response of the instrument is linear, and that the same tin(II) chloride reaction time is used throughout.

The presence of matrix interference is indicated by a lower slope for the standard addition graph than for the original calibration graph. If this occurs the method of standard additions should be used for all samples of that type.

3. *Aeration flasks.* It is recommended that the same aeration flask be used for the elution of standard and sample solutions. Between each test, rinse

the aeration flask with water. To guard against the effect of tin(II) chloride residues, a small amount of bromine water may be added to the rinse water. Always finish by rinsing carefully with water before re-using the aeration flask.

4. *Reagent dispensers.* To minimize contamination, the reagents to be used for the mineralization should be stored in flasks fitted with dispensing syringes of the appropriate volume. This arrangement, if used permanently, minimizes the need for pipettes.

TESTING THE METHODS

The methods were tested in three ways. During the development stage of the methods, tests were made by adding different amounts of mercury compounds to different sample types to test recovery rates. At that stage some comparative tests were also performed on a small scale. Finally, inter-laboratory tests were performed by many of the laboratories that participate in BITC in order to prove that comparable results can be obtained with the different methods by different laboratories.

Recoveries of mercury

Many experiments were done to see how much mercury could be recovered by analysis of samples to which different mercury compounds had been added, or of samples of known mercury content. Samples with known mercury contents used, were Orchard Leaves (National Bureau of Standards, Standard Reference Material 1571, mercury content 155 ± 15 μg kg^{-1}) and tablets containing phenyl-mercury borate (mercury content 236 mg kg^{-1}). Other samples are given in Table 2, with recoveries. These recoveries were determined by standard addition of mercury(II) chloride to a mineralized sample for preparation of the calibration graph, as described in "Wet Oxidation" under "Remarks"; then a known amount of a mercury compound was added to another aliquot of the sample, the aliquot was mineralized, and the mercury content determined. The recovery rate was calculated from:

$$\frac{(\text{Hg found}) - (\text{Hg content of sample aliquot})}{\text{Hg added}} \times 100\ \%$$

It must be pointed out that the results in Table 2 are presented as the range between the lowest and highest results (obvious extreme values excluded), and that there was a tendency for the range to become larger as the number of determinations increased. Nevertheless, this form of reporting the results has been chosen, because it gives more information than the mean, which in most cases is close to 100 % recovery for the sample types for which the method is recommended (see Table 1). For Orchard Leaves, the results are in the range specified by N.B.S.; for the tablets, the results differ rather more, but because of the very high mercury content the sample size for each determination had to be very small.

TABLE 2

Recovery of mercury by the three methods of decomposition

Sample	Hg added[a] ($\mu g\ kg^{-1}$)	% Hg recovery		
		Wet digestion	Bomb	Wickbold
Orchard leaves	155 ± 15 (=±10 %)	95	98—107	93—94
Tablets	236000 ± 1.5 %	95—103	98—101	96—99
as solution in ethanol		94—99	n.r.[b]	99—105
Shellfish, fish	300—10000	86—105	94—117	72—120
Fish meal	100—150	95—102	100—105	98—108
Soya bean oil; sunflower oil	2000	n.a.[c]	n.a.	94—100
Soil	1000—2000	86	97	n.a.
Grass	100—500	94	n.r.	95—98
Urine	200—1000	99	97—113	n.r
Water	1000	98—105	98—105	100—105
Methanol, acetone		97—105	108—113	90—110
Chlorinated hydrocarbons	500—36500	n.a.	n.a.	87—112
Dimethylmercury, diethylmercury		(65—82)	n.r	n.r
in water/ethanol		n.a.		

[a] Mercury compounds added: methylmercury chloride, phenylmercury chloride, phenylmercury borate or mercury(II) chloride.
[b] n.r.; no results.
[c] n.a.; method not applicable (see Table 1).

During this work, many comparative tests were also performed to see if two laboratories could obtain the same results with one method or if another method gave the same result for a given sample. When these tests showed good results, it was agreed that the methods seemed to be reliable and that an interlaboratory test on a large scale could be set up to prove this.

Interlaboratory tests and results

An interlaboratory test of the methods by sending samples to the laboratorie that participate in BITC proved to be very difficult to organize. Many of the types of sample that can be analyzed by these methods are difficult to obtain in large homogeneous quantities, are subject to drastic changes in composition with time, are difficult to transport, or cannot be analyzed by all three methods (see Table 1). The NBS Standard Orchard Leaves could not be obtained in the quantity necessary for these interlaboratory tests. Finally, an attempt was made to use hair, wheat flour and fish meal. It is possible to analyze these samples by all the three methods given. This is important, not only for comparison of the performance of the three methods, but also to make possible the participation of more laboratories. Because BITC is an organization of chlorine producers, many laboratories are better equipped for inorganic analysis than for organic analysis, so that only a few have the equipment and experience necessary for all three methods of mineralization. It was possible to participate in two interlaboratory tests for wheat flour and fish meal, organized by a German group of government and research laboratories, but only the results of BITC member laboratories are presented here.

Sample preparation and results

The first interlaboratory test was carried out with wheat flour and fish meal. Samples were taken from a large quantity of material by the German group of laboratories and sent to the participants for analysis in mid-1974. From the results it was obvious that the mercury content of wheat flour was too low (about 3 μg kg^{-1}) for determination by any of the three methods. The fish meal was analyzed mainly by the wet oxidation procedure; only two laboratories used the bomb method and four the combustion method. However, some laboratories found very low results by the wet oxidation method, so that the results were not used for statistical evaluation. After the interlaboratory test, the description of the procedure for the wet oxidation method was improved. It was found that the mercury content of fish meal depends somewhat on the particle size of the meal. Accordingly, for the next interlaboratory test, fish meal of a certain, small particle size was used, the fraction was homogenized carefully, and some parts of this fraction were analysed in advance to see if consistent results could be obtained. As this proved to be the case, the fraction was used for the second interlaboratory test on fish meal during the spring of 1975, the results of which are given in Table 3.

An interlaboratory test with human hair was performed during December, 1974. Again, because of the large amount of material necessary, there were difficulties in preparing sufficient homogeneous material. When hair is mixed, static electric charges soon build up and make mixing very difficult; therefore, it was decided to grind and mix the hair at low temperature. The raw material was mixed with solid carbon dioxide and ground in a mill, and the resulting powder was homogenized in a tumbler mixer. In order to grind enough material, this procedure had to be repeated several times. In order to obtain an indication of the degree of homogeneity, five samples were taken when about half the material was ready. The results showed an average of 980 μg Hg kg^{-1} with a relative standard deviation of 6.2 %. Since this error was the total error arising from inhomogeneity and from the method itself, it was assumed that the procedure for grinding and mixing was satisfactory. Therefore, the second part of the material was treated in the same way; a single sample gave a result of 1000 μg Hg kg^{-1}, which was in good agreement with the previous results. Consequently the sample was distributed to the participants; the analytical results are given in Table 3.

TABLE 3

Results of interlaboratory analysis for mercury (in μg Hg kg^{-1})
(The numbering of the laboratories is the same for the different methods and samples)

Lab. No.	Hair sample					Fish meal sample				
				Mean	s_r (%)				Mean	s_r (%)
Method 1[a]										
2	924	912	941	926	1.6	277	300	284	287	4.1
4	830	980	960	923	8.8	250	280	280	270	6.4
6	1760	1720	1720	1733	1.3	302	328	318	316	4.2
7	3900	4100	4200	4067	1.3	360	355	360	358	0.8
8	800	770	710	760	6.0	310	310	280	300	5.8
10	3000	2810	2680	2830	5.7	260	300	280	280	7.1
11	1150	1050	1050	1083	5.3	260	300	280	280	7.1
12	3530	3200	3520	3417	5.5	300	300	330	310	5.6
13						264	279	298	280	6.1
14	6180	6260	4880	5773	13.4	279	316	308	301	6.5
15	999	942	1012	984	4.0	250	285	265	267	6.6
16						302	306	295	301	1.8
17	1060	1060	1070	1063	0.5	358	378	360	365	3.0
18	1070	1110	1170	1117	4.5	183	194	191	189	3.0
19	620	700	710	677	7.3	250	256	256	254	1.4
20						524	489	506	506	3.5
21	1530	1600	1560	1563	2.2	310	327	294	310	5.3
22	5100	4800	5800	5233	9.8					
23	3590	3730	3550	3623	2.6					
24	455	467	481	468	2.8					
25	2165	2190	2500	2285	8.2					
Method 2										
1	5080	4900	4920	4967	2.0	330	325	325	327	0.9
3	5700	5900	5300	5633	5.4	298	296	280	291	3.4
6	1880	1950	2100	1977	5.7	323	327	325	325	0.6
7[b]	3900	3700	3500	3700	5.4	330	360	340	343	4.4
7	830	800	900	843	6.1	350	340	345	345	1.4
7						350	355	345	350	1.4
9						465	340	330	378	19.9
11						270	310	300	293	7.1
14[b]	4180	4260	4250	4230	1.0	316	304	301	307	2.6
14	4060	4170	4120	4117	0.8	309	303	316	309	2.1
15	877	682	815	791	12.6					
17	1050	990	1020	1020	2.0	383	379	373	378	1.3
17	1190	1140	1010	1113	8.3					
19						308	315	315	313	1.3
21	1760	1740	1740	1747	0.7	319	327	331	326	1.9
21	1500	1500	1470	1490	1.2					

TABLE 3 (continued)

Lab. No.	Hair sample					Fish meal sample				
				Mean	s_r (%)				Mean	s_r (%)
Method 3										
1	4830	4710	4770	4770	1.3					
5						290	300	290	293	2.0
6	3600	3700	3500	3600	2.8	335	340	345	340	1.5
7	550	590	570	570	3.5					
17	1030	1050	1030	1037	1.1	260	250	390	300	26.0
17						390	400	390	393	1.5
21						251	260	251	254	2.0

[a]Methods: 1, Wet oxidation under reflux with nitric and sulphuric acids. 2, Digestion with nitric acid in a bomb. 3, Combustion in an oxy-hydrogen flame.
[b]Laboratories 7 and 14 analyzed two different hair samples.

Statistical procedures

The procedures followed were the same as those used in Part I [1]. The statistical evaluation was done according to the document ISO/TC 69/GTA (October, 1972) of the International Organization for Standardization and the German document DIN 51848. The means, repeatabilities and reproducibilities of the results are given in Table 4. For the interlaboratory test on fish meal, the results of the three methods were tested for significant differences by the F- and T-tests.

Discussion and conclusions

For hair, the results of the different laboratories show a great variety, with figures ranging from 500 to 6000 μg Hg kg^{-1}. The reproducibility is very bad with a relative standard deviation of 70 %! The results are so evenly spread that no set of results could be eliminated because of lack of reproducibility. However, the within-laboratory results show reasonably good repeatability, the relative standard deviation being 4.4 % (Table 4), which compares well with the value for fish meal. This strongly suggests that the original ground material was not mixed well, although the sample received by each participant was homogeneous in itself, because of mixing either during transport or before analysis started. This idea is supported by the following facts. When laboratory no. 7, which is closely related to the laboratory that prepared the sample and knew the results of the advance analyses, obtained high results, the rest of its sample was sent to laboratory no. 14 which also found a high mercury content (Table 3, method 2, lab. 7, first line; lab. 14, second line). Laboratory 7 then asked for a second sample and found a completely different result (method 2, lab. 7, second line). Some laboratories used more than one destruction method for the determination of mercury in the sample received (Table 3, labs. 1, 6, 7, 14, 15, 17, 21), and found consistent results. We

TABLE 4

Results of statistical evaluation of interlaboratory analysis for mercury

Sample	Hair	Fish meal			
Method	all	1	2	3	all
Number of participating laboratories	20	17	10	4	21
Sets of three results eliminated:					
Because of lack of repeatability	3	0	1	1	2
Because of lack of reproducibility	0	1	0	0	1
Results					
Arithmetic mean, $\mu g\ kg^{-1}$	2048	292	326	320	308
Repeatability[a]					
Standard deviation, $\mu g\ kg^{-1}$	90.3	14.7	9.2	5.4	12.0
Relative standard deviation, %	4.4	5.0	2.8	1.7	3.9
Reproducibility[a]					
Standard deviation, $\mu g\ kg^{-1}$	1423	42.4	26.4	60.3	41.8
Relative standard deviation, %	70	14.5	8.1	18.8	13.6

[a] Repeatability means single-laboratory, single-operator and single-apparatus precision; reproducibility means multi-laboratory, multi-operator and multi-apparatus precision.

therefore decided to include these results in this paper, because some of the goals of the interlaboratory test were achieved, and because it shows something of the great difficulties encountered with interlaboratory tests of this kind.

For the second test on fish meal, the results were much better. As can be seen from Table 4, the mean of the results is lowest for method 1. This method seems to be the easiest to carry out and needs no costly apparatus, so that some laboratories without much experience with this type of analysis used only this method; losses of mercury are then somewhat more likely (see "Introduction"). If the lower result with method 1 is not the result of inexperience in some laboratories, tests can be used to establish if the results obtained with the methods differ significantly; statistically, this proved not to be the case, so that all results belong to the same population. The results of this interlaboratory test and the results of the recovery tests indicate the value of the three procedures given.

ZUSAMMENFASSUNG

Beschrieben werden drei Verfahren zur Zerstörung organischen Materials in Proben, in denen anschliessend das gesamte Quecksilber durch flammenlose Atomabsorptions-Spektrophotometrie bestimmt werden kann. Die Methoden sind auf eine grosse Zahl von Probenarten anwendbar. Sie sind für spezielle Probenarten nicht immer die schnellsten Verfahren; aber sie sollten als Schiedsmethoden gesehen werden, mit deren Hilfe man andere Methoden auf ihre Zuverlässigkeit überprüfen kann und die von den Mitgliedsfirmen des Bureau International Technique du Chlore als verbindliche Methoden anerkannt wurden. Die Ergebnisse von Ringanalysen mit 25 teilnehmenden Industriellaboratorien werden dargestellt. Bei einer Fischmehlprobe ergab die statistische Auswertung einem

Quecksilbergehalt von 308 μg kg^{-1} und eine Wiederholbarkeit von 3,9 % und eine Reproduzierbarkeit von 13,6 %.

RÉSUMÉ

Comme le prétraitement de la détermination de mercure total par absorption atomique sans flamme on décrit trois méthodes permettant la destruction de matériaux organiques. Cettes méthodes étaient acceptées comme des méthodes de réference par les sociétés membres du Bureau International Technique du Chlore. Les méthodes sont applicables à une grande variété de types d'échantillons. Celles-ci ne seraient pas toujours les plus rapides pour chaque type d'échantillons, mais celles on doit considérer comme des méthodes de référence. Pour vérifier les méthodes, on a procédé à des essais circulaires auxquels ont pris part 25 laboratoires industriels. Pour une échantillon de farine de poisson une teneur en mercure de 308 μg kg^{-1} est trouvée avec un échantillon de farine de et une reproductibilité de 13,6 %.

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AN ENZYME ELECTRODE BASED ON IMMOBILIZED ARYLSULFATASE FOR THE SELECTIVE ASSAY OF SULFATE ION

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SUMMARY

An enzyme electrode has been constructed for the assay of sulfate ion based on inhibition of the reaction

$$\text{4-Nitrocatechol sulfate} + H_2O \xrightarrow[\text{sulfatase}]{\text{aryl-}} \text{4-nitrocatechol} + SO_4^{2-}$$

The steady-state current arising from oxidation of the product, 4-nitrocatechol, is measured at +0.8 V vs. S. C. E. The competitive inhibition of this reaction by added sulfate ion causes a decrease in this steady-state current in a linear relationship to pSO_4 in the range 2—4. The enzyme arylsulfatase (arylsulfate sulfohydrolase, EC 3.1.6.1) is chemically immobilized in a layer on a platinum electrode. This enzyme electrode also gives linear calibration plots for phosphate ion (10^{-2}—10^{-4} M) based on its competitive inhibition of the above reaction, and for fluoride ion (10^{-2}—10^{-4} M) based on its activation of the reaction. The assay of 4-nitrocatechol sulfate (NCS) in the range 10^{-4}—10^{-6} M is possible. By proper control of the NCS concentration the electrode can be made almost completely specific for sulfate: only molybdate interferes. To establish the best operating conditions for the electrode, the effect of pH on the V_m and K_m were determined.

Because of the high sensitivity and selectivity of enzymes, their application as analytical reagents has been quite fruitful, especially in the assay of organic substrates of biological importance [1]. Such techniques have also been suggested for the assay of a few inorganic anions, such as nitrate, nitrite and phosphate ion [1], and have advantages over standard procedures which require prior separation steps to avoid interference from other species [2]. A non-enzyme type of electrode for sulfate was proposed by Mohan and Rechnitz [3], but is difficult to fabricate.

Enzymatic assays for anions based on soluble enzymes and spectrophotometric methods have been proposed for phosphate [2, 4—6] and sulfate [6]. A new principle for assay of such anions (phosphate), an enzyme electrode with immobilized enzymes, was described by Guilbault and Nanjo [7], and is the only enzyme electrode for either of these oxy anions. These authors used the alkaline phosphatase-catalyzed hydrolysis of glucose-6-phosphate, which is inhibited by phosphate ion (eqn. (1)). The reaction was followed by an indicator reaction (eqn. (2)) with glucose oxidase

$$\text{Glucose-6-phosphate} + H_2O \xrightarrow[\text{Phosphatase}]{\text{Alkaline}} \text{Glucose} + HPO_4^{2-} \tag{1}$$

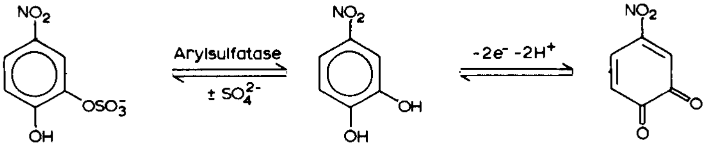
$$\text{Glucose} + O_2 \xrightarrow[\text{Oxidase}]{\text{Glucose}} \text{Gluconic Acid} + H_2O_2 \tag{2}$$

A similar enzymatic principle has been applied in this work to the electrochemical assay of sulfate. The hydrolysis of arylsulfate catalyzed by arylsulfatase (arylsulfate sulfohydrolase, EC 3.1.6.1) is used

$$\text{Ar—O—}SO_3^- + H_2O \xrightarrow{\text{Arylsulfatase}} \text{Ar—OH} + HSO_4^- \tag{3}$$

There are two types of arylsulfatase: Type I, which is not inhibited by sulfate, and Type II, which is [8]. However, there are three subclasses of Type II enzyme, differences occurring in the activation effect of chloride and the basic kinetic properties. The enzyme from *Helix pomatia* [9] has been shown to exhibit normal kinetics, and is not affected by chloride. The kinetic data for this arylsulfatase and the substrates most commonly used are given in Table 1.

Since the electrochemical oxidation of the catechol is a fairly reversible 2e$^-$ process at solid electrodes in aqueous media [13], the 2-hydroxy-5-nitrophenyl sulfate (4-nitrocatechol sulfate, NCS) was chosen as substrate for an amperometric enzyme system as follows:



(4)

It can be seen from Table 1 that there are at least three serious interfering anions of this reaction. An enzyme electrode fabricated with immobilized arylsulfatase was found to give linear responses toward sulfate, phosphate and fluoride anions as well as to the substrate, NCS. However, at a certain NCS concentration, phosphate and fluoride ions do not interfere in the assay of sulfate ion. Nor do any common cations, except those which tend to precipitate sulfate (e.g. Ba^{2+}).

EXPERIMENTAL

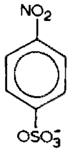
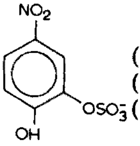
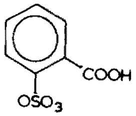
Construction of the electrodes

The various electrode types used are shown in Fig. 1. For the preliminary experiments in solution with soluble enzymes, the first two types were used. Type I is a platinum disc electrode (Beckman Model 39273) with an active surface area of about 0.2 cm^2; this electrode was also the solid base of the other constructions.

The Type II electrode was almost free of the effect of stirring on the current because of the soluble permeable membrane (cellophane dialysis membrane) secured by an "O" ring on the lectrode body [14].

TABLE 1

Kinetic data of arylsulfatase (EC 3.1.6.1) from *Helix pomatia*

Substrate	pH[a]	K_m mM	Activity in presence of anions[b]				Ref.
			SO_4^{2-} (%)	PO_4^{3-} (%)	F^- (%)	SO_3^{2-} (%)	
 NPS	(A) 6.25	0.27	61	20	35	7	9
	(A) 7.5	5.1	86	27	47	5	
 NCS	(A) 6.6	0.09	89	18	11	1	
	(A) 7.4	0.73	95	26	55	5	
	(M) 7.2	0.45	(a)20	(b)30	(c)47	(d)72	10, 11
				(b) 2			12

[a]Buffer systems: (A) 0.25 M Tris-acetate; (M) 0.1 M Tris-maleate.
[b]Concentrations: all 25 mM except: (a) 50 mM; (b) 10 mM; (c) 2.5 mM; (d) 0.25 mM.

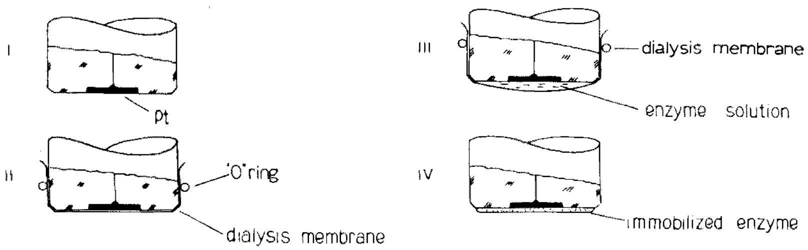


Fig. 1. Four types of amperometric electrodes. Type I, Uncoated Pt disc electrode. Type II, Pt electrode covered with a dialysis membrane — no enzyme. Type III, Soluble enzyme-type electrode. Type IV, Glutaraldehyde-bound arylsulfatase on Pt disc electrode.

The Type III electrode was constructed for preliminary enzyme electrode experiments by placing an enzyme solution layer on the platinum surface, held in place by a cellophane dialysis membrane. This simple immobilization was carried out with 5 mg of sulfatase powder (Type H-1, from *Helix pomatia*, approximately 0.5 IU mg^{-1} of solid, containing also β-glucuronidase activity; Sigma, St. Louis, Mo.). The electrode was soaked for several hours in buffer solution to dissolve the enzyme. This electrode could be used for only a couple of days, because the osmotic pressure difference effected a slow dilution of the enzyme solution. In addition, denaturation of the enzyme occurred in this time interval.

In the Type IV electrode, the enzyme was immobilized by the well known glutaraldehyde—albumin matrix entrapment procedure. When a slight modification of the recently reported coating method for glass electrodes [15] was used, a good, thin active and very homogeneous solid layer with amazingly good adherence to the flat platinum and the surrounding glass surfaces was obtained.

Layers with three different enzyme contents were made as follows: sulfatase (100 mg for 50 % w/w, 50 mg for 33 % w/w and 11 mg for 10 % w/w) was dissolved in 0.5 ml of 0.25 M acetate buffer (pH 4.76) and 0.5 ml of 17.5 % (w/w) albumin solution (albumin powder, Sigma Fraction V, from bovine, 96—99 %) was added and the mixture was stirred; then 0.05 ml of 25 % solution of glutaraldehyde (Sigma, Grade II, aqueous solution) was added to the mixture and stirred for 20 s. Within the next 30 s approximately 0.05 ml of this solution was dropped onto the flat surface of the platinum electrode turned upside down, and an even layer was made with a spatula. This layer was allowed to solidify for 15—20 min. After this binding time the electrode was rinsed with distilled water and stored in acetate buffer solution (pH 4.76) at room temperature. Thus, the actual amounts of the enzyme on the electrodes were approximately 2.5 U (50 %), 1.25 U (33 %), and 0.28 U (10 %).

This construction technique does not require any securing support such as nylon net or membranes, and the active layer is much more homogeneous and thinner than can be achieved by previous methods. To make 5—10 parallel electrodes takes only 25—30 min and after that the electrodes are ready to use.

The lifetime of these electrodes was 25—50 runs, depending on the enzyme content. It is most likely from the observations, that the loss of the activity is caused by some further coupling reactions between the *o*-benzoquinone product of the electrode process and the matrix of entrapped enzyme.

Substrate and buffers

p-Nitrocatechol sulfate (dipotassium salt, Sigma) was used as substrate without further purification. 4-Nitrocatechol (Aldrich, Milwaukee; reagent grade, 97 %) was used to test the proper conditions of amperometric oxidation, and to calibrate the reaction-rate measurements.

Acetate buffers were prepared from 0.5 M stock solutions of acetic acid and sodium acetate; the pH was adjusted by using the proper ratio in the mixture (pH range 2.70—6.80), and then diluted with distilled water to twice the volume.

Tris-acetate buffers were made from 0.5 M acetic acid and 0.5 M tris(hydroxymethyl)aminomethane (Sigma) solutions in the same way as above, adjusting the pH to 7.0—9.5.

Other chemicals were of reagent grade and were used without further purification.

Apparatus and procedures

For the voltammetric and amperometric measurements, a Heath polarograph system (Model EUA-19-2) was used with a potentiometric amplifier (Model EU-200-01) and a strip-chart recorder (Model EU-205-11) to record the current changes vs. time.

The electrochemical cell comprised the test electrode and a S.C.E. with a 1.0 M KNO_3-agar salt bridge to avoid the inactivation of the enzyme by the calomel electrode [16]. The electrodes were immersed in the stirred and thermostated (25 °C) buffer solution. The polarizing potential applied was +0.8 V vs. S.C.E. (except at pH 7.0, when it was +0.6 V).

In the amperometric experiments the steady-state background current was measured before the injection of the substrate, and after use the electrodes were rinsed well with distilled water and dried with a soft tissue.

For the bulk of enzymatic reactions, an aqueous solution of the enzyme (5 mg ml^{-1}) was used. This stock solution kept its activity over two weeks in a refrigerator.

For the kinetic measurements in the bulk reaction of NCS, the slope of the initial velocity of the reaction was recorded as $\mu A\ min^{-1}$; the rate in $\mu M\ min^{-1}$ was calculated for standard solutions of nitrocatechol.

The steady-state method was used in the experiments with enzyme electrodes (Types III and IV). After the current had reached a constant level in the buffer, and NCS medium, the solution of sulfate to be assayed was injected, and the new steady-state current was observed. The sulfate present was calculated from a calibration plot.

RESULTS AND DISCUSSION

Bulk reaction study

A study of the bulk reaction of the soluble enzyme seemed to be important for two reasons. First, the preliminary runs had shown that the kinetic behavior of the sulfatase from *Helix pomatia* is not strictly normal; there is a product activation effect besides the inhibition effect, depending on the initial NCS concentration. Secondly, Mell and Maloy [17] have shown, by modeling an amperometric enzyme electrode (for glucose oxidase) through digital simulation, that the most important factor of this system is

$$V = k_3 C_E d^2 / D K_m \tag{5}$$

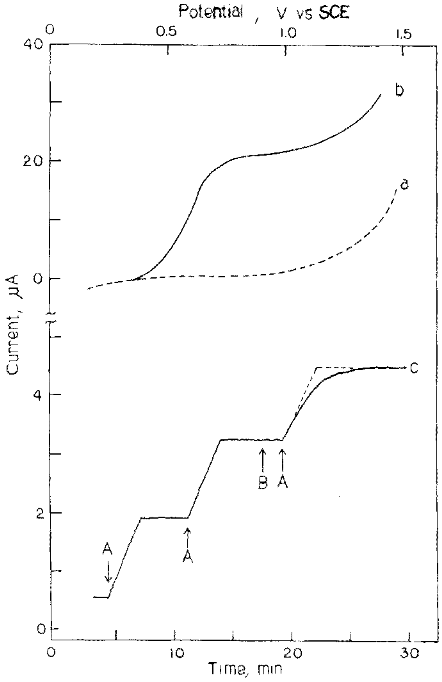
where $k_3 C_E = V_m$, the maximum velocity of the enzyme reaction; d is the thickness of the enzyme layer; D the diffusion coefficient of the substrate in the membrane thin layer; and K_m is the Michaelis—Menten constant.

This parameter (V) compares the rate of chemical reaction in the membrane to the rate of diffusion through the membrane. If the value of V is below

1.0, the response of the electrode is catalysis-controlled while above 10.0 it is diffusion-controlled.

From Fig. 2 it can be seen that the product of the enzymatic hydrolysis of the NCS has a well-defined oxidation wave at the platinum electrode in acetate buffer (a, b). The time study of the bulk reaction (c) shows a very low K_m value and a sulfate inhibition effect on it. Without the enzyme the substrate is stable in the pH range examined.

Logarithmic plots of the V_m and K_m vs. pH were constructed from the Lineweaver—Burke diagrams of the bulk reaction, and are shown in Fig. 3. The breaks of these curves show the pK values of the free enzyme and substrate as well as the enzyme-substrate compound [18]. The breaks in pK_m and log V_m (dashed line) around pH 6.5, must be caused by the dissociation of the phenolic hydroxyl group in the NCS and 4-nitrocatechol since



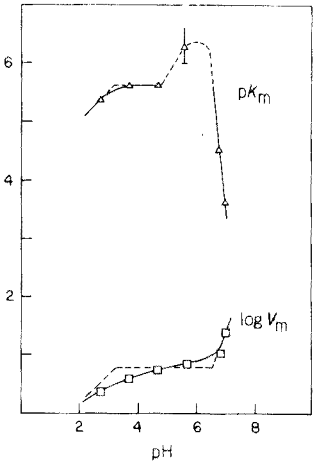


Fig. 2. Bulk enzymatic reactions. (a) Voltammetric curves of buffer + enzyme mixture (10 ml acetate buffer, pH 4.76 +0.25 ml of sulfatase solution), polarization rate 0.1 V min^{-1}, electrode Type I. (b) Voltammetric curve taken 1 h after adding 0.1 ml of 10^{-2} M NCS solution to the mixture, under the same conditions as above. (c) Time study of the bulk reaction at pH 4.76 (10 ml acetate buffer +0.25 ml of sulfatase solution) measured with electrode Type III, E = +0.8 vs. S.C.E. A, 0.1 ml of 10^{-2} M NCS solution was injected B, 0.1 ml of 0.5 M K_2SO_4 injected. (-----) Curve predicted in absence of sulfate ion.

Fig. 3. Plots of log V_m and pK_m vs. pH for arylsulfatase from *Helix pomatia*. 0.1 ml of enzyme solution in 10 ml of buffer; electrode type II; E = +0.8 V up to pH 6.8 and +0.6 V at pH 7.0. (------) Curves normalized.

their pK values are 6.4 and 6.6, respectively [8]. The others (at about 5.6, 4.7 and 3.2) are the results of pK_e (enzyme) and pK_{es} (enzyme-substrate). There is a narrow range between pH 5.6 and 6.5 where the K_m value is almost zero, above this the K_m increases very quickly.

The smallest influence of the pH on the kinetic parameters falls between the 3.2 and 4.7 break-points. This pH range seems to be the best for an amperometric enzyme electrode system based on reaction inhibition.

Enzyme electrode with soluble enzyme layer (Type III)

Figure 4 shows the responses of the enzyme electrode containing soluble enzyme to changes in sulfate ion concentration at different pH values. This electrode had linear response to the NCS substrate at every pH applied. These curves verified that the most sensitive inhibition occurs around pH 3.7 and that there is no inhibition in the range of the very small K_m values. At pH 7.0 and above, the electrode behavior became irregular with an activation effect of sulfate ion. This activation effect by sulfate ion had already been observed in the bulk reaction experiments at higher than 10^{-4} M substrate concentrations. The dual activating and inhibiting effect of anions and cations is quite well established [20], and a careful control of experimental conditions (i.e. pH, substrate concentrations) is always required for optimum results.

Enzyme electrode with immobilized enzyme layer (Type IV)

Enzyme electrodes with three different enzyme contents in the layer were tested at different pH values (from 3.70 to 6.70) and at two substrate concentrations.

Figure 5 shows typical responses to sulfate injections under the different conditions. It can be seen that the responses observed are becoming normal

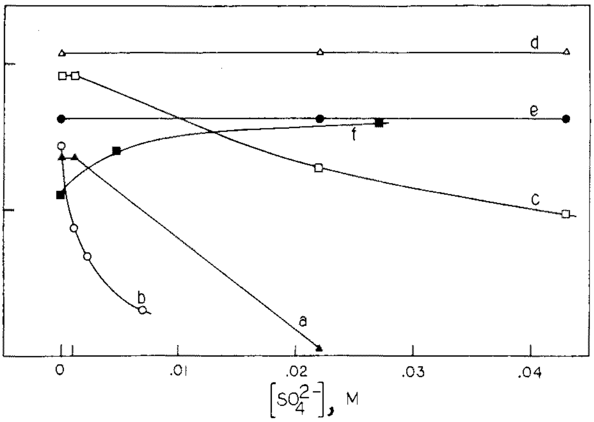


Fig. 4. Calibration curves for sulfate ion with the enzyme electrode containing soluble enzyme (Type III) at different pH values. [NCS] = $5 \cdot 10^{-5}$ M. E = +0.8 V vs. S.C.E. (a) pH 2.70; (b) pH 3.70; (c) pH 4.70; (d) pH 5.70; (e) pH 6.60; (f) pH 7.00.

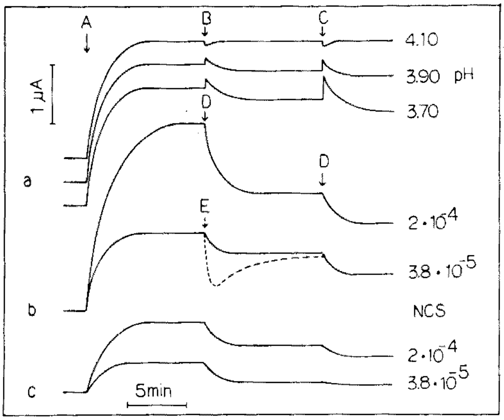


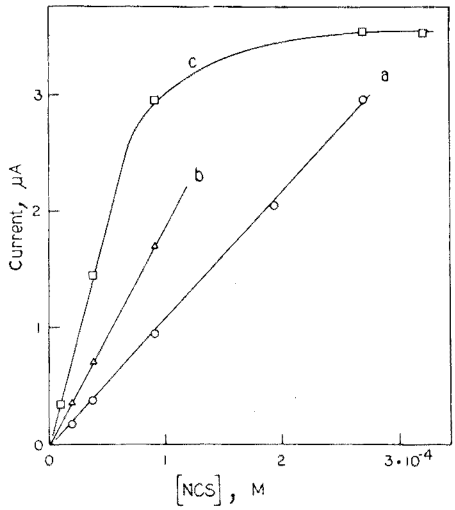
Fig. 5. Response curves of the enzyme electrodes containing immobilized enzyme layers with different amounts of sulfatase (Type IV). Medium contains 10 ml of buffer. $E = +0.8$ V vs. S.C.E. (a) 50 % (w/w) enzyme, $2 \cdot 10^{-4}$ M NCS; (b) 33 % (w/w) enzyme, pH 3.70; (c) 10 % (w/w) enzyme, pH 3.70. The NCS was injected at point A; at points B and E, 0.1 ml, at C 0.5 ml, at D 0.05 ml of 0.1 M K_2SO_4 solution were added to the solution.

inhibition with decreasing enzyme concentration in the layer. In agreement with Fig. 4, the results are better at lower pH. However, an irregularity was observed in the responses of the electrodes containing 33 % of enzyme (b curves). If the first sulfate injection was 0.1 ml of 0.1 M K_2SO_4 into the 10-ml medium, instead of 0.05 ml, a transient curve was recorded with a maximum peak observed between the steady-state conditions. This is shown in Fig. 5 by the dashed line. This behavior could be observed only at lower concentrations of the substrate and at this intermediate enzyme content. Thus, such conditions are not recommended.

The calibration curves of the various electrodes to the substrate are in good agreement with the theoretical predictions of Mell and Maloy [17]. Decreasing the enzyme concentration causes a decrease in the value of V (eqn. (5)), and the electrode response becomes mostly catalysis-controlled (Fig. 6). The electrode with the 50 % (w/w) sulfatase layer was found to have linear response to NCS up to $5 \cdot 10^{-3}$ M NCS with a detection limit of $5 \cdot 10^{-5}$ M. The electrode with 10 % sulfatase had a linear range 10^{-6}—10^{-4} M NCS. It must be noted that every electrode needs individual calibration because the thickness of the enzyme layer formed during the electrode construction cannot be strictly controlled.

Figure 7 shows the sulfate calibration curves of two enzyme electrodes at two substrate concentrations. The pH used was chosen at the center of the constant pK_m range (Fig. 3).

The inhibition by the sulfate ion was expressed as the relative change of current, $\Delta I/I$, where I is the steady-state current observed in the buffer-substrate medium before the potassium sulfate is added, and ΔI is the change on addition of sulfate sample. In the semilogarithmic plot, these curves are linear over two decades change of the sulfate concentration (10^{-4}—10^{-2} M).



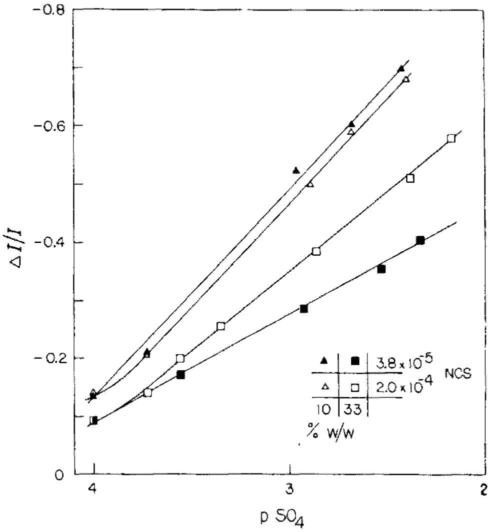


Fig. 6. Calibration curves of the enzyme electrodes with immobilized sulfatase to NCS. (a) 50 % (w/w) enzyme, pH 3.70; (b) 33 % (w/w) enzyme, pH 3.70; (c) 10 % (w/w) enzyme, pH 4.10.

Fig. 7. Sulfate calibration curves of various sulfatase electrodes with different enzyme content. $\Delta I/I$ is the relative inhibition form, where I is the steady-state current without sulfate ion added; ΔI is the lowering of the steady-state current due to addition of sulfate. Electrode type IV; pH 4.1; E = +0.8 V vs. S.C.E.; other conditions are indicated on the figure.

The electrode containing 10 % (w/w) sulfatase gave almost twice the sensitivity of one containing 33 % (w/w) sulfatase; which verifies the importance of the catalysis-controlled behavior. However, at the higher concentration of the substrate, this difference was smaller.

Effect of pH on the electrode response to sulfate

Although studies of the bulk reactions had shown that the smallest effect of the pH on the electrode response should be expected around pH 4.10, a pH study showed a strong relation between the inhibition response to $2 \cdot 10^{-3}$ M sulfate of an electrode having a 33 % (w/w) sulfatase active layer, and the pH (Fig. 8). The slope of the linear relationship was 0.66 relative inhibition unit/pH unit. This may be caused by the slight changing of the V_m in this pH range (see Fig. 3), and a still high sensitivity coming from the Mell—Maloy's V factor, and also because of a difference in enzyme behavior caused by immobilization.

Further investigations are needed to determine the optimal conditions (enzyme content in the active layer and substrate concentration) at the point where the effect of pH is smallest. A pH of 3.70 was optimal for all electrodes containing 50 % and 33 % (w/w) of enzyme, and 4.10 was best for the 10 % (w/w) enzyme electrode.

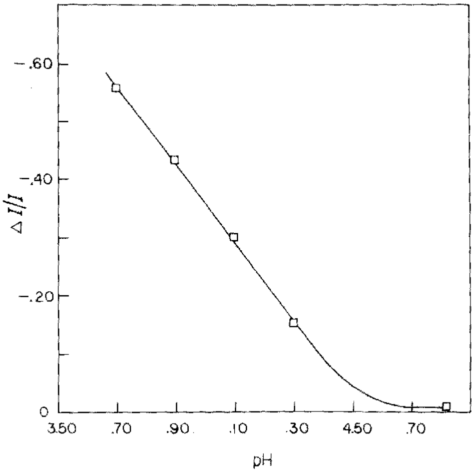
Electrode responses to other anions

The response of the sulfatase electrode containing 10 % (w/w) enzyme was examined at pH 4.1, and two different substrate concentrations to Cl^-, Br^-, CN^- and F^- ions and to oxyacid anions, other than SO_4^{2-}.

Chloride, nitrate and arsenate (applied as Na_2HAsO_4 solution) had no influence on the steady-state current of the enzyme electrode up to 0.01 M.

As can be seen from Fig. 9, the phosphate (P_i, applied as NaH_2PO_4), bromide, fluoride, and cyanide ions had some effect on the electrode system. At the higher concentration of substrate tested ($2 \cdot 10^{-4}$ M NCS), however, the effects of these anions are negligible if their concentrations are under 10^{-3} M (solid lines and open signs). In this case, the phosphate ion has no interference at any concentration, nor has bromide up to $6 \cdot 10^{-3}$ M or fluoride up to 10^{-3} M. This means that sulfate can often be measured without prior separation from these ions, and the electrode is very highly selective.

At a lower NCS concentration ($3.8 \cdot 10^{-5}$ M), the phosphate ion yields a linear calibration curve in the 10^{-4}—10^{-2} M range with a decrease in the



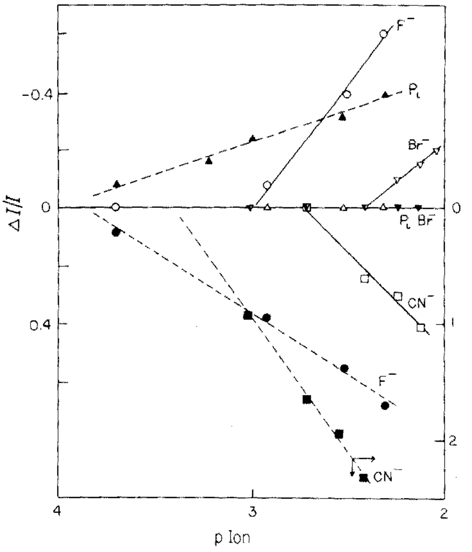


Fig. 8. Effects of pH on the sulfate response. $\Delta I/I$ relative inhibition by $2 \cdot 10^{-3}$ M sulfate plotted against the pH; [NCS] = $2 \cdot 10^{-4}$ M; E = +0.8 V vs. S.C.E.; 33 % (w/w) sulfatase in the active layer (Type IV).

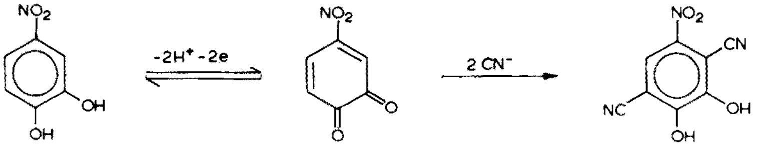
Fig. 9. Anion effects on the sulfatase electrode. $\Delta I/I$ is plotted against the p Ion. Electrode type IV; 10 % (w/w) enzyme in the active layer; pH 4.10; E = +0.8 V vs. S.C.E. Open marks with the solid lines are at a $2 \cdot 10^{-4}$ M NCS concentration; closed (solid)marks with dashed lines are at $3.8 \cdot 10^{-5}$ M NCS concentration. △ Phosphate. □ Cyanide. ○ Fluoride. ▽ Bromide.

steady-state current of the electrode, while fluoride ion also yields a linear calibration curve in the same concentration range, but with an increase in the current. Hence, the electrode offers some promise for the assay of phosphate and fluoride.

Molybdate ion (applied as Na_2MoO_4) was found to be an irreversible inhibitor of arylsulfatase, even in concentrations as low as 10^{-4} M. Hence it interferes in all phosphate assays.

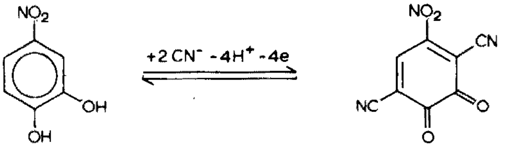
The effect of the cyanide ion on the steady-state response of the electrode to the substrate was found to be a very strong apparent activation. However, even in the absence of enzyme at an uncoated platinum electrode, cyanide increases the anodic current because of the oxidation of nitrocatechol under the same operating conditions.

In the specific fluorimetric determination of cyanide [19], the reaction of cyanide with *p*-benzoquinone to form a hydroquinone derivative was used. It is most likely that a similar reaction occurs with the *o*-benzoquinone type nitrocatechol at the electrode surface, reforming the electroactive species as follows



(6)

The overall reaction, therefore, is a 4e¯ process



(7)

The cyanide interference through these reactions could be eliminated by using other derivatives of catechol containing substituents in proper positions on the ring to prevent the addition of cyanide to the *o*-benzoquinone form. However, with a $2 \cdot 10^{-4}$ M NCS concentration, cyanide does not interfere in the determination of sulfate up to $2 \cdot 10^{-3}$ M, a concentration higher than that usually found in any environmental sample. Thus the proposed new enzyme electrode is judged to be very selective for the assay of sulfate, provided that a high concentration of NCS substrate is used.

Assays of 10 sulfate samples, ranging in concentration from 10^{-2} to 10^{-4} M, were effected with the proposed electrode in the presence of 10^{-2} M chloride; the accuracy was better than ± 3 %, and the precision between samples was about 4 %. By comparison, these same assays performed by the method of Weetall and Jacobsen [6] showed an accuracy and precision of 5—10 %.

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ÉTUDE SPECTROMÉTRIQUE D'UN PLASMA INDUIT PAR HAUTE FRÉQUENCE
PARTIE I: PERFORMANCES ANALYTIQUES

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RÉSUMÉ

Un nouveau générateur haute fréquence de plasma fonctionnant à 40 MHz a été conçu comme source d'excitation en spectroscopie d'émission atomique et source d'atomisation en absorption atomique. De bonnes performances analytiques ont été obtenues en émission et en absorption atomique. On peut néanmoins préférer l'émission pour sa simplicité de mise en oeuvre.

SUMMARY

A new design of inductively coupled plasma generator operating at 40 MHz is described. Data are presented to show that the generator gives satisfactory performance when used in both atomic emission and absorption spectrometry, although the former has the advantage of simplicity of operation.

Le plasma induit par haute fréquence est maintenant une source bien connue en spectroscopie d'émission. Plusieurs groupes de chercheurs [1–10] se sont attachés à l'étudier et ont montré qu'il pouvait conduire à de bonnes performances analytiques, généralement supérieures aux résultats trouvés par l'absorption atomique classique. Cette source présente de plus un intérêt certain en analyse multiéléments, même dans une gamme étendue de concentrations.

Néanmoins, la plupart du temps, les générateurs h.f. utilisés pour engendrer le plasma n'ont pas été conçus spécialement comme sources spectroscopiques mais adaptés à cet usage. Aussi avons-nous été conduits à mettre en commun avec la Sté Electronique Scientifique et Industrielle Durr [11] nos expériences et recherches antérieures. Les études préalables effectuées dans le domaine 1–220 MHz ont montré qu'un bon compromis entre les différentes technologies possibles consiste en la construction d'un générateur d'un principe entièrement nouveau, à lignes accordées fonctionnant à 40 MHz. Nous l'avons utilisé comme source d'excitation en spectrométrie d'émission sur solutions et comme source d'atomisation en analyse par absorption atomique. Les études spectroscopiques sont menées en parallèle de part et d'autre. De plus nous avons perfectionné la spectrométrie d'absorption atomique avec plasma en mettant au point un appareillage électronique à deux longueurs d'onde conçu spécialement pour s'affranchir des parasites dus au plasma.

Dans cette première partie, nous avons spécialement étudié les limites de détection et les courbes de dosage d'un certain nombre d'éléments en comparant les performances analytiques de l'émission et de l'absorption atomique. L'étude des effets interéléments fera l'objet d'une seconde partie.

APPAREILLAGE

Le générateur de plasma

Le générateur a été construit par la Sté Electronique Scientifique et Industrielle Durr. Il s'agit d'un générateur inductif 40 MHz dont l'oscillateur est du type à lignes accordées. Son schéma de principe est représenté Fig. 1. La puissance appliquée au générateur est réglable par l'intermédiaire de la haute tension d'alimentation *V*. L'intensité plaque est mesurée: le générateur fonctionne correctement de 0,6 à 5 kVA. L'inducteur est composé de cinq spires. Nous disposons ainsi d'un temps de séjour élevé du gaz et des particules dans le champ haute fréquence.

Dans les générateurs classiques généralement utilisés par les autres auteurs, l'oscillateur est constitué par un circuit L.C. qui détermine la fréquence de travail. La précision en fréquence est limitée par la précision des composants

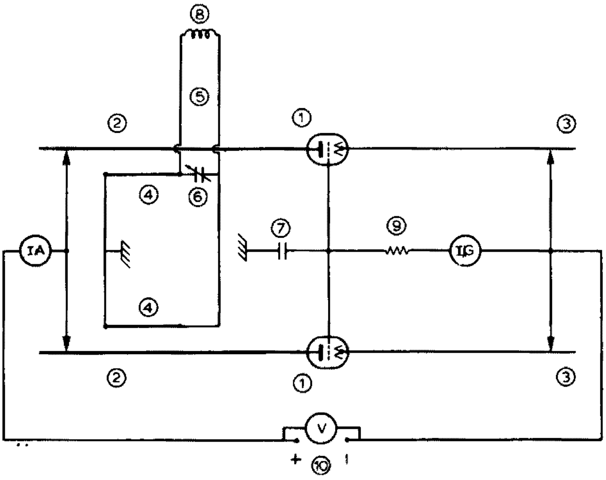

Fig. 1. Schéma de principe du générateur à lignes accordées 1. Triodes V.H.F. 2. Lignes anodiques en $\lambda/4$. 3. Lignes cathodiques en $\lambda/4$. 4. Lignes de couplage. 5. Lignes feeder de l'inducteur. 6. Capacité d'accord. 7. Capacité de découplage. 8. Inducteur. 9. Résistance de grille. 10. Entrée haute tension.

du circuit et l'adaptation du générateur aux variations de la charge introduite dans l'inducteur se fait généralement par un dispositif mécanique asservi à la mesure de la puissance réfléchie. Ce dernier agit sur un composant réglable: self ou capacité.

Par contre, dans le générateur que nous utilisons, l'asservissement est entièrement électronique. La fréquence centrale f_0 de l'oscillateur est déterminée par la longueur l des lignes suivant la relation

$f_0 = \frac{c}{4\,l}$ où c est la vitesse de la lumière,

et la précision sur la détermination de f_0 n'est liée qu'à la précision sur la longueur l des lignes. Ce type de générateur a donc une excellente stabilité en fréquence; celle-ci ne varie pas au cours du temps.

Par ailleurs les lignes d'accord 4 jouent un double rôle (Fig. 2). D'une part elles constituent un transformateur adaptateur d'impédance permettant d'opérer à 40 MHz avec un inducteur de cinq spires ce qui est impossible avec les générateurs "classiques". D'autre part elles servent à l'asservissement du générateur à la charge (feedback). En effet, si la charge n'était constituée que d'une self pure, le courant dans le circuit secondaire serait en quadrature avec la tension. Le fait que l'inducteur 8 soit le siège de pertes (l'énergie transmise au plasma) entraîne une variation de phase du courant. Cette variation de phase permet la réalisation de l'accord par l'intermédiaire de l'induction mutuelle entre les lignes 2 et 4. Dans ce montage, la puissance réfléchie est donc quasi invariante. En effet, les variations de fréquence entraînées par les variations de charge sont faibles: $2 \cdot 10^{-3}$ pour des variations extrêmes de la charge, $5 \cdot 10^{-5}$ en régime permanent. Un avantage considérable de ce générateur est qu'aucune intervention n'est nécessaire ni en cours de fonctionnement, ni au cours de l'allumage et les corrections que le générateur effectue lui-même sont absolument instantanées: il est possible d'effectuer une série d'analyses sur un aérosol sec puis de travailler immédiatement après avec un aérosol humide sans avoir à intervenir ni à attendre. Les réglages sont toujours optimum. Après plusieurs mois d'usage intensif aucun réglage n'a été nécessaire et les caractéristiques sont absolument inchangées.

Optimisation des conditions de fonctionnement

Le plasma est produit à l'intérieur d'une enceinte ou tête d'amenée des gaz placée dans l'inducteur. Nous avons conservé le principe de têtes à trois

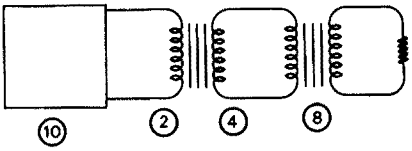

Fig. 2. Schéma équivalent du générateur à lignes accordées.

tubulures aussi bien pour l'émission (Fig. 3a) que pour l'absorption atomique (Fig. 3b). L'étude des paramètres expérimentaux (Tableau I), diamètres des tubes de la tête, débits de gaz a été faite avec le souci d'obtenir de bonnes performances analytiques et un faible coût de fonctionnement.

Nous avons établi que la stabilité du plasma est liée à la vitesse du gaz plasmagène (argon). En dessous de la vitesse critique (2 m s^{-1}) le plasma n'est pas stable et n'est pas expulsé hors de la zone située à l'intérieur de l'inducteur. Cette vitesse est fonction, à un débit donné, de la surface de la couronne d'alimentation du gaz plasmagène.

L'échantillon à l'état d'aérosol produit par un nébuliseur à ultrasons est entraîné par de l'argon et introduit, après désolvatation, dans le plasma d'argon [9]. Bien que l'on utilise trois tubulures aucun autre courant gazeux n'est nécessaire.

Optique et exploitation du signal

Les conditions opératoires des points de vue optique et électronique sont résumées dans le Tableau 2. Dans le cas de l'émission, l'installation utilisée est d'un type classique doué de bonnes performances.

Pour l'absorption atomique, nous avons mis au point un appareillage spécialement conçu sur le principe de la méthode à deux longueurs d'onde, utilisée d'abord par Menzies [12]. Cette méthode consiste à effectuer le rapport des intensités de deux raies d'un même élément provenant de la même source et séparées dans un polychromateur [13]. L'une des raies est susceptible de subir une absorption de résonance et l'autre non. Les deux raies subissent dans le milieu absorbant l'absorption non résonante et la diffraction: on a ainsi un moyen de compenser efficacement les perturbations

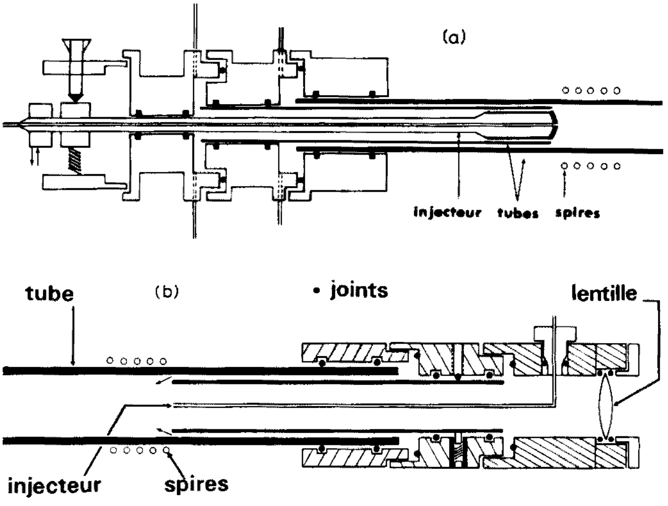

Fig. 3. Schéma de la tête utilisée (a) en émission, et (b) en absorption atomique.

TABLEAU 1

Paramètres physiques du générateur à plasma et conditions de fonctionnement en émission et absorption atomique

I Tête du plasma	Emission	Absorption atomique	
Tube extérieur			
diamètre extérieur (mm)	30	29,5	
diamètre intérieur (mm)	27	25,4	
Tube intermédiaire			
diamètre extérieur (mm)	22	23,0	
diamètre intérieur (mm)	19,7	19,0	
Surface de la couronne d'alimentation (mm^2)	50	91	
Tube d'injection ou injecteur			
diamètre extérieur (mm)	18	2	
diamètre intérieur (mm)	1,1 à 1.7	1,5	
Distance focale de la lentille	—	100 mm à 200 nm	
II Inducteur			
Nombre de spires	5	5	
Diamètre extérieur du tube des spires (mm)	6	6	
Hauteur de l'inducteur (mm)	50	50	
Hauteur du tube externe par rapport au sommet de l'inducteur (mm)	40—70	90—200	
III Débits de gaz ($l\ min^{-1}$)			
Débit du gaz plasmagène min.	6		
normal	10		
Débit d'injection de l'aérosol	1,0 à 2,5		
IV Générateur			
Tension du générateur (V) min.	1800	normal 2900	max. 3300
Courant plaque (mA)	260	440	500
Puissance appliquée (kVA)	0,47	1,27	1,65

du fond continu qui ont jusqu'ici considérablement limité les performances de la méthode d'absorption atomique appliquée aux sources à plasma [14—19].

Cet appareillage est composé de deux canaux identiques d'amplification à détection synchrone et d'amplification logarithmique: le signal de chaque radiation est traité séparément. On forme ensuite la différence de ces deux signaux: le signal ainsi obtenu est proportionnel au logarithme du rapport des deux raies et à la concentration en atomes absorbants dans le milieu. La modulation du signal de la lampe à cathode creuse s'effectue par modulation du courant de décharge. Cette méthode présente deux avantages: d'une part l'oscillateur qui pilote la modulation fournit directement le signal de référence

TABLEAU 2

Caractéristiques de l'optique et de l'appareillage électronique utilisés

Monochromateur	SOPRA, 2 m de distance focale. Réseau holographique 2400 traits mm^{-1}. Dispersion linéaire réciproque 1,45 Å mm^{-1} à 6323 nm. Peut être utilisé en polychromateur avec 3 fentes et 3 P.M. permettant d'observer simultanément 3 longueurs d'onde dans un intervalle de 13 nm environ.
Photomultiplicateurs	EMI 6256 S pour le monochromateur (faible courant d'obscurité 0,2 nA à 1800 V). EMI 6256 B pour le polychromateur.
Electronique émission	Amplificateur convertisseur courant—tension, impédance d'entrée 10^{12} Ω, bande passante 0—30 kHz. Constante de temps réglable de 0,05 à 20 s.
Electronique absorption	Amplificateur filtre à détection synchrone double canal, Q réglable de 1 à 15 000. Alimentation de lampe à cathode creuse à modulation électronique.
Enregistreur	SEFRAM, type Servorac à 2 voies de 250 mm, 1 mV—1 V

destiné à la détection synchrone, d'autre part, à courant moyen égal, l'intensité de la lampe est quatre à huit fois plus grande que dans le cas de la modulation optique.

ETUDE DE L'EMISSION ATOMIQUE

Limites de détection

Nous avons choisi treize éléments (Tableau 3) qui nous ont semblé représentatifs soit par leurs différentes valeurs d'énergie d'ionisation, soit par leur facilité d'excitation (Mg par ex.) soit au contraire par la difficulté de dissocier leur oxyde (oxydes réfractaires: W par ex.). Nous avons en effet observé [9] que les composés obtenus après désolvatation sont sous la forme d'oxydes, généralement hydratés.

Le choix des raies d'analyse a été effectué à l'aide des spectres des différents éléments. Généralement les raies II conduisent à de meilleurs résultats pour les limites de détection, bien que la température mesurée sur les éléments injectés soit inférieure à 5000 K [20]. Nous avons attribué cela aux mécanismes particuliers d'excitation liés à l'utilisation de l'argon comme gaz plasmagène [21].

Nous avons réalisé cette étude dans des conditions que l'on peut considérer comme des conditions de compromis (débit d'injection 2,0 l min^{-1}, diamètre intérieur de l'injecteur 1,3 mm). Il est possible pour des analyses particulières d'améliorer ces résultats en modifiant les paramètres suivants: puissance appliquée au générateur h.f., hauteur d'observation et débit d'entraînement de l'aérosol.

Nous indiquons sur le Tableau 3 les limites de détection obtenues en

TABLEAU 3

Comparaison des limites de détection en ng ml^{-1} obtenues avec le plasma fonctionnant à 40 MHz (tête verticale et tête horizontale) et le plasma fonctionnant à 5 MHz (tête verticale). Les limites sont prises comme 6 fois les fluctuations du fond continu émis par un blanc

Elément	40 MHz				5 MHz	
	Tête verticale		Tête horizontale		Tête verticale	
	λ(nm)	limite	λ(nm)	limite	λ(nm)	limite
Al	I 396,15	0,5	I 396,15	0,5	I 396,15	30
B	I 249,77	10	I 249,77	2	I 249,77	30
Cd	II 226,58	2,5	I 326,11	5		
Ce	II 413,30	2	II 413,30	4	II 394,27	30
Cr	I 357,87	5	I 357,87	2		
	II 267,72	10	II 267,72			
La	II 394,91	0,15	II 394,91	0,25	II 379,48	6
	II 408,67	0,5	II 408,67			
Mg	II 279,55	0,03	II 279,55	0,03	II 279,55	0,05
Nb	II 319,50	0,3	II 319,50	0,2	I 318,03	2
	II 292,78	0,3				
P	I 253,56	160	I 253,56	60		5000
Ta	II 296,51	25	II 296,51	5	I 296,33	30
Ti	II 323,45	0,4	II 323,45	0,2		
	II 334,90	0,25			II 334,90	2
V	I 437,92	4	I 437,92	1	II 309,31	1
	II 292,40	4				
W	II 276,43	2,5	I 400,88	2	I 400,88	100

observant la tête soit verticalement, soit horizontalement selon son axe de symétrie. Nous avons utilisé une constante de temps de 15 s. Rappelons que nous prenons pour limite de détection un signal égal à six fois les fluctuations du signal émis par le blanc. En dépit des recommandations de l'IUPAC AC [22] pour qui la limite de détection correspond à un signal égal à deux ou trois fois les fluctuations du fond continu émis par le blanc, nous préférons la définition que nous donnons, car elle correspond à un signal réellement observable. De plus nous effectuons la mesure au cours d'une série d'essais à des concentrations faibles, voisines de la limite de détection et non par extrapolation à partir de mesures à des concentrations beaucoup plus élevées [23]. Cette façon d'opérer nous semble plus proche des conditions pratiques par rapport à celles d'autres auteurs. Pour illustrer cela, nous avons choisi le vanadium dont nous indiquons comme limite de détection 4 ng ml^{-1}. Une détermination suivant le critère décrit par Boumans et de Boer [23] nous conduirait à une limite de détection de 0,2 ng ml^{-1}, ce qui abaisserait la valeur de la limite d'un facteur 20. Néanmoins seule la première valeur nous semble réellement exploitable car elle correspond à une concentration que l'on est certain d'observer.

Nous avons également fait figurer dans le Tableau 3 les résultats que nous avions obtenus sur le plasma fonctionnant à 5 MHz [9, 10] pour le phosphore à titre de comparaison. Le système d'introduction de l'échantillon et l'optique étaient identiques dans toutes ces expériences. Seule l'amplification du signal n'était pas effectuée du fait d'une intensité des raies beaucoup plus importante avec le générateur à 5 MHz.

Généralement, les mêmes raies pour l'étude des têtes placées verticalement et horizontalement ont été utilisées, sauf cas particuliers signalés dans le Tableau 3 pour le cadmium et le tungstène. Dans ces deux cas, le choix de raies I s'est avéré meilleur: cela peut s'expliquer du fait de la grande longueur observée de l'émission, la zone où les raies II sont les plus intenses étant réduite par rapport à la longueur totale de la zone d'excitation.

Nous voyons que le passage du plasma 5 MHz au plasma 40 MHz a entraîné une amélioration appréciable des limites de détection, spécialement pour des éléments comme le tungstène ou le phosphore. Par contre l'amélioration en passant de la tête placée verticalement à la tête horizontale est beaucoup moins sensible mais peut être encore utile dans certains cas (P).

La comparaison entre les résultats publiés par ailleurs [1, 2, 5, 6, 9] nous montre que cet appareillage conduit à de bonnes performances analytiques en émission atomique. La progression des résultats par rapport au plasma fonctionnant à 5 MHz s'explique essentiellement par une diminution importante du fond continu accompagnée d'une meilleure stabilité de ce fond. On a ainsi une amélioration importante du rapport signal/bruit bien que la température atteinte avec le plasma 40 MHz (inférieure à 5000 K) conduise à des intensités plus faibles qu'avec le plasma 5 MHz. La température d'excitation et la fréquence du plasma ne sont certainement pas les seuls paramètres qui permettent d'expliquer les résultats analytiques trouvés [21].

Courbes de dosage

Il nous a semblé intéressant d'étudier les variations de l'intensité en fonction de la concentration de l'élément afin de connaître leur allure et de voir quel est leur domaine de linéarité. Sur la Fig. 4, nous donnons ces courbes pour les huit éléments Al, Ce, Cr, Nb, P, Ti, V et W. Les raies utilisées sont celles indiquées dans le Tableau 3. Nous avons tracé des diagrammes en partant d'une valeur voisine de la limite de détection jusqu'à une concentration de 10^4 ng ml^{-1} et cela dans les deux cas d'utilisation de la tête: position horizontale et position verticale. Un décalage d'abscisse a été fait pour le phosphore à cause de la limite de détection moins bonne.

On peut voir que ces courbes présentent une linéarité sur un domaine d'au moins 10^3 en concentration.

ETUDE DE L'ABSORPTION ATOMIQUE

De même que pour l'emission, nous avons choisi un certain nombre d'éléments en fonction de leur caractère chimique ou spectroscopique.

Les raies d'analyse sont les mêmes que dans la méthode d'absorption sur

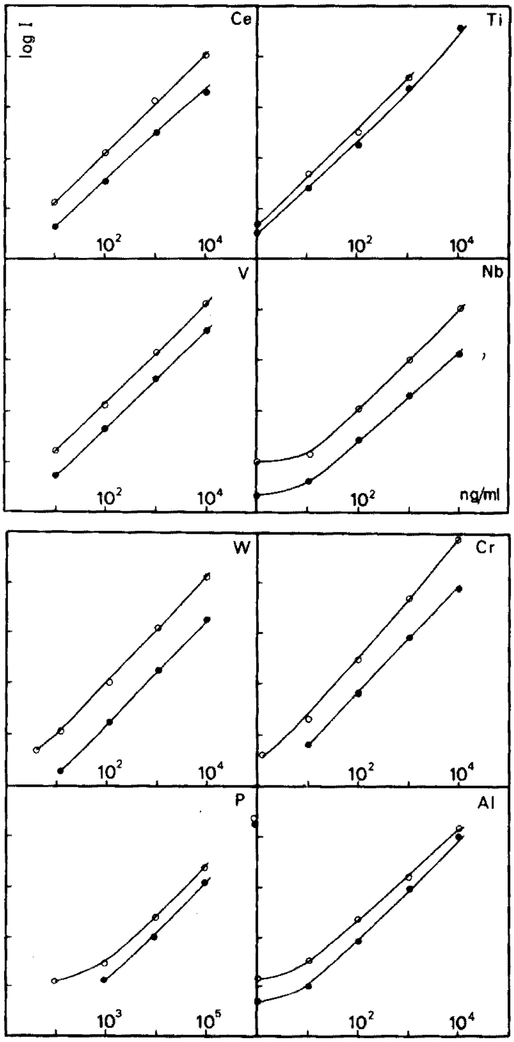

Fig. 4. Variation de l'intensité en fonction de la concentration en éléments en utilisant les raies du Tableau 3. ○ Tête horizontale ● tête verticale.

les flammes classiques: ce sont les raies de résonance. Mais l'efficacité de la méthode à deux longueurs d'onde repose sur le choix de la radiation de référence. En effet, il n'y a pas de compensation directe des fluctuations de la lampe comme c'est le cas dans les systèmes classiques à double faisceau, mais une compensation indirecte dans la mesure où l'intensité des raies d'une lampe à cathode creuse évolue dans le même sens (sauf lorsqu'on a auto-absorption dans la lampe). Si les deux raies d'absorption et de mesure d'un même élément ont la même énergie d'excitation la compensation des fluctuations de la lampe est totale car l'intensité des raies ne dépend que des probabilités de transition. Si la raie de référence ne peut répondre à ce critère, soit qu'il n'y ait pas d'autre transition partant du même niveau d'excitation, soit que la raie adéquate soit située trop loin de la raie de mesure pour le domaine spectral couvert, la compensation n'est que partielle.

Résultats expérimentaux

Le Tableau 4 donne les limites de détection obtenues pour sept éléments. La comparaison de ces résultats avec ceux obtenus par émission sur le même générateur à plasma, montre que, sauf cas très particuliers, la méthode d'absorption atomique ne présente pas d'intérêt en tant que méthode analytique. En outre, les courbes de dosages que nous avons pu tracer pour les divers éléments n'ont pas l'allure linéaire que l'on est en droit d'attendre théoriquement, ce qui serait gênant pour des applications analytiques. Ce phénomène a déjà été observé par d'autres auteurs [17] sans qu'une interprétation en ait pu être donnée. De notre côté, nous avons mis en évidence dans les cas de Ti et Al [24] une importante émission stimulée, sous certaines conditions de fonctionnement du plasma. Nous pensons que ce phénomène est de nature à expliquer en partie l'anomalie signalée des courbes d'étalonnage.

CONCLUSION

Les résultats analytiques que nous avons obtenus en utilisant un générateur inductif de plasma comme source spectroscopique confirment les hautes performances de cette technique, en particulier si, comme c'est notre cas, le générateur et l'appareillage électronique de mesure et de traitement des signaux sont spécialement adaptés à des fins analytiques.

Cet appareillage a aussi permis un progrès appréciable de la spectrométrie d'absorption atomique associée au plasma par rapport à l'absorption atomique classique utilisant une flamme. Néanmoins, cette méthode n'offrant pas de meilleurs résultats que l'émission atomique associée au plasma, on peut lui préférer cette dernière qui est plus simple à mettre en oeuvre tout en permettant facilement une analyse simultanée de plusieurs éléments.

Toutefois l'absorption atomique garde tout son intérêt comme moyen d'étude fondamentale du plasma conjuguée avec la spectrométrie d'émission.

TABLEAU 4

Limites de détection en ng ml^{-1} obtenues en absorption atomique (double et simple canal). Les valeurs des gA ont été prises dans [25]

Elément	λ Mesure (nm)	Energie cm^{-1}	gA $10^8\ s^{-1}$	λ Réf.	Energie	gA $10^8\ s^{-1}$	Concn. caract.	Limite double canal	Limite simple canal
Mg	285,213	0—35051	9,4	280,270 Mg	0—35669	5,3		0,05	10
Al	396,153	112—25348	1,3	394,403 Al	0—25348	0,66		6	$2 \cdot 10^4$
	309,271	112—32437	5,5	314,135 Ne II				200	
Bi	306,772	0—32588	7,0	302,464 Bi	15437—48489	38	300	100	1000
Ca	422,673	0—23652	1,0	430,253 Ca	15316—38552	7,1	0,2	0,04	5
Na	588,995	0—16973	1,8				2		0,5
Ti	334,188	0—29915	13	338,595 Ti	387—29912	3,4	200	10	500
W[a]	255,135	0—39183	8,2	265,654 W	2951—40583	9,1	$8 \cdot 10^3$	10^3	

[a] Dans le cas du tungstène, la raie de référence théoriquement adéquate (266,496 nm 1670—39183 cm^{-1}) ne peut être correctement séparée des raies voisines (266,432 et 266,577 nm).

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THE DETERMINATION OF TEMPERATURES IN A GRAPHITE TUBE ATOMIZER WITH A CONVENTIONAL ATOMIC ABSORPTION-FLAME EMISSION SPECTROMETER

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SUMMARY

Temperatures up to 3200 °C in graphite tube atomizers can be measured by a two-wavelength intensity ratio method. The melting point of gold serves as a standard to calibrate the spectral response and the transmittance of the optics. The errors in the temperatures measured are 20 –100 °C. A conventional two-channel atomic absorption-flame emission spectrometer was used, but any single-channel instrument is also suitable for measurements. The method can be used for any type of heated graphite or metal flameless atomizer.

The temperature of the inner wall of a graphite flameless atomizer must be known accurately in order to study the kinetic behavior of chemical species during the atomization process [1–3]. The contact method with a thermocouple is not suitable, because graphite has inadequate heat capacity, and thermal equilibrium cannot be maintained. Statistical analysis of spectra is very complicated [4, 5], and measurements with an optical pyrometer tend to be uncertain. Such measurements have been used [6] in studies of the temperature–time profiles of carbon filament atomizers.

In this report, a simple method with a conventional atomic absorption-flame emission spectrometer is discussed. The method is based on measurement of the intensity ratio between two wavelengths derived from the Wien formula; it compensates for spectral emissivity and transmittance of the optics, and no comparison with a standard black body or tungsten lamp is required. The theoretical treatment is analogous to that developed by Browner and Winefordner [7] for the measurement of flame temperatures. The temperature of the inner wall of the graphite tube can be measured simply and exactly. The minimum atomization temperatures of elements are discussed.

Principle of the method

The Wien formula for black body radiation shows good coincidence with the Planck formula for $\lambda T \leqslant 0.2$ cm K [8]. The Wien equation can be used up to 3500 K for wavelengths below 580 nm.

$$E(\lambda T) = \frac{C_1}{\lambda^5} \cdot e^{-\frac{C_2}{\lambda T}} \tag{1}$$

where $E(\lambda T)$ is the spectral radiant energy at wavelength λ and T K (the absolute temperature); $C_1 = 3.7353 \cdot 10^{-12}$ W cm^{-2}; and $C_2 = 1.4388$ cm deg.

The observed spectral radiant intensity $I(\lambda T)$ is expressed as follows

$$I(\lambda T) = \epsilon(\lambda T) \cdot \tau(\lambda) \cdot \frac{C_1}{\lambda^5} \cdot e^{-\frac{C_2}{\lambda T}} \tag{2}$$

where $\epsilon(\lambda T)$ is the spectral emissivity, and $\tau(\lambda)$ is the transmittance of the optics. The ratio $R(T_1) = I(\lambda_1 T_1)/I(\lambda_2 T_1)$ at different wavelengths λ_1 and λ_2 and a temperature T_1, whereas $R(T_2)$ is the same ratio at wavelengths λ_1 and λ_2 and another temperature T_2. The ratio of $R(T_1)/R(T_2)$ is therefore given by

$$K = \frac{R(T_1)}{R(T_2)} = \frac{I(\lambda_1 T_1)}{I(\lambda_2 T_1)} \bigg/ \frac{I(\lambda_1 T_2)}{I(\lambda_2 T_2)} \tag{3}$$

or

$$K = \frac{\dfrac{\epsilon(\lambda_1 T_1)\,\tau(\lambda_1)}{\epsilon(\lambda_2 T_1)\,\tau(\lambda_2)}}{\dfrac{\epsilon(\lambda_1 T_2)\,\tau(\lambda_1)}{\epsilon(\lambda_2 T_2)\,\tau(\lambda_2)}} \cdot e^{\frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} C_2 \left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \tag{4}$$

When the wavelengths λ_1 and λ_2 are close, $\epsilon(\lambda_1 T_1) \approx \epsilon(\lambda_2 T_1)$, and $\epsilon(\lambda_1 T_2) \approx \epsilon(\lambda_2 T_2)$, and we can write

$$K \approx e^{\frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} \cdot C_2 \left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \tag{5}$$

Equation (5) can be rewritten as

$$\ln K = \frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} \cdot C_2 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6}$$

or

$$T_2 = \frac{T_1 C_2 (\lambda_1 - \lambda_2)}{C_2(\lambda_1 - \lambda_2) - T_1 \lambda_1 \lambda_2 \ln K} \tag{7}$$

From eqns. (3) and (7), the final equation becomes

$$T_2 = \frac{T_1 C_2 (\lambda_1 - \lambda_2)}{C_2(\lambda_1 - \lambda_2) - T_1 \lambda_1 \lambda_2 \{\ln I(\lambda_1 T_1)/I(\lambda_2 T_1) - \ln I(\lambda_1 T_2)/I(\lambda_2 T_2)\}} \tag{8}$$

In eqn. (8), $I(\lambda_1 T_1)/I(\lambda_2 T_1)$ can be measured at T_1 K, e.g. the melting point of gold, so that the ratio $I(\lambda_1 T_2)/I(\lambda_2 T_2)$ is the only unknown parameter. The unknown temperature T_2 can therefore be calculated easily from eqn. (8).

EXPERIMENTAL

Apparatus and Materials

A Nippon Jarrell-Ash two-channel, dual-phase atomic absorption-flame emission spectrophotometer Model AA-8500, and a graphite-tube atomizer Model FLA-100 were used. The cross-sectional view of the graphite tube and the holder is shown in Fig. 1. The heating power was provided by a regulated sequential system. The two kinds of thermocouple used were made of alumel—chromel wire (0.5 mm diam.) and tungsten—rhenium wire (0.5 mm diam.). A Rikadenki Kogyo Model B-140 strip-chart recorder was used.

Test solutions were prepared from chloride salts. The purity of the metals used for the determination of temperatures was 99.9 % or higher.

Measurement techniques

Intensity ratio at two wavelengths. The graphite tube atomizer was installed in the atomic absorption-flame emission spectrometer instead of the burner head. A graphite plate (3 mm diam., 1 mm long) was inserted longitudinally in the centre of the graphite tube. Electric power was provided to the graphite tube in the step-wise mode, and emission intensities were measured. Of course, both channels of the atomic absorption-emission spectrometer were adjusted so that same electric output could be recorded for the same emission intensity. The emission intensities at 500 nm and 580 nm were measured simultaneously. Figure 2 shows the block diagram of the two-channel atomic absorption-emission spectrometer.

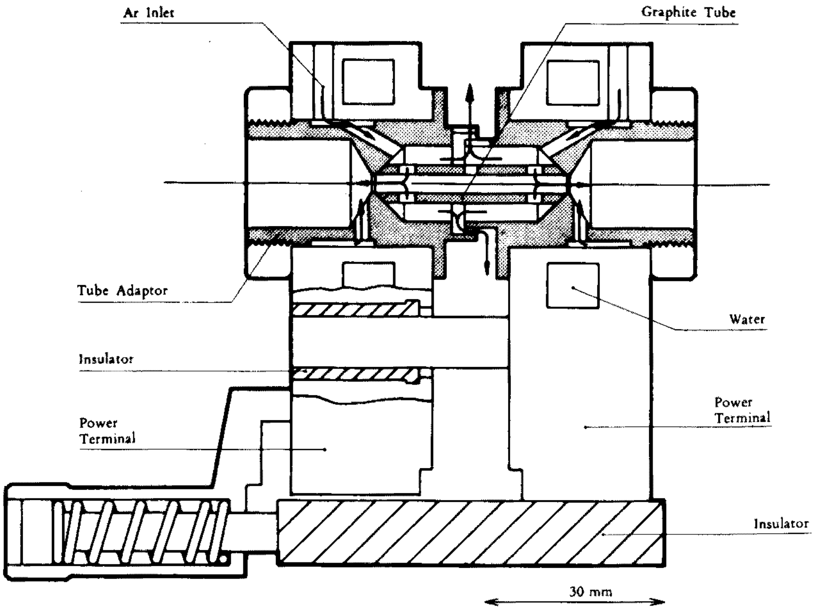

Fig. 1. Graphite tube atomizer.

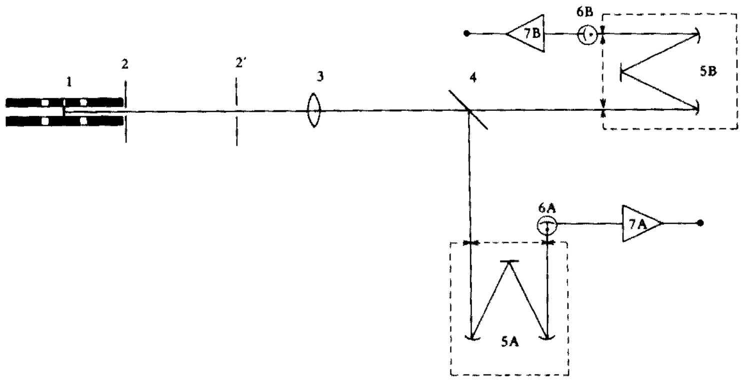

Fig. 2. Diagram of optics for measuring intensity ratios at two wavelengths. 1, Graphite cell. 2,2′ Pin hole. 3, Lens. 4, Half transmission mirror. 5A,B, Monochromator. 6A,B, Photomultiplier. 7A,B, Amplifier.

TABLE 1

Balanced intensity ratios versus currents
(Model AA-8500. Slit width, 0.3—0.5 mm Wavelengths: λ_1, 500 nm, λ_2, 580 nm)

Current (A)	Balanced intensity ratio *I* (500 nm/580 nm)	Current (A)	Balanced intensity ratio *I* (500 nm/580 nm)
80	0.206	200	0.690
90	0.250	220	0.747
100	0.300	240	0.800
110	0.353	260	0.844
120	0.399	280	0.892
140	0.448	300	0.940
160	0.562	320	0.980
180	0.630	330	1.010

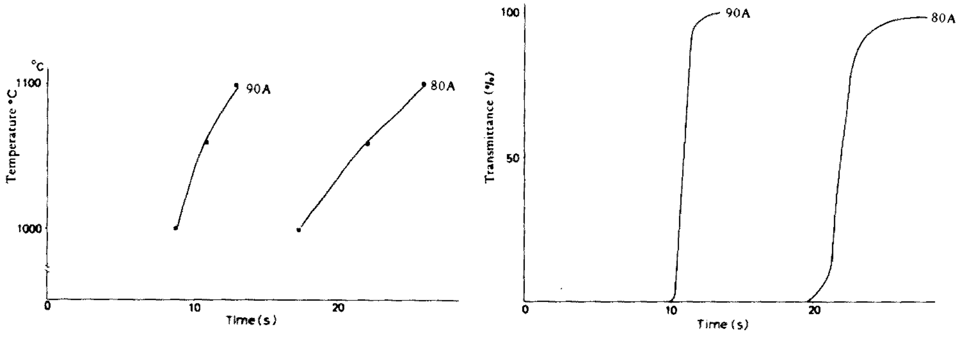

Fig. 3. Atomization time and melting point of gold.

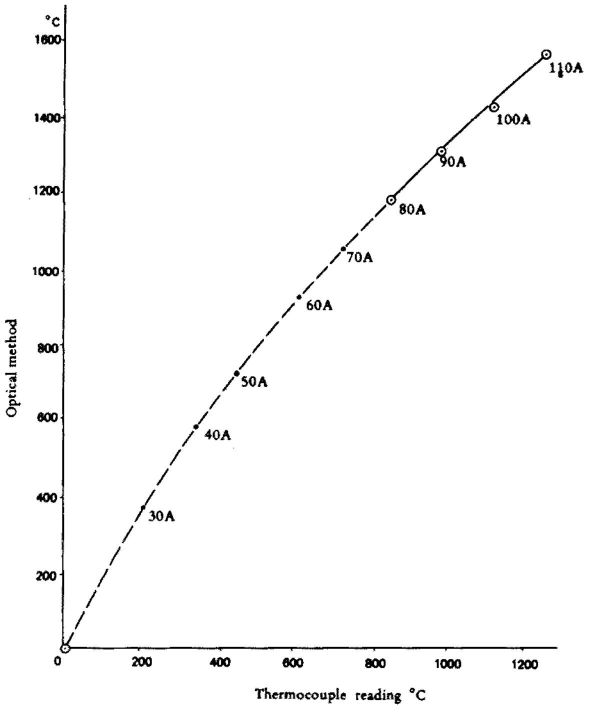

Fig. 4. Calibration of a thermocouple below 800 °C by the optical method.

When a single channel was used, the emission intensities at 500 nm and 580 nm were measured in turn at the same electronic gain with identical time schedules.

Standard temperature. On account of the heat capacity of the graphite tube, the balanced temperature was obtained after a certain period of time.

TABLE 2

Results of measuring high temperatures by the two-wavelength intensity ratio method with the melting point of gold for calibration
(Melting point of gold, 1064 °C; 80 A, 22 s; intensity ratio, 0.161)

Current (A)	$\ln \frac{0.161}{R}$	Temperature (°C)	Current (A)	$\ln \frac{0.161}{R}$	Temperature (°C)
80	−0.246	1184	200	−1.455	2349
90	−0.440	1297	220	−1.534	2495
100	−0.622	1418	240	−1.603	2634
110	−0.785	1544	260	−1.656	2750
120	−0.908	1653	280	−1.712	2885
140	−1.113	1866	300	−1.764	3023
160	−1.249	2036	320	−1.806	3141
180	−1.364	2201	330	−1.836	3233

A small gold plate was inserted into the centre of the graphite tube so as to cut off the beam of the hollow-cathode lamp. The graphite tube was then heated with a certain current. When the light transmittance of the hollow-cathode lamp showed 50 %, the temperature of the graphite tube was assumed to be that of the melting point of gold. The transmittance became 50 % after 22 s with a current of 80 A and after 11 s with 90 A (Fig. 3).

RESULTS AND DISCUSSION

Table 1 shows the relationship between the currents provided to the graphite tube and the intensity ratios when the intensity was obtained under thermal equilibrium. The times required for balanced temperatures of the graphite tube were about 25 s and 10 s with 100 A and 300 A, respectively.

The base intensity ratio, $I(500\ \mathrm{nm})/I(580\ \mathrm{nm})$, at the melting point of gold (1064 °C) was measured after application of 80 A for 22 s; the result was 0.161. The unknown temperature T_2 was then derived from eqn. (8). Results are given in Table 2.

The procedure for the determination of low temperatures which did not provide adequate emission intensity was as follows.

Determination of graphite temperature

The temperatures observed by the optical method and measured with the

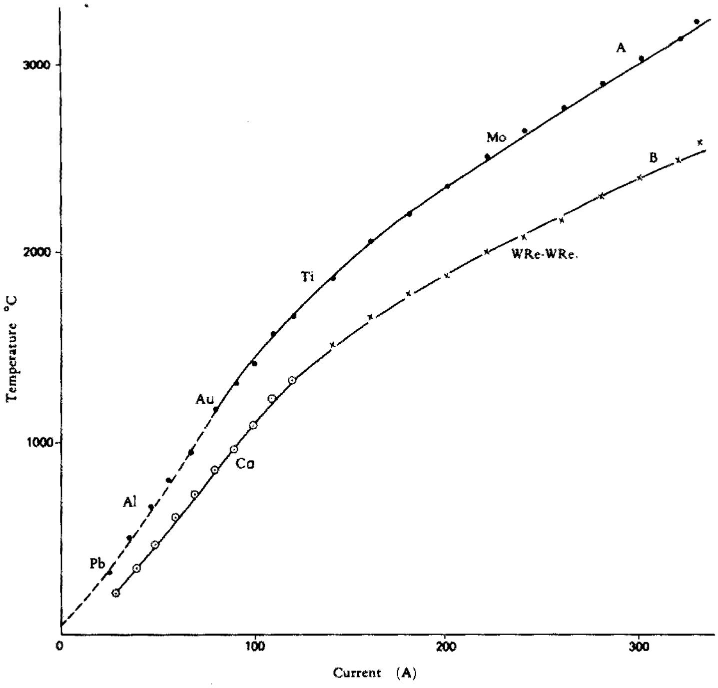

Fig. 5. Current and temperature achieved. A, Two-wavelength, one-point calibration method. B, Thermocouples.

thermocouple were plotted; the result is shown as a solid line in Fig. 4. Extrapolation was done as indicated by the dotted line in Fig. 4; this dotted line represents the correction coefficient for the observed temperature of the thermocouple. The calibration curve for the temperature of the graphite tube of the flameless atomizer finally obtained is shown as curve A in Fig. 5.

This calibration curve was confirmed by using the melting points of lead, aluminum, molybdenum and titanium; these temperatures showed good coincidence with the calibration curve. Tungsten and tantalum were tested in order to confirm the calibration curve, but the observed melting points fell outside the calibration curve, as shown in Table 3. Both elements are well known to form metal carbides easily in the graphite tube, because the theoretical carbon content in the metal carbide is 6 % or less (Table 3).

Table 4 shows the minimum atomization temperatures for some elements obtained by using the calibration curve. These temperatures correspond to absorbance measurements of 0.01 A.U. obtained by using 20 μl of 1000 μg ml^{-1} test solutions. In order to keep the partial pressure of oxygen as low as possible, the argon flow rate was set high. Figure 6 shows the relation between argon flow rate and minimum atomization temperature for different metals.

TABLE 3

Melting point of metal carbides

Element	M.p. of pure metal (°C)	M.p. of metal carbide (°C)	M.p. of metal in graphite tube (°C)	Theor. *C* content of metal carbide (%)	Metal carbide formation temp. (°C)
B	2300 ± 300	2450	—	20	2000
Ti	1820 ± 100	3250	1820 ± 100	22	1200
Si	1430 ± 20	2600	1700 ± 50	—	2290
Mo	2625 ± 20	2690	2575 ± 50	—	1100
V	1735 ± 50	3830	—	—	—
W	3410 ± 20	2867	3100 ± 100	6	1200
Ta	2996 ± 50	3880	3300 ± 100	6.2	1600

TABLE 4

Minimum atomization temperatures (°C)

Element	Present work	Aggett · Sprott (ref. 1)	Campbell · Ottaway (ref. 2)
Al	1350	1550	2027
Fe	1200	1230	1477
Mn	1200	1210	1327
Pb	600	860	727
Cr	1300	1380	1527
Zn	800	800	823
Cd	400	270	577
Mg	1150	1210	1277

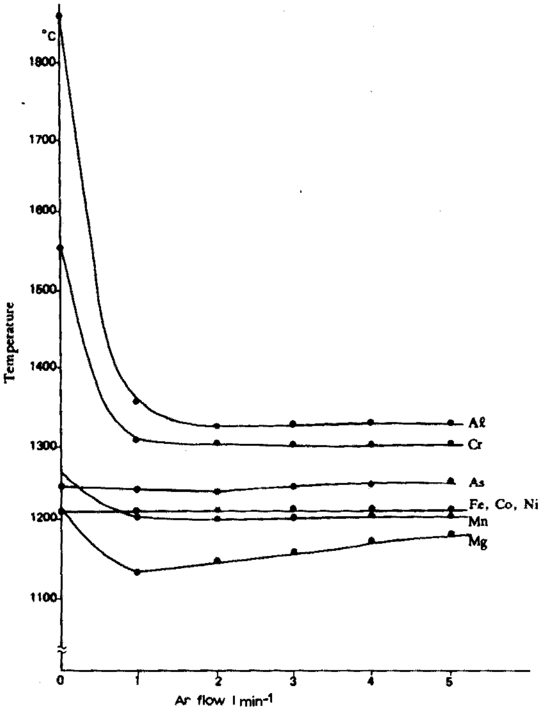

Fig. 6. Effect of argon flow rate on the minimum atomization temperature for different metals.

It can be seen that the atomization temperatures of elements such as aluminum and chromium which form stable oxides may be affected considerably by the argon flow rate. Probably the high flow rate of argon swept out any residual oxygen from the graphite tube and prevented diffusion of oxygen from the outside. The temperature of the inner wall of the graphite tube was almost unaffected by the argon flow rate when the graphite tube and holder described here were used.

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VAPORIZATION AND THERMAL DECOMPOSITION OF TRANSITION METAL SALTS IN FLAMELESS ATOMIC ABSORPTION SPECTROMETRY WITH A CARBON TUBE ATOMIZER

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SUMMARY

Vaporization and thermal decomposition of Cr, Mn, Fe, Co, Ni and Cu salts were investigated by measuring the absorption spectra observed when aqueous solutions of these salts were heated in the carbon tube atomizer. Gaseous metal halides are vaporized in the atomizer at temperatures above 300–500 °C. SO_2 and NO are produced by thermal decomposition of metal sulfates and nitrates, respectively. The vaporization of metal halides is also confirmed by the spectra for solutions of metals in hydrochloric acid and for mixtures of metal nitrates and ammonium halides.

Recently, various designs of flameless atomizers have been widely applied to the trace metal analysis of small liquid and solid samples. These techniques generally give better sensitivities and detection limits than conventional flame techniques. The higher sensitivity frequently allows chemical separations to be avoided and is especially valuable in work with very small samples. However, various types of interference effect occur in the application of flameless atomizers to trace metal analysis in a variety of samples [1–9]. In most cases, the formation and vaporization of undissociated molecules causes tedious kinds of interference such as molecular absorption, light scattering, and loss of test elements before formation of atoms [6–9]. These molecules are generally considered to be produced by the sublimation and thermal decomposition of salts in the sample, by the interaction of test elements with concomitants, and in some cases by vapor-phase reaction of free atoms with other atoms or molecules [1–3].

Molecular absorption of alkali and alkaline earth metal halides, oxides and hydroxides is well-known in flames and flameless atomizers [10–13]. These absorbing molecules have been confirmed by comparison with their emission spectra and with absorption spectra described in the literature. The other absorbing molecules, however, have not yet been confirmed in detail.

The present paper describes the absorption spectra observed when aqueous solutions of halides, sulfates and nitrates of transition metals such as chromium, manganese, iron, cobalt, nickel and copper are heated in the carbon tube atomizer. In addition, absorbing molecules produced by the vaporization and thermal decomposition of these salts are discussed with regard to their spectra.

EXPERIMENTAL

Apparatus

Absorption spectra were measured with Simazu MAF-1 atomic absorption spectrometer combined with Nippon Jarrell-Ash FLA-1 flameless carbon tube atomizer [9]. A deuterium lamp of the hollow-cathode type (Hamamatu TV, L233-1DQ) was used as a continuous light source operated at 30 mA. Argon gas was employed as the inert sheath gas at a flow rate of 2.0 l min^{-1}. Eppendorf micropipettes fitted with disposable plastic tips were used for placing test solutions in the atomizer. Temperatures of the atomizer were measured with a calibrated chromel-alumel thermocouple or an optical pyrometer.

Reagents

Test solutions of halides, sulfates and nitrates of chromium, manganese, iron, cobalt, nickel and copper were prepared by dissolving reagent-grade chemicals in distilled water without any purifications.

Procedures

Absorption spectra were measured by procedures similar to those for the usual flameless atomic absorption method [9]. The aqueous solution (20 μl) was dried for 10 s at 20 A (ca. 130 °C) and ashed for 15 s at 40 A (ca. 250 °C). The voltage was then increased rapidly to a higher value for 5 s to give a temperature high enough to obtain the most intense spectra. The spectra were plotted by point-by-point measurements of absorbances from 200 to 400 nm at intervals of 10, 5, 2.5 nm or less. The optimal tube current and temperature for the spectral measurement of each test solution are summarized in Table 1 together with the minimum temperature at which an absorption signal can be obtained. In all cases, the absorption intensities of each band increased gradually with increasing temperatures up to the optimal values listed and beyond this temperature intensities decreased slowly. However, there were no differences in the spectra obtained at any temperatures up to about 2600 °C.

RESULTS AND DISCUSSION

Chromium and iron halides

Absorption spectra for fluorides and chlorides of chromium and iron are shown in Fig. 1. Weak absorption bands below 300 nm were observed for $CrF_3 \cdot 3H_2O$ and $FeF_3 \cdot 3H_2O$ solutions heated at 500—2600 °C. From these spectra, however, it was impossible to determine the molecular species produced in the atomizer. When $CrCl_3 \cdot 9H_2O$ solution was heated above 500 °C, absorption was observed at wavelengths below 370 nm with intense bands near 202 and 305 nm, a weak band near 232 nm and shoulders near 210 and 275 nm. This spectrum is almost identical with that of gaseous

TABLE 1

Experimental conditions for the measurement of absorption spectra

Reagent	Concn. of metal (μg ml^{-1})	Tube current (A)	Temp. after 5 s (°C)	Minimum temp. (°C)
$CrF_3 \cdot 3H_2O$	500	230	1800	500
$CrCl_3 \cdot 9H_2O$	500	210	1600	500
MnF_2	500	180	1200	400
$MnCl_2 \cdot 4H_2O$	200	180	1200	400
$MnBr_2 \cdot H_2O$	200	180	1200	350
$FeF_3 \cdot 3H_2O$	500	230	1800	500
$FeCl_2 \cdot 4H_2O$	200	180	1200	350
$FeCl_3 \cdot 9H_2O$	200	180	1200	350
$CoF_2 \cdot 3H_2O$	500	230	1800	500
$CoCl_2 \cdot 6H_2O$	200	160	1000	350
$CoBr_2 \cdot 6H_2O$	200	140	800	300
CoI_2	500	140	800	300
$NiF_2 \cdot 4H_2O$	500	230	1800	500
$NiCl_2 \cdot 6H_2O$	200	160	1000	350
$NiBr_2$	200	140	800	300
$NiI_2 \cdot 6H_2O$	500	140	800	300
$CuF_2 \cdot 2H_2O$	500	230	1800	500
$CuCl$	200	140	800	300
$CuCl_2 \cdot 2H_2O$	200	140	800	300
$CuBr_2$	200	140	800	300
Sulfates	1000	140—160	800—1000	300—400
Nitrates	1000	30	150	100

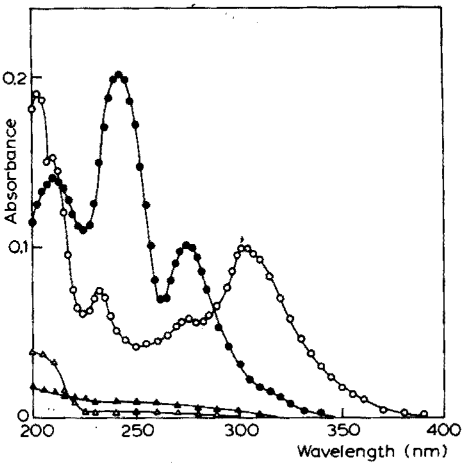
$CrCl_2$ reported by DeKock and Gruen [14]. The result shows that gaseous $CrCl_2$ is formed in the atomizer during heating of this chloride solution.

When $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 9H_2O$ solutions were heated above 350 °C, three absorption bands near 210, 242 and 275 nm were obtained. These bands correspond quite well with those of gaseous $FeCl_2$ [14, 15]. Christian and Gregory [16] have noted that the spectrum of gaseous $FeCl_3$ has two bands near 243 and 361 nm because of the dimeric Fe_2Cl_6. However, such bands were not observed in the present measurements for iron chlorides. Consequently, it is clear that gaseous $FeCl_2$ is vaporized in the atomizer during heating of $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 9H_2O$ solutions.

Manganese halides

Figure 2 shows the absorption spectra for manganese fluoride, chloride and bromide. Because of the lower atomization temperature of manganese than the other metals tested here, the atomic absorption signal of manganese near 279.5 nm was observed when these halides were heated above 800 °C.

When MnF_2 solution was heated above 400 °C, absorption was observed in the two wavelength regions 200—270 and 330—370 nm. The former band



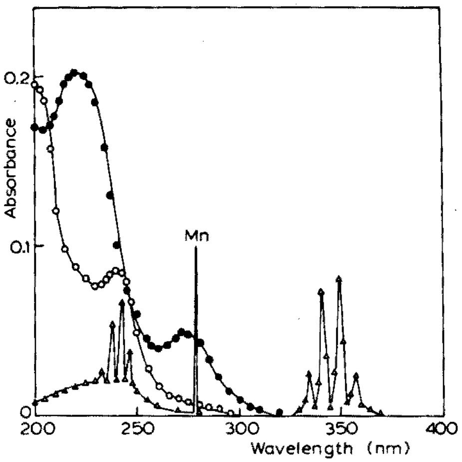


Fig. 1. Absorption spectra for chromium and iron halides. (△) $CrF_3 \cdot 3H_2O$; (○) $CrCl_3 \cdot 9H_2O$; (▲) $FeF_3 \cdot 3H_2O$; (●) $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 9H_2O$.

Fig. 2. Absorption spectra for manganese halides. (△) MnF_2; (○) $MnCl_2 \cdot 4H_2O$; (●) $MnBr_2 \cdot H_2O$.

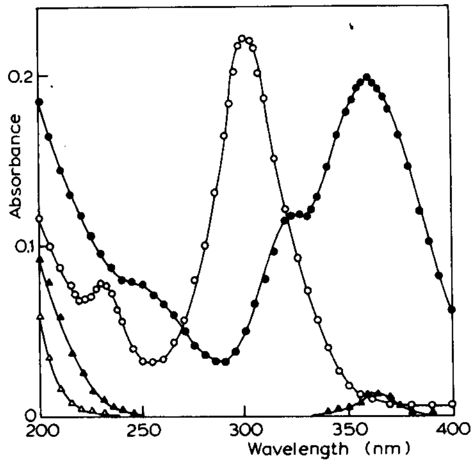
consisted of four maxima near 235, 238, 242 and 245 nm, while the latter band had four maxima near 334, 342, 349 and 357 nm. These two bands correspond to those of gaseous MnF and MnF_2 [17—19] respectively. It is considered from this spectrum that two gaseous fluorides are vaporized in the atomizer during heating of MnF_2 solution.

When $MnCl_2 \cdot 4H_2O$ solution was heated above 400 °C, an intense band below 210 nm and a weak band near 240 nm were obtained. The u.v absorption spectrum of gaseous $MnCl_2$ has not been published, but absorption by gaseous MnCl near 240—250 nm has been reported by Bacher [17]. Therefore, the observed spectrum is probably due to gaseous MnCl and $MnCl_2$, which would be expected to be vaporized in the atomizer during heating of $MnCl_2 \cdot 4H_2O$ solution.

When $MnBr_2 \cdot H_2O$ solution was heated above 350 °C, an intense band near 220 nm and a weak band near 272 nm were obtained. The u.v. absorption spectrum of gaseous $MnBr_2$ has not been reported; absorption by gaseous MnBr near 370—390 nm has been recorded [17], but this band was not observed in the present study. Therefore, the spectrum obtained for $MnBr_2 \cdot H_2O$ solution is probably due to gaseous $MnBr_2$.

Cobalt halides

Absorption spectra for cobalt halides are shown in Fig. 3. Weak absorptions below 240 nm were observed for $CoF_2 \cdot 3H_2O$ solution heated at 500—2600 °C, but the vaporized molecules could not be identified. In the case of $CoCl_2 \cdot 6H_2O$ solution heated above 350 °C, an intense band near 300 nm and a weak band near 230 nm were obtained. This spectrum is in good



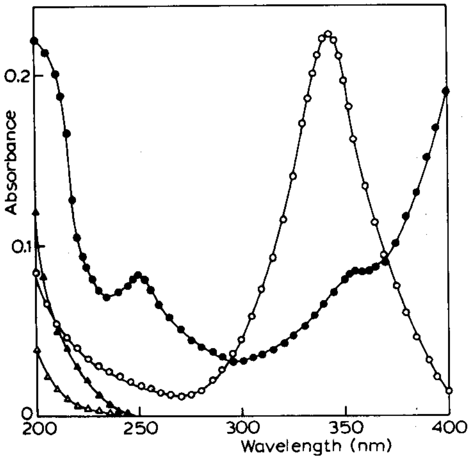


Fig. 3. Absorption spectra for cobalt halides. (△) $CoF_2 \cdot 3H_2O$; (○) $CoCl_2 \cdot 6H_2O$; (●) $CoBr_2 \cdot 6H_2O$; (▲) CoI_2.

Fig. 4. Absorption spectra for nickel halides. (△) $NiF_2 \cdot 4H_2O$; (○) $NiCl_2 \cdot 6H_2O$; (●) $NiBr_2$; (▲) $NiI_2 \cdot 6H_2O$.

agreement with that of gaseous $CoCl_2$ [14, 15] which indicates that gaseous $CoCl_2$ is vaporized during heating.

When $CoBr_2 \cdot 6H_2O$ solution was heated above 300 °C, an intense band near 360 nm and shoulders near 245 and 325 nm were obtained. Although the u.v. absorption spectrum of gaseous $CoBr_2$ has not been reported, Leroi et al. [20] have obtained an i.r. spectrum of gaseous $CoBr_2$ when the anhydrous salt is heated at 800—1000 °C in an argon atmosphere. The spectrum obtained here is probably due to gaseous $CoBr_2$ in the atomizer.

In the case of CoI_2 solution heated above 300 °C, absorption was observed at 200—250 nm and 340—380 nm. Absorption below 250 nm is probably due to I_2 vapor produced by thermal decomposition of CoI_2 [21]. The weak band near 360 nm corresponds to that of gaseous CoI_2 suggested by Butkow and Wojeiechowska [21].

Nickel halides

Figure 4 shows the absorption spectra for nickel halides. Weak unidentifiable absorption below 240 nm was observed for $NiF_2 \cdot 4H_2O$ solution heated at 500—2600 °C.

An intense band near 342 nm was observed for $NiCl_2 \cdot 6H_2O$ solution heated above 350 °C. This spectrum corresponds quite well with that of gaseous $NiCl_2$ [14, 15], hence it is clear that gaseous $NiCl_2$ is vaporized in the atomizer.

When $NiBr_2$ solution was heated above 300 °C, absorption was observed at all wavelengths studied, with a weak band near 250 nm and a shoulder near 355 nm. Beyond 360 nm, the absorption increased rapidly up to near

420 nm; this 420-nm band was not observed for the other bromides studied here. Butkow and Wojeiechowska [21] have noted that gaseous $NiBr_2$ absorbs near 353 nm in the narrow temperature range 640—660 °C, the band being overlapped by Br_2 absorption near 420 nm at higher temperatures because of thermal decomposition of $NiBr_2$. To follow up their results, the spectrum for $NiBr_2$ solution was investigated at various temperatures over the range 300—2600 °C, but the same spectra were observed at all temperatures. In an i.r. study, DeKock and Gruen [22] obtained the spectrum of gaseous $NiBr_2$ from the anhydrous salt heated at 786 °C in a quartz cell. Furthermore, Schafer and Jacob [23] have reported that $NiBr_2$ is sublimed at 919 °C under 1 atm. From these results, it is considered that gaseous $NiBr_2$ is formed under the present experimental conditions.

In the case of $NiI_2 \cdot 6H_2O$ solution heated above 300 °C, absorptions below 250 nm were observed, probably because of I_2 vapor produced by thermal decomposition of NiI_2 [21], as in the case of CoI_2.

Copper halides

Figure 5 shows the absorption spectra for copper fluoride, chlorides and bromide. Weak unidentifiable absorption below 300 nm was observed for $CuF_2 \cdot 2H_2O$ solution heated at 500—2600 °C.

When CuCl and $CuCl_2 \cdot 2H_2O$ solutions were heated above 300 °C, both chlorides gave almost identical spectra below 350 nm with an intense band near 223 nm. This spectrum agrees with that of gaseous Cu_3Cl_3 assigned recently by Hilden and Gregory [24]. The results indicate that gaseous Cu_3Cl_3 is produced in the atomizer during heating of both chloride solutions by the following processes:

$$CuCl_2 \cdot 2\,H_2O(s) \rightarrow CuCl(s) + 1/2Cl_2\,(g)$$

$$CuCl(s) \rightarrow CuCl(g)$$

$$3\,CuCl(g) \rightarrow Cu_3Cl_3\,(g)$$

In the case of $CuBr_2$ solution heated above 300 °C, an intense band near 230 nm was observed. This spectrum agrees closely with that of gaseous Cu_3Br_3 [24], which indicates that gaseous Cu_3Br_3 is produced in the atomizer, analogously to the formation of Cu_3Cl_3.

Metal sulfates and nitrates

It is well known that most oxy-anion salts such as metal sulfates and nitrates are decomposed to the corresponding metal oxides in flameless atomizers during heating of these salt solutions. In order to confirm this process, the gaseous products of thermal decomposition of these salts were identified from the absorption spectra for the solutions of metal sulfates and nitrates given below:

$Cr_2(SO_4)_3 \cdot n\,H_2O$, $MnSO_4 \cdot 4–6\,H_2O$, $FeSO_4 \cdot 7\,H_2O$, $CoSO_4 \cdot 7\,H_2O$, $NiSO_4 \cdot 7\,H_2O$, $CuSO_4 \cdot 5\,H_2O$, $Cr(NO)_3 \cdot 9\,H_2O$, $Mn(NO_3)_2 \cdot 6\,H_2O$, $Fe(NO_3)_3 \cdot 9\,H_2O$, $Co(NO_3)_2 \cdot 6\,H_2O$, $Ni(NO_3)_2 \cdot 6\,H_2O$ and $Cu(NO_3)_2 \cdot 3\,H_2O$.

The absorption spectrum of sulfur dioxide [12] was observed for all metal sulfates heated above 300—400 °C. Nitric oxide gamma bands [12] near 204.6, 214.6 and 226.0 nm were observed for all nitrates during drying at about 100—150 °C. In both cases, no absorption by other molecules was observed at any higher temperatures in the wavelength region studied. The result shows that metal sulfates and nitrates are decomposed to oxides in the atomizer after evolution of SO_2 and NO, respectively. Similar results have been found for alkali metal sulfates and nitrates [12].

Metals in solutions containing halogen ions

The formation and vaporization of metal halides in flames and flameless atomizers have been suggested in chemical interference studies of hydrochloric acid and halides [3—5]. In order to investigate this mechanism, absorption spectra for mixtures of the above-mentioned metal ions and halides were measured by the procedures described above.

Initially, solutions containing 1.0 mg ml^{-1} of the metal were prepared by dissolving the high-purity metal in hydrochloric acid, with dilution to a final acidity of about 1 M. When these solutions were heated above 300—500 °C, the spectra observed were the same as those of the metal chlorides (Figs. 1—5).

Next, mixtures of metal ions (1.0 mg ml^{-1}) and halide ions (1.0 mg ml^{-1}) were prepared by the addition of ammonium halides to the metal nitrate solutions used in the preceding section. Except for the spectra of NO and

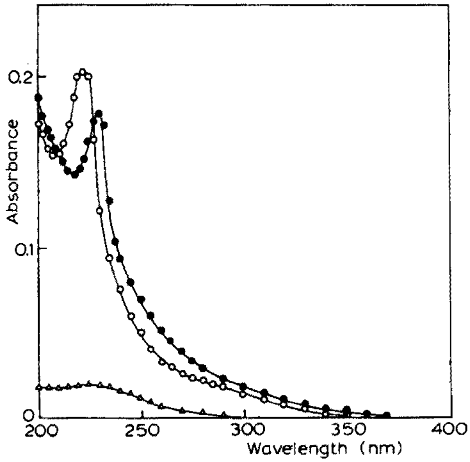


Fig. 5. Absorption spectra for copper halides. (△) $CuF_2 \cdot 2H_2O$; (○) CuCl and $CuCl_2 \cdot 2H_2O$; (●) $CuBr_2$.

NH_3 produced by thermal decomposition of the salts during drying at 100—150 °C, the same spectra as those of the respective metal halides and discussed above were obtained for the mixtures heated above 300—500 °C. These results are similar to those obtained for mixtures of alkali metal nitrates and ammonium halides [12].

The above results suggest that the interfering effects of hydrochloric acid and halogen ions on atomic absorption measurements of metals should be attributed to the vaporization of considerable amounts of undissociated metal halides before the formation of atoms. Consequently, standard metal solutions of oxy-anion salts should be preferred for flameless atomizers rather than the chloride solutions normally used in flame atomization.

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THE DETERMINATION OF METALS IN PETROLEUM SAMPLES BY ATOMIC ABSORPTION SPECTROMETRY
PART II. DETERMINATION OF NICKEL

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SUMMARY

Some atomic absorption characteristics of xylene solutions of eight organometallic compounds of nickel in air—acetylene and nitrous oxide—acetylene flames are described. Different absorbances from various nickel organometallic compounds were observed; these differences were not eliminated by using the nitrous oxide—acetylene flame. Serious errors may arise when different organometallic compounds are used for calibration in the determination of nickel in xylene solutions of various petroleum samples. These errors are much less pronounced when nickel is determined by a standard addition technique. The effects of different sample matrices are discussed.

In petroleum samples, nickel — as well as vanadium — is present in the form of organometallic compounds, which may be either of the porphyrin or non-porphyrin type [1—3]. In the porphyrin compounds, nickel is bound by four nitrogen donor atoms, while in the non-porphyrin compounds, oxygen and sulphur can also act as donor atoms [4—6].

When atomic absorption spectrometry is used for the determination of nickel in petroleum samples, considerable troubles have been found in some cases, and these have been attributed to a complex matrix effect of the petroleum samples [7, 8]. For example, Takeuchi et al. [9] observed a dependence of the nickel absorbance on the type of nickel complex extracted into MIBK; the cupferrate, diethyldithiocarbamate and dithizonate exhibited higher absorption signals than the hydroxyquinolinate and salicylaldoximate. Kashiki and Oshima [10] have shown that the addition of halogen eliminates the differences in the atomic absorption signals from various nickel compounds such as nitrate, naphthenate and acetylacetonate in MIBK media. Leonard and Swindall [11] suggested that either a single nickel—ligand complex should be used in samples and reference solutions, or that the high-temperature nitrous oxide—acetylene flame should be employed. They showed, for instance, that in the low-temperature air—acetylene flame, the burner height

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for maximum absorption of nickel cyclohexanebutyrate, which contains metal—oxygen bonds, and that for samples which do not contain such bonds, can differ significantly.

In the work described here, the effects of using different organometallic compounds of nickel for the preparation of nickel reference solutions for the direct determination of nickel in petroleum samples diluted with xylene, are described. The compounds tested were tetraphenylporphyrin, cyclohexanebutyrate, naphthenate, acetylacetonate, benzoylacetylacetonate, monothioacetylacetonate, dithioacetylacetonate and Conostan nickel standard. The measurements were carried out in air—acetylene and nitrous oxide—acetylene flames.

EXPERIMENTAL

Apparatus

All measurements were carried out with a Varian-Techtron model AA-6 atomic absorption spectrometer equipped with an AB-51 burner for an air—acetylene flame and an AB-50 burner for a nitrous oxide—acetylene flame. A shielded nickel hollow-cathode lamp (A.S.L.) was used as the primary line source. Other experimental conditions were as follows: analytical line, 232.0 nm; spectral bandwidth, 0.2 nm; lamp current, 8 mA; air flow rate, 7.7 l min^{-1} and acetylene flow rate, 1.0 l min^{-1} for the air—acetylene flame; nitrous oxide flow rate, 5.0 l min^{-1} and acetylene flow rate, 4.4 l min^{-1} for the nitrous oxide—acetylene flame; rate of solution aspiration, 2.0 ml min^{-1}; height of observation, 0 mm (just above the burner top).

Stock solutions

Stock xylene solutions of organometallic compounds were prepared following, in general, the prescriptions of Dean and Rains [12], except for the nickel tetraphenylporphyrin, nickel naphthenate and nickel Conostan standards.

Nickel tetraphenylporphyrin (NiTPP; 10 μg Ni ml^{-1}). The synthesized compound [13] (0.0129 g) was dissolved in 30 ml of hot xylene; after cooling, the solution was transferred to a 100-ml volumetric flask and diluted to the mark with xylene.

Nickel cyclohexanebutyrate (NiCHB; 100 μg Ni ml^{-1}). The compound (0.0649 g; BDH Chemicals) was dissolved in 30 ml of xylene with the addition of 10 ml of 2-ethylhexanoic acid, 5 ml of 6-methyl-2,4-heptanedione and 2 ml of dimethylaniline; when all the material had dissolved, the solution was transferred to a 100-ml volumetric flask and diluted to the mark with xylene.

Nickel acetylacetonate (NiAA) and *nickel benzoylacetonate* (NiBA).

Solutions (100 μg Ni ml^{-1}) were prepared by dissolving 0.0502 g and 0.0701 g of the synthesized compound [14, 15], respectively, in the same way as for NiCHB.

Nickel naphthenate (NiNaph; 100 μg Ni ml^{-1}). The compound (0.1059 g; Setuza Lovosice, Czechoslovakia) was dissolved in hot xylene; after cooling, the solution was transferred to a 100-ml volumetric flask and diluted to the mark with xylene.

Conostan nickel standard (NiCON; 100 μg Ni ml^{-1}). This standard (2.0000 g; Continental Oil Company, U.S.A.) was dissolved in 30 ml of hot xylene with the addition of 0.5 ml of a Conostan solubilizer; after cooling, the solution was transferred to a 100-ml volumetric flask and diluted to the mark with xylene.

Stock solutions of nickelmonothioacetylacetonate (NiMTAA) and nickeldithioacetylacetonate (NiDTAA) containing 100 μg Ni ml^{-1} were prepared by dissolving 0.0492 and 0.0546 g of the compound, respectively, in the same way as for NiCHB.

All the compounds synthesized were checked gravimetrically for their nickel content.

Sample preparation

The effect of the nickel bonding was studied with synthetic mixtures of the standards in xylene, as well as with real petroleum samples. The following petroleum samples were used: 1. a deasphalted sample from Romashkino vacuum residuum (U.S.S.R.); 2. a deasphalted sample from Kuwait vacuum residuum; 3. Karathoug crude oil (Syria); 4. Morgan crude oil (Egypt); 5. a hydrogenated atmospheric residuum from Romashkino crude oil: 6. an atmospheric residuum from Romashkino crude oil; 7. a Romashkino propane asphalt; 8. a Saratoff propane asphalt (U.S.S.R.).

Appropriate amounts of these samples — not more than 1 g per 10 ml of xylene — were dissolved with slight heating in xylene; after cooling, the solutions were diluted to a definite volume with xylene.

The nickel contents of these samples, which were considered as reference values, were determined by conventional atomic absorption spectrometry after mineralization of the samples with *p*-xylenesulfonic acid. The results are shown in Table 1.

TABLE 1.

Nickel content (μg g^{-1}) in petroleum samples determined by a.a.s. after mineralization

Sample	1	2	3	4	5	6	7	8
Ni (p.p.m.)	43.5	13.8	50.0	28.1	18.6	51.3	59.5	130.5

RESULTS AND DISCUSSION

Calibration curves were constructed by using reference solutions prepared from all the organometallic compounds investigated, and were measured (under the experimental conditions described above) in both the air—acetylene and the nitrous oxide—acetylene flames. To evaluate possible effects of a hydrocarbon matrix, series of the reference solutions were prepared also with the addition of Conostan base oil No. 245 (2 g of the oil per 10 ml) and of a paraffin oil.

In both the flames studied, reference solutions containing the same concentration of the metal but prepared from different organometallic compounds gave different absorption signals. (These differences, however, were less pronounced than in the case of vanadium [17].) To simplify the evaluation, the maximum permissible experimental error (r.s.d., 5 %) was taken into account; with this reservation, a single calibration curve could be plotted in some cases for several organometallic compounds, as can be seen in Fig. 1. In both the flames, the calibration curve corresponding to NiTPP exhibited the highest slope, while that corresponding to NiMTAA and NiDTAA exhibited the lowest slope. The simulated hydrocarbon matrix (measured in the air—acetylene flame) had no effect on the results; calibration curves measured with reference solutions with and without addition of base oil were identical within experimental error (Fig. 1a).

The existence of several calibration curves for different organometallic compounds of nickel has obvious consequences for the analytical results of real petroleum samples; the more different calibration curves, the more different results for one sample are possible. Table 2 shows the results for the eight petroleum samples studied. When the nickel contents determined after mineralization (see Table 1) are compared with those determined in xylene solutions in the air—acetylene flame (Table 2), it can be seen that an evaluation from the calibration curves of all the organometallic compounds investigated (except for MTTA and DTAA) gives lower results in almost all cases. In the nitrous oxide—acetylene flame, the values obtained after mineralization correspond best to those obtained from the calibration curves of MTAA and DTAA and, in some cases also to those evaluated from some other calibration curves with lower slope.

To verify the utility of a standard addition technique, the additivity of the analytical signals from binary combinations of the organometallic compounds investigated was examined in the air—acetylene flame. Additions of 1 and 2 μg Ni ml^{-1} prepared from one organometallic reference solution were added to the reference solution (1 μg Ni ml^{-1}) prepared from a second organometallic compound. In the case of real petroleum samples, which were diluted to a concentration level of about 1 μg Ni ml^{-1}, additions were made analogously. Table 3 shows that the application of the addition technique to binary combinations of pure organometallic compounds yields results different from those which would be expected from the calibration curve profiles of the

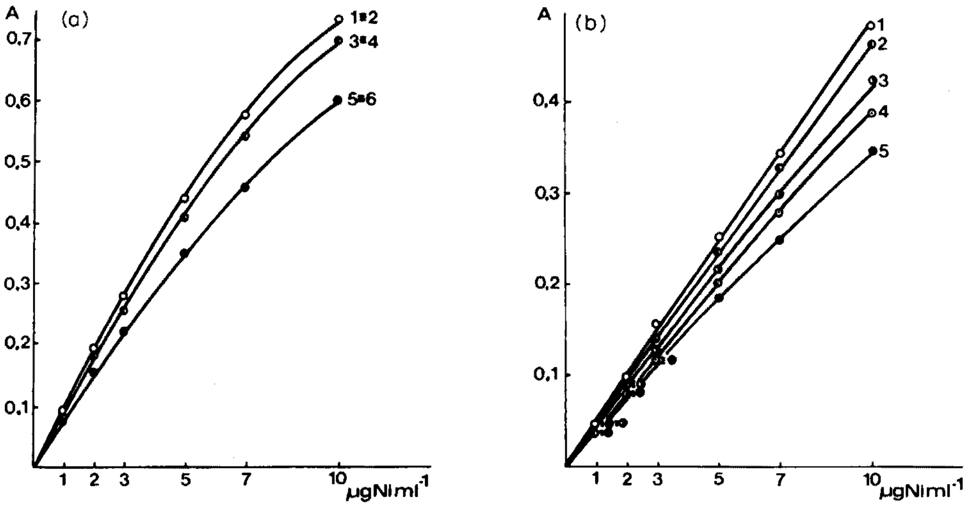

Fig. 1. Calibration curves for nickel obtained with reference solutions prepared from different organometallic compounds.
(a) Air—acetylene flame
1, NiTPP, NiAA, NiBA (in xylene).
2, NiTPP, NiAA, NiBA (in oil matrix).
3, NiCHB, NiCON, NiNaph (in xylene).
4, NiCHB, NiCON, NiNaph (in oil matrix).
5, NiMTAA, NiDTAA (in xylene).
6, NiMTAA, NiDTAA (in oil matrix).
(b) Nitrous oxide—acetylene flame
1, NiTPP, NiAA (in xylene).
2, NiBA, NiNaph (in xylene).
3, NiCHB (in xylene).
4, NiCON (in xylene).
5, NiMTAA, NiDTAA (in xylene).

corresponding organometallic compounds. This can be partly explained by the fact that the measurements must be done within a linear part of the calibration curves, i.e. at low nickel concentrations, where the differences between individual calibration curves are small and where an experimental error of measurement of the analytical signals may play a significant role.

Application of the addition technique to the real petroleum samples gave the results listed in Table 4. It is apparent that, again, these results exhibit little analogy with those obtained from the calibration curves or with those listed in Table 3. This can be attributed to a significant effect of the complex structure of petroleum samples.

The discussion presented above is primarily of a descriptive character. Although many more real petroleum samples were investigated than are included in this paper, no typical and significant relation between the type of the sample (sample matrix) and the results obtained could be found. It is clear, however, that without a perfect knowledge of the sample structure, i.e.

TABLE 2

Nickel contents in petroleum samples determined by the calibration curve technique in air—acetylene and nitrous oxide—acetylene flames (All results are given in μg g^{-1}.)

Sample	NiTPP[a]	NiCHB	NiAA	NiBA	NiNaph	NiMTAA	NiDTAA	NiCON
Air—acetylene flame								
1	33.8	36.2	33.8	33.8	36.2	44.9	44.9	36.2
2	10.9	11.3	10.9	10.9	11.3	13.2	13.2	11.3
3	41.8	45.9	41.8	41.8	45.9	55.6	55.6	45.9
4	27.5	29.3	27.5	27.5	29.3	35.4	35.4	29.3
5	17.9	18.8	17.9	17.9	18.8	22.6	22.6	18.8
6	40.7	44.0	40.7	40.7	44.0	53.4	53.4	44.0
7	50.1	54.4	50.1	50.1	54.4	65.4	65.4	54.4
8	117.1	127.6	117.1	117.1	127.6	160.4	160.4	127.6
Nitrous oxide—acetylene flame								
1	35.3	39.8	35.3	32.0	38.6	47.1	47.1	42.2
2	10.2	11.8	10.2	10.6	11.3	13.2	13.2	12.5
3	42.7	48.7	42.7	44.9	47.3	58.9	58.9	51.7
4	25.8	29.5	25.8	27.1	28.6	34.1	34.1	31.0
5	16.2	18.6	16.2	17.2	18.1	21.1	21.1	19.5
6	41.6	47.3	41.6	43.8	46.0	55.8	55.8	50.1
7	51.6	59.5	51.6	54.1	57.8	70.3	70.3	62.5
8	124.7	144.6	124.7	132.8	140.0	175.0	175.0	154.0

[a]For abbreviations, see Experimental.

TABLE 3

Nickel contents in xylene solutions of organometallic standards determined by the addition technique (All results are given in μg ml^{-1}.)

Sample	Standard							
	NiTPP[a]	NiCHB	NiAA	NiBA	NiNaph	NiMTAA	NiDTAA	NiCON
NiTPP	—	1.06	1.05	1.16	1.11	1.53	1.76	1.14
NiCHB	0.96	—	0.99	1.03	1.16	1.46	1.35	0.96
NiAA	1.03	0.98	—	0.88	1.06	1.59	1.50	0.86
NiBA	1.05	0.92	0.99	—	1.02	1.46	1.17	1.02
NiNaph	0.79	0.71	0.75	0.63	—	0.91	0.95	0.65
NiMTAA	0.65	0.79	0.73	0.75	0.90	—	1.00	0.72
NiDTAA	0.76	0.89	0.86	0.70	0.91	0.74	—	0.60
NiCON	1.45	1.33	1.41	1.34	1.43	1.85	1.76	—

[a]For abbreviations, see Experimental.

TABLE 4

Nickel contents in petroleum samples determined by the addition technique (All results are given in μg g^{-1}.)

Sample	NiTPP	NiCHB	NiAA	NiBA	NiNaph	NiMTAA	NiDTAA	NiCON
1	47.9	46.1	43.3	44.2	47.0	73.7	65.0	50.7
2	14.2	12.8	14.3	13.5	13.6	18.1	17.8	13.7
3	53.8	44.9	49.3	51.5	55.5	72.2	70.2	53.5
4	31.9	32.2	31.0	34.4	34.9	44.4	40.0	33.1
5	22.7	24.0	20.9	15.7	17.7	32.7	31.2	26.1
6	48.9	47.2	47.2	46.1	50.6	70.4	71.0	48.3
7	62.3	52.1	60.8	55.7	65.9	95.8	70.1	67.9
8	129.9	139.0	—	129.9	144.1	187.0	179.2	132.5

which donor atoms are involved in binding nickel in each petroleum sample, and of the behaviour of all metal-containing components of the sample in the flame, etc., no satisfactory explanation and interpretation of the observed effects is possible. The solution of these complex problems is not within the capacity of the atomic absorption technique alone, and the integration of a number of modern instrumental analytical techniques will be necessary. An attempt to make a more detailed evaluation of the facts observed will be reported in a later communication.

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THE DETERMINATION OF ZINC, CADMIUM, LEAD AND COPPER IN A SINGLE SEA-WATER SAMPLE BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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SUMMARY

A comparative study is described of the anodic stripping voltammetry of sea water at its natural pH and at acetate-buffered pH, with a mercury film electrode. The reproducibility of the oxidation current peaks for copper and lead is improved and the electrode memory effect decreases, when the sample is acetate-buffered (pH 5.8). Determinations of zinc at the natural pH of sea water are inaccurate, because of the formation of Zn—Cu and Zn—Ni intermetallic compounds in the mercury film. The formation of such compounds can be prevented by the addition of gallium ions to acetate-buffered samples. A procedure for the determination of Cu, Pb, Cd and Zn in sea water is described.

The high sensitivity of anodic stripping voltammetry has attracted a great deal of attention to the potentiality of the method for the determination of metals at the 10^{-9} M level. Such a technique is suitable for direct determination of metal ions in natural waters and obviates the preconcentration step needed [1, 2] for analysis by the more conventional methods such as atomic absorption spectrometry. Anodic stripping voltammetry (a.s.v.) has been discussed in several reviews which deal with its principles [3], applications [4, 5] and theory [6, 7, 8] as well as the behaviour of the various electrodes commonly used in either linear sweep (d.c) or differential pulse stripping mode [9]. Differential pulse a.s.v. offers a much improved detection limit compared to linear sweep a.s.v., the non-faradaic component of the peak current being greatly reduced.

The application of a.s.v. to natural waters has been confined to the determination of only a few elements such as copper, lead and cadmium [10—12]. Although a.s.v. is suitable for the determination of other metals such as zinc, the formation of intermetallic compounds such as Cu—Zn and Ni—Zn and others in the mercury film or hanging mercury drop [5, 13—15] can introduce large errors because of lack of peak reproducibility [14]. In spite of this, the determination of zinc in the presence of copper in natural waters

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has been attempted [16—18].

The elimination of the Cu—Zn intermetallic compounds by the presence of gallium ions has recently been suggested [14]. An examination of the effect of gallium ions on other intermetallic compounds is presented here, together with a comparison between the determination of Cu, Pb, Cd and Zn in sea water at natural pH and in buffered solution by means of differential pulse a.s.v.

EXPERIMENTAL

Apparatus

A Southern-Analytical Pulse Polarograph (A3100) and a Princeton Applied Research pulse polarographic analyser (174) were used with a Metrohm polarographic cell (EA 880—20) fitted with a saturated calomel electrode (SCE), a platinum counter electrode and a mercury film electrode (MFE). Stirring was effected with a purified nitrogen stream which also served to remove oxygen. The flow of nitrogen was controlled by a capillary pressure-limiting valve.

A comparative study of linear sweep a.s.v. was made with an ESA (2014) 4-cell a.s.v. analyser. The cells were fitted with three electrodes (MFE, Ag—AgCl and Pt) and the solution was stirred with a nitrogen stream.

Reagents

Mineral acids used were Merck Suprapur grade or double-distilled from an all-quartz distillation unit. Acetate buffers were made up from analytical-grade reagents and cleaned electrolytically for 2 weeks. A series of acetate buffers (2 M) of pH 7.8—5.4 were prepared from appropriate amounts of K_2CO_3 and acetic acid, the excess of CO_2 being boiled off. When cold, the solutions were placed in the purifying apparatus and purged with nitrogen for 1 h, and the final pH was adjusted with 2 M acetic acid before purification commenced.

Preparation of the mercury film electrode

Spectrographic-grade graphite rods (6 mm diameter) were chosen for the working electrode because of availability, low cost, ease of preparation and simplicity of cell assembly. Untreated graphite usually exhibits high residual current characteristics, but when impregnated with wax, an improvement in the S/N ratio is obtained. Different impregnating materials have been used and when ceresin wax is employed, the S/N ratio is improved [19] by a factor of more than 12. Slight improvement was reported when a glassy carbon electrode was used. However, this advantage is often not realised because of the lower sensitivity connected with the smaller active surface area of such electrodes.

For impregnation, a batch (4—6) of graphite rods was placed in a glass tube packed with shavings of ceresin wax. The whole was evacuated to less than 0.1 mm Hg for a minimum of 1 h, placed upright in a water bath set at 90 °C for 30 min, still under vacuum, and then allowed to cool to 40—50 °C before the electrodes were removed. The conductive surface was then accurately machined and shaped on a small lathe. The electrode was mounted in the cell with a PTFE plug fitting.

The stability of the mercury film was found to depend on the preparation of the conductive surface of the electrode. When a highly polished surface was produced, the film was composed of an even distribution of fine droplets of mercury. However, this film proved to be very unstable; on removal from the plating solution, coalescence of the droplets produced patchiness in the texture and marked increase in the residual current. It is probably for this reason that the formation of the mercury film in situ has been adopted by some workers [10, 11]. When the conductive surface was roughened (crocus paper, grade 112), the film produced had an even distribution of fine and coarse mercury droplets; this film was quite stable and withstood repeated removal from the solution and repeated washing with a stream of water.

The mercury film was plated from 10^{-4} M $Hg(NO_3)_2$ (oxygen-free) initially at —0.4 V in a quiet solution for 20 min, and then at —0.7 V in a stirred solution for 40 min. The electrode was then conditioned by repeated plating (at —1.30 V) and stripping in a 0.2 M $CaCl_2$ solution, and finally held at —0.1 V for 20 min before being placed into service. In order to maintain its life time and sensitivity, the electrode should not be held at a potential more positive than —0.02 V vs. SCE and hydrogen should not be allowed to evolve at the electrode surface. Hydrogen evolution caused serious deterioration in the electrode performance. Carefully maintained electrodes performed satisfactorily for 2—3 weeks of daily use.

Procedure

A 25-ml aliquot of sea water previously filtered through a membrane (0.45 μm) was placed in the electrolysis cell, and purged with purified nitrogen for at least 10 min. Deposition of Cu, Pb and Cd was made at —0.90 V vs. SCE, and zinc at —1.25 V vs. SCE, for 5 and 2 min, respectively, with nitrogen stirring. The current—potential plot was then obtained in a quiet solution; the pulse height was 25 mV at 0.5 s, and the scan rate 5 mV s^{-1}. After oxidation of the metals, the electrode was held at —0.1 V.

RESULTS AND DISCUSSION

A.s.v. of sea water at the natural pH

Measurements of Cu, Pb and Cd were made by plating at —0.90 V. The oxidation current peaks occurred at —0.35, —0.54 and —0.68 V vs. SCE, respectively. The reproducibility of the peak measurements assessed by repeated (10) plating and stripping was ± 10 %. Such errors can be quite serious, particularly when standard addition calibration is used. The total analytical error may be much higher because errors can accumulate when the current peak values of the standard increments are calculated. The lack of reproducibility for the oxidation peaks was found to be due to (a) non-attainment of equilibrium with respect to the CO_2 system during the purging with nitrogen, which necessitates initial purging for a minimum of 10 min and preferably for 15 min, and (b) electrode memory. The electrode memory effect was established by stirring the sample at the end of the oxidation scan for a known period of time, allowing the sample to come to rest and immediately repeating the potential scan. The oxidation current peaks found represented the amount of metal remaining as an amalgam in the mercury film. Because electrolysis and oxidation of metals by the technique described here is not stoichiometric, a large memory characteristic will, after repeated plating and stripping, cause an increase in the metals in the mercury film unrelated to their concentration in the solution. Experiments showed that the memory effect for cadmium was negligible, and that a few seconds hold was sufficient to oxidize all plated cadmium. In the case of lead, a 2-min hold was needed for the quantitative oxidation of plated lead. Copper, however, exhibited a very large and significant memory effect. Table 1 shows that after a 12-min hold at —0.1 V the copper oxidation peak current was about 8—10 % of the original peak and that when a larger amount of copper was plated initially, a much longer hold time was required to reduce an appreciable build-up of copper in the mercury film. The effect of pH on the memory for copper was examined by acidifying the sea water with 1 M HCl to pH 5.8 and 3.2. There was a slight improvement at pH 5.8, and at pH 3.2 there was no measurable copper after a 1-min hold. For the analysis of sea water at its natural pH, it was therefore necessary to employ a longer hold time in order to obtain acceptable reproducibility for the peak current. However, prolonged hold at low potential tended to reduce the thickness of

TABLE 1

Electrode memory for copper in sea water
(Peak heights (in μA) are given for the original peaks and for the memory peaks after the stated hold period.)

Time of hold (min)	Natural pH			Acidified to pH	
				5.8	3.2
—	3.5	6.2	12.0	6.0	11.5
1	1.5	2.5	4.5	1.5	0.0
2	1.0	2.0	3.5	1.2	
3	0.8	—	—		
4	0.6	1.5	2.5		
6	0.5	1.0	—		
8		0.75	2.0		
12	0.2	0.5	1.5	0.4	
20	—	0.4	—		
30	—	0.3	—		
40	—	—	0.5		

the mercury film. Although the thickness is not critical [8], the re-solution of significant amounts of mercury can cause a marked change in the pH of the sample thus altering the analytical conditions significantly.

Calibrations for copper, lead and cadmium made by standard addition, plating for 5 min at —0.90 V and holding the electrode for 10 min at —0.05 V were linear in the ranges 0—2 p.p.b. Cu and Pb and 0—1.2 p.p.b. Cd. Slight non-linearity was observed in the copper calibration when the concentration exceeded 2 p.p.b. However, linearity could be restored when a longer hold time was used (Fig. 1).

The a.s.v. of zinc in sea water (pH 8.1) was investigated by electrolysis at —1.25 V for 2 min. The potential scan was then made at 5 mV s^{-1} terminating at —0.05 V. The zinc peak occurred at —1.05 V vs. SCE. The electrode memory for zinc was found to be low: less than 10 % of plated zinc remained as an amalgam after the first scan and after a 2-min hold no measurable zinc remained in the mercury film. The reproducibility of the zinc peak, assessed by plating for 2 min and holding after oxidation for 2 min at —0.1 V, was unsatisfactory; the peak current decreased gradually from 575 μA to 525 μA on 6 successive runs. This decrease is attributed to the formation of Zn—Cu intermetallic compounds which have greater stability in the mercury film and, thus, are not completely oxidized by the treatment adopted. When the hold was made at —0.05 V for 5 min, to allow for oxidation of more of the copper-bound zinc, the reproducibility of the zinc peak on successive plating was improved significantly; on 6 successive runs, the peak currents lay within

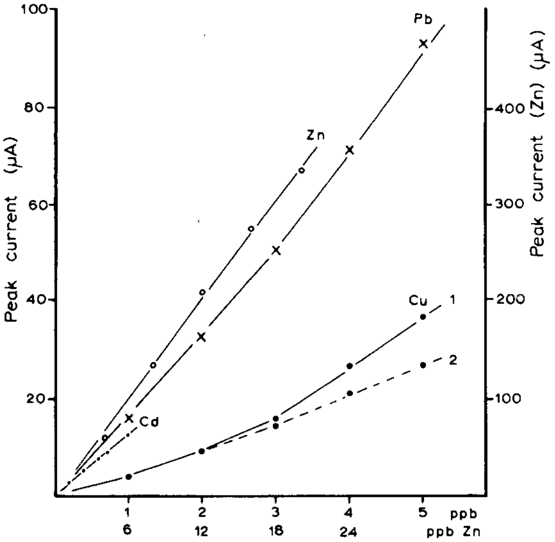


Fig. 1. Relationship between the oxidation current peaks of Cu, Pb, Cd and Zn and their concentration in sea water. Measurements were made at the natural pH of sea water. Lines (1) and (2) for copper are for 10 and 15-min hold at —0.05 V, respectively.

the range 512–520 μA.

Although reproducible zinc current peaks could be obtained, the peak height was found to decrease on addition of copper to the sample (Table 2). A similar decrease in the zinc current peak was also observed when nickel was added. Both decreases must be attributed to the formation of Zn–Cu and Zn–Ni intermetallic compounds, the peak observed representing only the unbound zinc in the amalgam and not the zinc in the intermetallic compounds. When the hold conditions under which a reproducible zinc peak was obtained, were used, the decreases in the zinc current peak observed on successive addition of nickel or copper showed that the molar ratio of Zn:Cu and Zn:Ni bound as intermetallic unoxidizable (under present analytical conditions) compounds was approximately 1:1.

The use of citrate to complex nickel ($\log \beta_1 = 5.4$ [20]) at pH 5–6 reduced the effect of nickel on the zinc peak to a negligible level (Table 2).

The formation of Zn–Cu intermetallic compounds in the mercury film or drop has been reported by many authors [6, 9, 13] and ^{65}Zn has been used

TABLE 2

Effect of Cu, Ni and Ga on the zinc peak in sea water

Metal or salt added	pH	A.s.v. mode[a]	Zn peak (μA)
20 p.b.b. Zn	5.8 (Ac)	DP	290
20 p.p.b. Zn + 4 p.p.b. Cu	5.8	DP	257
20 p.p.b. Zn + 8 p.p.b. Cu	5.8	DP	215
20 p.p.b. Zn + 12 p.p.b. Cu	5.8	DP	177
20 p.p.b. Zn + 40 p.p.b. Ga	5.8	DP	275
20 p.p.b. Zn + 80 p.p.b. Ga	5.8	DP	287
445 p.p.b. Zn	8.1	LS	53.8
445 p.p.b. Zn + 5 p.p.b. Ni	8.1	LS	38.0
445 p.p.b. Zn + 10 p.p.b. Ni	8.1	LS	26.6
445 p.p.b. Zn + 15 p.p.b. Ni	8.1	LS	17.5
0.02 M Sodium citrate		LS	18.5
+ 40 p.p.b. Zn		LS	86.4
+ 40 p.p.b. Zn + 10 p.p.b. Ni		LS	87.4
+ 40 p.p.b. Zn + 30 p.p.b. Ni		LS	85.6
0.16 M acetate			
+ 32 p.p.b. Zn	5.8	DP	560
+ 40 p.p.b. Ni	5.8	DP	440
+ 80 p.p.b. Ni	5.8	DP	335
+ 80 p.p.b. Ni + 40 p.p.b. Ga	5.8	DP	530
+ 80 p.p.b. Ni + 80 p.p.b. Ga	5.8	DP	600
+ 80 p.p.b. Ni + 120 p.p.b. Ga	5.8	DP	595

[a] DP = Differential pulse
LS = Linear sweep

to identify such compounds in the mercury film [15]. The results suggest that reproducible zinc peaks can be obtained only after complete oxidation of the deposited zinc, including the fraction bound with the copper, by adopting a long hold time at low potential. Under such conditions a correction can be applied to the zinc value if the copper concentration is known. The calibration of the zinc peak in the presence of constant amounts of copper is linear in the range of 0—20 p.p.b. Zn (Fig. 1).

A.s.v. of Cu, Pb and Cd in sea water at controlled pH

The use of acetate buffer has often been recommended for a.s.v. work, and was therefore tested. With plating at −0.90 V, the memory of the electrode was less pronounced than in the chloride medium (sea water). Table 3 shows that when sea water was buffered with acetate to pH 5.8, only 2 % of the plated lead and copper remained on the electrode after a 30-s hold at −0.1 V; after 1 min, about 1 % was detected which was entirely a polarographic peak. Only a slight improvement in the memory characteristic of the electrode was observed when the sea water was buffered to pH 5.05.

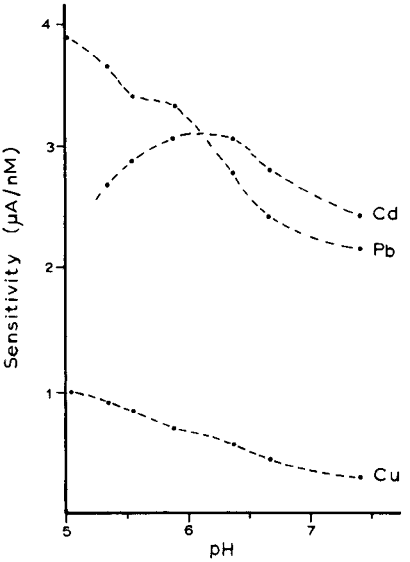
The sensitivity of the copper, lead and cadmium current peaks after pre-electrolysis for 5 min in sea water buffered in the range pH 7.4—5.05 increased at low pH values (Fig. 2). The pH value chosen was 5.80. At this pH there was a minimum change in the peak sensitivity and oxidation potential with small changes in pH for both copper and lead; moreover, the hydrogen overvoltage occurred at −1.30 V vs. SCE, which is sufficiently negative to allow the detection of the zinc peak in the same sample. Calibration graphs for Cu, Pb and Cd based on standard addition, plating for 5 min at −0.9 V, and holding at −0.1 V for 2 min, were linear in the range 0—1.2 p.p.b. Cd and 0—2 p.p.b. lead or copper (Fig. 3).

The formation of intermetallic compounds was investigated in acetate-buffered sea water (pH 5.8) by plating at −1.25 V. Both Cu—Zn and Ni—Zn complexes were formed; the composition of these compounds in the mercury

TABLE 3

Electrode memory for Cu, Pb and Cd in acetate-buffered sea water
(Peak heights (in μA) are given for the original peaks and for the memory peaks after the stated hold period.)

Time of hold (min)	pH 5.8			pH 5.05		
	Cd	Pb	Cu	Cd	Pb	Cu
—	47.5	180	108	65	235	145
0.5	0.0	3.5	2.6	0.25	5.0	2.5
1		3.0	1.9	0.25	5.0	1.5
2		3.0	1.7	0.25	5.0	1.5
5		3.0	1.5	0.25	5.0	1.5
6		3.0	1.5	0.25	5.0	1.5



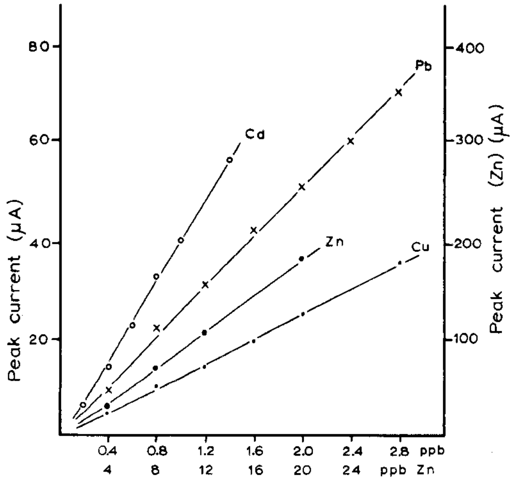


Fig. 2. Variation of the sensitivity of Cu, Pb and Cd with pH of the sea water.

Fig. 3. Relationship between the oxidation current peaks of Cu, Pb, Cd and Zn and their concentration in acetate-buffered sea water (pH 5.8).

film was the same as that measured in the chloride medium (i.e. 1 : 1). It is concluded, therefore that whenever these metals are deposited on mercury electrodes, intermetallic compound formation will cause a decrease in the observed zinc peak and that a single pre-electrolysis at —1.25 V will not yield a quantitative measurement of either zinc or copper.

A.s.v. of zinc in sea water at controlled pH

The zinc peak in acetate-buffered sea water (pH 7.0—5.0) appears at —1.05 V vs. SCE. The sensitivity and peak potential varied very little with the pH of this medium [17]. Gallium ions have been reported [14] to reduce the formation of Zn—Cu intermetallic compounds in acetate medium; quantitative oxidation of the zinc becomes possible, because a Ga—Cu compound of higher stability than the Cu—Zn compound is formed preferentially.

The oxidation current peak of gallium in chloride—acetate medium appears at —0.90 V vs. SCE. Experiments carried out in metal-free sea water buffered to pH values between 7.0 and 5.0, showed that the gallium peak varied markedly with pH (Fig. 4). No peak was observed above pH 6.1, possibly because of hydrolysis [21]. The current peak increased linearly with decrease in pH down to pH 5.1 where it remained constant; hydrogen evolution was just apparent at this pH. When copper was added in the presence of gallium at pH 6.2, it interfered with the zinc peak, which was decreased by formation

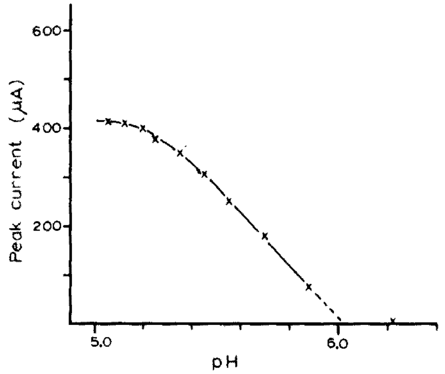


Fig. 4. Variation of the gallium oxidation current peak with pH.

of Cu—Zn compounds. This suggests that at pH values where no oxidation current is observed for gallium, this element is not reduced to the metallic form on the mercury film. At all other pH values, the addition of copper did not affect the zinc peak, when gallium was present.

The effect of the concentration of gallium on the Zn—Cu intermetallic compounds formed at pH 5.8 was investigated by the electrolysis of metal-free sea water enriched with 20 p.p.b. Zn and 12 p.p.b. Cu; the gallium concentration was increased by 10 p.p.b. increments. It was found that the zinc peak increased on addition of gallium, reaching a constant value when the gallium level was 40 p.p.b., at which point the gallium peak was just apparent (Table 2). The addition of up to 20 p.p.b. nickel to the solution (containing 120 p.p.b. Ga) had no effect on the zinc peak. However, the gallium peak showed a linear decrease on successive additions of nickel (Table 4). This suggests that Ga—Ni intermetallic compounds were also formed in the mercury film and that the stabilities of both the Ga—Ni and Ga—Cu compounds are greater than those of the Zn—Ni and Zn—Cu compounds.

An approximate assessment of the composition of the Ga—Ni and Ga—Cu compounds in the mercury film was attempted. First, the relationship between the gallium concentration and its oxidation peak was established, and then the decrease in the gallium peak on successive addition of Ni and Cu was observed. Metal-free sea water acetate-buffered (0.16 M) to pH 5.8 and containing 20 p.p.b. Zn and 120 p.p.b. Ga, was electrolyzed at —1.25 V for 2 min. After the potential scan, the electrode was held in a stirred solution at —0.05 V for 10 min to allow for complete oxidation of all metallic compounds. The observed gallium peak after each addition of copper or nickel should represent the free proportion of gallium. The results (Table 4) showed an apparent decrease in the gallium peak of 2.4 p.p.b. Ga per 1 p.p.b. Cu, and 0.47 p.p.b. Ga per 1 p.p.b. Ni. Thus the molar ratios for Ga: Ni and Ga: Cu are approximately 1 : 2 and 2:1, respectively. Table 4 also shows that

TABLE 4

The effect of copper and nickel on the zinc and gallium peaks
(Metal-free sea water enriched with 20 p.p.b. Zn was used as the sample.)

Metals added (p.p.b.)			Peak current (μA)	
Cu	Ga	Ni	Zn	Ga
12	40	—	260	20
12	80	—	259	105
12	120	—	258	190
16	120	—	258	170
20	120	—	257	150
24	120	—	258	135
28	120	—	259	120
28	120	4	258	115
28	120	12	258	107
28	120	20	257	100

no change is observed in the zinc peak current which suggests that formation of zinc compounds with the other metals were insignificant under the conditions used.

The minimum of gallium ions necessary to remove the interference of both copper and nickel (including copper added during standard addition) in the determination of zinc can, therefore, be calculated. For the analysis of coastal waters, 60 p.p.b. of gallium was used. This concentration was found suitable for waters containing up to 5 p.p.b. Cu (the maximum copper added for calibration is 10 p.p.b.) and 5 p.p.b. Ni. Higher concentrations of gallium can lead to difficulties (and error) in the measurement of the zinc peak because of their proximity.

The following procedure was adopted for the analysis of sea-water samples for Cu, Pb, Cd and Zn. A 25-ml aliquot was used to which 2 ml of acetate buffer (2 M, pH 5.8) was added. The solution was purged with a stream of purified nitrogen for at least 10 min. A nitrogen stream was used to stir the sample while Cd, Pb and Cu were first plated at —0.90 V vs. SCE for 5 min. The potential scan was then done (differential pulse mode) for the quiet solution, with a scan rate of 5 mV s^{-1} (25-mV pulse height every 0.5 s). The scan was terminated at —0.1 V and the electrode was held at this potential for at least 2 min while the solution was being stirred. The procedure was repeated to ascertain reproducibility. Calibration was then done by standard additions, The Cu, Pb and Cd concentrations in the cell being increased in steps of 0.4, 0.4 and 0.2 p.p.b., respectively. Four or five standard additions were made to check the linearity of the calibration.

Zinc was determined after the addition of 1.5 μg of gallium(III) as chloride (cell concentration, 60 p.p.b. Ga), by plating at —1.25 V for 2 min. Scanning was then done under the same conditions as above. The scan was terminated at —0.05 V and held for 5 min, before the process was repeated for either reproducibility check or calibration. The zinc calibration by standard addition was found to be linear between 0 and 30 p.p.b. (Fig. 3).

Oslofjord water, collected from a depth of 40 m at Drobak and filtered through a 0.45-μm membrane filter, was analysed by the procedure described here. The average of 10 replicate analyses for Zn, Cd, Pb and Cu was found to be 35.6 ∓ 1, 0.35 ∓ 0.02, 0.68 ∓ 0.08 and 0.41 ∓ 0.02 p.p.b., respectively.

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DETERMINATION OF TOTAL MERCURY IN WORKROOM AIR BY ATOMIC ABSORPTION OR X-RAY FLUORESCENCE SPECTROMETRY AFTER COLLECTION ON CARBON-LOADED PAPER

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SUMMARY

The routine determination of total mercury in workroom air of an alkali chloride electrolysis plant equipped with mercury cells, is described. The procedure is based on atomic absorption spectrometry (a.a.s.) (cold vapour technique) or x-ray fluorescence spectrometry (x.r.f.s.) after collection on carbon-loaded paper fixed in a disposable Millipore filter holder. The lowest quantity of mercury that can be determined is 0.2 μg by a.a.s. and 2 μg by x.r.f.s. Samples taken in the plant gave a relative standard deviation of about 2 % for a.a.s. and 3 % for x.r.f.s.

In air, mercury may be encountered as the element either as vapour or adsorbed on dust, or as compounds in particulates or in gaseous form. Because mercury is poisonous, its determination in workroom air is of great importance in evaluation of health hazards. In 1971 the American Conference of Governmental Industrial Hygienists adopted a threshold limit value (TLV) of 50 μg Hg m^{-3} for mercury and its compounds (except alkyl, TLV = 10 μg m^{-3}) [1].

Numerous analytical methods for the determination of mercury in various matrices have been described. Reviews have been published recently by Ure [2] and Chilov [3]. Because of the numerous forms in which mercury may exist in air, sampling is complicated. Sampling and determination of mercury in air generally involve two basic principles: direct-reading methods or methods in which the mercury and mercury compounds are removed from air by bubblers, filters, adsorbents or amalgamable collectors.

Direct-reading methods. Portable detectors (gas vapour meters), which have been introduced by several manufacturers, are mostly used. These exploit the fact that mercury vapour absorbs radiation at the resonance 253.7-nm line. The mercury-containing air is passed directly through the instrument, and mercury compounds are not detected. Measurement with these instruments can be affected by high magnetic fields such as may be present in the cell rooms of alkali chloride plants; also, over-estimation can occur because of molecular absorption by organic and inorganic species, or by light scattering by particulate material.

Analysis after collection of mercury from the air. The most popular scrubbing solution is acidic potassium permanganate [4]. Collection in solutions has some disadvantages; for example, the method cannot be used if particulate matter is present [4], and much effort is involved in cleaning and preparing the bubblers, whilst they are vulnerable during transport. Moreover, sampling is time-consuming, for the gas must not be allowed [4] to pass at a rate exceeding 50 l h^{-1}.

Sampling can be simplified by using solids instead of solutions. Examples are the use of glass fibre paper [5], activated charcoal [6] (both impregnated with iodine), manganese dioxide [7] and silver wool [8].

Van der Sloot and Das [9] as well as Scaringelli et al. [10] have used charcoal for sampling total mercury from air, followed by neutron activation analysis or flameless atomic absorption, respectively. The first publication deals with unpolluted air containing more than 0.5 ng of total mercury per m^3, and the second with the determination of total mercury in ambient air, maximum precision and accuracy occurring at 1 μg Hg m^{-3}.

In the investigations described here a relatively fast, convenient method was developed for the determination of total mercury in air in the range 0.2—100 μg m^{-3}. The principle of adsorption on non-impregnated charcoal [9, 10] was adapted, the method being modified by using carbon-loaded paper containing about 50 % charcoal. Mercury was determined by the atomic absorption "cold-vapour technique" [11] (a.a.s.) or x-ray fluorescence spectrometry (x.r.f.s.); the lower limits of detection are, respectively, 0.2 μg Hg (3 times the standard deviation of the blank determination) and 2 μg Hg [12] per sample. The great advantage of x.r.f.s. is its speed, because the mercury can be determined after collection on the carbon-loaded paper without further preparation. However, fewer laboratories are equipped for x.r.f.s. than for atomic absorption.

EXPERIMENTAL

Sampling

For sampling a Millipore Aerosol Field Monitor MAWG 037 AO is used. This is a transparent disposable plastic filter holder, pre-assembled with a 0.8-μm membrane filter disc in place (the exposed surface is 8 cm^2). The filter disc is replaced by three discs of carbon-loaded paper (Schleicher and Schüll, no. 508) and one 0.22-μm membrane filter. The sampler must be used in conjunction with an adapter so that a vacuum source can be attached through a limiting orifice.

In the direction of suction the layers are piled as follows: (a) one disc of carbon-loaded paper to adsorb the mercury present as vapour and to remove most of the mercury present as particles; (b) one membrane filter disc GSWP

03700 (0.22 μm) to remove any particles that break through the carbon-loaded paper; (c) two discs of carbon-loaded paper. The membrane filter does not adsorb mercury vapour. The membrane filter is not used as the first layer because its surface is so smooth that the retained particles do not adhere well; the pore size of this filter is that recommended by Philips [13] and by Hammerle et al. [14]. The vapour pressure of mercury salts in the particulate form retained on the upper carbon disc or the membrane filter, can be considerable, so that volatilization may occur as sampling proceeds. The final two carbon discs adsorb this vapour.

The amount of air to be sampled depends on the mercury concentration expected and is measured with a wet gas meter. The maximum quantity of air sampled in this work was 10 m^3; for all experiments the sampling rate was 200 $l\ h^{-1}$. This flow rate and the number of filters in the sampler may not be optimal. To check on breakthrough two samplers were placed in series.

Cold-vapour atomic-absorption spectrometry

Boil the filters (per sampler) gently for 20 min with 20 ml of nitric acid (ca. 14 M) to dissolve mercury. Cool and filter through a 0.8-μm membrane filter. Wash the filter with 5 ml of nitric acid (1 + 1) and dilute the filtrate to 50 ml. Transfer an aliquot of the solution (maximum 10 ml) to a 100-ml conical flask containing 5 ml of potassium permanganate solution (40 $g\ l^{-1}$) and 1 ml of sulphuric acid (1 + 4). Rinse the walls with 5 ml of distilled water. Heat to boiling, keep the solution boiling for a few seconds, and cool. Add 0.5 ml of sodium chloride solution (300 $g\ l^{-1}$). Decolourize the solution by dropwise addition of hydroxyammonium chloride solution (100 $g\ l^{-1}$). After transferring the solution to an aeration flask, determine the mercury content by the procedure given by the Mercury Analysis Working Party of BITC [4].

If the aliquot of solution taken is 1 ml or more, the method of standard additions must be applied for calibration to eliminate any matrix effect.

If the presence of organic mercury compounds on the filters is suspected, the yield of the extraction procedure can be checked in a parallel determination by total combustion of the filters in an oxy-hydrogen flame (Wickbold combustion) [15], followed by a.a.s.

X-ray fluorescence spectrometry

The combined discs from the sampler are examined directly in a Philips PW 1410 x-ray spectrometer. Corrections are made for counting loss caused by the dead time of the counting circuit and background. The corrected intensity can be divided by the intensity of the Hg Lα line from a monitor in the form of combined discs loaded with elemental mercury, to compensate for long-term instrumental drift. The necessary calculations are made with an on-line Hewlett-Packard 9830 A desk calculator. The instrumental conditions used are shown in Table 1. The combined discs are placed in the sample holder; the carbon layer which was nearest the sampled air entry must be

TABLE 1

Operating conditions for the Philips PW 1410 x-ray spectrometer

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Chromium target tube operated at 60 kV and 45 mA.
LiF 200 analyzing crystal
Scintillation counter
Coarse collimation
Pulse-height analyzer : lower level 2 V, window 5 V
Medium : air
Fixed time 100 s, or fixed count 10^6counts
Spinner : on
Spectral line : HgLα (35.90° 2θ, wavelength 1.247 A)
Background : on each side of the peak (34.90° and 36.90° 2θ)
Backing : austenitic stainless steel
Philips PW 1427/10 sample holder with an aluminium mask (32 mm aperture)
Ratio monitor : combined discs loaded with elemental mercury

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closest to the x-ray tube, and the discs are kept in the same order for both counting and sampling. A spectroscopic standard in the form of a disc (1.5 in. dia. 0.75 in. thick) is used as backing (to depress scatter).

Calibration

The calibration is carried out with a known amount of elemental mercury loaded on combined discs. The mercury is formed by reduction of mercury (II) with a tin(II) chloride reducing solution, removed from the solution in a stream of air, and adsorbed on the discs.

Procedure. Transfer 2 ml of reduction solution [4] and 50 ml of distilled water to a 100-ml aeration flask supplied with a glass frit. Introduce, during 15 min, 10 ml of standard mercury solution [4] containing 1—10 mg Hg l^{-1}, into the aeration flask with the aid of a syringe pump (e.g. Sage Instruments, model 220-1). During the introduction of the mercury solution, pass air through the flask at a rate of 3 l min^{-1}, to expel the mercury formed. Continue passing air for 5 min after stopping the introduction of the mercury solution. Lead the mercury-containing air successively through a drying tube (magnesium perchlorate) and then through a sampler, the top of which has been removed (for "open" analysis). The drying tube and the sampler are connected by a tube (20 cm long, 4.1 cm i.d.) to simulate open sampling. Examine the mercury-loaded discs in the x-ray spectrometer as described above. Plot the measured net intensities or the calculated ratios (corrected for the blank) versus the amounts of mercury taken.

RESULTS AND DISCUSSION

In order to investigate the adsorption efficiency of the samplers in the cell room of a mercury cell electrolysis, plant combinations of coal filters and bubblers, containing sulphuric acid — permanganate as absorbing solution [4], were tested. Table 2 shows that the efficiency of the coal filter sampler is higher than that of the bubblers. Experiments proved that impregnation of the coal with iodine is unnecessary; this is advantageous because of the interference of iodine in the determination of mercury by a.a.s.

The efficiency of the extraction of mercury from the filter discs with nitric acid as described above was checked with 50 μg Hg^0 or Hg^{2+} loaded on the discs. The residual amount on the extracted discs was less than 0.04 μg Hg (determination after complete digestion of the discs with HNO_3 — H_2SO_4 under reflux). Samplers connected in parallel and loaded in the plant, gave the same results after extraction with nitric acid and after complete digestion with nitric acid — sulfuric acid, which is a more cumbersome procedure.

To check for losses of mercury during sampling, 1 m^3 of air (purified with charcoal) was passed at a rate of 200 $l\ h^{-1}$ through a sampler which had been loaded in the laboratory with 50 μg Hg as Hg^{2+} or Hg^0 or loaded in the plant. There was no detectable loss of mercury in any case (Table 3). After storage of discs loaded with 50 μg Hg for a week in a closed weighing bottle at room temperature, no significant loss of mercury was detected. No loss of mercury was found during x.r.f.s. measurements.

To establish the effectiveness of the different layers of carbon-loaded paper and the membrane filter in the samplers, the separate layers of a sampler which had been loaded in the cell room of the plant were measured by x.r.f.s. The greater part of the mercury was present on the outermost filter and a little on the membrane filter (Table 4). During sampling part of the air sample touches the ring that holds the discs in place. Three rings of samplers loaded in the plant were therefore inspected for mercury by a.a.s. The amount found in each case was 0.8 μg, which is negligible in comparison with the 140 μg determined on this occasion.

TABLE 2

Collection of mercury in cell-room air (analysis by a.a.s.)

Exp.	μg Hg (→ direction of air flow)					
	Bubbler 1	Bubbler 2	Sampler 1	Sampler 2	Bubbler 1	Bubbler 2
1			6	< 0.2	< 0.1	< 0.1
			6	0.3	< 0.1	< 0.1
2			23	< 0.2	< 0.1	< 0.1
			21	< 0.2	0.14	< 0.1
3	33	0.2	6	1		
			44	0.4	0.4	0.2
4	16	< 0.1	0.2	< 0.2		
			15	0.2	0.2	< 0.1

TABLE 3

X.r.f.s. testing of loss of mercury during passage of air through loaded samplers

Loading	Air passed (m^3)	Net intensity (c.p.s.)	
		Before passage	After passage
50 μg Hg^{2+}	0.9	694	694[a]
50 μg Hg^0	0.9	396	392[a]
Cell-room air	1.15	213	212

[a]For the different sensitivities, see Fig. 1.

TABLE 4

Loading of the separate layers of a sampler

	Net intensity[a] (c.p.s.)
Complete sampler filling	716
First carbon layer	707
Millipore filter 0.22 μm	9
Second carbon layer	2
Third carbon layer	3

[a]Corrected for a blank set of discs.

TABLE 5

Effect of drying the mercury-containing air on the collection of 100 μg of elemental mercury (analysis by a.a.s.)

Exp.	Drying agent	μg Hg (→ direction of air flow)			
		Sampler 1	Sampler 2	Bubbler 1	Bubbler 2
1	$Mg(ClO_4)_2$	95	0.1	< 0.1	< 0.1
2	None[a]	62	11	17	< 0.1
3	$Mg(ClO_4)_2$	97	0.1	< 0.1	< 0.1

[a]Relative humidity ca. 100 %.

Calibration of the x.r.f.s. method

Originally, a simple method was tested in which standards were prepared by depositing a small volume of standard mercury(II) solutions on to a set of discs. The papers were dried at room temperature and measured with the impregnated surface facing the x-ray tube. The calibration curve obtained was a straight line up to 100 μg Hg and reproducibility was good. However, for samples taken in the plant, the results for the same discs were about twice as high by a.a.s. as by x.r.f.s., although when a standard mercury(II) solution was deposited on a sampler before sampling in the plant, the added quantity was recovered after analysis by either method. In further investigations, attempts were made to simulate the actual conditions for field sampling in the preparation of the specimens for calibration. These studies led to the calibration procedure described; passage through the aeration flask makes the humidity of the mercury-containing air higher than that of the air commonly sampled, hence a drying agent must be used (see Table 5).

The calibration samples were also analysed by a.a.s.; there was very good agreement. There is no obvious reason for the differences in the slopes of the graphs shown in Fig. 1.

Results for cell-room air

The results for mercury in cell-room air obtained by a.a.s. and x.r.f.s. agree well (Table 6). Samples taken in the plant gave a relative standard deviation of about 2 % by a.a.s. and 3 % by x.r.f.s. Figure 2 shows the correlation of the results obtained by the two techniques.

TABLE 6

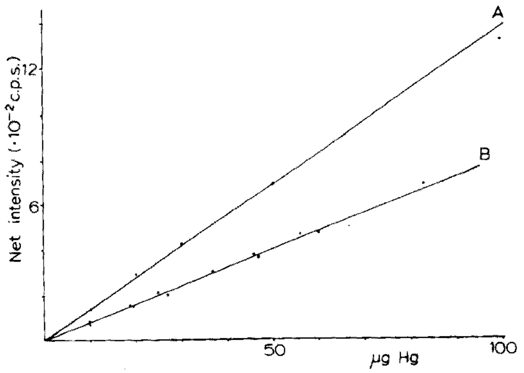
Analysis of cell-room air by a.a.s. and x.r.f.s.
(The quantity of air sampled varied; a maximum of 10 m^3 of air was sampled.)

	Hg (μg)				
	A.a.s.				X.r.f.s.
Exp.	Blank[a]	Sampler 1	Sampler 2	Total	Total
1	0.2	88	0.3	88	90
		91	0.4	91	85
		88	0.4	88	86
2	0.1	22	< 0.2	22	23
		21	< 0.2	21	23
		22	< 0.2	22	22
3	0.2	10	0.2	10	10
		10	0.2	10	9
		10	0.2	10	10
4	0.1	26	0.2	26	27
		27	0.2	27	26
		28	0.3	28	20
5	0.1	129	1.0	130	140
		119	5.8	125	130
		127	6.5	134	135

[a] Blank value of a sampler filling.

CONCLUSIONS

The described method of collecting mercury and mercury compounds on carbon-loaded paper before determination by a.a.s. or x.r.f.s. is suitable for



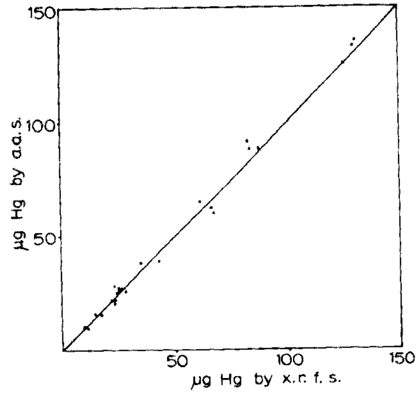


Fig. 1. Correlation of x.r.f.s. intensity and quantity of mercury. A. Sampler impregnated with Hg^{2+} solution. B. Elemental mercury adsorbed on a sampler.

Fig. 2. Correlation of a.a.s. and x.r.f.s. results.

cell-room air of a mercury cell electrolysis plant. The lower limit of detection is 2 µg Hg by x.r.f.s. and 0.2 µg Hg by a.a.s. per volume of air sampled.

To increase the sensitivity of the x.r.f.s. method, analyses could be done with an x-ray tube provided with a molybdenum target instead of a chromium target [13].

A method of collecting mercury on manganese dioxide [7] is under investigation for the a.a.s. determination. If this is successful, the filtration step necessary with carbon-loaded papers, could be avoided, because the manganese dioxide can be dissolved completely; the a.a.s. determination would then be accelerated and the chance of contamination diminished.

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DETERMINATION OF TRACE IMPURITIES AT THE P.P.B. LEVEL IN FUSED SILICA BY SPARK-SOURCE MASS SPECTROMETRY

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SUMMARY

A sample dissolution-concentration technique for the determination of trace elements in fused silica by spark-source mass spectrometry (s.s.m.s.) is described. The fused silica is dissolved by ultra-pure hydrofluoric acid, and most of the silicon tetrafluoride formed is then removed at 80—100 °C, leaving behind the impurities in the solution as fluorides. After addition of ultrahigh-purity graphite and internal standards (Tl and Rb), the mixture is dried to give a sample suitable for pressing into electrodes. The method not only concentrates the trace impurities but also reduces the interferences originating from silicon oxide and carbide species in the mass spectra and thus allows the determination of a larger number of elements at p.p.b. levels. More than 30 trace impurities in 6 fused silica boules and J. T. Baker's Ultrex silicon dioxide are determined and compared with data obtained by other methods.

The amount of trace impurities in vitreous silica prepared by the flame pyrolysis of silicon tetrachloride [1] is important for the development of optical waveguides and optical glasses, since small (p.p.b., $\mu g\ g^{-1}$) concentrations of certain elements can cause drastic changes in optical transmission characteristics in different regions of the energy spectrum [2, 3]. Precise determination of all trace impurities present in high-purity fused silica is thus of utmost importance.

Similarly to other non-conducting materials, fused silica can be analyzed by spark-source mass spectrometry (s.s.m.s.) by means of the method of pressed electrodes, which contain a mixture of the sample and a conducting binder material such as graphite or silver powder. However, the introduction of a second material into the electrode system gives rise to complications owing to the additional lines caused by the presence of heterogeneous polymeric species whose m/e ratio is equal to that of the element or elements under investigation. The use of graphite with fused silica is particularly troublesome in this respect since all of the major components are of very low mass number (i.e., Si: m = 28, 29, 30; O: m = 16; C: m = 12, 13). As a result, numerous molecular complexes are present in the spectrum as silicon oxides (SiO_x^+), silicon carbides (SiC_x^+), polymers of silicon (Si_x^+) and carbon (C_x^+)

throughout the normal ($m = 7$—270) region. The presence of these molecular species, especially the oxides and carbides, drastically reduces the number of elements that can be determined, especially when low levels of impurities must be measured. In principle, the high mass resolution capability of photographic detection (e.g., $M/\Delta M > 5000$) permits many of these molecular species to be separated from the elements of interest. Unfortunately, for p.p.b. determinations where as much as 3000-nanocoulomb (nC) exposure is required, many of the interfering molecular lines are broadened because of over-exposure, so that separation is actually not possible. Furthermore, in high mass resolution determinations, narrower slits are usually required, so that a much longer time would be needed for a given exposure. As much as 8-h exposure time has been required for p.p.b. level determinations. In view of these difficulties, a sample dissolution—concentration technique was developed so that the instrument time per analysis can be reduced considerably and, more important, element coverage can be increased owing to the reduction of molecular interferences. The dissolution and drying of samples onto silver and graphite before s.s.m.s. analysis has been reported previously [4—6]. The technique described here incorporates the removal of the matrix elements to achieve concentration and to reduce the interference deriving from molecular species, in addition to sample dissolution before s.s.m.s. analysis.

EXPERIMENTAL

Apparatus

An AEI MS-702R double-focusing spark-source mass spectrometer equipped with photographic detection was used. The analysis of the photographic plates was made by the usual method described by Owens and Giardino [7]. Corrections were made for mass effect, energy effect and blank level. Line-width correction was found to be unnecessary since only those lines of about equal width were used for calculation. The platinum ware used was that especially reserved for trace analysis. It was cleaned by boiling in 4 M nitric acid for 20 min followed by thorough rinses with double-distilled deionized water. Drying of the platinum ware and sample dissolution were all performed in a clean room equipped with a Class 100 (Federal Standards 209A) laminar flow hood, which removed 99.99 % of particles 0.3 μm or larger.

Sample preparation and dissolution

Weigh about 0.5 g of the sample (20—30 mesh) into a 30-ml platinum crucible. Add 2 ml of Baker's Ultrex hydrofluoric acid, cover with a fitted platinum lid, and digest on a hot plate set at 80—100 °C for 24—36 h. If necessary, add a few more drops of acid to complete the dissolution. Add 1.00 ml of solution containing 5 p.p.m. thallium and rubidium to the samples as internal standard. Transfer the sample from the crucible to a 5-ml Nalgene vial with the aid of a small plastic funnel. Wash crucible 3 or 4 times with double-distilled deionized water. Reduce the volume of solution slowly to less than 1 ml at 95 °C. After the addition of 50 mg of graphite (UltraCarbon, outgassed ultra-superior purity) and a few drops of acetone for wetting the graphite, dry the sample completely at 95 °C overnight. Homogenize the dry mixture with a Spec mixer mill for at least 2 h and press into electrodes by the usual method.

Run a reagent blank following the same procedure described above.

RESULTS AND DISCUSSION

The use of this sample dissolution—concentration procedure removes several difficulties usually encountered in regular s.s.m.s. analysis on sample—graphite mixture. By removing the matrix, the sample can be concentrated so that very high sensitivity can be achieved without unreasonably long exposure times. For instance, when 500 mg of fused silica and 50 mg of graphite are used, the maximum exposure required to detect 1 p.p.b. level of impurities is only 200 nC. This reduces the instrument time from 8 h to less than 0.5 h. Furthermore, with relatively short exposures, all the problems associated with long exposure are eliminated. These problems, some of which are critical for the determination of very low levels of impurities, include uniformly high background level, secondary fogging extending not only to the one or two lines neighboring the matrix lines but to large regions near the matrix lines, changes in the electrode geometry owing to over-consumption of the sample material and possible instability of the instrument during the very long exposure time.

The removal of the matrix elements has also eliminated a large number of the molecular interferences. With the procedure described, the silicon content is usually reduced to the 10—100 p.p.m. level so that the molecular species originating from silicon are no longer of concern. Therefore, a larger number of elements can be determined at the p.p.m. or p.p.b. level. For instance, iron and nickel are usually very difficult to determine in a silica—graphite matrix at low levels. Iron (m = 54, 56, 57, 58) cannot be determined because of the presence of Si_2^+ ($^{28}\mathrm{Si}\,^{28}\mathrm{Si}^+$, $^{28}\mathrm{Si}\,^{29}\mathrm{Si}^+$, $^{28}\mathrm{Si}\,^{30}\mathrm{Si}^+$); thus, the only line that can be used is the less abundant mass 54. Since Al_2^+ is also at mass 54, the detection limit for iron is dependent on the amount of aluminum present. In many of the fused silica samples analyzed, the iron detection limit is usually around 20 p.p.m. In the case of nickel (m = 58, 60, 61, 62 and 64), the interferences are due to $^{29}\mathrm{Si}\,^{29}\mathrm{Si}^+$ and $^{28}\mathrm{Si}\,^{30}\mathrm{Si}^+$ for mass 58, $^{30}\mathrm{Si}\,^{30}\mathrm{Si}^+$ and $^{28}\mathrm{Si}\,^{16}\mathrm{O}_2^+$ for mass 60, $^{29}\mathrm{Si}\,^{16}\mathrm{O}_2^+$ and $^{28}\mathrm{Si}\,^{16}\mathrm{O}\,^{17}\mathrm{O}^+$ for mass 61, $^{30}\mathrm{Si}\,^{16}\mathrm{O}_2^+$ and $^{28}\mathrm{Si}\,^{16}\mathrm{O}\,^{18}\mathrm{O}^+$ for mass 62, and $^{28}\mathrm{Si}\,^{12}\mathrm{C}_3^+$ for mass 64, so that in most cases, the detection limit is only around 10 p.p.m. With the sample dissolution—concentration technique, iron can be determined at mass 56 and 57, and nickel at mass 60 and 62 without any observable interferences at the low p.p.b. level.

Since the removal of the silicon tetrafluoride is accomplished at 80—100 °C, one potential source of error is the volatilization of impurities as fluorides. The list of elements that may be lost during the removal of silicon tetrafluoride is not particularly long and includes B, P, S, As, Se and Hg. Fortunately, many of these elements, such as B, P, S and As, can be determined by the usual graphite mixed electrode method without much interference. Table 1 lists the results of analyses of J. T. Baker Ultrex silica prepared at three different temperatures. It shows that at the temperature used there is no appreciable loss of the elements listed.

The data in Table 1 can also be used as a reproducibility study to determine the precision of this method. In general, the data indicate that the precision of determination is better than ± 35 % relative which is about the same as one can expect for the usual photographic detection method. To

TABLE 1

S.s.m.s. analysis of J. T. Baker Ultrex Silica (Lot No 329183) prepared at different temperatures (p.p.b.w.)

Element	Temperature (° C)		
	85	100	125
Al	550	440	430
Au	< 3	< 3	< 3
Bi	< 4	< 5	< 5
Ca	340	400	540
Cd	< 6	< 10	< 8
Ce	< 2	< 2	< 2
Co	5.1	4.6	4.3
Cr	46	68	41
Cu	4.2	4.9	5.3
Fe	77	46	68
La	< 1	< 1	< 1
Mg	200	80	90
Mn	3.7	3.4	5.3
Mo	< 3	< 3	< 4
Nb	< 1	< 1	< 1
Ni	23	32	32
Pb	< 2	< 9	< 9
Pd	< 1	< 1	< 1
Ru	< 2	< 2	< 2
Sb	< 3	< 4	< 6
Sn	< 6	< 5	< 8
Sr	< 1	< 1	< 1
Ti	150	130	140
V	3.0	2.7	4.5
W	< 1	< 1	< 1
Y	< 1	< 1	< 1
Zn	6.9	11	5.9
Zr	< 6	< 1	< 3

TABLE 2

S.s.m.s. results obtained for code 7940 fused silica boules and comparison to other methods (p.p.b.w.)

Boule No.	1			2			3			4			5			6		
	S.s.m.s.	A.a.s.^{a}	S.p.^{b}	S.s.m.s.	A.a.s.	S.p.	S.s.m.s.	A.a.s.	S.p.	S.s.m.s.	A.a.s.	S.p.	S.s.m.s.	A.a.s.	S.p.	S.s.m.s.	A.a.s.	S.p.
Al	800	1000	570	960	340	< 200	510	340	310	610	390	< 200	240	30	<200	400	3200	2900
As	< 15^{c}			3.6^{c}			< 6^{c}			< 16^{c}			< 7^{c}			< 8^{c}		
Au	< 4			< 2			< 1			< 3			< 11			< 2		
B	690^{c}			80^{c}			6.9^{c}			16^{c}			57^{c}			2.1^{c}		
Bi	< 5	< 20		< 15	< 20		< 1			< 3			< 11			< 2		
Br	< 21			11			21			47			< 7			8.3		
Ca	600	450		480	300		200	450		260	1300		8200	1300		410	420	
Cd	< 7			< 19			< 2			< 4			< 10			< 2		
Ce	< 3			< 8			< 1			< 2			< 8			< 1		
Co	6.0	< 10		8.5	< 10		0.67	< 10		1.8	< 10		5.5	< 10		1.1	< 10	
Cr	56	50		71	61		7.7	16		11	17		4.5	63		1.1	1.4	
Cu	76	5		46	< 4		13	41		23	250		23	< 4		24	5	
Fe	210	370	200	330	400	230	340	270	<100	35	67	<100	280	250	<100	150	180	<100
Ga	< 1			7.1			< 1			< 15			< 5			< 1.0		
I	< 7^{c}			< 5^{c}			< 17^{c}			< 5^{c}			< 8^{c}			< 2^{c}		
In	< 2			< 5			< 1			< 3			< 5			< 1		
La	< 30			< 6			< 1			< 1			< 1			< 1		
Mg	230	180		170	410		30	130		130	200		100	370		160	120	
Mn	24	4.8		7.0	1.4		18	0.8		4.7	0.4		5.8	1.5		16	4.3	
Mo	< 6			< 19			< 1			< 4			< 16			< 2		
Nb	< 1			< 4			< 1			< 1			< 3			< 1		
Ni	130	58		36	66		19	14		18	18		17	4		38	< 2	
P	58^{c}			5.5^{c}			18^{c}			10^{c}			18^{c}			17^{c}		
Pb	< 9	1.2		< 29	2.5		< 1	19		< 6	24		< 20	3.8		< 1	35	
Pd	< 6			< 19			< 2			< 4			< 16			< 3		
Ru	< 6			< 8			< 1			< 3			< 12			< 1		
S	<2700^{c}			< 180^{c}			<1400^{c}			< 310^{c}			<2500^{c}			< 120^{c}		
Sb	< 4	< 20		< 13	< 25		< 1			< 3			< 8			< 2		
Sn	< 6	< 50		< 19	< 45		< 1			< 4			< 14			< 2		
Sr	< 4			< 1			< 1			< 3			< 3			< 3		
Ti	600	500	<220	440	< 100	<200	190	400	<200	140	200	<200	500	300	<200	1900	3500	2900
V	220	240	350	180	220	390	180	250	440	24	< 50	<200	7.2	< 50	<200	32	< 50	<200
W	< 12			< 33			< 3			< 8			< 1			< 4		
Y	< 2			< 4			< 1			< 1			< 3			< 0.5		
Zn	14	31		23	28		5.1	130		110	160		3.0	4		19	23	
Zr	32			1.2			17			< 7			100			22		

[a] Flameless atomic absorption spectrometry.

[b] Spectrophotometry.

[c] S.s.m.s. results without chemical preconcentration.

TABLE 3

S.s.m.s. results obtained for J. T. Baker Ultrex Silica and comparison to other methods (p.p.b.w.)

	S.s.m.s.	A.a.s.	O.e.s.[b]	Mfr[c] certified
Al	470	20	< 4	20
As	9.7[a]			
Au	< 3			
B	< 1[a]			<5000
Bi	< 5			< 1
Br	14[a]			
Ca	430	390		50
Cd	< 8			< 10
Ce	< 2			
Co	4.7, 1.0[a]	< 10		< 1
Cr	52	15	30	20
Cu	4.8	4		2
Fe	64	180	40	20
Ga	< 3			
I	< 7[c]			
In	< 1			
La	< 1			
Mg	120	40	15	20
Mn	4.1	4.1	5	3
Mo	< 1			< 1
Nb	< 1			
Ni	29	36		2
P	62[a]			
Pb	< 7	< 1	< 3	1
Pd	< 1			
Ru	< 2			
S	<2000[a]			
Sb	< 4	< 10		
Sn	< 6		6	
Sr	< 2			
Ti	140	<100	< 3	< 1
V	3.4	< 50	< 3	< 1
W	< 1			
Y	< 1			
Zn	7.9	41		20
Zr	< 5			< 5

[a] S.s.m.s. results without chemical preconcentration of impurities.
[b] Optical emission spectrography.
[c] Data obtained by optical emission spectrography supplied by manufacturer.

achieve better precision, such as ± 5—10 % relative, the peak switching mode of the electrical detection system was considered. Unfortunately, it is not practical to determine so many elements by this method since the technique is essentially used in the determination of one element at a time. However, this mode of detection should be extremely useful if a limited number of elements desired, and especially if they are within a narrow mass range.

Table 2 lists results for the Corning Code 7940 fused silica samples which have also been analyzed for some elements by atomic absorption and spectrophotometry. The agreement between these techniques is quite good considering the fact that the precision of the photographic detection is only about ± 35 % relative at the p.p.b. concentration level. In the case of Baker Ultrex silica (Table 3) the agreement between techniques is also reasonably good except for Mg, Ti and Al. Data on Ca, Fe, Ni and Co are somewhat higher than the certified values even though there is good agreement between the results obtained in the present study. The application of this sample dissolution—concentration technique is not limited to fused silica. Any materials such as arsenic, silicon and selenium that form volatile fluorides can be analyzed in a similar manner. Ion exchange, which separates the matrix from the impurities, can also be used to remove the matrix elements. Experiments to determine trace impurities in alumina by dissolution followed by ion exchange to separate aluminum ion from the trace impurities with a glass-immobilized chelating agent are in progress.

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THE RETENTION BEHAVIOR OF RADIONUCLIDES ON COPPER(II) SULFIDE

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SUMMARY

The adsorption properties of copper(II) sulfide in various acid solutions for different radiotracers are described. Column and batch equilibration methods are discussed. Copper(II) is selectively adsorbed on CuS; the decontamination factor exceeds 10^4 for column operations in 6 M hydrochloric acid solution. Among the 30 ions tested in 6 M hydrochloric acid, only copper and gold are adsorbed quantitatively; mercury, silver, bromine, technetium and molybdenum are adsorbed partially. The retention capacity for copper(II) is around 20 mg Cu/g CuS. The adsorption processes on CuS as functions of acid concentrations (HCl, $HClO_4$ and H_2SO_4) are described. The method seems applicable in activation analysis for trace elements in copper matrices.

In recent years inorganic ion-exchange chromatography has found a wide range of applications in analytical chemistry and in radiochemical separation [1—4]. The mechanism of uptake of ions on inorganic ion exchangers is generally quite complicated, involving physical adsorption, surface adsorption, isotope exchange, precipitation, coprecipitation, etc. In many cases, the ion-exchange process is interestingly connected with phenomena such as the formation of defined insoluble compounds with the matrix [3].

In ion-exchange properties of a wide range of insoluble sulfides, e.g. Ag_2S, FeS, ZnS, PbS, CdS, have been studied in dilute acid media [5—9]; these sulfides are selective towards cations forming insoluble sulfides. The exchange reaction proceeds primarily by metathesis, the metal ion in the exchanger being displaced by appropriate ions in the solution. For divalent cations, the order of selectivity corresponds to the order of solubilities of the freshly prepared amorphous sulfides [10], though there is no correspondence with the solubilities of the sulfide minerals [6, 10].

In the present study, the adsorption characteristics of ions on copper(II) sulfide precipitate from various acid media were examined and practical application of this material in radioanalytical separations were tested. Both column chromatographic and batch equilibration methods were used.

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In experiments done with radioactive tracers in 6 M hydrochloric acid solution, out of 30 elements tested on the CuS columns, only copper and gold were retained quantitatively, and silver, mercury, molybdenum, technetium and bromine partially; other ions were eluted quantitatively. The decontamination factor for copper ion in the column process was favorable, maintaining a constant high value ($>10^6$) up to the maximum adsorption capacity of CuS (20 mg Cu/g CuS). These desirable features (selectivity, high retention capacity and high decontamination factor) indicate useful applications in activation analysis for trace impurities in copper matrices.

EXPERIMENTAL

Preparation of copper(II) sulfide

Copper(II) sulfide was prepared by adding, with continuous stirring, excess of ammonium sulfide to a 0.5 M copper(II) chloride solution. The resulting precipitate was filtered and washed with water. To obtain materials with a large particle size, the precipitation was conducted at —10 °C [3]. The material was dried, ground and sieved, and the 80—150-mesh fraction was collected. The product was heated at 160 °C for 2 h before the adsorption study. This heating step was of critical importance in obtaining satisfactory adsorption.

Commercial reagent-grade CuS (Wako Company, Japan) was used to determine if the commercial material and the specially prepared compound possessed identical adsorption properties. Repeated studies showed that the two products possessed similar adsorption characteristics and the Wako product was thereafter used throughout this study.

Preparation of radiotracers

The radiotracers were prepared by neutron activation of the corresponding stable elements or oxides in the reactor of National Tsing Hua University. The neutron flux was $2 \cdot 10^{12}$ n cm^{-2} s^{-1}. The media for the radiotracer solution were adjusted as required.

Separation by column chromatography

The columns (1.5 cm^2 × 10 cm) were prepared by supporting a 5-cm bed of CuS (5 g) on a quartz wool plug. The flow rate obtained was then too low (about 0.10 ml min^{-1}) for practical uses, and a pressurized column was adapted for use; a flow rate of 0.35—0.40 ml min^{-1} was kept constant during washing, sorption and elution under pressure. The resin bed was washed with 10 ml of eluant before being loaded with the feed solution. In each experiment, 5 ml of feed solution containing 50—500 μg of tracers was sorbed on the column. The column was then washed with 50 ml of acid solution of the same concentration at the same flow rate. The effluent fractions and the precipitates were analyzed by γ-spectrometry.

To investigate if the adsorption characteristics of ions were affected by the presence of macro amounts of copper ion under fixed column conditions, 100 mg of copper carrier, which corresponded to the exchange capacity of the column, was added along with the various radiotracer ions to the column.

Separation by batch equilibration

Batch equilibration experiments were conducted by shaking 2 g of CuS in a 50-ml flask with 10 ml of the appropriate acid solution. The equilibration time for copper adsorption was tested with ^{64}Cu tracer.

Radioactivity measurement

A 1.75 × 3-in. NaI(Tl) crystal was used for routine radioactivity measurements. When the CuS column was used for determination of trace impurities in a copper matrix, a 43-cm^3 Ge(Li) detector was used for high-resolution measurements. The output from the detector was analyzed with a HP 4096-channel pulse-height analyzer.

RESULTS

Adsorption characteristics of transition metal ions on various metal sulfides have been studied in dilute acid solution [5—8]. The process was attributed primarily to displacement reactions. In the present study, the adsorbability of ions from strongly acidic media was examined.

Table 1 shows the results of column experiments carried out with 30 radiotracers in 1 M and 6 M hydrochloric acid solutions. The figures given show the percentage of the initial radioactivity eluted in the total 50-ml washings from the column. Of the 30 elements tested, only copper and gold were quantitatively adsorbed, while silver, mercury, molybdenum, technetium and bromine were partially retained. Most ions seem to be eluted more efficiently in 6 M than in 1 M HCl solution. Even higher HCl concentrations would probably be more favorable for the elution of most ions, but this would create problems from the solubility of CuS.

The results shown in Table 1 are in principle similar to those found by Girardi et al. [11], except that they reported copper to be only partially retained.

To elucidate the effect of a copper matrix on the retention behavior of radionuclides, systematic column experiments were done by adding copper carrier (100 mg) to each of the radiotracer solutions. Table 1 shows that the elution yields for most ions were similar to, or even appreciably higher than, those in the absence of carrier. This finding could be useful in activation analysis of copper for trace metals.

In studying the adsorption characteristics by batch equilibration the time required for equilibration was first examined. When the radioactivity of copper adsorbed on CuS was studied at different shaking times in 6 M HCl medium, it was found that equilibrium was established within 10 min; results

TABLE 1

Behavior of various ions in HCl solution on CuS columns
(Results are reported as percentage eluted in the 50-ml fraction and are the mean values of at least duplicate analysis.)

Ion	Radio-tracer	1 M HCl	1 M HCl + Cu (100 mg)	6 M HCl	6 M HCl + Cu (100 mg)
Ag(I)	$^{110\text{m}}$Ag	1.2	1.8	62	64
As[a]	^{76}As	98	98	99	99
Au(III)	^{198}Au	2.1	1.8	1.4	1.5
Ba(II)	^{140}Ba	98	99	99	99
Br^-	^{82}Br	28	35	28	31
Cd(II)	^{115}Cd	98	99	99	100
Co(II)	^{60}Co	96	97	96	98
Cr(III)	^{51}Cr	99	99	98	100
Cs(I)	^{137}Cs	98	98	99	100
Cu(II)	^{64}Cu	0	0	0	0
Eu(III)	^{152}Eu	99	100	100	100
Fe(III)	^{59}Fe	97	98	99	99
Hg(II)	^{197}Hg	68	71	95	96
La(III)	^{140}La	99	99	99	100
Mn(IV)	^{56}Mn	99	100	100	100
Mo(VI)	^{99}Mo	88	89	90	91
Na(I)	^{24}Na	98	99	99	100
Ni(II)	^{65}Ni	96	96	97	98
Pa(V)	^{233}Pa	98	99	98	99
Pb(II)	^{210}Pb	97	98	99	99
Rb(I)	^{86}Rb	96	98	98	99
Sb[a]	^{122}Sb	98	99	100	100
Sc(III)	^{46}Sc	97	98	98	99
Se(IV)	^{75}Sc	97	98	99	99
Sn[a]	^{113}Sn	97	97	99	100
Tc(VII)	$^{99\text{m}}$Tc	88	89	97	97
U(VI)	^{239}U	98	99	99	99
Y(III)	^{90}Y	96	97	97	98
Zn(II)	^{65}Zn	99	99	100	100
Zr(IV)	^{95}Zr	96	98	97	100

[a] Uncertain oxidation state.

were unchanged up to at least 50 min. There was no evidence to indicate a slow and continuous increase in the exchange rate because of diffusion within the solid phase [1].

Table 2 shows the retention behavior of ions on CuS in 1 M and 6 M hydrochloric acid solutions by batch equilibration. In general the results were similar to those found in column experiments. The retention of copper was, however, around 50 %, though this was connected with the acid concentration (see below) and may be due primarily to isotope exchange reactions.

TABLE 2

Behavior of various ions in HCl solution on CuS by batch equilibration
(Results are reported as percentage activity in the filtrate and are the mean values of at least duplicate analysis.)

Ion	Radio-tracer	1 M HCl	1 M HCl + Cu (100 mg)	6 M HCl	6 M HCl + Cu (100 mg)
Ag(I)	^{110m}Ag	2.3	1.5	56	54
As[a]	^{76}As	95	97	96	98
Au(III)	^{198}Au	3.5	3.2	1.8	2.4
Ba(II)	^{140}Ba	96	97	98	99
Br^-	^{82}Br	28	55	30	30
Cd(II)	^{115}Cd	98	98	98	99
Co(II)	^{60}Co	95	96	96	97
Cr(III)	^{51}Cr	98	99	98	99
Cs(I)	^{137}Cs	96	97	98	98
Cu(II)	^{64}Cu	44	45	44	43
Eu(III)	^{152}Eu	98	98	99	100
Fe(III)	^{59}Fe	95	98	96	98
Hg(II)	^{197}Hg	73	76	95	96
La(III)	^{140}La	99	99	99	100
Mn(IV)	^{56}Mn	98	99	100	100
Mo(VI)	^{99}Mo	87	88	90	90
Na(I)	^{24}Na	96	97	98	99
Ni(II)	^{65}Ni	98	98	97	99
Pa(V)	^{233}Pa	98	98	98	98
Pb(II)	^{210}Pb	96	96	97	97
Rb(I)	^{86}Rb	95	96	96	97
Sb[a]	^{122}Sb	98	98	99	99
Sc(III)	^{46}Sc	96	97	98	99
Se(IV)	^{75}Se	96	97	96	98
Sn[a]	^{113}Sn	95	96	96	97
Tc(VII)	^{99m}Tc	89	89	95	96
U(VI)	^{239}U	96	97	97	98
Y(III)	^{90}Y	95	96	96	97
Zn(II)	^{65}Zn	99	99	99	100
Zr(IV)	^{95}Zr	95	96	97	98

[a] Uncertain oxidation state.

The retention behavior of various ions on CuS was also examined in perchloric and sulfuric acid media. The results (Table 3) show that copper and gold were retained quantitatively in all cases, whereas silver and mercury which were retained partially in HCl medium, could be retained nearly quantitatively in H_2SO_4 and $HClO_4$ solutions. Technetium and molybdenum were retained only partially in all cases. Other ions such as lanthanum and zinc were quantitatively eluted as expected.

TABLE 3

Adsorption of ions from different acid media by the column method (Results are reported as percentage adsorbed on CuS.)

Ion	HCl		$HClO_4$		H_2SO_4	
	1 M	6 M	1 M	6 M	0.5 M	3 M
Cu	100	100	100	100	100	100
Au	98	99	99	99	97	99
Ag	99	38	98	100	98	99
Hg	32	5	97	97	96	97
Mo	12	10	30	82	10	9
Tc	12	3	25	70	65	66
Zn	< 1	< 1	< 1	< 1	< 1	< 1
La	< 1	< 1	< 1	< 1	< 1	< 1

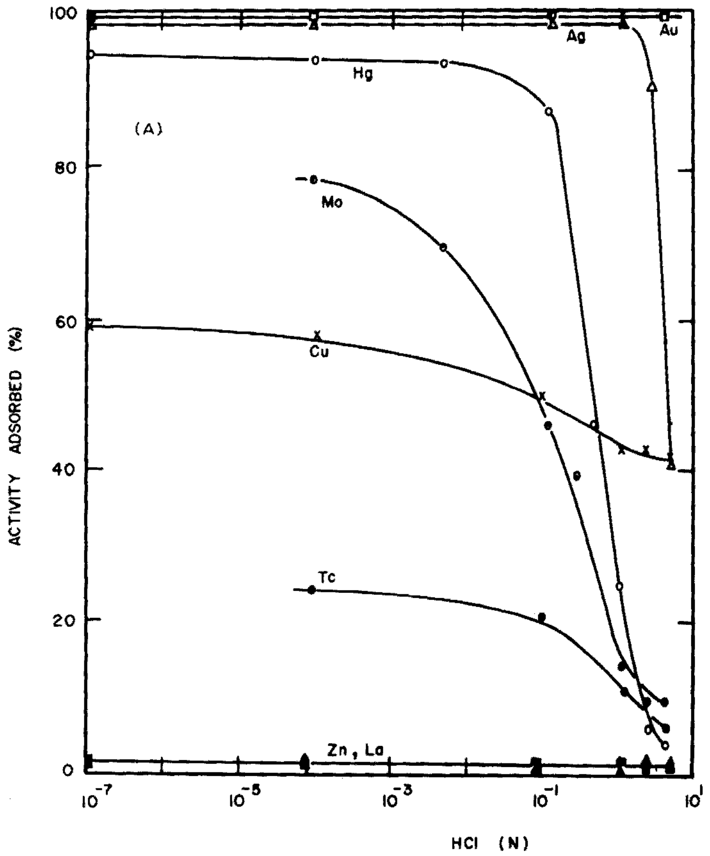
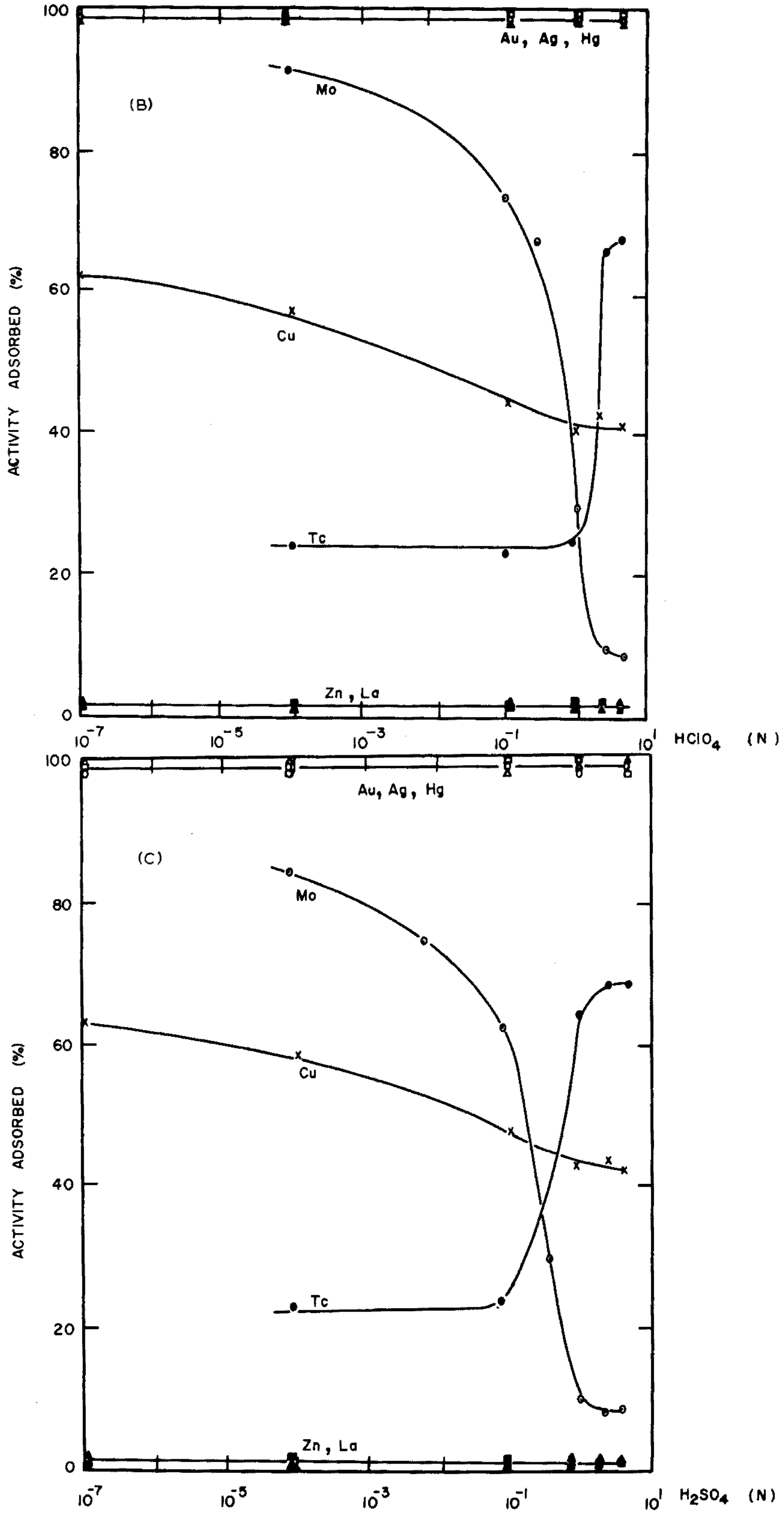


Fig. 1. Adsorption of several radionuclides on CuS from various acid concentrations (batch equilibration). (A). HCl media. (B) $HClO_4$ media. (C) H_2SO_4 media.


(B)
ACTIVITY ADSORBED (%)
100
80
60
40
20
0
Au, Ag, Hg
Mo
Cu
Tc
Zn, La
10^{-7}
10^{-5}
10^{-3}
10^{-1}
10^{1}
$HClO_4$ (N)
(C)
ACTIVITY ADSORBED (%)
100
80
60
40
20
0
Au, Ag, Hg
Mo
Cu
Tc
Zn, La
10^{-7}
10^{-5}
10^{-3}
10^{-1}
10^{1}
H_2SO_4 (N)

Retention capacity

To determine the total retention capacity of CuS for copper, column experiments were carried out with increasing amounts of $CuCl_2$ in 6 M HCl solution. The decontamination factor maintained a constant value of $1.3 \cdot 10^6$, as the amount of copper in the feed solution was increased from trace level to 100 mg, when the column contained 5 g of CuS. Increased loading did not appreciably affect the adsorption characteristics, as often happens with inorganic ion exchangers [12]. However, as the copper loading exceeded 100 mg, the decontamination factor decreased sharply, indicating that maximum capacity had been achieved at 20 mg Cu/g CuS.

The effect of acid concentration on ion uptake

In an attempt to understand the ion adsorption process on CuS, the influence of acid concentration was investigated. Figure 1 shows the results for adsorption from different concentrations of various acids (HCl, $HClO_4$ and H_2SO_4). In hydrochloric acid media (Fig. 1(A)), gold and silver were retained quantitatively irrespective of acidity from pH 7 to about 1 M. As the acidity increased further, retention of silver decreased sharply to 41 %, whereas retention of gold was unchanged. The adsorption of mercury decreased slightly as the acidity increased to about 0.1 M and then decreased dramatically to 4.8 % at 6 M. The adsorption of copper gradually decreased from a maximum value of 58 % at pH 7 to 44 % from 6 M HCl. Molybdenum and technetium were retained only partially and adsorption decreased with increasing acidity. There was no adsorption for zinc, lanthanum and many other ions over the acid range tested.

The adsorption behaviors of some of these ions were remarkably different in $HClO_4$ and H_2SO_4 solutions (Fig. 1 (B), (C)). Silver, mercury and gold were adsorbed quantitatively throughout the acid range tested (pH 7—6 M), which contrasts with the sharp drop in adsorption of mercury and silver from high HCl concentrations. The adsorption of technetium showed, interestingly, the opposite trend to that found with increasing HCl concentration; it persisted at around 23 % in lower acidities and then increased abruptly as the acidity increased to about 1 M for $HClO_4$ and 0.1 M for H_2SO_4.

DISCUSSION

Ion uptake process

The general trend of the results is that those ions (typically mercury, gold and silver) which form less soluble sulfides than copper are adsorbed quantitatively, whereas ions (typically zinc, manganese and iron) which form more soluble sulfides are eluted quantitatively from copper(II) sulfide*;

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*The solubility products [13] of the sulfides are; Hg(II) $1.6 \cdot 10^{-54}$; Ag(I) $5.5 \cdot 10^{-51}$; Cu(II) $8 \cdot 10^{-37}$; Pb(II) $7 \cdot 10^{-29}$; Cd(II) $1.0 \cdot 10^{-28}$; Zn(II) $7 \cdot 10^{-26}$; FeS $4 \cdot 10^{-19}$.

and the adsorption characteristics of several ions of interest, e.g. molybdenum, technetium and silver, generally depend on the acid concentration. Accordingly, the ion uptake process can be conveniently discussed in connection with acidity of the medium.

In very dilute acid solutions (roughly 10^{-7}—10^{-3} M), in which metal—anion complex formation is not considered possible for most ions, the solvated ion can be represented as M^{n+}; and, as suggested previously [9] the adsorption process involves principally displacement reactions

$$2/n\ M^{n+} + CuS \rightarrow Cu^{2+} + M_{2/n}S \qquad (1)$$

Selectivity for this reaction is related primarily to the solubility of the sulfides.

As the acidity increases (roughly from 10^{-3} to 1 M), the probability of a given ion forming metal—anion complexes in hydrochloric acid increases but may be significant only in perchloric or sulfuric acid. Elements such as Zn^{2+}, Cd^{2+}, Hg^{2+}, Au^{3+}, Ag^{+}, etc., are well known to form negatively charged complex ions over a wide range of hydrochloric acid concentration [14]. Since zinc, cadmium and many other ions are not appreciably adsorbed, whereas gold is adsorbed completely throughout the range pH 7 to 6 M acid, and the adsorption of silver and mercury is first complete and then quite suddenly incomplete when a critical acidity is reached, it seems reasonable to assume that adsorption is not related directly to the chemical environment of the exchanging metal. The governing factor for the adsorption of the metal ions appears still to be the solubility of the sulfides.

The differences in adsorption characteristics between mercury, gold, silver (which have lower K_{sp} values than CuS) and molybdenum, especially in hydrochloric acid media, require explanation. The variation in type and extent of the following successive reactions may be considered: adsorption via displacement reactions to form sulfides and subsequent desorption either because of the solubilities of the sulfides formed in acidic media or because of other interactions of sulfides with the media. The decrease in adsorbability for molybdenum, silver and mercury at increased HCl concentrations, may be due to increased solubility or to stronger interaction of sulfides with chloride ions.

The relatively high adsorption of molybdenum at low acidities (about 82 % at pH 4) can be attributed to the displacement reaction (eqn. 1). No solubility product for MoS_3 is available in the literature; molybdenum chemistry is very complicated, and the molybdenum species in a particular system can be affected markedly by small changes in conditions [15]. The nonquantitative adsorption of molybdenum at pH 4 could be attributed to numerous competing species.

The opposing trends for the adsorption of technetium(VII) from HCl and from H_2SO_4 or $HClO_4$ are of interest. Since copper sulfide is an effective carrier for traces of technetate in acid medium [15], the adsorption of technetate can be attributed to coprecipitation at the CuS surface, but the reaction is inefficient in any acid at pH 4 (Fig. 1). Strong hydrochloric acid can convert TcO_4^- to $TcCl_6^{2-}$, though the reaction may be slow, with several intermediate oxidation states [15]; however, such reactions could account for the reduced adsorption yield as the HCl concentration increases. The increased adsorption of technetium with increasing $HClO_4$ and H_2SO_4 concentrations, is more difficult to explain.

Application to neutron activation analysis

The complete removal of copper by a CuS column should find application in the determination of trace elements in high-purity copper metal. Table 3 shows that 6 M HCl should be a suitable medium in practice, since only gold and copper are adsorbed quantitatively. Although silver, mercury, technetium and molybdenum are eluted only partially, the percentage retentions are constant under controlled column conditions.

Figure 2 shows the spectra of irradiated copper metal before and after passage through a copper sulfide column. Clearly, several trace elements such

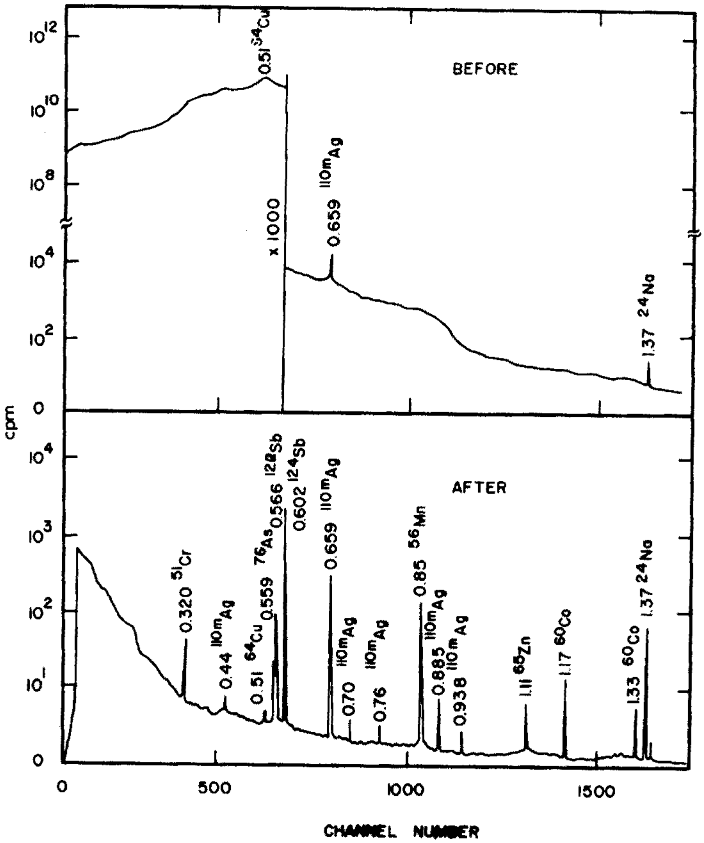

Fig. 2. γ-Spectra of irradiated copper metal before and after passage through CuS column.

as chromium, manganese, zinc, antimony and cobalt, can be detected by high-resolution γ-spectrometry only after the removal of the copper matrix.

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SEPARATION OF ZIRCONIUM FROM FISSION PRODUCTS IN SILICA GEL—NITRIC ACID SYSTEMS

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SUMMARY

A method for the separation of zirconium from fission products based on the system 100—200 mesh silica gel—2.0 M nitric acid is described. Decontamination factors are over 500 for ^{95}Nb, ^{106}Ru, ^{124}Sb, ^{137}Cs, molybdate and uranium(VI), and the yield of zirconium is 98 %.

Most known methods for the separation of zirconium from fission products are practiced in chloride systems, or less frequently in fluoride systems. However, nitrate systems are preferable for separations of macro amounts of zirconium from fission products originating from reprocessing wastes. Analytical separation of zirconium in nitrate media is possible by liquid—liquid extraction with thenoyltrifluoroacetone, but the reagent is not stable under radiation in nitrate media. The adsorption behavior of several elements on silica gel has been studied [1—4]; zirconium, niobium and antimony are adsorbed on silica gel in nitric acid from many fission product elements, but there have been no detailed reports on the behavior of antimony, plutonium and macro amounts of zirconium. In the present work, the behavior of these elements was studied radiochemically in the system silica gel—nitric acid to obtain basic data for separation of macro amounts of zirconium from fission products or irradiated uranium in nitrate media, e.g. waste solutions of spent fuel reprocessing.

EXPERIMENTAL

Chemicals

Silica gel (100—200 mesh) was prepared from commercially available desiccant. It was washed several times with 7 M nitric acid and with water in a column, and dried at 110 °C. Uranium dioxide, lanthanum oxide and zirconium oxynitrate (special grade, Yokozawa Chemicals) were used as nitrates in 2 M nitric acid. The other reagents used were all of JIS special grade. The radioactive nuclides, ^{95}Zr—Nb, ^{106}Ru—Rh, ^{137}Cs—Ba and ^{239}Pu, were imported; ^{124}Sb (1Ci g^{-1}) was obtained from the Radioisotope Centre, JAERI. Niobium-95 was prepared from ^{95}Zr—Nb by liquid—liquid extraction [5]. A mixture containing ^{99}Mo—Tc (about 1 m Ci g^{-1}) was obtained by (γ, n) reaction of molybdenum metal. Plutonium and molybdenum were used as Pu(IV) and Mo(VI), respectively.

Measurement

The gross γ-ray activity of ^{95}Nb, ^{106}Ru—Rh, ^{124}Sb and ^{137}Cs—Ba was measured by a 1.5-in. well-type NaI(Tl) scintillation counter. The γ-ray activity of ^{95}Zr and ^{95}Nb in a mixture of ^{95}Zr—Nb, as well as that of ^{99}Mo, was obtained from the areas of photopeaks in the γ-ray spectra, measured by a Packard 1024-channel pulse-height analyzer with a biased amplifier connected to a 30-cm^3 Ge(Li) detector. A gas-flow counter was used for measurement of α-ray activity of ^{239}Pu.

The concentrations of macro amounts of zirconium and uranium(VI) were determined by spectrophotometry with arsenazo(III) [6, 7].

Determination of distribution ratios

The batch equilibration method [8] was adopted. For ^{95}Zr—Nb or ^{124}Sb, 4.0 ml of the aqueous phase was shaken for 40 min with a weighed amount (0.5 g) of silica gel. For ^{239}Pu, 2.0 ml of the aqueous phase and 0.1 g of silica gel were used. The shaking time was decided by preliminary tests for ^{95}Zr—Nb and ^{124}Sb. The activity of the aqueous phases was measured before and after shaking to calculate the distribution ratio, K_d.

Column elution

The initial test solution was 2.0 M nitric acid containing a radioactive tracer and zirconium (6.65—22.2 μg Zr ml^{-1}). This solution (10 ml), 40 ml of 2.0 M nitric acid and 130 ml of 10 M nitric acid were passed successively through a silica gel column (10 mm i.d., 100 mm high). The elements examined were: 25.68 mg of uranium(VI) as the most abundant element in the irradiated uranium; ^{95}Zr, ^{95}Nb and ^{124}Sb as adsorbable elements; and ^{99}Mo, ^{106}Ru and ^{137}Cs as typical fission products. Zirconium carrier was added again to the loaded samples. The radioactivity was measured for both the effluent and the initial test solutions. The decontamination factors were calculated from the equation

$$\text{D.F.} = \frac{(\text{Total radioactivity of the initial soln. added})}{(\text{Total radioactivity of the zirconium fraction})} \qquad (1)$$

where the zirconium fraction is the eluate with 10 M nitric acid.

The break-through point of zirconium was measured with ^{95}Zr—Nb solution (740 μg Zr ml^{-1}) in 2.0 M nitric acid and silica gel columns of 6-mm diameter and 100-mm length. In all the column elutions, the flow rate was about 0.4 ml min^{-1}.

Solutions containing a radioactive tracer were always allowed to stand overnight before experiments in order to equilibrate the zirconium species [4]. The experiments were carried out at ambient temperature.

RESULTS AND DISCUSSION

Distribution ratio

Since the purpose of the present work was to obtain basic data for the separation of macro amounts of zirconium in the spent fuel or in the fission products, the adsorption isotherm was studied at 2.0 M nitric acid (Fig. 1). The errors were calculated from the statistical counting errors only. The distribution ratio, i.e. the tangential slope of the isotherm, increased with decreasing zirconium concentration, and below 10 μg Zr ml^{-1} showed the same value with that of carrier-free ^{95}Zr.

Tracer chemical study [3] showed that ^{95}Zr and ^{95}Nb were adsorbed ($K_d > 5$); ^{99}Mo(VI), ^{234}Th and ^{239}Np were slightly adsorbed (K_d = 1—5); and ^{60}Co, ^{65}Ni, ^{90}Sr, ^{88}Y, ^{99m}Tc, ^{106}Ru, ^{137}Cs, ^{139}Ba, ^{140}La, ^{144}Ce(III), ^{147}Pm and ^{237}U (VI) were not adsorbed ($K_d \leqslant 1$) on 30—80-mesh silica gel in 0.1—10 M nitric acid. Antimony-125 was also adsorbed on silica gel [4]. These values might be changed by the presence of macro amounts of elements in the postulated starting sample. Table 1 shows that the effect of non-adsorbable elements on the distribution ratio of zirconium is negligible from the practical point of view. Lanthanum was used as representative of the most abundant lanthanide in fission products [9]. The ratios of the concentrations, La/Zr and U/Zr, were decided by an assumed burn-up of 10,000 MWD.T^{-1} and the fission yields in ^{235}U fission with thermal neutrons. Since the amount of

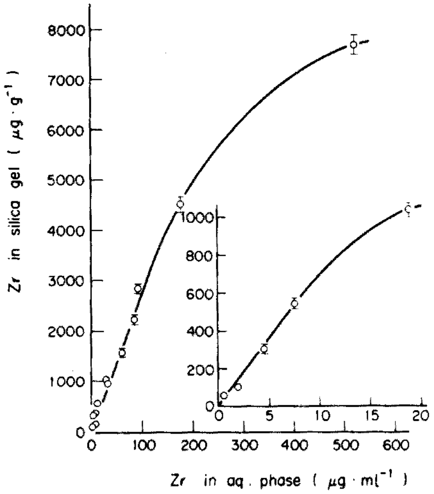

Fig. 1. Adsorption isotherm of zirconium on silica gel from 2 M HNO$_3$ at room temperature.

TABLE 1

Distribution ratio of zirconium in the presence of lanthanum or uranium(VI) nitrate at 2.0 M nitric acid

Initial concentration of			K_d
Zr (μg ml^{-1})	La (μg ml^{-1})	U (mg ml^{-1})	
6.65	0	0	$0.9 \cdot 10^2$
6.65	14.0	0	$1 \cdot 10^2$
2220	0	0	$1.5 \cdot 10$
2220	4270	0	$1 \cdot 10$
22.2	0	0	$7 \cdot 10$
22.2	0	21.4	$8 \cdot 10$

zirconium, the most abundant among the adsorbed elements, was expected to affect the adsorption of the other elements, the acidity dependence of the distribution ratios of ^{95}Zr, ^{95}Nb, ^{124}Sb and ^{239}Pu was measured in the presence of macro amounts of zirconium and of carrier-free ^{95}Zr (Fig. 2). An initial concentration of 6.65 μg Zr ml^{-1} lay in the region of constant distribution ratio of zirconium in Fig. 1. The concentrations of the other adsorbable elements were low enough [9] not to affect the adsorption. The distribution ratios reported by Caletka et al. [1] agreed with the present data. Fluctuating values for carrier-free ^{95}Zr and ^{95}Nb were averaged for several determinations in Fig. 2; the values for ^{95}Zr alone are considered practically the same as those

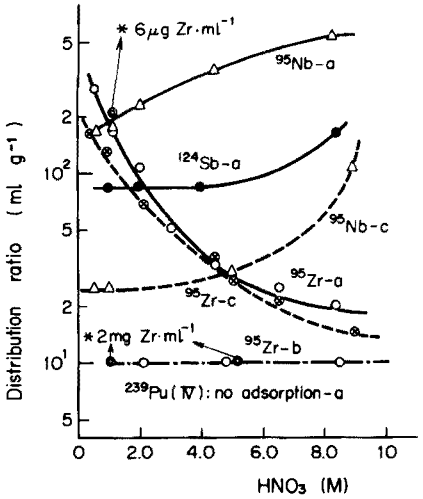

Fig. 2. Acidity dependence of distribution ratios of several elements. Asterisks indicate results obtained by Caletka et al. [1].
The initial concentrations of zirconium were; a, 6.65 μg Zr ml^{-1}, b, 2.22 mg Zr ml^{-1} and c, no zirconium carrier.

for ^{95}Zr with 6.65 μg Zr ml^{-1} present. In both cases, the distribution ratio for zirconium decreased with increasing acidity, but ratios for ^{95}Zr in 2.22 mg Zr ml^{-1} solutions were independent of the acidity. This may be attributed to the adsorption mechanism changing with nitric acid concentration as discussed by Caletka et al. [1]. Antimony was considered to be pentavalent after preliminary tests and earlier reports [10, 11]. Though the distribution ratio of ^{95}Nb was also affected by the presence of zirconium, the effect was not a problem in the separation of zirconium. No distribution ratio of americium and curium was measured because of their similarity to lanthanum.

Column elution

As the adsorption rate was similar to those of ion-exchange resins [3, 8], a separation scheme for column elution was worked out on the basis of the data on distribution ratios. After loading on the silica gel column as indicated under Experimental, elution with 2 M HNO_3 should remove ^{137}Cs, ^{106}Ru, U(VI), etc., elution with 10 HNO_3 should remove Zr, and Nb and Sb should remain on the column. Zirconium could also be eluted by 1 M sulfuric acid or by oxalic acid solution; the latter is often used for elution of carrier-free ^{95}Zr [1, 2, 12]. The results of the column elution tests are shown in Fig. 3, together with the reproducibility of the zirconium elution curve, where values below $2 \cdot 10^{-3}$ % were neglected. Decontamination factors (Table 2) defined by eqn. (1) were calculated from these results. The yield of zirconium was 98.1 ± 0.14 %, when 66.5 or 222 μg of zirconium was loaded on the column. More than 0.1 % of niobium and about 1.2 % of antimony appeared in the zirconium fraction, but all of them did not reappear in the same fraction on repeated column elution. This behavior cannot be explained by the distribution ratio only, but the repetition was effective for decontamination. The zirconium elution curve was asymmetrical, tailing being observed. This was attributed to the convex shape of the adsorption isotherm (Fig. 1), which corresponds to a Langmuir-type adsorption, as generally happens for silica gel adsorption [13].

The capacity of silica gel for zirconium in 2.0 M nitric acid was estimated to be 0.44 meq g^{-1}, from the break-through point found at 16 ml. This is similar to the value reported by Ahrland et al. [2], 0.40 meq g^{-1} at pH 1.5.

Conclusion

Zirconium showed a distribution ratio of over 70 for 2.0 M nitric acid at zirconium concentrations less than 100 μg Zr ml^{-1}. Further, the distribution ratio of zirconium was low enough for elution at high acidities where the values for niobium and antimony were over 10^2. Radioactive nuclides of niobium and antimony are the other species adsorbable on silica gel in nitrate media among fission products, but their concentrations are negligible. Thus, the silica gel adsorption can be used as a highly selective separation method for zirconium from fission products or from the irradiated uranium in nitrate media. Though the presence of 4.27 mg La ml^{-1} and 21.4 mg U ml^{-1}

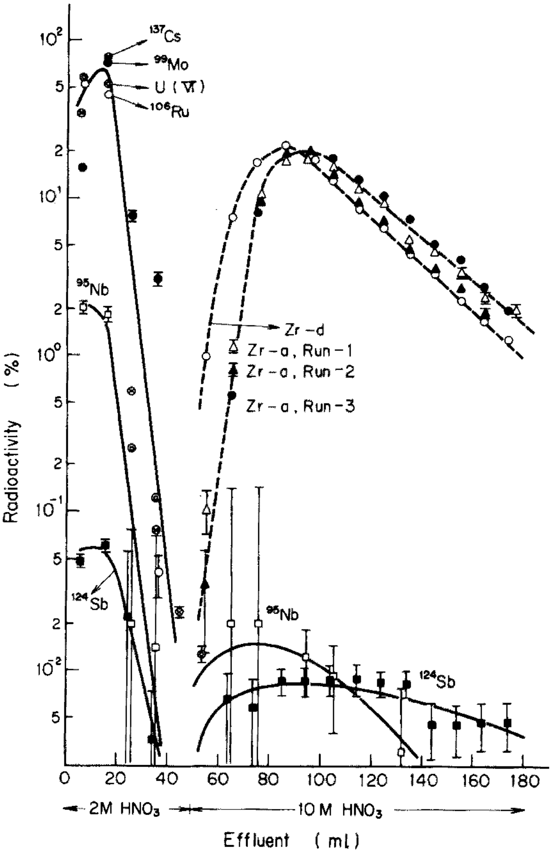

Fig. 3. Results of column elution experiments.
The initial concentrations of zirconium were; a, 6.65 μg Zr ml^{-1} and d, 22.2 μg ml^{-1}.

TABLE 2

Decontamination factors

Contaminant	Decontamination factor
^{95}Nb	1000 ± 390
^{106}Ru	500 ± 220
^{124}Sb(V)	590 ± 61
^{137}Cs	520 ± 56
Mo(VI)	about 10^3
U(VI)	about 10^3

did not lower the distribution ratio of zirconium, the presence of 6 mg U ml^{-1} plus 9 mg Cu ml^{-1} did [14]. This means that salts in high concentration can affect the adsorption of zirconium, and that this method is more suitable for fission products than for irradiated uranium with low burn-up, because of the existence of relatively large amounts of uranium. In the column elution, silica gel could be used in the same way as ion-exchange resins. The reproducibility was good under the conditions studied. Although silica gel has a smaller capacity than ion-exchange resins, it is stable under radiation. These facts indicate that silica gel adsorption could be applied directly to solutions from spent fuel reprocessing. The fission-product zirconium is the best for burn-up determinations of thorium—uranium fuel [15], and thorium is expected to behave similarly to uranium in silica gel adsorption [3]. Therefore, silica gel adsorption could also be used in this case.

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THE DETERMINATION OF SMALL AMOUNTS OF ORGANIC HYDROPEROXIDES WITH TRIPHENYLPHOSPHINE

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SUMMARY

A method for the determination of hydroperoxides has been devised which combines the sensitivity of iodimetric methods with the accuracy of the tin(II) reduction procedure. The hydroperoxide is reduced with a modest excess of triphenylphosphine (TPP) in cyclohexane solution. The amount of reagent consumed is followed by a g.l.c. procedure which measures the change in peak area ratio of TPP and an internal standard, hexacosane. The method has been used successfully with oxidized glycerides and simple esters of oleic and linoleic acid for which the Sully iodimetric method gives low results.

In the course of work on the low level autoxidation of the lipid components of palm oil, the need arose for accurate assays of hydroperoxide in small samples of pure and expensive substrates. A practical survey of the many methods of hydroperoxide estimation available indicated that, with t-butyl hydroperoxide as a standard, the Sully iodimetric technique [1] was the most satisfactory in terms of accuracy, precision and sensitivity. With samples of 0.01 mmol a value of 102.1 % of theory (against the purity determined by the accurate but more cumbersome tin(II) method [2]) was obtained with a standard deviation (s) of 0.4 %. However, the method gave hydroperoxide values lower by some 14 % and 7 % than those obtained by the tin(II) procedure on oxidized linoleate and oleate esters, respectively, or their glycerides. At least part of the explanation for this discrepancy lay in the reaction of iodine with the unsaturated substrate, as the addition of methyl linoleate to a t-butyl hydroperoxide sample lowered the apparent purity by ca. 5 %.

For the determination of trace levels of hydroperoxides, colorimetric methods are often used. The more popular of these involve the oxidation of iron(II) ions [3], the leucobase of methylene blue [4], or iodide ions [5, 6] by the hydroperoxide and the subsequent determination of the oxidized species spectrophotometrically. Their disadvantages lie in their poor selectivity and, frequently, poor precision and accuracy.

Other sensitive analytical methods for hydroperoxides include polarography

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[7—10] and g.l.c. [11—22]. Polarography has been used rather infrequently, probably because of the unavailability of, or unfamiliarity with, the necessary equipment; g.l.c. analysis is limited to hydroperoxides that are sufficiently stable and volatile. However, the reduction of the hydroperoxides with triphenylphosphine (TPP) and the estimation by g.l.c. of (i) the alcohol derived from the hydroperoxide, (ii) the triphenylphosphine oxide (TPPO) formed, or (iii) the residual TPP, was potentially attractive as a microanalytical procedure. Triphenylphosphine is stable and can be purified easily; reduction by TPP was reported to be quantitative, unequivocal and rapid for almost every hydroperoxide [23]. It proved to be impossible to determine the lipid alcohols quantitatively because of their ready dehydration on the g.l.c. column. Experimental difficulties were found in following the TPPO produced, as in the work of Holtz et al. [24]. The methods described [25] for the determination of residual TPP have not included g.l.c. and are too insensitive for the present purpose.

EXPERIMENTAL

Reagents

Triphenylphosphine (laboratory-reagent grade, m.p. 78—82 °C) was recrystallized from a 2 + 1 (v/v) mixture of ethanol and ether to give the pure compound (by g.l.c.), m.p. 80.5—81.5 °C. Hexacosane (Field Instruments) was pure by g.l.c. under the conditions described below. t-Butyl hydroperoxide had b.p. 30.3—31.3 °C/10 mm Hg and was 96.4 % pure by tin(II) chloride reduction [2].

Methyl linoleate, methyl oleate, trilinolein and triolein (Sigma Chemical Co.) were freed from hydroperoxides by column chromatography and were ca. 99 % pure by thin-layer chromatography. They were autoxidized at 55 °C to known extents, measured accurately by the oxygen absorption apparatus described by Cain and Knight [26]. When the requisite oxygen absorption had occurred, the reaction vessel was cooled rapidly in solid CO_2—acetone to prevent further oxidation.

Cyclohexane (commercial grade) was purified by fractional distillation. The middle fraction (b.p. 80.5 °C/760 mm Hg) was outgassed with nitrogen before use.

Procedure

The TPP reagent was prepared by dissolving accurately weighed quantities of TPP (6 mg) and hexacosane (3 mg) as the internal standard in cyclohexane (10 ml). The peroxide sample, containing ca. 10^{-2} mmol of hydroperoxide, was also dissolved in cyclohexane (10 ml). Portions (2 ml) of the reagent solution were pipetted into 2 ml of the hydroperoxide solution in a test tube which was flushed with a gentle stream of nitrogen and stoppered. The reaction mixture was left for 10 min at room temperature before being concentrated to ca. 1 ml volume by a rapid stream of nitrogen over the surface of the liquid. This concentration procedure took 5 min.

Gas-liquid chromatography was performed on a Philips gas chromatograph PV 4000 equipped with a flame ionization detector. A 2.5 m × 4 mm glass column, packed with 60—80 mesh Chromosorb G coated with 0.5 % of a silicone oil (OV 17) and 0.25 % terephthalic acid, was operated isothermally at 220 °C with N_2—H_2 as the carrier gas at 500 mm Hg pressure. Samples of 4 μl were injected; peak areas were measured by integration.

$$\% \text{ hydroperoxide estimated} = \frac{A_1 - A_2}{A_1} \times \frac{w_1}{W_1} \times \frac{W_2}{w_2} \times 100$$

where A_1 and A_2 are the ratios of the peak areas of TPP and hexacosane for the TPP reagent and the reaction mixture, respectively; w_1 is the weight (g) of TPP used; w_2 is the sample weight of the hydroperoxide; and W_1 and W_2 are the molecular weights of TPP and hydroperoxide, respectively.

RESULTS AND DISCUSSION

Determination of TPP by g.l.c.

The ratio of peak areas of TPP and hexacosane is linearly related to their weight ratio in the range 0.2—4.0. Table 1 shows the invariance with time of standing of the reagent solution of TPP—hexacosane peak area ratios, and of a reaction mixture of oxidized methyl oleate and excess of TPP. No steady decrease of these ratios over a period of 1 h at room temperature was observed with either solution, indicating that the TPP is stable under the experimental conditions used.

Determination of t-butyl hydroperoxide

The method was standardized against a sample of t-butyl hydroperoxide which had been assayed by both the tin(II) method [2] and the Sully method [1]. At low concentrations of t-butyl hydroperoxide ($1.15 \cdot 10^{-3}$ M), the reduction of the hydroperoxide at room temperature was incomplete even after a few hours, in agreement with previous observations on the reduction by phosphine of this tertiary hydroperoxide compared with secondary lipid hydroperoxides [27]. To obtain a conveniently fast rate, the reaction was carried out at an elevated temperature. Six test tubes, each containing the same reaction mixture, were purged with nitrogen, stoppered, and immersed in a constant-temperature bath at 65 °C. They were removed successively from the bath after known intervals of time and cooled, and their contents analyzed for residual TPP. Table 2 shows that the reduction of t-butyl hydroperoxide is complete after 40 min. A similar treatment of five test tubes containing only the reagent blank showed that the TPP—hexacosane peak area ratio did not fall with time over the period 0—80 min. A t-butyl hydroperoxide purity of 97.4 % was obtained in reasonable agreement with the values of 96.4 % and 98.4 % obtained by tin(II) reduction and the Sully procedure, respectively.

TABLE 1

Variation of TPP—hexacosane peak area ratios with time of standing of the reagent solution, and of a reaction mixture of TPP and oxidized methyl oleate ($[TPP]_0 = 2.13 \cdot 10^{-3}$ M, $[C_{26}] = 3.50 \cdot 10^{-4}$ M, $[ROOH]_0^a = 9.70 \cdot 10^{-4}$ M)

Time[b] (min)	TPP/C_{26} peak area ratio	
	Reagent blank	Reaction mixture
0	1.53	0.866
15	1.54	0.890
30	1.56	0.880
45	1.58	0.863
60	1.53	0.869
	$s = 0.02$	$s = 0.01$

[a] Methyl oleate hydroperoxide calculated from oxygen absorbed.
[b] After the concentration procedure.

TABLE 2

Dependence on time of the amount of t-BuOOH reduced by TPP ($[t\text{-BuOOH}]_0 = 1.15 \cdot 10^{-3}$ M, $[TPP]_0 = 2.13 \cdot 10^{-3}$ M. Time of heating at 65 °C is given in min.)

Time	0	5	10	20	40	80	100
% Reduced	10.6	68.4	82.0	93.6	97.0	97.7	97.5

Determination of lipid hydroperoxides

Table 3 compares the theoretical hydroperoxide yields based on oxygen uptake in the early stages of autoxidation of methyl linoleate, methyl oleate, trilinolein and triolein with those obtained by the TPP method and the Sully procedure. The following points may be noted.

(i) The increase in the hydroperoxide concentration determined by the TPP method is directly proportional to the increase in oxygen uptake of these compounds.

(ii) The methyl linoleate hydroperoxidic oxygen obtained by this TPP method averages 92.4 % of that calculated from the oxygen absorbed. Similar analyses indicate yields of 88.9 %, 96.6 % and 88.1 %, respectively, for the hydroperoxides derived from the autoxidation of methyl oleate, trilinolein and triolein. There is good general agreement between the TPP and the tin(II) methods, again emphasizing the error involved in the iodimetric method where linoleate or oleate hydroperoxides are concerned.

These secondary hydroperoxides did not exhibit the slow rate in the reduction of t-butyl hydroperoxide observed at similar concentrations, and the reaction proceeded readily to completion in less than 15 min at room temperature.

TABLE 3

Comparison of the hydroperoxide yields obtained by Sully's method with those obtained by the TPP method in the early stages of linoleate and oleate autoxidation

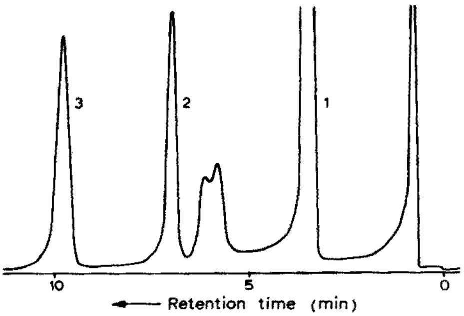
Sample	Extent of oxidation mole %[a]	Sully's method		TPP method		Tin(II) method
		% yield	Mean	% yield	Mean	% yield
Methyl linoleate	1.83	82.0		90.1		
	2.93	79.6		92.8		
	3.73	82.0	81.6	92.5	92.4	
	4.96	83.4		93.8		94.3
	6.36	82.5		92.8		
Methyl oleate[b]	2.00	76.0		95.5		
	2.35	79.5		89.5		
	2.98	81.5		90.5		
			78.4		88.9	
	3.57	78.5		84.0		
	3.62	78.0		83.5		
	4.56	77.0		90.5		85.6
Trilinolein	1.21	77.0		96.5		
	2.54	80.5		95.9		
			78.4		96.6	
	3.63	77.5		95.5		
	4.32	78.9		98.6		
Triolein[b]	1.23	79.0		92.8		
	2.24	74.9		86.6		
			77.4		88.1	
	3.00	77.0		85.9		
	4.51	78.5		87.1		

[a] Moles of oxygen absorbed per 100 mole of fatty acid residue.
[b] Oxidation was initiated by azobisisobutyronitrile.

CONCLUSIONS

These results indicate that small quantities of a hydroperoxide may be conveniently and accurately determined by reduction with an excess of TPP and estimation of the residual TPP by g.l.c. The usefulness of this method is limited only by the possible interference of the TPP peak by the other components present in the reaction mixture (e.g. the alcohol or its dehydration products). If required, as little as 0.5 μmol hydroperoxide can be determined.

The chromatograms of the reaction mixtures of methyl linoleate and methyl oleate hydroperoxides and TPP (Figs. 1 and 2) indicate that the TPP and hexacosane give two completely resolved peaks. Apart from these and the peaks of the esters, there are two other unresolved peaks in the autoxidized linoleate—TPP mixture (Fig. 1) and a multiplicity of peaks in



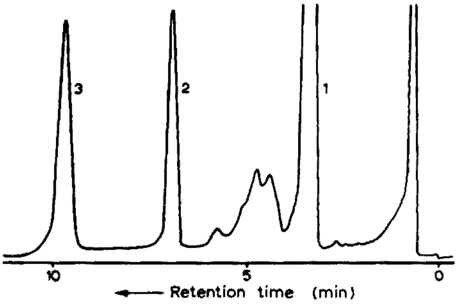


Fig. 1. G.l.c. trace of a reaction mixture of oxidized methyl linoleate and excess triphenylphosphine. Peaks: 1, methyl linoleate; 2, triphenylphosphine; 3, hexacosane.

Fig. 2. G.l.c. trace of a reaction mixture of oxidized methyl oleate and excess triphenylphosphine. Peaks: 1, methyl oleate; 2, triphenylphosphine; 3, hexacosane.

the autoxidized oleate—TPP mixture (Fig. 2). These probably arise from the alcohols derived from the reduction of the hydroperoxides, although it is suspected that the alcohols would be dehydrated on the column under the experimental conditions used. An attempt to correlate the sum of the peak areas derived from the TPP reduction of methyl linoleate autoxidized to different extents with the reduction in the TPP peak area was not successful. A significant point to note is the absence of the TPPO peak in all chromatograms. TPPO is quite polar and would have a very long elution time under the experimental conditions used, rendering its peak unsuitable for accurate quantitative work. Trilinolein and triolein, unlike the simple esters which have short elution times, were also observed to remain on the column.

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RE-ASSESSMENT OF CHELATING ION-EXCHANGE RESINS FOR TRACE METAL ANALYSIS OF SEA WATER

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SUMMARY

The behaviour of the chelating ion-exchange resin Chelex-100 for collection of trace metals from sea water has been studied by anodic stripping voltammetry after acid digestion of the sea water sample and the resin effluent. All the naturally occurring, electrochemically reducible species of Cu, Pb, Cd and Zn are chelated by the resin; this fraction of these metals is regarded as the dissolved fraction. Centrifugation showed that some of the metal liberated by acid digestion is associated with colloidal species. Neither this nor the metal adsorbed on fine particles is affected or removed by the chelating resin.

Studies of the behaviour of chelating ion-exchange resins with respect to some minor elements [1, 2], and the application of resins such as Chelex-100 [3] in trace metal analysis of sea water, have provided convenient methods for the concentration of some minor elements from large volumes of natural water samples. The significance of this technique lies in its ability to separate metals without prior chemical treatment of the sample which could produce contamination at the 10^{-9}-g l^{-1} level, and without, as some treatments of water samples often do, causing a change in the composition of the species of the metals in the sample.

Since the chelation of metals by these resins is pH-dependent [2, 4], their use in the H^+ form involves a decrease in the pH of the effluent because of the release of hydrogen ions, thus causing a deterioration in the efficiency of the uptake of metal ions on the resin. The maximum efficiency is observed when the resin is converted to forms other than H^+ (e.g. Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). However, when a strong electrolyte solution such as sea water is applied to the resin in its H^+ form, a rapid conversion to the Na^+ (and Mg^{2+}, Ca^{2+}) form is achieved after the passage of ca. 200—300 ml, thus converting the resin to the form in which it has maximum chelating efficiency. The loss caused by leakage of metal ions when 8—10 l of sea water is applied to the resin is, therefore, only a small proportion of the total. However, such losses can be significant when small volumes of sea water or fresh water are used.

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This has been emphasized [5] and it has been recommended that the chelating resin should be used in its NH_4^+ or Na^+ forms for maximum efficiency. Different forms of the chelating resin have been used. The calcium(II) form [6] was chosen for the separation of minor metals from sea water and fresh water, so that the major ion composition of the eluate remained constant (>99 % calcium salt) as necessitated by the subsequent pulse-polarographic method of determination.

More recently, and concomitantly with the widening use of anodic stripping voltammetry (a.s.v.), certain discrepancies in the behaviour of the chelating resins have been reported [7, 8], and it has been suggested that chelating resins such as Chelex-100 do not completely bind and remove the minor elements from sea water. In view of the chemical treatment the water sample was subjected to a.s.v. analysis and since such treatment was applied during the assessment of the chelating resin [8], a re-examination of this resin was undertaken by a.s.v. techniques with particular reference to the behaviour of the different metal species commonly found in natural waters.

EXPERIMENTAL

Equipment and reagents

The a.s.v. measurements were made with a Princeton Applied Research (PAR) Polarographic Analyser model 174 equipped with a Metrohm cell fitted with a standard calomel electrode (SCE), a mercury film (on graphite) electrode and a platinum-wire counter electrode.

Merck "Suprapur" hydrochloric and nitric acids were used. The acetate buffer (1.7 M, pH 5.8), sodium acetate (2 M) and $CaCl_2$ solution (0.5 M) were prepared from analytical-reagent grade salts and were purified electrolytically for a period of two weeks in the PAR reagent cleaner.

The chelating resin columns were prepared as described by Riley and Taylor [3], with a quartz wool plug to support the resin within the glass column. The Chelex-100 resin, initially in the NH_4^+ form, was found to change rapidly to the Na^+ form after the passage of ca. 300 ml of sea water [9]. Tests made on this resin during the present investigation confirmed this, and showed that when the top 1 cm of the resin bed was removed and washed with 2 M nitric acid, calcium accounted for over 80 % of the metals displaced. This suggests that in practice the resin is effectively in the Ca^{2+} form when sea water is applied to the resin. Consequently, the resin columns were prepared in the Ca^{2+} form for the present investigation. The columns were then washed with 10 bed volumes of distilled water before use.

Samples

Three different sea-water samples were obtained from the Oslofjord (20—40 m); 2 l of each were filtered through membrane filters (0.45 μm, previously washed with deionized distilled water) and stored in aged polythene bottles. A 1-l aliquot was passed through the chelating resin column, and all the effluent was collected in polythene bottles and stored for analysis. The columns were cleaned and regenerated after each application.

Analytical methods

Zinc, cadmium, lead and copper were determined in both the sample and the resin effluent by differential pulse a.s.v. Calibration was done by standard addition; for each determination, three increments of standard were made to ascertain linearity and the concentrations of the metals were found by extrapolation.

Sample A. The original sea water and the resin effluent were analysed directly at their natural pH. In view of the interference on the zinc determination caused by Zn—Cu and Zn—Ni intermetallic compounds [10], and in order to minimize this effect on both the copper and zinc determinations when the standard addition method was used, the zinc was determined in a separate aliquot.

Sample B and C. Single aliquots were analysed at a final pH of 5.4 (acetate buffer). Cu, Pb and Cd were determined first and the zinc was then determined after the addition of gallium ions to prevent the formation of Zn—Cu and Zn—Ni intermetallic compounds [11].

Aliquots of sample B were acidified with 1 M HCl to pH 2.2 and digested in PTFE beakers at 100 °C for 15 min. Similar treatment was carried out on other aliquots after centrifugation at 48,000 G in heavy-duty polythene tubes. Aliquots of sample C were acidified to pH 0.8 with 2 M HCl and digested at 100 °C for 15 min. The pH of the sample was adjusted to 5.4 with sodium acetate (2 M) before analysis.

Acid treatment has been used by many investigators in obtaining an estimate of the total trace metal content of natural waters [8, 12]. The treatment here was identical to that employed previously. However, hydrochloric acid was used in preference to nitric acid since the high concentration of free nitric acid produced a marked change in the baseline of the current—potential curve thus affecting the resolution and accuracy of the copper determination.

The acid treatment was applied to the original sample and to the chelating resin effluent. Each determination (digestion and centrifugation) was repeated a minimum of 4 times. The average values and error limits are listed in Table 1.

DISCUSSION

The speciation of trace metals in sea water has recently received a great deal of attention [13, 14]. Current ideas, however, have been derived largely from compilations of stability constants applied to multi-metal multi-ligand systems. In trace metal partition and budget studies, it must be remembered that the concept of "total metal" based on data obtained from water samples filtered through a filter of 0.45-μm pore size [8], must be regarded as being as arbitrary as the choice of the pore size of the filtration medium. In such studies it may be advisable to consider the entire water sample. Particles larger than 0.45 μm participate in reactions such as adsorption-desorption, and consequently could exert a strong influence on the level and distribution

TABLE 1

Concentrations of some trace metals in sea water and in the effluent from the chelating resin columns by a.s.v.[a]
(All results are given as p.p.b.)

	Zn	Cd	Pb	Cu
Sample A[b]				
Original sea water	28.8 ± 1.2	0.57 ± 0.03	0.77 ± 0.08	1.88 ± 0.1
Chelex effluent	0.5 ± 0.1	0.05 ± 0.02	0.06 ± 0.05	0.07 ± 0.02
Sample B[c]				
1. Untreated: original	21.9 ± 0.5	0.56 ± 0.03	1.32 ± 0.06	1.28 ± 0.05
effluent	0.3 ± 0.2	0.01 ± 0.006	0.1 ± 0.08	0.05 ± 0.06
Centrifuged:				
original	21.0 ± 0.4	0.58 ± 0.04	1.40 ± 0.1	1.34 ± 0.07
effluent	0.1 ± 0.2	0.01 ± 0.006	0.2 ± 0.08	0.01 ± 0.01
2. Acid digest (pH 2.2):				
original	23.7 ± 0.5	0.65 ± 0.02	1.82 ± 0.2	1.57 ± 0.1
effluent	0.98 ± 0.3	0.01 ± 0.006	0.70 ± 0.1	0.1 ± 0.05
Centrifuged and digested:				
original	23.6 ± 0.5	0.68 ± 0.02	1.90 ± 0.2	1.61 ± 0.1
effluent	0.7 ± 0.3	0.02 ± 0.006	0.1 ± 0.1	0.02 ± 0.05
Sample C[c]				
1. Untreated: original	35.6 ± 1	0.35 ± 0.02	0.68 ± 0.08	0.41 ± 0.02
effluent	0.35 ± 0.2	0.01 ± 0.01	0.06 ± 0.05	0.01 ± 0.01
2. Acid digest (pH 0.8):				
original	36.7 ± 1	0.52 ± 0.04	1.78 ± 0.1	0.98 ± 0.1
effluent	1.04 ± 0.1	0.12 ± 0.03	0.76 ± 0.1	0.43 ± 0.05
Centrifuged and digested:				
original	35.4 ± 0.2	0.43 ± 0.04	1.53 ± 0.1	0.72 ± 0.1
effluent	0.12 ± 0.02	0.02 ± 0.005	0.35 ± 0.03	0.22 ± 0.06

[a] Longer plating times were used for the analysis of the resin effluent in order to produce measurable oxidation peaks.
[b] Direct analysis at natural pH.
[c] Measurements made at pH 5.4 (acetate buffer).

of dissolved trace metals.

Present knowledge suggests that trace metals in natural waters may exist in any or all of the following categories:

1. as inorganic complexes such as chloro-complexes, hydroxides, carbonates and hydroxychloro-complexes;
2. as complexes with dissolved organic matter such as amino acids, humic material or extracellular metabolites;
3. in organometallic compounds where the metal forms an essential part of the structure: compounds such as porphyrin and humic substances are known to contain appreciable amounts of copper and iron [15, 16];
4. adsorbed on to colloidal matter and/or occluded within colloidal species;

5. adsorbed on fine mineral material or organic detritus, or bound within planktonic material, or co-precipitated with the hydrated oxides of iron and manganese.

A large proportion of the metal in category 5 is usually removed by filtration. Metal in categories 1 and 2 can easily be observed electrochemically by their reduction at the DME. Experiments have shown that copper and zinc chelated by organic compounds such as EDTA, alanine, humic and fulvic acids [17] are reduced at the DME and, furthermore, can be plated on solid electrodes such as the graphite electrodes with mercury film. Metals in categories 3, 4 and 5 cannot be detected by such techniques and they must therefore be liberated and presented as reducible species.

The release of adsorbed metal from either colloidal hydrated oxides or mineral matter can be achieved [18] by a pH adjustment to below 3.5; the release of bound metal in the dissolved organic matter, colloidal and mineral material requires a more rigorous destructive treatment such as acid digestion.

The results (Table 1) show that when a sea-water sample was applied to the chelating resin and the a.s.v. analysis for Zn, Cd, Pb and Cu was made directly without any chemical treatment, within the analytical accuracy, all the reducible species of these metals were retained by the resin (sample A). The same observation was made when the a.s.v. analysis was carried out at pH 5.4 in acetate medium (samples B and C).

The acid treatment of the original sample and the resin effluent at pH 2.2 and 0.8 resulted in an increase in the concentration of all the metals, while that of copper was significantly large. Larger increases were obtained after the treatment at pH 0.8, particularly for lead and copper. When both the original sea water and the resin effluent were centrifuged at 48,000 G, it was found that less metal was liberated after the acid treatment at pH 2.2 and 0.8. However, similar centrifugation and analysis without acid treatment showed no change in the metal levels in either the original sample or the resin effluent. This latter observation is of particular analytical significance since it suggests that a pH adjustment of the sea water to 5.4 with acetate buffer does not significantly release any of the adsorbed or bound metals. Attempts at centrifugation to 90,000 G had to be abandoned since the only suitable containers, namely, cellulose nitrate and polycarbonates, caused serious contamination by lead and to a lesser extent copper.

Since centrifugation reduced the amount of metal liberated after the acid digestion of sea water, it seems very probable that this fraction of the metal is associated with the colloidal and fine particulate matter, and is not affected by the chelating resin. Furthermore, the data suggest that complete separation of the dissolved Cu, Pb, Cd and Zn complexes with inorganic or organic ligands can be achieved by the use of chelating resin. In other words, colloidal species of metals, metals bound with organic material or colloidal species, or metals adsorbed on colloidal species are unaffected by the chelating resin. Although this fraction of the metal is important in geochemical studies of trace metals in sea water, its availability for primary production is doubtful until it is complexed in organic or inorganic ligands. In natural environments such release of metal from organic detritus or humic substances is usually achieved by bacterial activities and oxidative processes.

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SPECTROPHOTOMETRIC DETERMINATION OF MERCURY(II) AS THE TERNARY COMPLEX WITH RHODAMINE 6G AND IODIDE

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SUMMARY

The formation of a pink-coloured product when rhodamine 6G is treated with tetraiodomercurate(II) is used to determine mercury (5—25 μg) in a final volume of 25 ml. The reaction occurs immediately over the pH range 1—7 and, when the system is stabilized with gelatin, the absorbance remains unchanged at 575 nm for at least 24 h. The few interfering ions can be masked by the addition of appropriate reagent solutions. The method is simple and reliable and provides a molar absorptivity of $7.0 \cdot 10^4$ l $\mathrm{mole^{-1}}$ $\mathrm{cm^{-1}}$.

The determination of traces of mercury has attracted considerable attention owing to the toxicity of mercury and its compounds, and many colorimetric methods have been proposed [1]. Methods based on ternary complex formation seem to provide the best alternative choice to the conventional method based on extraction with dithizone [2], as they are associated with superior sensitivity and selectivity, in addition to high stability and reproducibility. Amongst the ternary systems proposed, the method of Lebedeva [3] involving the reaction of tetrabromomercurate(II) with methylene green is most sensitive ($\epsilon_{640\ \mathrm{nm}} = 1.06 \cdot 10^5$ l $\mathrm{mole^{-1}}$ $\mathrm{cm^{-1}}$) and selective since only gold(III), tellurium(III), antimony(V), lead(II) and cadmium(II) are reported to interfere. However, like most other ternary systems proposed for mercury, the method involves a selective extraction step because the species formed absorb at the same wavelength as the dye. Hence there appeared to be a need for a rapid precise method with minimum manipulation, suitable for routine determination of traces of mercury.

The survey of the various ternary systems proposed for mercury(II) suggested that the use of tetraiodomercurate(II) as the primary complex instead of tetrabromomercurate(II), would improve the selectivity of the method, as it would extend the number of masking agents available to prevent any interferences. A detailed examination of the reaction of several cationic dyestuffs with mercury(II) in the presence of potassium iodide showed that in weakly acidic solutions, rhodamine 6G offered the best possibilities. The colour reaction with tetraiodomercurate(II) was distinctive, as the species formed was pink in contrast to the red colour of the reagent solution under identical conditions. This indicated that the absorbances could be measured in the aqueous phase itself without any need for extraction. The nature of the reaction and the development of an analytical procedure were therefore examined in detail.

EXPERIMENTAL

Apparatus and reagents

A Carl-Zeiss PMQ-II spectrophotometer with 10-mm quartz cells, and a Knick pH meter with an Ingold combined glass—calomel electrode were used.

Mercury(II) solution (1 mg ml^{-1}). Dissolve 0.3385 g of mercury(II) chloride in water and dilute to 250 ml. Dilute appropriate volumes of this stock solution with water to provide a 5-p.p.m. solution of mercury, as required.

Buffered potassium iodide solution. Dissolve 5 g of potassium iodide and 5 g of potassium hydrogen phthalate in water, add a few crystals of sodium thiosulphate and dilute to 250 ml with water.

Rhodamine 6G solution (0.005 %). Dissolve 0.05 g of the reagent (Chroma Gesellschaft, Schmid & Co., Stuttgart) in water and dilute to 1 l.

Procedure

Transfer a suitable aliquot (up to 10 ml) of the sample solution containing not more than 25 μg of mercury to a 25-ml volumetric flask. Add with mixing 5 ml of the buffered potassium iodide and 5 ml of the rhodamine 6G solution followed by 1 ml of 1 % (w/v) gelatin solution prepared in the usual way. Dilute the solution to the mark with distilled water, and measure the absorbance in 10-mm cells at 575 nm against a reagent blank. Prepare a calibration curve for 5—25 μg of mercury by the above procedure.

RESULTS AND DISCUSSION

Preliminary studies indicated that the reaction proceeded immediately when iodide was added to mercury(II) solution before the addition of rhodamine 6G. The major difficulty was the gradual precipitation of the complex on standing, which made absorbance measurements difficult. The complex was colloidal in nature and stabilization was achieved by addition of the protective colloid gelatin, which successfully retarded precipitation of the complex even on leaving overnight. As a matter of routine, gelatin was therefore added after the other reagents for stabilization purposes.

Figure 1 shows the absorption spectra of rhodamine 6G with different molar proportions of mercury in the presence of excess of potassium iodide solution at pH 4. It is evident that the interaction between tetraiodomercurate-(II) and rhodamine 6G proceeds with a considerable bathochromic shift and

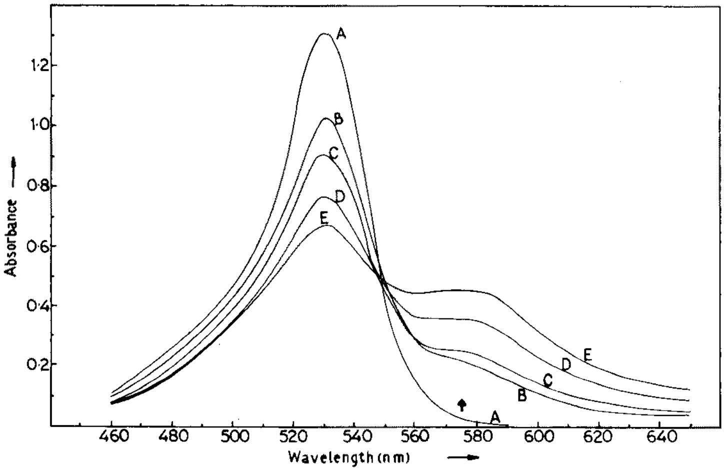

Fig. 1. Absorption spectra. (Total volume 25 ml, 4-cm cells) (A): 1 ml of $1 \cdot 10^{-4}$ M rhodamine 6G and 5 ml of buffered potassium iodide solution with gelatin. (B—E): As in (A) with the addition of 0.33 ml (B), 0.50 ml (C), 1.0 ml (D) and 2.0 ml (E) of $1 \cdot 10^{-4}$ M mercury solution.

that the complex shows maximal absorption at 575 nm, as against that of the reagent at 530 nm.

Effect of experimental variables

The optimal pH was examined with a universal buffer solution over the pH range 1—10. Measurements of the absorbances of the complex and the reagent blank showed that the colour system is independent of pH over the range 1—7. Below pH 1, iodine was liberated. Although the reaction proceeds over a wide pH range, the pH of the sample and the blank should not be widely different, as the blank absorbance varied slightly with change in pH. The pH was maintained at 4.0 in all subsequent investigations.

To avoid the use of the complex universal buffer solution with its possible subsequent interferences, simple buffers for pH 4.0 were tested. Either potassium hydrogenphthalate or acetate buffer could be used without affecting the colour system; the buffer concentration was not important. All subsequent investigations were done with the hydrogenphthalate buffer, which was incorporated into the iodide solution for convenience.

Two series of experiments were carried out to investigate the influence of the concentrations of the reagents on the development of the colour. In one, varying amounts of a 2 % solution of potassium iodide were added to a mixture of 4 ml of 5 p.p.m. mercury solution and 5 ml of 0.005 % rhodamine 6G solution. The optimum amount was 5 ml, but a large excess of iodide scarcely affected the sensitivity. In the second series, varying amounts of rhodamine 6G were added with 5 ml of 2 % potassium iodide solution. The colour development reached a maximum at 4 ml and then remained constant as the amount of rhodamine 6G was increased up to 10 ml.

The order of addition of the reagent solutions was not critical provided that gelatin was added after the other reagents. Prior addition of gelatin caused decreased absorbance.

Beer's law and precision

Beer's law was obeyed over the range 5—25 μg of mercury in a final volume of 25 ml. Under the conditions described, the molar absorptivity is $7.0 \cdot 10^4$ l mole^{-1} cm^{-1} for mercury.

A series of ten standard solutions containing 10 μg of mercury was analyzed; the standard deviation was 0.05 %.

Nature of the complex

With the large excess of iodide used, mercury(II) forms tetraiodomercurate(II) rather than triiodomercurate(II) (log $K_4 = 2.2$); HgI_4^{2-} then reacts with rhodamine 6G to form a neutral ternary complex which could be extracted into apolar solvents. The ratio of mercury to rhodamine 6G in the complex in the presence of excess of iodide was established by the conventional continuous variations and mole ratio methods. The evidence shown by Fig. 2 (a, c) is indentical with the expected ratio of two molecules of rhodamine 6G for each ion of mercury; thus the complex formed has the empirical composition R_2HgI_4 (where R^+ represents the rhodamine 6G cation). The ratio of mercury to iodide in the ternary complex was investigated in the presence of excess of rhodamine 6G. The plots (Fig. 2b, d) show evidence for the formation of the tri-iodomercurate(II) anion; the definite 3:1 ratio of iodide to mercury suggests that the empirical composition of the complex formed under these conditions is $RHgI_3$. This was confirmed by a slope ratio plot for the mole ratio of triiodomercury(II) (formed by mixing stoichiometric amounts of mercury(II) and iodide) to rhodamine 6G.

On the basis of all these results, it was concluded that the ternary complex formed at low concentrations of iodide has the empirical composition $RHgI_3$ and that it is very weak in nature (see Fig. 2d, e). The more stable species with Hg:4I:2R stoichiometry exists only at higher concentration of iodide (1000-fold excess over mercury). In any case, the $RHgI_3$ and R_2HgI_4 species had identical spectral characteristics.

There is a significant shift in the wavelength of maximum absorption on complex formation (Fig. 1). Such shifts in similar ternary systems featuring bulky organic dyestuffs have been attributed by Babko and Pilipenko [4] to weak bonding between the amine nitrogen atom of the dye and the metal ion. However, in the present complex, mercury(II) in tetraiodomercurate(II) anion is already coordinately saturated, so that R_2HgI_4 should probably be considered as an ion-pair.

Interference studies

The effect of various cations and anions on the determination of mercury was examined. In these tests, 10 μg of mercury and 1 mg of the foreign ion were used. The ions examined are listed in Table 1.

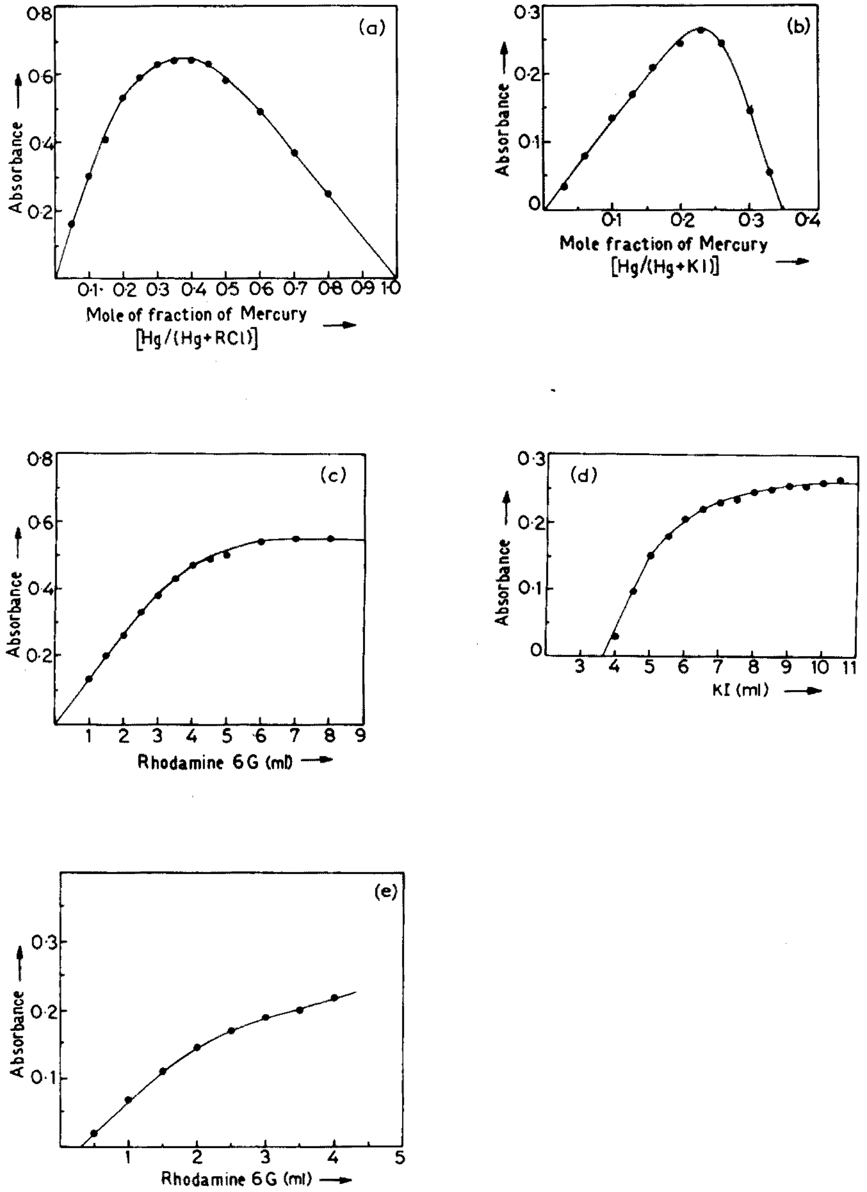

Fig. 2. Composition studies. (Total volume 25 ml; 1-cm cells at 575 nm.) (a, b) Continuous variation plots. (a) Total concentration of mercury and rhodamine 6G = 10 ml of 10^{-4} M solution. Buffered potassium iodide (5 ml) and gelatin (1 ml) added. (b) Total concentration of mercury and iodide = 10 ml of 10^{-4} M solution. Rhodamine 6G (10 ml of 10^{-4} M) and gelatin (1 ml) added. (c, d, e) Mole ratio plots. (c) 2 ml of 10^{-4} M mercury + x ml of 10^{-4} M rhodamine 6G + 5 ml of buffered iodide + gelatin (1 ml). (d) 2 ml of 10^{-4} M mercury + x ml of 10^{-4} iodide + 10 ml of 10^{-4} M rhodamine 6G in 0.05 M hydrogenphthalate + gelatin (1 ml). (e) 2 ml of 10^{-4} M mercury + 10 ml of 10^{-4} M iodide in 0.05 M hydrogenphthalate + x ml of 10^{-4} M rhodamine 6G + gelatin (1 ml). Ionic strength 0.2.

TABLE 1

Interference studies

Group	
I	Li^+, Cu^{2+}, Ag^+
II	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}
III	$B_4O_7^{2-}$, BO_3^{2-}, Al^{3+}, Ce^{3+}, Tl^{3+}, Tl^+, La^{3+}, Th^{4+}
IV	Sn^{2+}, Sn^{4+}, Pb^{2+}
V	NH_4^+, Sb^{3+}, Bi^{3+}, AsO_2^-, AsO_4^-, VO_3^-, PO_4^{3-}, NO_2^-, NO_3^-
VI	Cr^{3+}, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, SeO_3^{2-}, TeO_3^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-}
VII	Mn^{2+}, F^-, Cl^-, Br^-, ClO_4^-, IO_3^-
VIII	Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{4+}

Miscellaneous: Thiocyanate, citrate, oxalate

Under the conditions established, the interference encountered included (a) those that oxidized iodide to iodine: Cu^{2+}, $Cr_2O_7^{2-}$, Fe^{3+} and IO_3^-; (b) those which reduced mercury(II) to lower oxidation states: Sn^{2+} and AsO_2^-; (c) those that precipitated out as their iodides or hydrous oxides: Ag^+, Pb^{2+}, Bi^{2+}, Tl^+ and Cu^{2+}; and (d) those that formed coloured species similar to that formed by mercury(II): Pd^{2+}, Pt^{4+} and Cd^{2+}.

The deleterious effects of Cu^{2+}, Pb^{2+}, Bi^{3+}, Cd^{2+} and Fe^{3+} were overcome by the addition of 2 ml of 0.05 M EDTA solution. The addition of hydrazine sulphate reduced the higher oxidation state of chromium so that it no longer interfered; interferences of Sn^{2+} and AsO_2^- were prevented by oxidation with bromine water. Sulphite addition overcame the interference of Pt^{4+}, and the addition of ammonia similarly eliminated the effect of Pd^{2+}. The interference of silver(I) could not be removed by the addition of cyanide, which would mask mercury itself; the interference of silver was due to its precipitation as iodide, and could be avoided by centrifuging the precipitate before the addition of rhodamine 6G. Thus the relatively few interferences that were encountered were easily eliminated by properly conditioning the solution and under these conditions the sensitivity of the procedure remained unaffected.

Conclusion

The reaction between rhodamine 6G and tetraiodomercurate(II) provides a reliable means of determining traces of mercury. The method, although less sensitive ($\epsilon_{575\,\text{nm}} = 7.0 \cdot 10^4$ l mole^{-1} cm^{-1}) than that based on the reaction between tetrabromomercurate(II) and methylene green ($\epsilon_{640\,\text{nm}} = 1.06 \cdot 10^5$ l mole^{-1} cm^{-1}), compares favourably with the standard method based on dithizone ($\epsilon_{490\,\text{nm}} = 3.2 \cdot 10^4$ l mole^{-1} cm^{-1}). Also, the absorptiometric finish does not involve an extractive separation, so that the proposed method is simple and rapid. The method has also the advantage of virtual freedom from interferences of many extraneous ions and therefore should be of value in trace analysis for mercury in biological and pharmaceutical samples, plant materials and industrial effluents.

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A HIGHLY SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH CHROMAL BLUE G AND CETYLTRIMETHYLAMMONIUM CHLORIDE

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SUMMARY

A new spectrophotometric method for the determination of palladium with chromal blue G (Color Index 43835) and cetyltrimethylammonium chloride is described. The sensitivity of the color reaction between palladium and chromal blue G is greatly increased in the presence of cetyltrimethylammonium chloride. The palladium complex has maximal absorbance at pH 3.2—3.8 and at 670 nm. Beer's law is obeyed over the range 0.08—1.4 p.p.m. palladium; the molar absorptivity is $1.01 \cdot 10^5$ l mol^{-1} cm^{-1} at 670 nm and the sensitivity is $1 \cdot 10^{-3}$ μg Pd cm^{-2}. The mole ratio of palladium and chromal blue G in the complex in the presence of cetyltrimethylammonium chloride is 1:3. Only scandium interferes when sodium fluoride is used as masking agent.

The most widely used methods for the spectrophotometric determination of palladium are based on reactions with *p*-nitrosoaniline derivatives [1, 2] including *p*-nitrosodimethylaniline and *p*-nitrosodiphenylamine. More recently, procedures based on the palladium complexes with 2-mercaptobenzoic acid [3], naphthalene-1,8-dithiol [4], and 1,4-diphenylthiosemicarbazide [5] have been suggested. Some spectrophotometric methods for metals based on complex formation on the micelle surface formed in the presence of a quaternary ammonium salt have also recently been suggested [6—8]. Chromal blue G (sodium-2″-chloro-4″-nitro-4′-hydroxy-3,3′dimethylfuchsone-5,5′-dicarboxylate; color index 43835), a triphenylmethane dye, has been used as a spectrophotometric reagent for scandium [9] and beryllium [10].

It has been found that microgram amounts of palladium react very sensitively with chromal blue G in the presence of a quaternary ammonium salt. This paper describes a method for the determination of palladium based on the formation of a colored complex of palladium with chromal blue G in the presence of cetyltrimethylammonium chloride. Several conditions under which microgram amounts of palladium can be determined, the influence of diverse ions and the composition of the complex are discussed.

EXPERIMENTAL

Apparatus

Absorbances were measured with a Shimadzu spectrophotometer (QR-50 type) and a Hitachi automatic recording digital spectrophotometer (624 type) in 1.00-cm matched quartz cells. A Toa electrode pH meter (model HM-6A) was also used.

Reagents

Standard palladium solution. Prepare a stock solution of palladium by dissolving palladium chloride in distilled water, and then adding small amounts of hydrochloric acid; standardize gravimetrically by the dimethylglyoxime method [11]. Prepare working solutions (10 μg Pd ml^{-1}) by appropriate dilution.

Chromal blue G solution. Purify chromal blue G (Geigy Co. Inc., New York) by recrystallization from ethanol; prepare a 0.1 % (w/v) solution in 95 % ethanol.

Cetyltrimethylammonium chloride solution (CTMA). Prepare an aqueous 0.5 % (w/v) solution of CTMA (Tokyo Kasei Kogyo Co.).

Buffer solution (pH 3.5). Mix 0.2 M sodium acetate solution and 0.2 M acetic acid.

All other chemicals used were analytical-reagent grade.

Standard procedure

Transfer the sample solution containing 2—35 μg of palladium to a 25-ml volumetric flask, and add 2 ml of chromal blue G solution, 5 ml of acetate buffer, and then 1 ml of CTMA solution. If the pH of the resulting solution is not between 3.2 and 3.8, it should be preneutralized with hydrochloric acid or sodium hydroxide solution. After diluting to the mark with distilled water, mix, leave for color development for 10 min, and measure the absorbance at 670 nm against a reagent reference solution.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of chromal blue G have been presented previously [9]; the maximal absorption is at 480 nm below pH 4.0, at 430 nm over the pH range 5.5—10.0, and at 590 nm above pH 10.5. The absorption spectra of chromal blue G at various pH values in the presence of CTMA are shown in Fig. 1; maximal absorption of chromal blue G in the presence of CTMA occurs at 510 nm below pH 3.0, at 430 nm over the pH range 3.5—10.0 and at 640 nm above pH 10.5.

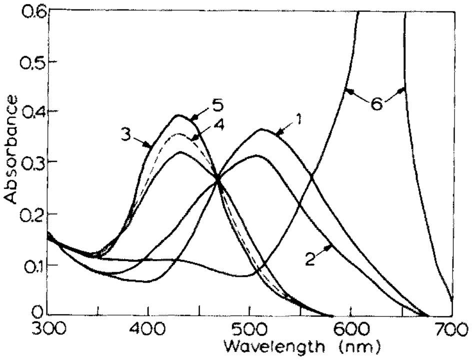
Figure 2 shows the absorption spectra of chromal blue G and its palladium complex at pH 5.4, and the effect of CTMA on the absorbances at pH 3.5. The presence of CTMA in the palladium complex produces a pronounced bathochromic shift (635 nm to 670 nm) and increases greatly the absorbance of the complex. The spectral changes on varying the pH in the presence of CTMA are shown in Fig. 3. Below pH 8.5, maximal absorbance of the complex occurs between 660 and 680 nm; above pH 6.5, two absorbance maxima occur, one at about 670 nm and one at 550 nm.

Effect of experimental variables

The effect of pH on the color development was examined by measuring, at 670 nm, the absorbance of the palladium complex over the pH range 2.8—8.0. The absorbance increases sharply up to pH 3.2, remains constant in the pH range 3.2—3.8 and then decreases gradually up to pH 8.0. A pH of 3.5 was, therefore, maintained in subsequent work. A 0.2 M acetate buffer solution (pH 3.5) was satisfactory. The amount of buffer solution added had no effect on the absorbance measured by the standard procedure over the range 3—10 ml.

The effect of changes in the concentration of chromal blue G on the absorbance of palladium complex at pH 3.5 was determined. In the presence of CTMA, the absorbance of the complex formed from 0.6 p.p.m. palladium is almost constant when more than 1.5 ml of a 0.1 % chromal blue G solution is added; in the absence of CTMA, the absorbance is increased by an increase in the concentration of chromal blue G. In the presence of CTMA, 2 ml of the dye solution in 25 ml of the solution is sufficient for less than 35 μg of palladium. This concentration represents a 12.9-fold molar excess of chromal blue G over 35 μg of palladium.

The effect of variable amounts of CTMA on the color development was examined by measuring the absorbance, at 670 nm, of solutions containing



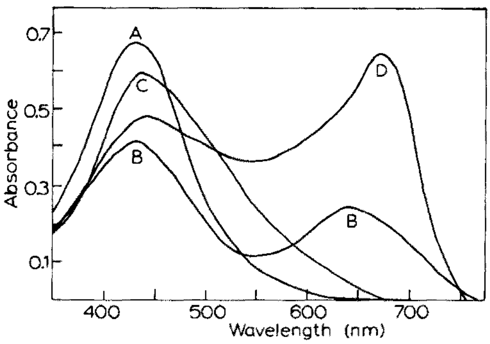


Fig. 1. Absorption spectra of chromal blue G in the presence of CTMA. Chromal blue G, 20 p.p.m.; CTMA, 200 p.p.m. pH: (1) 2.0, (2) 3.0, (3) 4.0, (4) 5.0, (5) 6.0—6.5, (6) 12.

Fig. 2. Absorption spectra of chromal blue G (40 p.p.m.) and its palladium complex. (A) Blank of B; (B) 0.8 p.p.m. Pd, pH 5.4; (C) blank of D; (D) 0.8 p.p.m. Pd, 200 p.p.m. CTMA, pH 3.5.

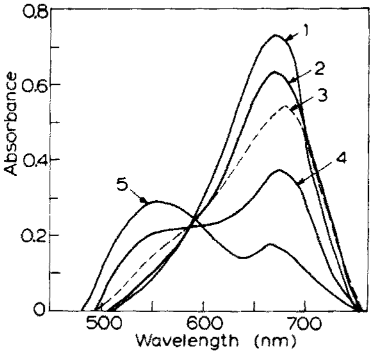


Fig. 3. Absorption spectra of palladium complex at various pH. Chromal blue G, 80 p.p.m.; Pd, 0.8 p.p.m.; CTMA, 200 p.p.m. pH: (1) 3.5, (2) 4.5, (3) 5.5, (4) 6.5, (5) 8.0. Reference: reagent blank.

constant concentrations of palladium and chromal blue G. The absorbance is gradually decreased by an increase in CTMA concentration in the range 150—300 p.p.m. CTMA, but shows a rapid decrease with more than 300 p.p.m. CTMA. Hence it is necessary to keep the CTMA concentration constant.

The color of the palladium complex develops almost instantaneously, and its intensity is stable for at least 2 h; only a 2 % decrease in absorbance occurs after 2 h when measured against a reagent blank. The absorbance for a given amount for palladium is independent of temperature in the range 10—30 °C.

Calibration curve, sensitivity and precision

Calibration curves were prepared by the standard procedure. Beer's law is obeyed over the range 0.08—1.4 p.p.m. palladium. The molar absorptivity (ϵ) is $1.01 \cdot 10^5$ l mol^{-1} cm^{-1} at 670 nm, and the Sandell sensitivity of the reaction is $1 \cdot 10^{-3}$ μg Pd cm^{-2}. The proposed method is very sensitive. Its sensitivity is much greater than that of the methods based on 2,2′-dipyridylketoxime (ϵ = 12,000) [12], 2,1,3,-benzoselenadiazole (ϵ = 19,000) [13], xylenol orange (ϵ = 26,000) [14], chromeazurol S (ϵ = 18,600) [15], and pontachrome azure blue B (ϵ = 47,900) [16]; and is slightly higher than that achieved with eriochrome cyanine R and tetradodecyldimethylbenzylammonium chloride (ϵ = 99,000) [8].

A standard solution containing 15 μg of palladium was analyzed 10 times by the standard procedure; the average absorbance was 0.575, with a standard deviation of 0.002 absorbance unit and a relative error of ±0.7 %.

Effect of diverse ions

Beryllium, aluminum, scandium, copper(II), iron(III), nickel, yttrium, and rare earth elements also form colored complexes with chromal blue G in weakly acidic solutions [9, 10]. These ions were therefore included in a study of possible interference with the determination of palladium. Some common ions, including these cations, were added individually to a solution containing 15.0 μg of palladium, and their effects were examined under the conditions of the standard procedure. The results (Table 1) show that some diverse ions, especially beryllium, iron(III), aluminum, scandium, and thorium(IV), interfere seriously. Copper(II), nickel, yttrium, and rare earth elements do not form colors in acetate-buffered solutions of pH 3.5. Chloride, acetate, nitrate, fluoride, sulfate, and phosphate are without effect even in large amounts. Fluoride effectively masks the more seriously offending ions, beryllium, aluminum, iron(III), and thorium(IV) (Table 2). Scandium (more than 20 μg) causes low results, but can be effectively masked by phosphate without further separation.

Complex formation

The method of continuous variations was employed to establish the palladium—chromal blue G ratio in the presence of CTMA. The constant concentration of CTMA was $6.08 \cdot 10^{-4}$ M, and measurements were made at pH 3.5 and 670 nm. The results indicated that a 1:3 complex between palladium and chromal blue G is formed in the presence of CTMA, and a 1:2 complex in the absence of CTMA, These results were confirmed by the mole ratio method.

It is expected that this method will find many applications where a highly sensitive reaction for palladium is desired.

TABLE 1

Effect of diverse ions on the determination of palladium (palladium taken: 15.0 μg)

Ion	Added (μg)	Pd found (μg)	Ion	Added (μg)	Pd found (μg)
Be(II)	15	30.9	Gd(III)	100	14.8
Ca(II)	150	15.1	Dy(III)	100	14.7
Mg(II)	150	15.2	Ru(III)	150	14.9
Cu(II)	150	15.0	Rh(III)	150	15.0
Pb(II)	150	14.9	Os(III)	150	15.1
Cd(II)	150	14.8	Au(III)	150	14.9
Ni(II)	150	15.0	Pt(IV)	150	14.7
Co(II)	150	14.7	Th(IV)	15	19.7
Mn(II)	150	14.9	Mo(VI)	150	15.0
Zn(II)	150	15.0	Cl^-	1000	14.9
Fe(III)	15	31.3	Ac^-	1000	15.2
Al(III)	10	49.1	NO_3^-	1000	15.2
Sc(III)	15	28.9	F^-	5000	15.0
Y(III)	100	14.8	SO_4^{2-}	1000	14.8
La(III)	100	14.7	PO_4^{3-}	5000	15.1
Nd(III)	100	14.9			

TABLE 2

Effect of fluoride as a masking agent (palladium taken, 15.0 μg; fluoride added, 5 ml of 0.1 M NaF solution)

Ion	Added (μg)	Pd found (μg)	Error (%)
Be(II)	50	15.0	0
	150	14.7	−2.0
Al(III)	50	15.1	+0.7
	150	14.6	−2.3
Fe(III)	50	15.0	0
	150	15.1	+0.7
Sc(III)	15	14.8	−1.3
	50	9.3	−38.0
	50[a]	14.7	−2.0
	100[a]	14.6	−2.3
Th(IV)	50	15.0	0
	150	14.6	−2.3

[a] Addition of 5 ml of 0.1 M Na_3PO_4 solution.

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ÉTUDE THERMODYNAMIQUE DE LA COMPLEXATION DES LANTHANIDES TRIVALENTS AVEC L'ACIDE HYDROXYÉTHYLÉTHYLÈNEDIAMINOTRIACÉTIQUE ET D'AUTRES ACIDES AMINOACÉTIQUES

I. DÉTERMINATION, PAR POTENTIOMÉTRIE, DES CONSTANTES D'ACIDITÉ DE CERTAINS ACIDES AMINOPOLYACÉTIQUES

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RÉSUMÉ

Les auteurs ont déterminé, par potentiométrie, à 25 °C et en milieu de force ionique égale à 1 (KCl) les pK d'une série d'acides polyaminopolyacétiques, à savoir la glycine (2.48, 9.67), l'acide iminodiacétique (1.84, 2.57, 9.27), l'acide nitrilotriacétique (1.03, 1.75, 2.31, 9.34), l'acide éthylènediaminotétraacétique (1.50, 1.95, 2.45, 6.21, 9.79), ainsi que les complexes Ln—EDTA—H (La, 3.1; Nd, 2.14; Sm, 2.03; Eu, 1.89; Gd, 1.82; Dy, 1.44; Ho, 1.35; Er, 1.27; Tm, 1.19; Yb, 1.17; Lu, 1.15).

SUMMARY

Several polyaminoacetic acids have been studied by potentiometry at an ionic strength 1 (KCl) and 25 °C, in order to determine their acidity constants. The pK values found are: 2.48, 9.67 (glycine); 1.84, 2.57, 9.27 (iminodiacetic acid); 1.03, 1.75, 2.31, 9.34 (nitrilotriacetic acid); 1.50, 1.95, 2.45, 6.21, 9.79 (ethylenediaminetetraacetic acid). The pK values of the lanthanide complexes Ln—EDTA—H are: 3.1, 2.14, 2.03, 1.89, 1.82, 1.44, 1.35, 1.27, 1.19, 1.17, 1.15 (Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu).

Dans une publication précédente [1], nous avons décrit en détail la mise au point et les performances d'un appareil de titrage automatique dont la précision, la reproductibilité et l'exactitude sont telles qu'il est possible de mesurer, en tout point d'une courbe de titrage, la valeur du pH avec une erreur inférieure au millième d'unité. Cet appareil est destiné principalement à la détermination des constantes d'acidité des complexes doubles ou mixtes formés entre les lanthanides et certains acides aminopolyacétiques.

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Dans le cadre de ce travail, nous avons été amenés à déterminer les constantes d'acidité des acides chélatants utilisés à 25 °C et en milieu de force ionique égale à 1 (KCl); il s'agit des acides aminoacétique ou glycine (GLY), iminodiacétique (IMDA = X), nitrilotriacétique (NTA = Z), éthylènediaminotétraacétique (EDTA = Y') ainsi que des acides LnY'H formés par complexation des lanthanides trivalents par l'EDTA. L'acide hydroxyéthyléthylènediaminotriacétique (HEDTA = Y) a également été étudié. La détermination de ses constantes d'acidité, ainsi que l'interprétation de certaines particularités de sa courbe de titrage feront l'objet d'une publication ultérieure.

Nous comparons, dans cet article, les valeurs des constantes que nous obtenons avec les données de la littérature.

PARTIE EXPERIMENTALE

Réactifs

IMDA. Le sel disodique de l'acide iminodiacétique (Aldrich) est neutralisé par l'acide chlorhydrique bidistillé. L'acide précipite lorsque la solution, par évaporation, atteint une concentration de 2 mol l^{-1} environ. L'acide est ensuite purifié par cinq cristallisations successives dans l'eau tridistillée en appareil de quartz.

NTA, EDTA, Glycine. Le NTA (Fluka), l'EDTA (Titriplex II, Merck) et la glycine (Riedel de Haen A.G.) sont utilisés sans purification préalable.

Les différents acides sont séchés sous vide à 40 °C pendant 24 h; leur pureté est ensuite contrôlée par titrages acide—base et complexométrique [2]. La glycine possédant un p*K* trop élevé, est titrée en milieu acide acétique glacial, le réactif titrant étant l'acide perchlorique préalablement étalonné, dans le même milieu, au biphtalate de potassium (P.A. Merck). Le terme est détecté visuellement au moyen du violet de cristal.

La pureté de tous les acides est supérieure à 99.8 %. Bien que certains soient réputés hygroscopiques, nous n'avons remarqué aucune augmentation de poids suite à une exposition à l'air pendant plus de 12 h; néanmoins, tous les acides sont conservés en récipients hermétiquement clos.

Ln_2O_3. Les oxydes de lanthanides (Fluka) de pureté supérieure à 99.9 % sont décarbonatés par calcination à 1100 °C pendant 1 à 2 h avant usage.

KCl. Le chlorure de potassium (P.A. Merck) est déshydraté par chauffage prolongé (24 h) à 350 °C.

Préparation des solutions

Les solutions d'acides aminopolyacétiques 0.01000 *M*, à force ionique 1 (KCl), sont préparées par pesée exacte des réactifs solides et transvasement ultérieur, au moyen d'eau tridistillée sur quartz et décarbonatée, dans des ballons jaugés étalonnés.

Les solutions de complexes LnY'H 0.01000 *M*, en milieu de force ionique égale à 1 (KCl), sont obtenues par réaction, à 100 °C, de quantités stoechiométriques d'EDTA et d'oxyde de lanthanide

$$Ln_2O_3 + 2H_4Y' \rightleftarrows 2LnY'H + 3H_2O$$

La préparation de KOH décarbonaté ne peut de faire par précipitation du carbonate en solution alcaline concentrée; la solution titrante de KOH est obtenue par passage d'une solution de KCl sur une colonne de résine anionique Dowex 1-X4, 100/200 mesh préalablement conditionnée sous forme OH^- par de la soude exempte de carbonate. L'éluat est recueilli, à l'abri de CO_2 atmosphérique, dans un ballon jaugé étalonné d'un litre. La colonne est rincée par 10 fois son volume libre d'eau décarbonatée et la quantité de KCl nécessaire pour ajuster la force ionique est ajoutée dans le ballon jaugé; le passage de 100 ml d'une solution de KCl *M* permet ainsi d'obtenir 1 l de solution de potasse 0.1 *M*.

Conditions du titrage

Les conditions expérimentales relatives aux titrages sont identiques pour tous les acides envisagés; le fonctionnement de l'appareil ayant été décrit précédemment [1], nous nous bornerons à rappeler brièvement ces conditions dans le Tableau 1.

TABLEAU 1

Titrage des acides aminoacétiques. Conditions expérimentales

Electrode indicatrice	H_2 sur électrode Pt/noir de Pt
Electrode de référence	Ag/AgCl (E° = 0.22230 V)
Cellule de référence	KCl 1 *m* ($\gamma^{\pm}_{HCl}$ = 0.720)
Pont de jonction	KCl 1 *m*
p_{H_2},	760 mm/Hg
Débit H_2	100 ml min^{-1}
Température	(25.00 ± 0.01) °C
Solution à titrer	100.08 ml de solution 0.01000 *M* en acide aminopolyacétique[a]
Solution titrante	0.0987 *M* en KOH μ = 1 (KCl)
Volume d'une injection	0.1007 ml
Durée des titrages	environ 6 h par proton titré

[a] Dans le cas de la glycine, on ajoute dans la cellule de titrage 10.05 ml de HCl 0.1000 *M* afin d'être en mesure de déterminer le p*K* de la forme H_2G^+. Dans le cas de l'EDTA, les solutions sont 0.00500 *M* pour des raisons de solubilité.

PRINCIPE DE LA METHODE

La méthode a été décrite dans une publication précédente [3]; rappelons simplement que la courbe de titrage, par une base, d'un acide aminopolyacétique peut s'exprimer mathématiquement de la façon suivante [3, 4]

$$v = \left(n - \frac{[\mathrm{H}^+] - [\mathrm{OH}^-]}{f\, C_{\mathrm{H}_n\mathrm{Y}}} - \frac{\sum_1^N \beta_{\mathrm{H}_n}\ [\mathrm{H}^+]^n}{1 + \sum_1^N \beta_{\mathrm{H}_n}\ [\mathrm{H}^+]^n} \right) \frac{v_{\mathrm{O}} C_{\mathrm{H}_n\mathrm{Y}}}{C_{\mathrm{OH}}} \tag{1}$$

n = nombre de groupements carboxyliques de l'acide considéré
v = volume de titrant ajouté (ml)
v_0 = volume initial de la solution à titrer (ml)
$f = v_0/(v_0 + v)$ = facteur de dilution

$$\beta_{\mathrm{H}_n} = \frac{[\mathrm{H}_n\mathrm{Y}]}{[\mathrm{Y}^{n-}]\ [\mathrm{H}^+]^n} = \frac{1}{K_{\mathrm{H}_1} K_{\mathrm{H}_2} \cdots K_{\mathrm{H}_n}} \quad \text{constantes globales de formation } (\mathrm{l\ mol}^{-1})^n$$

$K_{\mathrm{H}_1}, K_{\mathrm{H}_2}, \cdots K_{\mathrm{H}_n}$ = constantes d'acidité de l'acide envisagé (mol l^{-1})
$C_{\mathrm{H}_n\mathrm{Y}}$= concentration totale de l'acide dans le volume v_0 (mol l^{-1})
C_{OH} = concentration de la base titrante (mol l^{-1})
$[\mathrm{H}^+]$, $[\mathrm{OH}^-]$ = concentration en protons et en ions hydroxyles (mol l^{-1}).

Les différents termes de la formule (1) sont exprimés en molarité, alors que la différence de potentiel mesurée entre l'électrode de référence (Ag/AgCl) et l'électrode indicatrice (Pt/H_2) est liée à la molalité en ions H^+ par la relation:

$$\Delta E = E^\circ_{\mathrm{Ag/AgCl}} - \frac{RT}{F} \ln m_{\mathrm{H}^+}\, m_{\mathrm{Cl}^-} - \frac{RT}{F} \ln (\gamma_{\mathrm{HCl}}^{\pm})^2 + E_{\mathrm{J}} \tag{2}$$

$m_{\mathrm{H}^+}, m_{\mathrm{Cl}^-}$ = molalité en protons et en ions chlorures
$\gamma^{\pm}_{\mathrm{HCl}} = (\gamma_{\mathrm{H}^+}\ \gamma_{\mathrm{Cl}^-})$ = coefficient d'activité molal moyen de HCl
E_{J} = potentiel de jonction (V)

Le calcul de la molalité en protons nécessite la connaisance du $\gamma^{\pm}_{\mathrm{HCl}}$ dans nos conditions expérimentales, ainsi que la valeur du potentiel de jonction en chaque point de la courbe de titrage.

A 25 °C et en milieu de force ionique molale (KCl), la valeur de $\gamma^{\pm}_{\mathrm{HCl}}$ proposée par Harned et Hamer [5] est de 0.720.

Afin de vérifier une nouvelle fois l'exactitude des résultats fournis par notre dispositif expérimental, nous avons déterminé la valeur de $\gamma^{\pm}_{\mathrm{HCl}}$ en mesurant la force électromotrice de la pile

$$\mathrm{Pt};\ \mathrm{H}_2(\mathrm{g})\ \begin{matrix}\mathrm{HCl}\ x\,m \\ \mathrm{KCl}\ (1-x)m\end{matrix} \Big|\ \mathrm{KCl}\ m,\ \mathrm{AgCl};\ \mathrm{Ag}$$

en fonction de la molalité en HCl (x). La valeur du potentiel de jonction est calculée par la formule de Henderson avec: Λ_{HCl} (25 °C, $\mu = 1$) = 332.3 [6], et Λ_{KCl} (25 °C, extrapolée à $\mu = 1$) = 82.3 [5], $\Lambda(\mathrm{cm}^2 . \Omega^{-1})$ étant les conductivités équivalentes de HCl et KCl. Les résultats sont repris dans le Tableau 2.

Des expériences similaires ont été menées en milieu basique; l'activité en ions OH^- est liée à l'activité en ions H^+ par la relation $a_{H^+} \cdot a_{OH^-} = K_W$ (3). A 25 °C et en milieu de force ionique molale (KCl), $K_W = 1.008 \cdot 10^{-14}$ [5]. Exprimée en molalité, la relation (3) devient

$$m_{H^+} \cdot m_{OH^-} = \frac{K_W a_{H_2O}}{\gamma_{H^+} \gamma_{OH^-}} \tag{4}$$

A 25 °C et en milieu de force ionique égale à 1 (KCl), le terme $a_{H_2O}/\gamma_{H^+} \gamma_{OH^-}$ vaut 1.689; on obtient ainsi

$$m_{H^+} \cdot m_{OH^-} = 1.703 \cdot 10^{-14} \tag{5}$$

Par la mesure de la f.e.m. d'une pile semblable à celle décrite précédemment, dans laquelle nous générons des ions hydroxyles par coulométrie, on peut, grâce aux relations (2) et (5), déterminer la molalité en ions OH^-. Elle est comparée à la molalité théorique dans le Tableau 3. Etant donné que, d'une part, la zone de pH explorée ne dépasse pas 12 et que, d'autre part, la mobilité des ions OH^- est nettement inférieure à celle des protons, aucune correction n'est apportée pour le potentiel de jonction. La concordance entre les valeurs théoriques et les valeurs mesurées est très satisfaisante, surtout si l'on envisage tous les facteurs qui peuvent l'influencer: $E^\circ_{\mathrm{Ag/AgCl}}$, molalité de KCl dans le pont de jonction et dans le cellule de référence, $\gamma^{\pm}_{\mathrm{HCl}}$, K_W, $a_{H_2O}/\gamma_{H^+} \gamma_{OH^-}$, précision du coulomètre et stabilité de la température.

Tous les termes de l'éqn. (1) sont maintenant connus ou mesurés, à l'exception des constantes β_{H_n}; on peut donc les déterminer à partir de la

TABLEAU 2

Détermination du coefficient d'activité molal moyen de HCl
(t = (25 ± 0.01) °C; μ = 1 (KCl))

C_{HCl} (mol l^{-1})	m_{HCl}	ΔE(V)	E_j (V)	γ
$5.014 \cdot 10^{-2}$	$5.186 \cdot 10^{-2}$	0.31825	0.00364	0.728
$4.015 \cdot 10^{-2}$	$4.154 \cdot 10^{-2}$	0.32350	0.00296	0.725
$2.006 \cdot 10^{-2}$	$2.077 \cdot 10^{-2}$	0.34045	0.00152	0.717
$1.002 \cdot 10^{-2}$	$1.038 \cdot 10^{-2}$	0.35764	0.00077	0.715
$5.013 \cdot 10^{-3}$	$5.194 \cdot 10^{-2}$	0.37504	0.00039	0.715
$2.506 \cdot 10^{-3}$	$2.597 \cdot 10^{-2}$	0.39235	0.00020	0.720
$1.006 \cdot 10^{-3}$	$1.043 \cdot 10^{-2}$	0.41577	0.00008	0.718
$5.020 \cdot 10^{-4}$	$5.202 \cdot 10^{-3}$	0.43368	0.00004	0.718
				γ = 0.72 ± 0.01 à 95 % de confiance

TABLEAU 3

Comparaison des valeurs théoriques et calculées de la molalité en ions hydroxylés (t = (25.00 ± 0.01) °C; μ = 1 (KCl))

$-\log m_{OH(théor.)}$	ΔE (V)	$-\log m_{OH(calc.)}$	$\Delta = \log m_{OH} - \log m_{OH(calc.)}$
2.855	0.88427	2.864	0.009
2.808	0.88684	2.821	0.013
2.781	0.88838	2.795	0.014
2.719	0.89228	2.729	0.010
2.693	0.89385	2.702	0.007
2.690	0.89440	2.693	0.003
2.641	0.89705	2.648	0.007
2.615	0.89858	2.622	0.007
2.569	0.90140	2.575	0.006
2.507	0.90554	2.505	−0.002
2.504	0.90540	2.507	0.003
2.479	0.90686	2.482	0.003
2.444	0.90899	2.446	0.002
2.422	0.91019	2.426	0.004
2.316	0.91687	2.313	−0.003
2.156	0.92641	2.152	−0.004
1.969	0.93746	1.965	−0.004
1.883	0.94247	1.880	−0.003

courbe de titrage expérimentale en résolvant cette équation par ordinateur, au moyen d'un programme basé sur la méthode des moindres carrés par approximations successives dont le principe est détaillé dans une publication antérieure [3]. Il a cependant été modifié de façon à calculer, en chaque point de la courbe de titrage, la concentration en protons et en ions hydroxyles, les valeurs de $[H^+]$ et $[OH^-]$ de la formule (1) étant calculées à partir des relations (2) (3) et (5).

Les constantes ainsi obtenues sont exprimées en concentration et sont, par conséquent, fonction de la force ionique du milieu.

RESULTATS

Les tracés de la Fig. 1 représentent les courbes de titrage des acides aminopolyacétiques et d'un complexe TmY'H. Les valeurs des constantes d'acidité obtenues dans chaque cas sont données dans les Tableaux 4 et 5. L'écart-type calculé par ordinateur sur les x points d'une courbe de titrage ($100<x<150$) est en général de 0.002 unité pK sauf pour les pK des formes H_{n+1} L où il peut atteindre 0.03 unité pK. Nous l'appellerons erreur "instrumentale" ($\epsilon_{inst.}$).

Par contre, la dispersion entre les résultats obtenus pour différentes expériences, en vue de déterminer le même pK d'un même acide est supérieure à 0.002 unité pK. Ce manque de reproductibilité est dû essentiellement aux

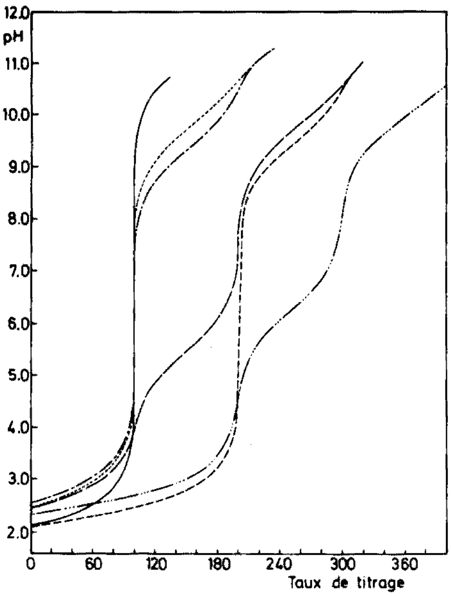

Fig. 1. Courbes de titrage de la glycine, l'IMDA, de l'NTA, de l'EDTA, de l'HEDTA et d'un complexe LnEDTAH par la potasse. Conditions expérimentales reprises dans le Tableau 1. Un taux de titrage de 100 correspond à la neutralisation de un proton. -------- Glycine; —·—·— IMDA; — — — — NTA; —— —— HEDTA; — ··· — EDTA; ——— Tm—EDTA—H.

erreurs "expérimentales" dans la préparation des solutions: volume des ballons jaugés, des pipettes, pesée des réactifs, standardisation de la potasse, étalonnage de la burette . . . Cette dispersion étant due aux facteurs "expérimentaux", elle ne dépend pas de la nature de l'acide considéré; on peut donc estimer cette erreur en sommant, pour tous les pK de tous les acides, c'est-à-dire pour l'ensemble des constantes déterminées, les carrés des

TABLEAU 4

Constantes d'acidité des acides aminoacétiques (Milieu = KCl 1 M. Température = (25.00 ± 0.01) °C. $pK_i = -\log \frac{(H_{n-i}L)(H^+)}{(H_{n+1-i}L)}$; n = nombre de groupements carboxyliques.)

Acides	pK_0	pK_1	pK_2	pK_3	pK_4
Glycine (GLY)	2.48 ± 0.01	9.67 ± 0.01			
IMDA (X)	1.84 ± 0.01	2.57 ± 0.01	9.27 ± 0.01		
NTA (Z)	1.03 ± 0.03	1.75 ± 0.01	2.31 ± 0.01	9.34 ± 0.01	
EDTA (Y′)	1.50 ± 0.02	1.95 ± 0.01	2.45 ± 0.01	6.21 ± 0.01	9.79 ± 0.01

TABLEAU 5

pK des complexes LnY'H
(Ln = ion lanthanide. Milieu KCl 1 M. Y' = EDTA. Température = (25.00 ± 0.01) °C.)

Lanthanides	Nos valeurs	Valeurs de la littérature
Lanthane	3.1 ± 0.1[a]	2.00 [7]
Cerium		2.04 [8] 3.2 [9] 1.83 [10]
Praséodyme		1.94 [8]
Néodyme	2.14 ± 0.02[a]	1.86 [8] 2.5 [11] 2.0 [7] 3.7 [12]
Samarium	2.03 ± 0.02[a]	1.69 [8] 2.6 [11] 2.2 [13]
Europium	1.89 ± 0.01	1.67 [8] 2.6 [11]
Gadolinium	1.82 ± 0.01	1.53 [8] 2.7 [11] 2.00 [14]
Terbium		1.2 [8] 2.6 [11] 1.7 [10]
Dysprosium	1.44 ± 0.01	1.1 [8] 2.8 [11]
Holmium	1.35 ± 0.01	1.0 [8] 2.7 [11]
Erbium	1.27 ± 0.01	0.9 [8] 2.8 [11]
Thulium	1.19 ± 0.01	0.8 [8] 2.6 [11]
Ytterbium	1.17 ± 0.01	0.8 [8] 2.7 [11]
Lutécium	1.15 ± 0.01	0.7 [8] 2.5 [11]

[a] Le manque de précision sur la valeur de ces constantes est dû à la faible solubilité des complexes LnY'H.

différences entre les valeurs mesurées et les valeurs moyennes et en divisant cette somme par le nombre de grandeurs sommées. La racine carrée ($\epsilon_{\text{expér.}}$) de cette valeur vaut 0.011 unité pK.

L'erreur dont nous affectons nos constantes est calculée par l'expression: $\epsilon = (\epsilon^2_{\text{inst.}} + \epsilon^2_{\text{expér.}})^{\frac{1}{2}}$.

DISCUSSION

Si l'on excepte le cas de la glycine, les données concernant le pK_0 de la forme $(H_{n+1}L)^+$ sont peu abondantes dans la littérature. Pour interpréter correctement les courbes de titrage en milieu acide, nous avons été forcés d'introduire cette espèce; pour les acides du type $(CH_2{-}COOH)_n NH_{(3-n)}$, son caractère acide est d'autant plus marqué que le nombre de groupements acétiques fixés sur l'azote est grand. Comme on peut le voir sur la Fig. 2, en passant de la glycine au NTA, la fixation d'un groupement acétique supplémentaire diminue, d'environ 0.7 unité, le pK_0 de $(H_{n+1}L)^+$. Pour l'EDTA, on obtient une valeur de 1.50. Les quelques valeurs de la littérature sont reprises dans le Tableau 6.

Comment de comparent nos valeurs avec celles de la littérature? Dans le cas particulier de l'EDTA, il existe une base de comparaison en considérant les valeurs sélectionnées par Anderegg dans un rapport récent d'une commission I.U.P.A.C. [17]. En milieu KCl 1 M, à 25 °C, l'auteur propose pour les deux derniers pK de l'EDTA les valeurs respectives de 9.88 ± 0.06 et 6.21 ± 0.04; dans les mêmes conditions, nous obtenons 9.79 ± 0.01 et

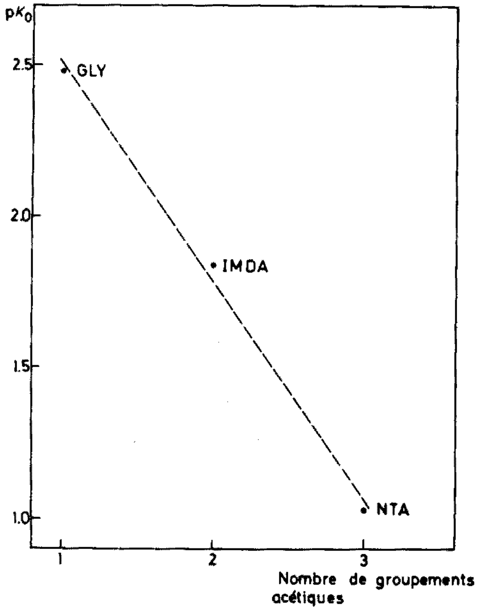

Fig. 2. Evolution du pK_0 de la forme $(H_{n+1}L)^+$ en fonction du nombre de groupements acétiques fixés sur l'azote de l'acide.

6.21 ± 0.01, alors que les valeurs récentes de Brücher et al. [18] dans le même milieu sont 9.78 et 6.18. L'accord est très satisfaisant.

Si nous considérons maintenant le cas de la glycine, il existe de nombreuses valeurs dans la littérature, ainsi qu'il ressort de la Fig. 3 qui reprend les données répertoriées dans les tables de Sillen et Martell [15] d'une part et dans celle

TABLEAU 6

pK_0 de la forme $(H_{n+1}L)^+$ des acides aminopolyacétiques
(Milieu KCl 1 *M*. Température: (25.00 ± 0.01) °C)

Acides	Nos valeurs	Valeurs de la littérature
Glycine	2.48 ± 0.01	voir Fig. 3
IMDA	1.84 ± 0.01	1.82 (μ = 0.1 KCl, t = 25 °C) [15]
		1.88 (μ = 1 $NaClO_4$, t = 25 °C) [15]
NTA	1.03 ± 0.01	0.8 (μ = 0.1, t = 20 °C) [16]
		1.1 (μ = 1, t = 20 °C [16]
EDTA	1.50 ± 0.02	1.55 (μ = 0.1 KCl, t = 25 °C) [17]
		1.91 (μ = ?, t = 25 °C) [17]
		1.62 (μ = variable, t = 20 °C) [17]
		0.96 (μ = 2 NaCl, t = 25 °C) [17]
		1.51 (μ = 0.1 $NaNO_3$, t = 25 °C) [17]
		1.51 (μ = 1.2 ?, t = 25 °C) [17]
		1.34 (μ = 0.1 KCl, t = 25 °C) [17]

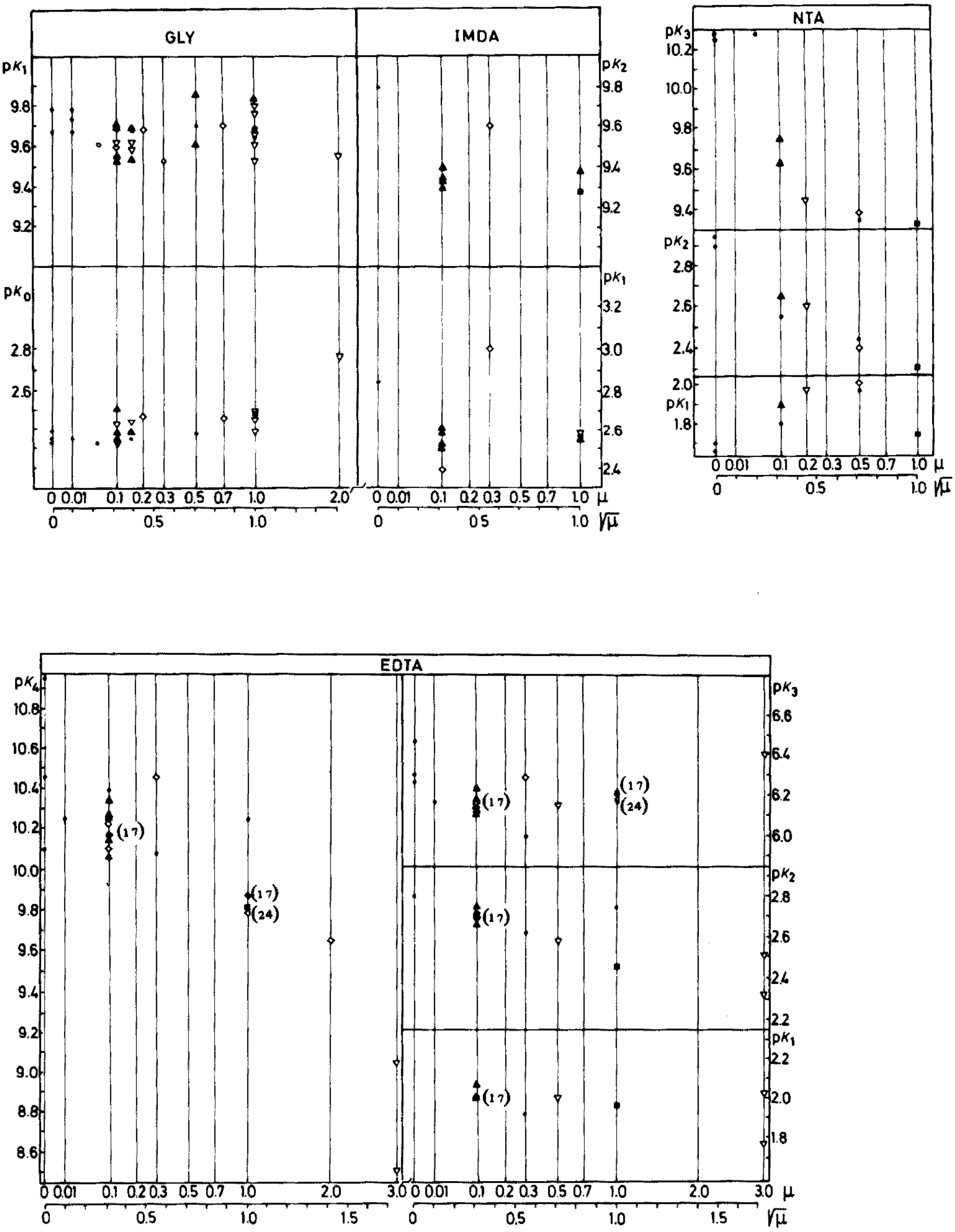

Fig. 3. Evolution des p*K* des acides suivants: glycine, IMDA, NTA et EDTA en fonction de la racine carrée de la force ionique, *t* = 25 °C. Sauf indication contraire, les valeurs sont tirées des ouvrages de Sillen et coll. [15, 16]. ▲ milieu KNO_3; ▽ milieu $NaClO_4$; ○ milieu K_2SO_4; ◇ milieu KCl; ■ nos valeurs; ◆ valeurs sélectionnées par Anderegg [17] en milieu KCl; ● milieu non défini.

de Martell et Smith [16] d'autre part. Nous y avons adopté des modes de représentation différents suivant le milieu considéré, ainsi qu'il est indiqué dans la légende. Les valeurs de pK_0 et pK_1 ont été portées en fonction de la racine carrée de la force ionique. On peut constater que la dispersion des données est considérable mais on ne doit pas perdre de vue que les conditions expérimentales sont très différentes d'un auteur à l'autre, soit qu'elles diffèrent par la nature, la concentration du sel qui fixe la force ionique et éventuellement les unités choisies; il est clair dans ces conditions, il est illusoire de vouloir tirer des conclusions sur la validité et l'exactitude de nos valeurs sur la base d'une simple comparaison directe avec l'ensemble de ces données de la littérature. Si nous retenons uniquement les données de la littérature obtenues à 25 °C, en milieu de force ionique connu et constituée par un sel potassique, nous obtenons les valeurs rassemblées dans la Tableau 7. Parmi celles-ci, il faut encore faire remarquer que la valeur de Keefer [21] a été obtenue par titrage á la soude dans un milieu de force ionique fixée par KNO_3. En ce qui concerne celle de James et Williams [22], l'étalonnage du pH mètre a été fait au moyen de borax 0.05 *M* alors que le titrage s'est effectué en milieu K_2SO_4 de force ionique 3.

Si l'on compare alors les valeurs du Tableau 7 obtenues en milieu KCl, on peut constater que nos données paraissent se situer de façon non aberrante, mais il serait difficile d'en tirer des conclusions précises concernant l'exactitude de nos déterminations.

En ce qui concerne les autres acides aminoacétiques considérés, à savoir IMDA, NTA et EDTA, les différentes données de la littérature, ainsi que nos propres valeurs sont rassemblées dans la Fig. 3. Ici encore, pour les mêmes raisons que celles qui viennent d'être invoquées à propos de la glycine, la dispersion des données est considérable et il serait difficile d'en tirer des conclusions sur la validité de nos propres résultats.

TABLEAU 7

Valeurs des pK de la glycine proposées par la littérature

pK_0	pK_1	Milieu	Temp.	Réf.
2.34	9.60	0.1 KCl	25 °C	(19)[a]
	9.69	0.15 KNO_3	25.15 °C	(20)[a]
	9.69	0.1 KNO_3	25 °C	(21)[a]
	9.84	1 KNO_3	25 °C	(21)[a]
	9.53	0.3 K_2SO_4	25 °C	(22)[a]
2.46	9.70	0.65 KCl	25 °C	(23)[a]
2.47	9.68	0.2 KCl	25 °C	(24)[a]
2.51	9.70	0.1 KNO_3	25 °C	(25)[a]
	9.61	0.5 KNO_3	25 °C	(26)[a]
2.48 ± 0.01	9.67 ± 0.01	1 KCl	25 °C	Nos valeurs

[a] Détermination potentiométrique au moyen d'une électrode de verre.

En ce qui concerne le p*K* des complexes LnY'H, il suffit de consulter la Fig. 4 et le Tableau 5 pour se rendre compte de la dispersion des valeurs proposées; non seulement les valeurs absolues des p*K* varient d'un auteur à l'autre, ce qui peut être partiellement attribué à des différences de milieu, de température et d'unités, mais, en plus, fait plus difficilement explicable, leur évolution en fonction du nombre atomique est également très différent d'un auteur à l'autre.

Nous tenons à remercier le Professeur G. Anderegg pour les remarques constructives qu'il a bien voulu nous faire. L'un de nous tient à remercier l'I.R.S.I.A. (Institut pour l'Encouragement de la Recherche dans l'Industrie et l'Agriculture) pour la bourse de doctorat qui lui a été octroyée. L'Institut Interuniversitaire des Sciences Nucléaires est également remercié pour le soutien financier accordé à notre laboratoire.

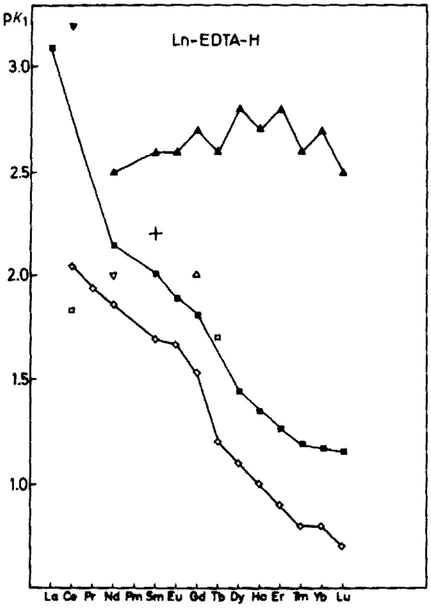

Fig. 4. Evolution des p*K* des acides LnY'H en fonction du nombre atomique des lanthanides.

▲Kolat et Powell [11]; μ = 0.015 (KNO_3), *t* = 20 °C.
◇Brücher et coll. [8]; μ = 0.1 (KCl), *t* = 25 °C.
■Nos valeurs; μ = 1 (KCl); *t* = 25 °C.
□Brücher et Kukri [10].
▼Kusakina et Yakimets [9]; μ = variable, *t* = 25 °C.
▽Schwarzenbach et coll. [7]; μ = 0.1 (KNO_3), *t* = 20 °C.
△Petushkova et Tananaev [14]; μ = variable, *t* = indéterminée.
+Tananaev et Shevchenko [13]; μ = variable, *t* = 25 °C.

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THE EXTRACTION OF ANIONIC TITANIUM(IV), VANADIUM(IV) AND ZIRCONIUM(IV)—THIOCYANATE COMPLEXES FROM AQUEOUS SOLUTIONS BY TRICAPRYLMETHYLAMMONIUM CHLORIDE

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SUMMARY

The extraction of anionic titanium(IV), vanadium(IV) and zirconium(IV)—thiocyanato complexes from aqueous solutions with a long-chain alkylammonium salt in benzene has been investigated under different conditions. Both the aqueous and organic phases have been examined spectrophotometrically. Infrared spectroscopy has been applied to the organic extracts, and electron spin resonance to the organic vanadyl complex. The mechanisms of the extractions and the structures of the extracted species are discussed on the basis of the results obtained.

Tricaprylmethylammonium thiocyanate has been utilized as a selective agent in the spectrophotometric determination of cobalt(II) [1]. The present authors have also investigated extractions of thorium(IV) [2] and uranium (VI) [3] from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate by quaternary compounds. This paper extends the work to the extraction of titanium(IV), vanadium(IV) and zirconium(IV).

EXPERIMENTAL

Reagents

Tricaprylmethylammonium chloride (General Mills; Aliquat-336; $R_3R'NCl$) used as the quaternary compound, was purified by washing several times with aqueous sodium chloride solution and n-hexane [4], and was diluted with benzene. The stock solution of titanium chloride was prepared from titanium hydroxide precipitated with aqueous ammonia from titanium sulphate solution (24 % $Ti(SO_4)_2$) and washed thoroughly with ammonium nitrate solution and distilled water; the hydroxide was dissolved in hydro-

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chloric acid solution of the selected concentration. The stock solutions of vanadium and zirconium chloride were prepared by dissolving vanadyl chloride, $VOCl_2$, and zirconium chloride, $ZrCl_4$, respectively, in hydrochloric acid solutions of the required concentrations. The other chemicals were analytical-reagent grade.

Extraction and analytical procedures

The procedure for obtaining distribution coefficients (the ratio of the equilibrium concentration of titanium, vanadium or zirconium in the organic phase to that in the aqueous phase) was as follows. Equal volumes (15 ml) of Aliquat-336 in benzene and the aqueous metal chloride solutions containing hydrochloric acid in the presence of potassium thiocyanate, were shaken for 10 min in a stoppered 50-ml conical flask in a water-bath thermostatted at the required temperature (preliminary experiments showed that equilibration for each metal is complete in 10 min); the organic phases centrifuged from the aqueous phases were stripped with 2 M nitric acid for titanium, and with 1 and 2 M hydrochloric acid for vanadium and zirconium, respectively, and then the distribution coefficients were determined.

Titanium was determined by back-titration of the aqueous solution after adding an excess of EDTA, with an aqueous solution of zinc sulphate to an Erio T (eriochrome black T) end-point [5]; vanadium with an aqueous solution of thorium nitrate at pH 3 to a xylenol orange end-point [6]; and zirconium with an aqueous solution of bismuth nitrate at pH 2 to a xylenol orange end-point [6]. The concentrations of chloride and thiocyanate in the organic phase were determined as follows: the precipitate from the organic solution with silver nitrate was decomposed by boiling for 1 h in the presence of concentrated nitric acid, and the residue was weighed as silver chloride [7]; accordingly, the loss in weight from the initial precipitate was equivalent to the concentration of thiocyanate.

Spectrophotometric, i.r. and e.s.r. spectral measurements

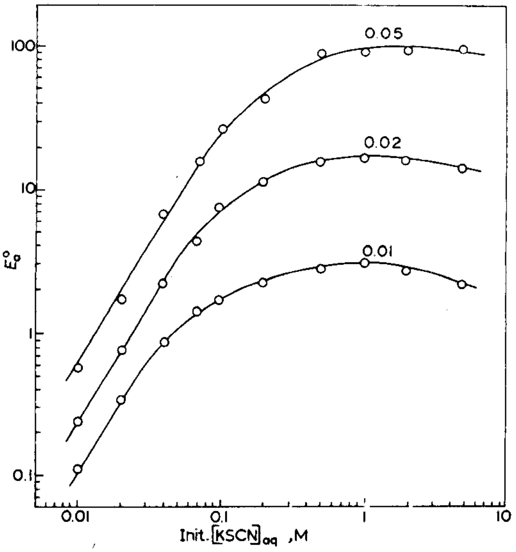
The absorption spectra were obtained on a Hitachi Model EU-2 recording spectrophotometer and a Shimazu Model QV-50 spectrophotometer, with matched 1.00-cm fused silica cells. The i.r. spectra of the samples prepared by evaporation of diluent in the organic phases were determined on a Japan Spectroscopic Co. Ltd. spectrometer Model IR-S, equipped with potassium chloride prisms for measurement at 4000—550 cm^{-1}, and Model IR-F, a grating model for measurement at 700—200 cm^{-1}, as a capillary film between thallium halide plates.

Electron spin resonance (e.s.r.) spectra of the organic extract for vanadium were determined on a high-sensitivity e.s.r. spectrometer, designed in the Research Institute of Electronics, Shizuoka University and made by Shimada Rikakogyo Co. Ltd. Measurement was made in the solid state by superheterodyne detection [8]; the wave-guide units in the spectrometer are standard X-band components with 1-s response, and the amplitude of the modulating field is 3 gauss at room temperature. The calculation of e.s.r. derivative line shape of samples was done with a HIPAC 103 computer.

RESULTS AND DISCUSSION

Extraction isotherms

The extraction of titanium(IV), vanadium(IV) and zirconium(IV) from their solutions (1 g l^{-1} as $TiCl_4$, $VOCl_2$ and $ZrCl_4$) containing hydrochloric acid in the presence of potassium thiocyanate by Aliquat-336 in benzene at 20 °C gave the results shown in Figs. 1—3. These show that the extraction efficiency follows the order zirconium(IV) > vanadium(IV) > titanium(IV) and decreases with increasing initial aqueous hydrochloric acid concentration. The distribution coefficients (E_a^o) for titanium, vanadium and zirconium first rise with aqueous thiocyanate concentration, pass through maxima at initial concentrations of 1, 0.15 and 0.5 M, respectively, and then fall again. The variation of the distribution coefficients may be attributed to formation of the metal ion—thiocyanato complex, competition between metal ion and thiocyanate for association with the quaternary compound providing a check on this rise. In extractions of solutions of the metal ions (1 g l^{-1}) containing



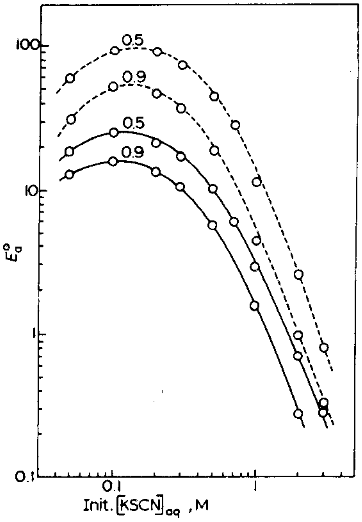


Fig. 1. Extraction of titanium(IV)—thiocyanato complex from 0.1 M hydrochloric acid solutions in the presence of potassium thiocyanate at different concentrations by Aliquat-336 in benzene. Numerals on curves are Aliquat-336 concentrations (M).

Fig. 2. Extraction of vanadium(IV)—thiocyanato complex from hydrochloric acid solutions in the presence of potassium thiocyanate at different concentrations by Aliquat-336 in benzene. Continuous and broken lines represent extractions with 0.02 and 0.03 M, Aliquat-336, respectively; numerals on curves are initial aqueous hydrochloric acid concentrations (M).

hydrochloric acid (0.1 M for titanium, 0.3 M for vanadium and 0.7 M for zirconium) and lithium chloride at various concentrations in the presence of 1.0 M potassium thiocyanate with Aliquat-336 (0.01 M for titanium, 0.02 M for vanadium and 0.03 M for zirconium) in benzene at 20 °C, however, the distribution coefficients are not appreciably influenced by chloride concentration. Additionally, log E_a^o decreases linearly with log $[HCl]_{aq}$ at a fixed total chloride concentration ([HCl] + [LiCl] = 1.0, 1.0 and 1.5 M for titanium, vanadium and zirconium, respectively), analogously to the curve for hydrochloric acid alone. It is thus presumed that the species containing chloride ion is not extractable; when the hydrochloric acid in the aqueous phase is partly replaced by lithium chloride the decrease in the distribution coefficient is checked, owing to the removal of the competition for titanium(IV), vanadium(IV) or zirconium(IV)—thiocyanato complex between hydrochloric acid and quaternary salt.

The electronic spectra of the vanadyl ion in aqueous solution indicate the formation of the species $[VO(H_2O)_5]^{2+}$ [9, 10]. The extraction of vanadium(IV) in the presence of thiocyanate probably depends on an ion-exchange reaction similar to that for uranium(VI) [3], viz.

$$SCN^- \text{ (a)} + R_3R'NCl \text{ (o)} \rightleftharpoons R_3R'NSCN \text{ (o)} + Cl^- \text{ (a)} \tag{1}$$

$$VO^{2+} \text{ (a)} + n\, SCN^- \text{ (a)} \rightleftharpoons [VO(SCN)_n]^{2-n} \text{ (a)} \tag{2}$$

$$VO(SCN)_n{}^{2-n} \text{ (a)} + (n-2)\, R_3R'NSCN \text{ (o)} \rightleftharpoons$$
$$(R_3R'N)_{n-2}[VO(SCN)_n] \text{ (o)} + (n-2)\, SCN^- \text{ (a)} \tag{3}$$

in which (a) and (o) represent aqueous and organic phases, respectively. Accordingly, the following relationship would be expected:

$$\log E_a^o = \log K + m \log(C_A - m\, C_V)/C_{SCN} \tag{4}$$

where E_a^o is the distribution coefficient, K the equilibrium constant, C_A the total quaternary compound concentration, C_V the vanadium concentration of the organic phase, and C_{SCN} the aqueous thiocyanate concentration, and in addition $m = n - 2$. In the extraction of vanadium(IV) from its solution (1 g l^{-1}) containing hydrochloric acid in the presence of 1.0 M potassium thiocyanate at 20 °C, log—log plots of E_a^o vs. $(C_A - m\, C_V)/C_{SCN}$ show that eqn. (4) is satisfied for $m = 3$ at initial $[R_3R'NCl] > 0.015$ M, and for $m = 2$ at initial $[R_3R'NCl] < 0.015$ M. It is therefore thought that each vanadium(IV)—thiocyanato complex ion is associated with three molecules of quaternary compound in the extraction at low vanadium concentrations, so that eqn. (3) becomes

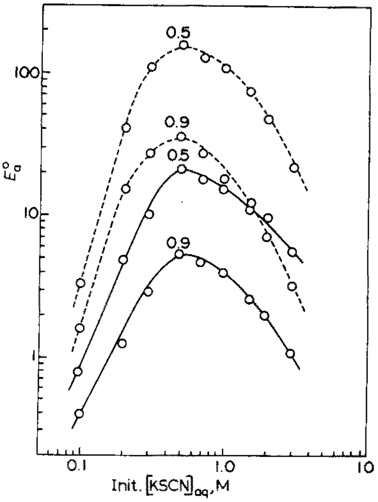
$$[VO(SCN)_5]^{3-} \text{ (a)} + 3\, R_3R'NSCN \text{ (o)} \rightleftharpoons$$
$$(R_3R'N)_3[VO(SCN)_5] \text{ (o)} + 3\, SCN^- \text{ (a)} \tag{5}$$

In the extraction of higher vanadium concentration, however, two molecules of quaternary compound are associated with each vanadium(IV)—thiocyanato complex ion, thus:

$$[VO(SCN)_4]^{2-}\ (a) + 2\ R_3R'NSCN\ (o) \rightleftharpoons$$
$$(R_3R'N)_2[VO(SCN)_4]\ (o) + 2\ SCN^-\ (a) \qquad (6)$$

This is supported by the fact that the molar ratios of the vanadium and thiocyanate concentrations in the organic phase to the concentration of Aliquat-336 as a function of initial aqueous vanadium concentration under the conditions indicated in Fig. 4, approach the limiting values of 0.5 and 2, respectively, as shown in Fig. 4. This implies that the complex in the organic phase contains vanadium/thiocyanate/Aliquat-336 in the molar ratio 1:4:2 as in eqn. (6).

In contrast, the titanyl ion, TiO^{2+}, does not appear to exist in solutions; the prevailing species in dilute acid solutions is hydrolyzed, e.g. $[Ti(OH)_2(H_2O)_4]^{2+}$ [11, 12]. The zirconyl ion, ZrO^{2+}, is considered in the older literature as the prevailing species in aqueous solutions of zirconium salts [13], but there is little reliable evidence for its existence [10(b)]. Recently the existence of Zr^{4+} ion in acidic solutions has been reported [14]; the prevailing species in fresh solutions of zirconium salts is Zr^{4+}, although slow hydrolysis occurs to form polymeric hydrolysed species [15]. Accordingly, the extrac-



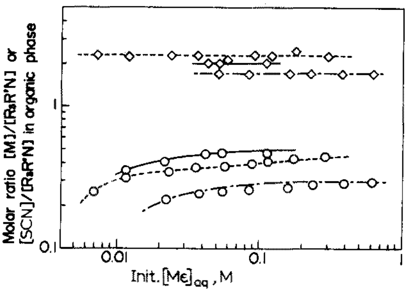


Fig. 3. Extraction of zirconium(IV)—thiocyanato complex from hydrochloric acid solutions in the presence of potassium thiocyanate at different concentrations by Aliquat-336 in benzene. Continuous and broken lines, and numerals on curves have the same meaning as in Fig. 2.

Fig. 4. Variation in the concentrations of metal and thiocyanate in the organic phase with initial aqueous metal concentration for extraction from hydrochloric acid solutions in the presence of potassium thiocyanate (1.0 M) by Aliquat-336 in benzene. ○ and ◇ denote the molar ratios of $[M]/[R_3R'N]$ and $[SCN]/[R_3R'N]$, respectively. Continuous, broken and chain lines represent the extractions of titanium(IV), vanadium(IV) and zirconium(IV) from hydrochloric acid solutions (2, 0.5 and 1 M) with Aliquat-336 (0.01, 0.02 and 0.01 M), respectively.

tion of titanium(IV) and zirconium(IV) may be expressed, similarly to that for vanadium(IV), as:

$$M(OH)_z^{4-z}\ (a) + n\ SCN^-\ (a) \rightleftharpoons [M(OH)_z(SCN)_n]^{4-z-n}\ (a) \qquad (7)$$

$$[M(OH)_z(SCN)_n]^{4-z-n}\ (a) + (n+z-4)R_3R'NSCN\ (o) \rightleftharpoons$$
$$(R_3R'N)_{n+z-4}[MO_{z/2}(SCN)_n]\ (o) + (n+z-4)\ SCN^-\ (a) + z/2\ H_2O\ (a) \qquad (8)$$

in which M denotes Ti or Zr. This leads to the following relationship:

$$\log E_a^o = \log K_1 + p\log(C_A - p\,C_M)/C_{SCN} \qquad (9)$$

where K_1 is a constant, and $p = n + z - 4$. When titanium(IV) and zirconium(IV) are extracted from their solutions (1 g l^{-1}) containing hydrochloric acid in the presence of 1.0 M potassium thiocyanate, and $\log E_a^o$ is plotted against $\log(C_A - p\,C_M)/C_{SCN}$, eqn. (9) is satisfied for $p = 2$ in titanium(IV), and for $p = 3$ in zirconium(IV).

Moreover, the molar ratios of titanium or zirconium and thiocyanate in the organic phase to Aliquat-336 as a function of initial aqueous titanium or zirconium concentration under the conditions indicated in Fig. 4, approach limiting values of 0.5 and 2 for titanium, and 0.33 and 0.6 for zirconium, respectively. This suggests that the complexes formed in the organic phase contain titanium or zirconium/thiocyanate/Aliquat-336 in the molar ratios 1:4:2 and 1:5:3, respectively. Equation (8) can therefore be rewritten as:

$$[Ti(OH)_2(SCN)_4]^{2-}\ (a) + 2\ R_3R'SCN\ (o) \rightleftharpoons$$
$$(R_3R'N)_2[TiO(SCN)_4]\ (o) + 2\ SCN^-\ (a) + H_2O\ (a) \qquad (10)$$

and

$$[Zr(OH)_2(SCN)_5]^{3-}\ (a) + 3\ R_3R'SCN\ (o) \rightleftharpoons$$
$$(R_3R'N)_3[ZrO(SCN)_5]\ (o) + 3\ SCN^-\ (a) + H_2O\ (a) \qquad (11)$$

Temperature effect

The extraction of titanium(IV), vanadium(IV) and zirconium(IV) from solutions (1 g l^{-1}) containing 0.1—0.9 M hydrochloric acid in the presence of 1.0 M potassium thiocyanate by 0.01—0.03 M Aliquat-336 in benzene at temperatures between 10 and 50 °C gave the results shown in Fig. 5. The decrease in the distribution coefficients for titanium and vanadium with rising temperature is similar to the result for extraction of thorium(IV) [2], but the temperature-dependence for vanadium is in the opposite direction. The heat reactions (change in enthalpy, kcal mol^{-1}) for eqns. (5), (10) and (11) were estimated to be 12.6 in 0.1 M HCl with 0.01 M $R_3R'NCl$ for titanium; 3.43 and 2.29 in 0.5 and 0.9 M HCl, respectively, with 0.03 M $R_3R'NCl$; —1.94 and —1.37 in 0.5 and 0.9 M HCl, respectively, with 0.02 M $R_3R'NCl$.

Absorption and i.r. spectra

The absorption spectra of both the aqueous and organic phases from the extraction of vanadyl chloride solutions under the conditions given in the legends, are shown in Figs. 6 and 7. The spectrum of the aqueous solution containing 0.5 M potassium thiocyanate exhibits the characteristic absorption bands at 610 and 765 nm, whose absorptions shift to shorter and longer wavelengths, respectively, as the thiocyanate concentration increases (Fig. 6). This perhaps corresponds to the transformation from penta- to hexa-

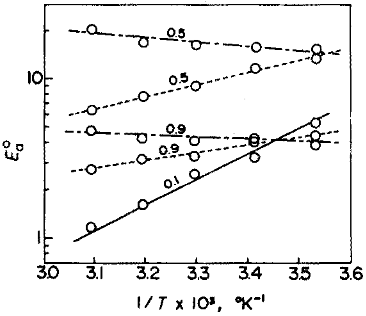
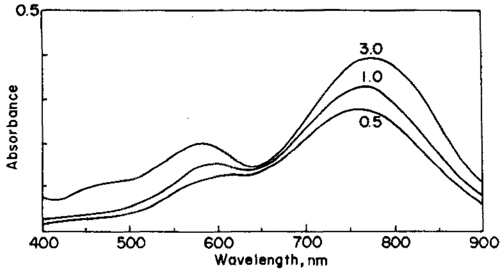


Fig. 5. Temperature-dependence of distribution coefficient for the extraction of metal—thiocyanato complex. Numerals on curves are initial aqueous hydrochloric acid concentrations (M). Continuous, broken and chain lines indicate the extractions of titanium(IV), vanadium(IV) and zirconium(IV) with Aliquat-336 (0.01, 0.03 and 0.02 M, respectively).



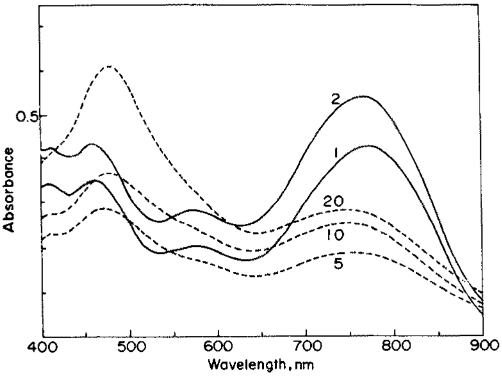


Fig. 6. Absorption spectra of aqueous solutions of vanadyl chloride (1 g l^{-1}) containing 0.5 M hydrochloric acid and potassium thiocyanate. Numerals on curves are initial potassium thiocyanate concentrations (M). 1.00-cm cells; 20 °C.

Fig. 7. Absorption spectra of organic solutions from extraction of vanadyl chloride solutions containing 0.5 M hydrochloric acid and 1.0 M potassium thiocyanate with 0.02 M Aliquat-336 in benzene. Numerals on curves are initial aqueous vanadyl chloride concentrations, g l^{-1}. Continuous and broken lines indicate 1× and 5× dilution, respectively. 1.00-cm cells; 20 °C.

coordination of the thiocyanato group for vanadium. For the spectrum of the organic solution from the extraction of vanadyl chloride solution (1 g l^{-1}) under the conditions mentioned (Fig. 7) the absorptions at 575 and 775 nm are accompanied by the charge-transfer band at 465 nm which is due to the $^2B_2 \rightarrow {}^2A_1$ transition. With increasing vanadium concentrations, these absorptions increase in intensity and shift slightly to 480, 575 and 750 nm, respectively; simultaneously the organic phase changes from blue to brown. The spectral results suggest that the extracted species is transformed from $[VO(SCN)_5]^{3-}$ to $[VO(SCN)_4]^{2-}$ as the vanadium concentration in the organic phase increases (cf. eqns. 5 and 6).

The brown complex prepared by evaporation of benzene from the brown organic solution was found to contain a water molecule. Drying in vacuo above 60 °C dehydrated this complex and the colour changed from brown to green. However, since the V—O stretching band [17—20] in the i.r. spectrum of the anhydrous (green) complex is little different from that of the hydrated (brown) complex, the water molecule is probably not coordinated directly to vanadyl ion; this is also consistent with the electronic spectral results (Table 1). In the spectrum of the hydrated complex, if the species $[VO(SCN)_4]^{2-}$ is in a point group C_{4v} symmetry, the absorption bands at 575 and 750 nm can be assigned to the transitions $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E(I)$, respectively [9]. The anhydrous complex shows these transitions at 585 and 750 nm, respectively. If the transformation from the penta- to hexa-coordinated structure is caused by the bonding of a water molecule to vanadyl ion, the lowering in the e* level should be observed as a shift to lower frequency [18]. There is no change in the absorption band due to the transition $^2B_2 \rightarrow {}^2E(I)$, hence the symmetrical configuration of the hydrated complex is probably similar to that of the anhydrous complex.

In the extraction of titanium(IV) and zirconium(IV) from aqueous solution containing hydrochloric acid and thiocyanate with Aliquat-336 in benzene, the organic phases show absorption bands at 420 and 480 nm, respectively, which arise from the charge-transfer transition [21], and are independent of the concentrations of acid and thiocyanate. When the variations in the absorbances of the organic solutions with increasing initial aqueous concentrations of titanium and zirconium were examined at 420 and 480 nm,

TABLE 1

Absorption spectral data for the vanadium(IV)—thiocyanato complexes with Aliquat-336

Hydrated complex			Anhydrous complex			Probable assignment
λ_{max} (nm)	ν (cm^{-1})	ϵ	λ_{max} (nm)	ν (cm^{-1})	ϵ	
480	20800	80	465	21600	42	$^2B_2 \rightarrow {}^2A_1$
575	17400	50	585	17100	38	$^2B_2 \rightarrow {}^2B_1$
750	13300	84	750	13300	78	$^2B_2 \rightarrow {}^2E(I)$

respectively, the absorbances approached limiting values; this suggests that anionic titanium and zirconium—thiocyanato complexes are extracted.

The organic extracts from vanadium(IV) solutions (1, 5, 10 and 20 g l^{-1}) containing 0.5 M hydrochloric acid in the presence of 1.0 M potassium thiocyanate with 0.094 M Aliquat-336 in benzene at 20 °C were examined by i.r. spectroscopy. Similar experiments were also done with titanium(IV) and zirconium(IV). The frequencies and probable band assignments for the anhydrous complexes, prepared by drying the organic solutions saturated with the titanium, vanadium and zirconium complexes, are given in Table 2, compared with those for the organic extract from the aqueous potassium thiocyanate solution only.

The spectrum of the organic extract without metal shows OH stretching and bending bands, the CN stretching band at 2092 cm^{-1} and the SCN bending frequency at 468 cm^{-1}, which implies that the compound $R_3R'NSCN \cdot H_2O$ [2] is formed as in eqn. (1). In the presence of vanadium, the absorptions caused by the stretching vibrations of the vanadyl group [17—20] appear at

TABLE 2

Infrared spectral data for titanium(IV), vanadium(IV) and zirconium(IV)—thiocyanato complexes with Aliquat-336

Frequency (cm^{-1})				Probable assignment
$R_3R'NSCN \cdot H_2O$	$(R_3R'N)_2$ $[TiO(SCN)_4]$	$(R_3R'N)_2$ $[VO(SCN)_4]$	$(R_3R'N)_3$ $[ZrO(SCN)_5]$	
3400 (wb)[a]				OH stretching
3200 (sh)				
2920 (s)	2920 (s)	2920 (s)	2920 (s)	CH stretching (sym. and asym.)
2820 (ms)	2860 (ms)	2860 (ms)	2860 (ms)	
2092 (s)	2040 (s)	2088 (s)	2080 (s)	CN stretching
1710 (vw)				OH bending
1620 (wb)				
1465 (m)	1465 (m)	1465 (m)	1465 (m)	CH_3 degenerate bending CH_2 scissoring
1375 (w)	1375 (w)	1375 (w)	1375 (w)	CH_3 sym. bending
	1070 (m)	1003 (m)		M—O stretching
	850 (w)	956 (w)		
	790 (vw)	786 (vw)	792 (vw)	CS stretching
720 (w)	720 (w)	720 (w)	720 (w)	CH_2 rocking
	650 (wb)		648 (w)	CS stretching
468 (w)	490 (m)	479 (m)	485 (m)	NCS bending
			445 (w)	M—O stretching
			418 (w)	
	385 (s)	380 (s)		M—N stretching
	355 (ms)	346 (ms)	280 (sb)	

[a] s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, b = broad, sh = shoulder.

1003 and 952 cm^{-1}, and the intensities of the OH bands decrease, in accordance with the results of Karl Fischer titrations; the CN stretching band appears at 2088 cm^{-1}, the SCN bending band at 479 cm^{-1}, and the V—N stretching bands at 380 and 346 cm^{-1}. All this suggests that the thiocyanate ion coordinates to vanadium through the nitrogen atom [22]. The spectrum of the hydrated complex shows absorptions analogous to those of the anhydrous complex, except for the presence of the OH bands.

Similar spectra were observed in the organic extracts from titanium and zirconium solutions (Table 2), although the M—O stretching band appears at 1070 and 850 cm^{-1} for titanium, and at 445 and 418 cm^{-1} for zirconium. These results confirm that titanium(IV), vanadium(IV) and zirconium(IV) are extracted according to eqns. (5) and/or (6), (10) and (11).

Structure of extracted species

The e.s.r. spectrum of the anhydrous vanadyl complex is shown in Fig. 8, compared with the calculated spectrum based on the line shape arising from randomly oriented sample in a tetragonal pyramidal symmetry [23, 24]. The experimental spectrum shows a hyperfine structure consistent with the

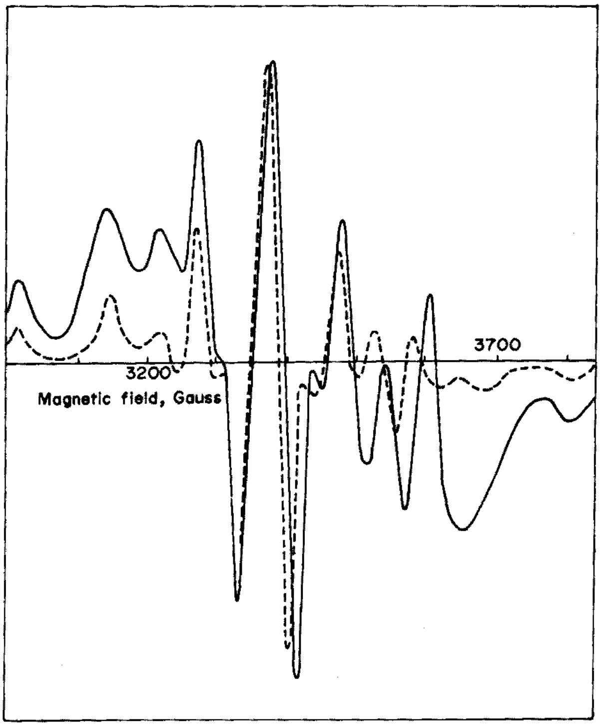
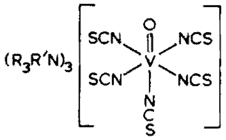


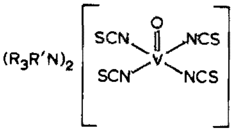
Fig. 8. E.s.r. spectrum of vanadium(IV)—thiocyanato complex. Continuous and broken lines are the observed and calculated spectra, respectively.

calculated curve. The calculated g values [23—34] are $g_{\parallel} = 1.951$ and $g_{\perp} = 1.991$, being isotropic in the thiocyanato group coordinated to vanadyl ion.

Hence structures [I] and [II] are proposed for the species extracted at low and higher vanadium concentrations, respectively.



(I) C_{4v} symmetry



(II) C_{4v} symmetry

It is reasonable to assume that the structures of the extracted species of titanium(IV) and zirconium(IV) are similar to those of [II] and [I], respectively.

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ADSORPTION CHARACTERISTICS OF TRACES OF BARIUM, BERYLLIUM, CADMIUM, MANGANESE, LEAD AND ZINC ON SELECTED SURFACES

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SUMMARY

The adsorption characteristics of Ba, Be, Cd, Mn, Pb and Zn on Pyrex, flint glass and polythene surfaces during storage under different conditions are described. It is concluded that the method of stabilization of water samples recommended by EPA, i.e. addition of 5 ml of 16 M HNO_3 per liter, is satisfactory. Stabilization and concentration with a mixed ligand system is recommended, except for Mn and Ba which are not extracted quantitatively. Extraction with APDC and MIBK is unsatisfactory for storage purposes.

Previous communications [1, 2] from this laboratory reported the adsorption losses of chromium(III) and (VI) and selenium from dilute aqueous solutions to the walls of beakers made out of Pyrex, flint glass, or polyethylene. The stability of chromium(VI) in solution as the Cr(VI)—APDC (ammonium pyrrolidinedithiocarbamate) complex extracted in methyl isobutyl ketone (MIBK) was also studied. The present work is an extension of this study to include barium, beryllium, cadmium, lead, manganese and zinc.

Recently there has been an increasing concern over the quality of drinking water and the degeneration of the quality of waters in rivers and lakes. The Environmental Protection Agency (EPA) and other laboratories are routinely monitoring these waters for trace metal contaminants and organic pollutants. The general practice has been to collect the water samples and transfer them to the laboratory for analysis. Often, considerable time elapses between collection and the actual analysis. During the storage time, significant losses can occur if proper precautions are not taken to stabilize the trace metals. These losses often cause serious errors in reported values.

The standard procedure recommended by EPA is to stabilize the trace metals by acidifying the water with nitric acid (5 ml of concentrated nitric acid to 1 l of sample). Although it is generally accepted that acidification of water considerably reduces the rate of adsorption of metals, there has been little or no systematic study to validate this assumption. The present work was undertaken to determine the adsorption losses of the metals investigated in 0.5 % nitric acid solutions (EPA recommendation), in solutions with a pH of 3, in solutions with a pH of 7, in solutions of the metals complexed with "mixed ligand" (dithizone, 8-quinolinol and acetylacetone) and

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extracted into ethyl propionate [5], and in solutions of the metals complexed with APDC (ammonium pyrrolidinedithiocarbamate) and extracted into MIBK (methyl isobutyl ketone) [4]. The adsorption process was monitored by means of the following radioactive tracers: ^{133}Ba, ^{7}Be, ^{115}Cd, ^{210}Pb, ^{54}Mn and ^{65}Zn. Pyrex, flint glass and polyethylene beakers were selected as containers for the solutions being studied. These three materials were chosen because they are commonly used for sample storage.

EXPERIMENTAL

Apparatus and Materials

Since ^{210}Pb emits β-rays, a Geiger-Müller tube Model EWH-141 (Atomic Accessories) having a 1.2—1.4 mg cm^{-2} mica end window mounted in a steel tube was used. Details of the detector assembly were given previously [6]. Three $\frac{1}{8}$-in. legs on the bottom of the steel tube mount provided a fixed geometry for counting the bottom of the beaker. For the other metals, which were γ-emitters, scintillation counting equipment was used; a 5 × 5 cm NaI (Tl) well-type crystal was mounted in such a way that it could be inserted into a beaker conveniently and with reproducible geometric orientation. The other accessories for counting both β- and γ-rays included a Hewlett-Packard Harrison 6515A d.c. power supply, a Canberra Model 815 amplifier, an Ortec Model 719 preset timer and an Ortec Model 775 counter.

The tracers were obtained from New England Nuclear, Boston, Mass. Deionized water (5 ml) was added to each vial containing the tracer and the solutions were then carefully mixed.

Radioactive stock solutions were prepared by adding the desired quantity of each isotope separately to a 100-ml volumetric flask and diluting to the mark with a (1 : 20) nitric acid solution. The quantities of isotopes used were as follows: ^{133}Ba (0.8 ml), ^{7}Be (3.0 ml), ^{115}Cd (2.0 ml), ^{210}Pb (1.0 ml), ^{54}Mn (1.0 ml) and ^{65}Zn (0.1 ml).

Metal carrier solutions (100 p.p.m.) were prepared by diluting 1000-p.p.m. stock solutions. For barium and beryllium, stock solutions were made as follows: 1.78 g of barium chloride and 19.64 g of beryllium sulfate tetrahydrate were dissolved separately in 100 ml of deionized water and diluted to 1 l. The cadmium, lead and zinc stock solutions were prepared by dissolving 1.0 g of each metal (analytical grade) in a minimum amount of nitric acid, evaporating to dryness, redissolving in deionized water and diluting to 1 l. The manganese stock solution was made by the procedure given on page 440 of ref. 4. Appropriate volumes of the tracer stock solutions were used to spike the respective carrier solutions such that the final solution provided at least 2000 c.p.m. per ml.

The mixed ligand extraction solution was prepared by dissolving 0.5 g of dithizone (diphenylthiocarbazone), 3.75 g of 8-quinolinol and 100 ml of acetylacetone in ethyl propionate and made up to 500 ml with ethyl propionate [5]. The APDC solution was prepared by dissolving 4 g of APDC in 100 ml of deionized water.

All chemicals used were of the highest purity commercially available. Kimax low-form Pyrex beakers and polyethylene beakers (250 ml; Bel-Art Products) were used. Flint glass bottles having about the same diameter as the beakers were cut to size and used. The flint glass containers are referred to as flint beakers throughout the text. The vessels were thoroughly hand cleaned with soap solution (no abrasives), rinsed three times with tap water and rinsed again five times with deionized water. The beakers were drained, dried and wrapped in plastic bags until they were ready to be used.

Procedure

The same general procedure was used for each individual metal. A 5-ml aliquot of the 100-p.p.m. spiked carrier metal solution was added to a 500-ml volumetric flask together with 2.5 ml of concentrated nitric acid [3, 4]. The solution was diluted to the mark with deionized water and mixed thoroughly, then a 100-ml aliquot was transferred to one treated beaker of each type. A 5-ml aliquot of the spiked metal carrier solution was added to a second 500-ml flask. The solution was made up to about 495 ml, and adjusted to pH 3 or 7, with nitric acid or ammonia solution. The solution was then diluted to the mark and the final pH was measured. Portions (100 ml) of the pH-adjusted solution were then added to a set of the beakers.

For the studies with the metal—APDC and metal—mixed ligand complexes, 5-ml aliquots of the spiked 100-p.p.m. carrier solution were diluted to about 100 ml and extracted according to established procedures [4, 5]. The solution of the metal—APDC complex was diluted to 500 ml with methyl isobutyl ketone (MIBK) and 100-ml portions were added to Pyrex, flint and polyethylene beakers. The metal—mixed ligand complex solution was diluted to 500 ml with the mixed ligand extractant and 100-ml portions were added to a set of beakers.

Each of the beakers containing 100 ml of the test solution was covered with a double layer of Saran Wrap and held at 23 ± 2 °C. After contact periods of 6, 12 and 24 h and 3, 5, 8, 12 and 15 days, the contents of each beaker were transferred to a corresponding holding beaker. Each test beaker was rinsed seven times with either deionized water (for aqueous solutions), pure MIBK (for metal—APDC—MIBK solutions), or pure ethyl propionate (for metal—mixed ligand solutions), and then dried and counted. Throughout the experiment the same corresponding holding beaker was used.

To calculate the percentage of metal ions adsorbed on the beakers, it was necessary to determine the total activity of the respective 100-ml test solutions prepared at the beginning of the experiment. To do this the normal contact area of each test solution had to be simulated. This was achieved by uniformly adding 5 ml of each standard solution to filter paper and carefully evaporating to dryness. The filter paper was cut into a strip 25 cm long and 2.8 cm wide and into a disc 5.5 cm in diameter. The paper was fixed with double-stick Scotch tape to the inside of the beaker. Standards were prepared for each variable studied by following the above procedure and these standards were always counted before the test beakers.

The percentage adsorption for each solution was then calculated from the formula:

$$\text{Percentage adsorption} = \frac{B}{20A} \times 100$$

where B is the total activity (c.p.m.) adsorbed on the test beaker and A is the total count obtained by adding 5 ml of the standard solution to the filter paper.

All beakers were counted by inverting the beakers on top of the crystal which was housed in a lead castle. Halfway down the length of the crystal, a metal O-ring with an indexing notch was set. By positioning the pouring spout of the beaker in the notch of the O-ring, the same geometrical orientation was obtained for each beaker. Background counts were checked to determine if the crystal had been contaminated inadvertently by any of the beakers.

When the G-M counter was used, the effective area was determined as follows: a 10-μl drop of 1-p.p.m. ^{210}Pb solution was dried on the center of a large inverted Petri dish. The G-M tube was centered above the spot and the counts per min were recorded. The G-M tube was then displaced in 0.5-cm steps along the x- and $-x$-axes and again the c.p.m. were recorded; this procedure was continued until the point was reached where there were no significant counts. By plotting the c.p.m. on the ordinate and the displacement on the abcissa, a Gaussian distribution was obtained from which the effective area of the G-M tube was calculated. By integrating the area under the curve, the efficiency of the G-M detector was calculated to be 43.2 %. The total activity of the 100-ml test solution was determined by evaporating to dryness 10 μl of the solution on the center of each of the beakers and counting the residue. The counts were then multiplied by 10,000 to give the total c.p.m. in 100 ml. The adsorbed activity in each beaker was calculated by the formula:

$$\text{Adsorbed c.p.m.} = \text{Observed c.p.m.} \times \frac{100}{43.2} \times 2.61$$

where 43.2 was the percentage efficiency of counting for that geometry and 2.61 was an area factor (contact area of beaker/effective area).

The percentage of lead adsorbed was then calculated from (Adsorbed c.p.m./Total c.p.m. in 100 ml) × 100.

RESULTS AND DISCUSSION

All of the studies were conducted at a concentration of 1 p.p.m. for the six metals. The aqueous samples were studied at 0.5 % nitric acid (EPA recommendation), and at pH levels near 3 and 7. The percentages of metals adsorbed on the surfaces of container materials during a period of 15 days are shown in Tables 1, 2 and 3. The stabilities of the metal—mixed ligand solutions and the metal—APDC—MIBK solutions are shown in Tables 4 and 5, respectively. It is evident from Table 1 that metal ions in water samples with 0.5 HNO_3 acidity are generally stable against adsorption. However, it is interesting to note that there was some adsorption of lead in the polyethylene beaker. From Table 4 it is clear that the metal—mixed ligand complex solutions were remarkably stable over the period of the study and thus the concentrated and extracted complexes are recommended for stabilizing and storing the metal ions from water samples. The metal—APDC complexes, however, behaved rather strangely. In some instances, such as for zinc and cadmium, in flint beakers losses may reach as much as 95 %. This loss may be due solely to adsorption or there may be some other associated phenomena responsible. It is quite possible that the reagent or the metal—APDC complexes are not stable and that slow decomposition of the APDC liberated sulfide ions which precipitated the metal sulfides.

There are some interesting trends and anomalies in the Tables. In general, adsorption increases as the pH increases. But in the case of lead, the Pyrex beakers with solutions at pH 3.10 showed more adsorption that at pH 7.10.

TABLE 1

Percentage adsorption of Ba, Be, Cd, Pb, Mn and Zn solutions containing 0.5 % HNO_3 on storage in Pyrex, flint and polyethylene containers

Time	Pyrex			Flint			Polyethylene		
	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
6 h	0.05	0	0.06	0.11	0	0.24	0.01	0	2.01
12 h	0.05	0	0.13	0.11	0	0.25	0.02	0	2.12
1 d	0.05	0.05	0.16	0.10	0.04	0.27	0.02	0.05	2.14
3 d	0.07	0.06	0.32	0.10	0.08	0.47	0.03	0.05	3.28
5 d	0.07	0.08	0.42	0.12	0.08	0.49	0.04	0.06	3.23
8 d	0.07	0.08	0.56	0.12	0.08	0.56	0.09	0.07	3.33
12 d	0.07	0.09	0.62	0.13	0.10	0.85	0.09	0.09	3.31
15 d	0.07	0.10	0.72	0.16	0.12	0.71	0.11	0.10	3.20

Time	Pyrex			Flint			Polyethylene		
	Mn	Be	Ba	Mn	Be	Ba	Mn	Be	Ba
6 h	0	0	0.03	0	0	0	0	0	0
12 h	0	0	0	0.03	6	6	0	0	0
1 d	0	0	0	0.05	0	0	0	0	0
3 d	0	0	0	0.02	0	0	0	0	0
5 d	0	0	0	0	0	0	0	0	0
8 d	0.023	0	0	0	0	0	0	0	0
12 d	0.026	0	0	0	0	0	0	0	0
15 d	0	0	0	0	0	0	0	0	0

TABLE 2

Percentage adsorption of Ba, Be, Cd, Pb, Mn and Zn solutions at pH 3[a] on storage in Pyrex, flint and polyethylene containers

Time	Pyrex			Flint			Polyethylene		
	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
6 h	0.05	0	1.3	0.10	0	2.57	0.02	0	4.91
12 h	0.06	0.05	1.6	0.10	0	2.72	0.02	0	5.08
1 d	0.06	0.08	2.15	0.10	0.02	2.87	0.03	0.02	4.92
3 d	0.06	0.09	3.67	0.11	0.11	5.53	0.03	0.02	8.0
5 d	0.07	0.10	3.43	0.11	0.14	9.09	0.03	0.02	8.17
8 d	0.12	0.10	7.15	0.11	0.14	13.20	0.05	0.02	9.11
12 d	0.12	0.13	17.91	0.14	0.14	11.55	0.05	0.03	12.24
15 d	0.14	0.14	21.48	0.15	0.15	10.98	0.06	0.03	9.76

Time	Pyrex			Flint			Polyethylene		
	Mn	Be	Ba	Mn	Be	Ba	Mn	Be	Ba
6 h	0		0.066	0.11		1.49	0		0
12 h			0.062	0.06		1.78	0		0
1 d	Less		0.043	0.15	Less	1.99	0	Less	0
3 d	than		0.093	0.10	than	2.08	0	than	0
5 d	0.01 %		0.06	0.09	0.01 %	2.07	0	0.01 %	0
8 d			0	0.15		1.96	0		0
12 d			0	0.15		1.94	0		0
15 d			0	0.10		1.88	0		0

[a] Zn solution at pH = 3.10; Mn solution at pH = 3.15;
Cd solution at pH = 3.05; Be solution at pH = 3.17;
Pb solution at pH = 3.10; Ba solution at pH = 3.55.

TABLE 3

Percentage adsorption of Ba, Be, Cd, Pb, Mn and Zn solutions at pH 7[a] on storage in Pyrex, flint and polyethylene containers

Time	Pyrex			Flint			Polyethylene		
	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
6 h	0.23	0.07	3.10	2.37	0.19	5.36	0.28	0.02	2.20
12 h	0.28	0.19	3.37	2.70	0.37	6.83	0.31	0.46	2.81
1 d	0.31	0.39	4.04	4.33	1.15	6.90	0.34	0.47	3.22
3 d	0.45	0.46	7.95	4.59	1.18	14.22	0.34	0.51	7.90
5 d	0.63	0.46	9.07	4.95	1.31	18.67	0.38	0.56	11.26
8 d	0.79	0.51	10.99	5.02	1.42	21.82	0.49	0.54	14.32
12 d	0.94	0.61	13.96	5.25	1.72	23.54	0.53	0.62	16.49
15 d	1.27	0.60	15.32	6.46	1.80	23.09	0.56	0.67	16.68

TABLE 3 (continued)

Time	Pyrex			Flint			Polyethylene		
	Mn	Be	Ba	Mn	Be	Ba	Mn	Be	Ba
6 h	0.06	0.23	0.37	0.98	4.18	5.90	0.04	3.45	0.05
12 h	0.08	0.49	0.32	1.06	4.73	5.96	0.05	5.64	0.05
1 d	0.09	0.60	0.39	1.16	5.71	6.04	0.06	8.22	0.08
3 d	0.11	1.21	0.39	1.12	8.40	6.44	0.06	14.34	0.07
5 d	0.15	1.52	0.23	1.07	10.09	6.98	0.08	16.67	0.09
8 d	0.16	1.48	0.27	1.26	9.36	6.86	0.09	17.00	0.10
12 d	0.10	1.78	0.31	1.17	10.24	7.60	0.11	19.17	0.10
15 d	0.12	2.02	0.34	1.20	9.04	7.89	0.11	16.65	0.12

[a] Zn solution at pH = 6.85; Mn solution at pH = 6.92;
Cd solution at pH = 7.15; Be solution at pH = 6.92;
Pb solution at pH = 7.10; Ba solution at pH = 6.97.

TABLE 4

Percentage adsorption of Be, Cd, Pb and Zn—mixed ligand complexes in ethyl propionate on storage in Pyrex, flint and polyethylene containers[a]

Time	Pyrex			Flint			Polyethylene		
	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
6 h	0.00	0.00	0.00	0.02	0.00	0.00	0.04	0.00	0.00
12 h	0.00	0.00	0.00	0.02	0.00	0.00	0.04	0.00	0.00
1 d	0.02	0.00	0.00	0.02	0.00	0.00	0.04	0.00	0.00
3 d	0.02	0.00	0.01	0.02	0.00	0.00	0.04	0.00	0.02
5 d	0.02	0.02	0.03	0.02	0.01	0.02	0.04	0.04	0.02
8 d	0.07	0.03	0.06	0.05	0.02	0.02	0.10	0.04	0.03
12 d	0.08	0.04	0.06	0.06	0.04	0.03	0.11	0.05	0.03
15 d	0.08	0.04	0.05	0.08	0.05	0.05	0.13	0.05	0.03

Time	Pyrex	Flint	Polyethylene
	Be	Be	Be
6 h	0	Less than 0.01 %	0.12
12 h	0		0.44
1 d	0		0.82
3 d	0		1.13
5 d	0		1.14
8 d	0		1.44
12 d	0		1.76
15 d	0		2.12

[a] Mn and Ba are not quantitatively extracted by this procedure.

Also, in the case of zinc, the trends of adsorption on all three surfaces at all three pH levels were similar except at pH 6.85 in the flint beaker where there was an abnormally high loss. Such anomalies can only be explained

TABLE 5

Percentage adsorption of Zn, Cd, Pb and Mn—APDC complexes in MIBK on storage in Pyrex, flint and polyethylene containers

Time	Pyrex			Flint			Polyethylene		
	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
6 h	0	0	0	0	0	0	0	0	0
12 h	0	0	0	0	0	0	0	0	0
1 d	60.1	11.7	0.8	73.3	44.6	1.19	53.1	15.8	0.55
3 d	66.2	14.8	41.11	81.1	57.1	20.41	60.97	19.1	28.63
5 d	72.6	47.6	51.07	85.1	65.7	43.05	66.2	20.9	38.83
8 d	73.7	49.9	50.17	85.8	81.3	43.72	66.6	24.3	41.86
12 d	76.9	52.8	49.21	94.4	95.0	47.96	74.1	31.8	40.25
15 d	8.5	59.5	54.07	95.3	95.7	47.75	74.87	36.3	42.66

Time	Pyrex	Flint	Polyethylene
	Mn	Mn	Mn
6 h	4.1	8.18	0.94
12 h	6.8	14.97	1.39
1 d	18.05	44.03	3.96
3 d	57.70	66.70	27.40
5 d	66.72	69.27	26.33
8 d	70.17	72.34	26.84
12 d	71.52	71.97	24.51
15 d	75.49	73.62	23.23

by assuming some abnormally active sites of adsorption on those particular beakers chosen for the study. For the same reason, the numbers in the Tables should be used as only general indicators rather than as absolute values. Also, in the calculation of the percentage adsorbed, the tacit assumption was made that the metal ions were adsorbed uniformly over the contact area. In actuality, this is not the case as has been proved previously [1, 6] by autoradiography of the adsorbed metals.

In conclusion, the following observations are in order from this study.

(1) The EPA recommended method of stabilizing the metal ions (Pb, Cd, Zn, Ba, Be, Mn) by adding 5 ml of nitric acid to 1 l of water sample is valid.

(2) An alternative method for stabilizing and concentrating the metal ions in water samples by extracting them with the mixed ligand system (except for Mn and Ba which are not quantitatively extracted by this procedure) can be recommended.

(3) Unless analyzed immediately, the APDC—MIBK system is not stable against adsorption losses and should not be used when storing metal ions.

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Short Communication

THE DETERMINATION OF GOLD IN ORES BY ATOMIC ABSORPTION SPECTROMETRY AFTER CHROMATOGRAPHIC SEPARATION

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(Received 23rd December 1975)

Many methods have been described for the determination of gold by atomic absorption spectrometry with methyl isobutyl ketone as preconcentration agent [1–8]. Gold(III) chloride in acetone–hydrochloric acid solution has been determined spectrophotometrically by Fritz and Millen [9]. This communication describes the determination of gold in acetone medium by atomic absorption spectrometry. The sensitivity is comparable to that obtained with the use of MIBK; the determination is free from interference if gold(III) chloride is separated from other elements with Amberlite XAD-7 resin.

Experimental

Reagents. All reagents were of analytical grade unless otherwise stated.

For the acetone–1 M hydrochloric acid solution, mix 4 volumes of reagent-grade acetone with 1 volume of aqueous 1 M hydrochloric acid.

Gold(III) chloride solution in 1 M HCl containing 1 mg Au ml^{-1} (BDH; for atomic absorption) was used, from which working solutions containing 0.1–5.0 p.p.m. of gold(III) in acetone–1 M hydrochloric acid were prepared.

Gold ores were kindly donated by National Institute for Metallurgy, Johannesburg, South Africa.

Apparatus. A Perkin-Elmer 290B atomic absorption spectrophotometer with a three-slot burner and a cathodeon hollow-cathode gold lamp was used. The operating conditions specified in the instrument manual were followed, except that the flow-meter settings for acetylene and air were adjusted to 14.00 and 11.80, respectively.

Digestion of samples. For gold levels of 0–10 p.p.m. use 10.0-g samples; if more than 10 p.p.m. of gold is present, use 5.0-g samples. Weigh the finely ground sample (325-mesh) into a 150-ml beaker, add 80 ml of aqua regia, cover the beaker with a watch glass, and digest on a hot plate to near dryness. Add 10 ml of 12 M hydrochloric acid and dilute to 150 ml with demineralized water. Filter the solution and wash the residue twice with 20 ml of 1 M hydrochloric acid. It is not necessary to remove nitrogen oxides by repeated evaporation with hydrochloric acid, and the acidity need not be exact as Amberlite XAD-7 resin absorbs gold from a wide range of acid concentrations [9].

Separation of gold. The pre-treatment of the resin was adapted from the method of Fritz and Millen [9]; add a slurry of Amberlite XAD-7 resin in 1 M hydrochloric acid to the glass column [10] to give a 30-mm resin bed supported by a plug of glass wool. Pass the solution through the column at 5 ml min^{-1}, and wash the column with 20 ml of 1 M hydrochloric acid to remove the base metals. Elute the gold with 20 ml of acetone—1 M hydrochloric acid at 2 ml min^{-1}. Collect the eluate in a 25-ml volumetric flask and adjust to the mark with acetone—1 M hydrochloric acid to obtain the solution for spectrometry.

Results and discussion

In preliminary experiments, the effect of solutions containing 70—100 % of acetone in 1 M hydrochloric acid was studied to check the recovery of gold from Amberlite XAD-7 resin. The gold was recovered quantitatively with all these solutions, but with acetone concentrations of 85—100 %, gas bubbles formed in the column.

The effect of acetone concentration on the sensitivity of the determinatio was studied. Solutions of gold(III) (5.0 p.p.m.) in acetone—1 M hydrochloric acid mixtures containing 10—100 % of acetone were prepared. The appropriate acetone concentrations in 1 M hydrochloric acid were used as blanks. Figure 1 shows the absorbance readings plotted against acetone concentrations. The effect of hydrochloric acid concentration was also studied. Solutions containing 2.0 p.p.m. of gold(III) in 4 volumes of acetone, plus 1 volume of acid ranging from 0.1 M—6.0 M, were prepared. The absorbance readings were constant in all cases. Attempts to increase the sensitivity by evaporating the eluate to dryness and redissolving it in acetone were unsucce ful because colloidal gold formed during the evaporation.

Interferences in the separation and determination of gold. The effect of matrix constituents was also studied. Ore samples were digested as described and the solutions were spiked with 10 μg of ^{198}AuCl$_3$. The uptake was calculated by measuring the activity of the solution before and after passage through the column. The uptake and recovery were greater than 99 %. The ores contained up to 30 % of iron, 0.1 % of copper, and 0.17 % of nickel.

The purity of the gold(III) chloride in the eluate was checked by neutron activation analysis [11]. The eluate was counted in a multi-channel analyser; the only peak observed was that of gold-198 at 0.412 MeV, although Cu, Ni, Zn, Fe, W, Co, Cr, As, Ag and Sc were present in the ores.

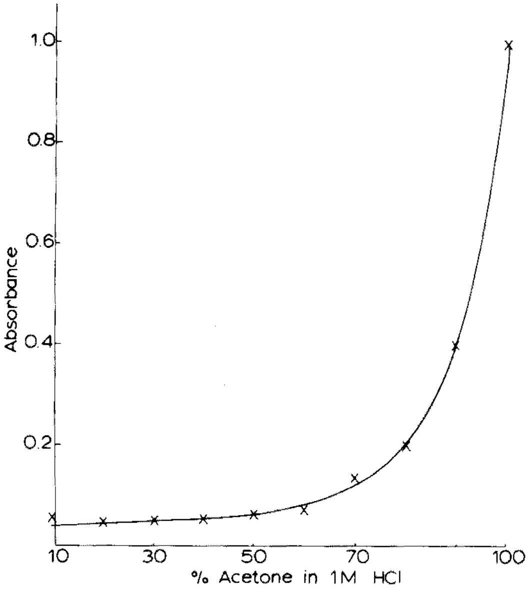

Fig. 1. Effect of acetone concentrations on the absorbance of 5.0 p.p.m. gold(III) chloride.

The interference of base metals on the proposed determination was studied by adding known amounts of iron, copper, nickel, zinc and cobalt to a solution of gold(III) chloride in acetone—1 M HCl. Even without separation on XAD-7 resin, high concentrations of base metals could be tolerated (Table 1).

This method is sensitive to variations in the acetone concentration (Fig. 1). The first 5 ml of the eluate contains the residual acid left in the column after washing and must be discarded. The blank absorbances were unaffected by the acetone concentration.

Accuracy, precision and sensitivity. The proposed method was used to analyse the standard reference gold ore MA-1 (Canadian Centre for Mineral and Energy Technology) with a certified value of 17.8 p.p.m. of gold. The result from four determinations was 18.05 ± 0.62 p.p.m. with a relative standard deviation of 3.4 %. The accuracy and precision of this method are therefore similar to those of established techniques. The sensitivity (for 1 % absorption) of the method was found to be 0.1 μg Au ml^{-1}.

Conclusion

The method described is reasonably simple and straightforward. The concentration factor can be increased by decreasing the flow-rate of the eluate to give a smaller volume of eluate. The Amberlite XAD-7 resin can be used repeatedly; its efficiency was unchanged after regular use for 8 weeks.

TABLE 1

The effect of possible interfering elements on the determination of gold in acetone—1 M HCl solution

Ions	Amount added (μg)	$AuCl_3$ added (μg)	$AuCl_3$ found (μg)	Difference %
Zn^{2+}	50,000	200	192	−4.0
	50,000	500	475	−5.0
Cu^{2+}	100,000	200	201	+0.5
	100,000	500	493	−1.4
Fe^{3+}	100,000	200	178	−11.0
	100,000	500	483	−3.4
Co^{2+}	50,000	200	195	−2.5
	50,000	500	473	−5.4
Ni^{2+}	50,000	200	197	−1.5
	50,000	500	448	−10.4
All	[a]	200	175	−12.5
	[a]	500	437	−12.6

[a] Combination of all the ions added in the amounts shown above.

The accuracy, precision and sensitivity of the method are comparable with those of established atomic absorption methods.

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Short Communication

INTRAMOLECULAR HYDROGEN BONDING IN SOME SUBSTITUTED ARYLSULFONATES

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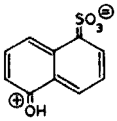
The sulfonate group occurs widely in aromatic compounds, where it is often introduced to enhance solubility. Many analytical reagents, especially colorimetric and fluorimetric reagents, rely on the solubility imparted by the sulfonate group, to optimize their analytical utility.

Although it is well known that the sulfonate group is slightly electron-withdrawing, in the resonance sense, and may therefore influence the analytical parameters of reagents by lowering pK_a or by raising the oxidation potential of amino or hydroxy groups, very little information appears to be available concerning the effects of proximity of sulfonate groups to other functional groups on substituted arylsulfonates. The protons of acidic functional groups, for example, should be capable of entering into intramolecular hydrogen-bonded interactions with the sulfonate group, if the molecular geometry is appropriate. These interactions may influence the analytical as well as the physical behavior of the sulfonated materials.

Our interest in the hydrogen-bonding properties of arylsulfonates arose when, during the course of spectroscopic investigations of these compounds, it became apparent that the pK_a values of 8-substituted 1-naphthalenesulfonates were higher than those of the 5-substituted 1-naphthalenesulfonates. The spectrophotometrically determined pK_a values of some substituted 1-naphthalenesulfonates (Pfaltz and Bauer, Inc., Flushing, N.Y.) are presented in Table 1 along with the pK_a values of the corresponding unsulfonated compounds, taken from the literature.

The hydroxynaphthalenesulfonates studied here are all sulfonated derivatives of 1-naphthol. In the 5-hydroxy (I) and 4-hydroxy (II) compounds, intramolecular hydrogen bonding between the $-OH$ and $-SO_3^-$ groups is impossible and the sulfonate group therefore exerts its influence by induction and electromerization. The pK_a of the 5-hydroxy isomer is only slightly lower than that of 1-naphthol while the pK_a of the 4-hydroxy-1-naphthalenesulfonate is appreciably lower. Since both isomers can have direct conjugation between the sulfonate and hydroxy groups, the weaker acidity of the 1,5-derivative relative to that of the 1,4-derivative is probably due to the greater distance through which the electronic effect in the former must be trans-



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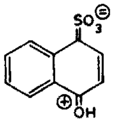

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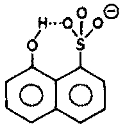

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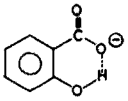


IV

mitted. In 8-hydroxy-1-naphthalenesulfonate (III) the acidity is clearly several orders of magnitude lower than in 1-naphthol, an observation which is explicable only if a moderately strong attractive association between the hydroxylic proton and the sulfonate group stabilizes the singly charged anion (conjugate acid). This is suggestive of an intramolecular hydrogen bond of strength comparable to that involving the phenolic proton [5] in the singly charged salicylate anion (IV).

It is interesting that in 8-hydroxy-1-naphthalenesulfonate the proposed hydrogen-bond is part of a 7-membered ring. Moreover, framework molecular models indicate that because of the large size of the sulfur atom, the orbital overlap of the hydroxyl hydrogen atom and the 2 sp^3 lone-pair electrons of the oxygen atoms of the sulfonate group is very poor if the hydrogen bond lies in the plane of the aromatic ring. This would amount to an intramolecular ion—dipole interaction and would not possess the additional stability derived from the covalent aspect of hydrogen bonding. Consequently, it is proposed that the hydrogen bond between the 8-hydroxy group and the 1-sulfonate group has its axis out of the plane of the naphthalene ring.

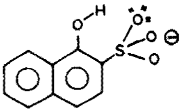
In 1-hydroxy-2-naphthalenesulfonate (V), the pK_a is very slightly lower than that of 1-naphthol. However, the proximity of the hydroxy and

TABLE 1

pK_a values (determined spectrophotometrically) of some naphthylaminesulfonates, naphtholsulfonates, and quinolinesulfonates. (Each pK_a value is the average of 6 points in the spectrophotometric titration.)

Acid	Wavelength (nm)	pK_a
8-Hydroxy-1-naphthalenesulfonate	364	12.83 ± 0.05
5-Hydroxy-1-naphthalenesulfonate	352	9.31 ± 0.03
4-Hydroxy-1-naphthalenesulfonate	299	8.10 ± 0.03
1-Hydroxy-2-naphthalenesulfonate	314	9.32 ± 0.04
8-Ammonium-1-naphthalenesulfonate	335	4.90 ± 0.05
5-Ammonium-1-naphthalenesulfonate	330	3.72 ± 0.05
Quinoline-8-sulfonate	312	3.87 ± 0.07
Isoquinolinium-5-sulfonate	332	4.50 ± 0.05
1-Naphthol		9.39 [1]
1-Naphthylamine		3.90 [2]
Quinoline		4.94 [3]
Isoquinoline		5.40 [4]

sulfonate groups, as well as the possibility of *ortho* conjugation between them, suggests that in the absence of direct interactions between the two groups, the pK_a of the 1,2-derivative should be at least as acidic as that of 4-hydroxy-1-naphthalenesulfonate. That this is not so suggests a direct attractive interaction between the hydroxy and sulfonate groups, although not as strong an interaction as in the 1,8-isomer. Framework molecular models, in this case, indicate that the closest approach between the sulfonate oxygen atoms and the hydroxyl hydrogen atom occurs when the axis between the two is in the plane of the naphthalene ring. However, σ-overlap along this axis, although better than in any other conformation, is poor. This also is related to the large size of the sulfur atom. Consequently, it is proposed that in 1-hydroxy-2-naphthalenesulfonate the hydroxy and sulfonate groups enter into a very weak intramolecular hydrogen bond or ion-dipole interaction whose axis lies in the plane of the naphthalene ring.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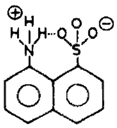
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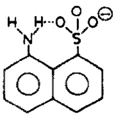
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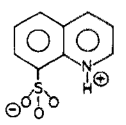
VIII

The 5-ammonium derivative (protonated 5-amino derivative) of 1-naphthalenesulfonate (VI) is very slightly more acidic than 1-naphthylamine. However, the 8-ammonium derivative is about an order of magnitude less acidic. As in the case of the corresponding hydroxy derivative, this can be explained on the basis of an intramolecular hydrogen bond lying out of the plane of the ring. The reason that the acidity of the 8-ammonium derivative is not diminished as much relative to 1-naphthylamine, as the 8-hydroxy derivative is relative to 1-naphthol, is readily understood if it is considered that in the conjugate base of the ammonium compound there is also a stabilizing (albeit weaker) intramolecular hydrogen bond, so that the stabilization of the ammonium ion relative to its conjugate base is weaker than the stabilization of the hydroxy derivative relative to its conjugate base.

Isoquinolinium-5-sulfonate has no possibilities for intramolecular hydrogen bonding. The pK_a is almost an order of magnitude more acidic than that of the unsubstituted isoquinolinium ion. Similarly, quinolinium-8-sulfonate, which does have the proper positioning with respect to the aromatic ring for hydrogen-bonding to occur between the sulfonate group and the proton of the protonated heterocyclic nitrogen atom, is more than an order of magnitude more acidic than the quinolinium ion. By comparison, quinoline-8-carboxylic acid [6] and its protonated methyl ester have pK_a values which are greater than that of the quinolinium ion and anomalously very high compared to the pK_a values of other quinoline carboxylic acids and esters. These results clearly indicate intramolecular hydrogen bonding in the 8-carboxy derivatives of quinoline and appear to abnegate the likelihood of such a phenomenon being extant, to an appreciable extent, in quinolinium-

8-sulfonate. Why this is so, is also clearly seen to be the result of the large size of the sulfur atom of the SO_3^- group. This prevents close approach and therefore strong interaction between the $-SO_3^-$ group and the hydrogen atom of the protonated heterocyclic group.

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Short Communication

THE ENHANCEMENT OF THE FLUORESCENCE OF FLUORESCAMINE DERIVATIVES IN MIXED DIMETHYLSULFOXIDE—WATER SOLVENTS

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Fluorescamine is a useful and versatile reagent for the rapid sensitive determination of primary amines [1]. The reagent reacts rapidly with a wide variety of species, including amino acids [2], peptides [3] and drugs [4, 5] to form fluorescent derivatives which are quite stable, while the reagent and its hydrolysis products do not fluoresce.

The choice of experimental conditions for the formation of the derivatives and the measurement of the luminescence poses problems when aqueous samples must be analyzed. The hydrolysis of fluorescamine competes with the formation of the desired fluorophore; this problem is usually overcome by the use of an excess of the reagent in an aprotic solvent. The fluorescence of various compounds, including tyrosine [6] and tryptophan [7] is higher in mixed aqueous solvents, e.g. 20 % methanol—80 % water, than in pure water. It is believed that water takes part in an additional energy-wasting process with the excited state to form an excited-state complex. The formation of this complex reduces the fluorescence quantum yield and decreases the sensitivity of the assay.

However, the removal of water from samples is usually not a viable procedure for routine analyses, and the buffer systems necessary for the reaction are aqueous. Since the fluorescamine procedure is quite useful, improvements would be of interest. A study of the effect of aqueous solvent systems containing dimethylsulfoxide (DMSO) on the fluorescence intensity of some fluorescamine derivatives is reported below.

Experimental

Amino acids and peptides (Sigma Chemical Co.), n-hexylamine and aniline (Chem-Service Inc., West Chester, Pa.), fluorescamine (Roche Diagnostics, Hoffman-La Roche), and dimethylsulfoxide and acetone (ACS reagent; Fisher Scientific Co.) were used as received.

An Aminco-Bowman spectrophotofluorimeter (American Instrument Co.) equipped with a Hamamatsu 1P21 photomultiplier and a Hanovia 901C mercury—xenon arc, was used at a constant excitation wavelength of 390 nm. The fluorescence was measured at the λ_{max} of each derivative, as discussed below.

A stock solution of fluorescamine (30 mg/100 ml) in acetone was permitted to age for 24 h as suggested by de Silva and Strojny [5]. A similar solution in DMSO was also permitted to age.

Fluorescamine derivatives were prepared by mixing one volume of the sample ($1.0 \cdot 10^{-4}$ M for amino acids and amine hydrochlorides; $1.0 \cdot 10^{-3}$ g l^{-1} for peptides) with one volume of 0.05 M NaH_2PO_4 (pH 8.50) and then with one volume of the fluorescamine solution in the appropriate solvent. The tubes were shaken on a Vortex Mixer during the addition of the fluorescamine and for 30 s thereafter. An aliquot (0.3 ml) of this mixture was mixed with additional phosphate solution and aprotic solvent to prepare 5.0 ml of the desired solution.

Results and discussion

The effect of the composition of the mixed DMSO—water solvents on the fluorescence of the tryptophan, alanine and albumin derivatives may be seen in Fig. 1. The trends shown were also observed for derivatives of several amino acids, primary amines and peptides (Table 1), and seem to be quite general. Thus where possible, the fluorescence of fluorescamine derivatives should be measured in solutions containing 30—50 % DMSO, rather than in a system containing only water (and the small amount of acetone used as solvent for the reagent). The fluorescamine derivatives of alanine (Fig. 1) and phenylalanine exhibited a higher fluorescence intensity in 50 % DMSO—50 % water than in 70 % DMSO—30 % water. Possibly an intensity maximum occurs for most fluorescamine derivatives at some concentration of DMSO, and this concentration must be found to obtain maximum sensitivity.

The wavelength of maximum emission of the fluorescamine derivatives shifted slightly towards the blue as the solvent became less aqueous. This

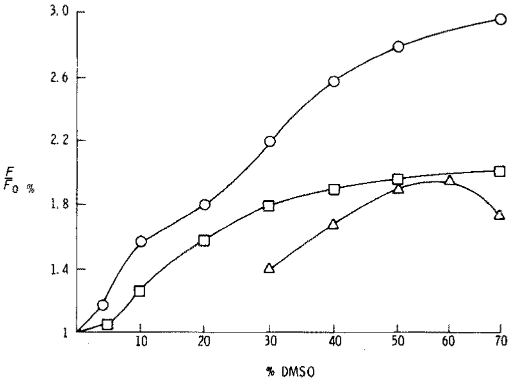

Fig. 1. Luminescence of fluorescamine derivatives as a function of solvent composition. $F/F_{0\%}$ refers to the fluorescence intensity of the sample compared to a completely aqueous solution. □, Albumin; ○, Tryptophan; △, Alanine.

TABLE 1

Relative fluorescence intensity of fluorescamine derivatives in various mixed solvents^a

	Aprotic solvent			Aprotic solvent	
	30 %	50 %		30 %	50 %
Alanine^b	1.38	1.88	Aniline^c	3.2	2.9
Albumin^b	1.36	1.94	Benzylamine^c	1.7	1.1
Aniline^b	1.73	2.33	n-Butylamine^c	2.2	2.2
Chymotrypsin^b	1.28	1.48	Glycine ethyl ester^c	0.6	0.3
Glycine^b	1.58	2.17	β-(3,4-Dimethoxy-phenylethylamine^c	1.4	1.5
n-Hexylamine^b	1.94	2.47			
Histone^b	1.39	1.79	Leu—Ala^c	1.1	0.9
Leucine^b	1.30	1.77	Pentaglycine^c	1.0	0.8
Isoleucine^b	1.39	1.84	Isoleucine^d	1.3	1.4
Phenylalanine^b	1.75	2.32			
Tryptophan^b	1.98	2.77			
Serine^b	1.39	2.02			

[a] Fluorescence intensity with respect to the fluorescence of that derivative in neat water. All data from duplicate results.

[b] This work; aprotic solvent is DMSO.

[c] From ref. 9; aprotic solvent is acetone.

[d] From ref. 8; aprotic solvent is ethanol. Data extrapolated from table, assuming linear relationship between intensity and concentration, which may not be totally valid for the 50 % entry.

shift was approximately 4 nm as the solvent was changed from pure water to 50 % DMSO—50 % water, and has also been observed in ethanol—water systems [8] and acetone—water systems [9].

DMSO has been suggested as a useful solvent for fluorescamine [9]. In the present work, the fluorescamine derivative of tryptophan was prepared with the reagent in either acetone or DMSO. Table 2 shows that acetone is the better solvent, possibly because of its low viscosity (η = 0.30 cP) compared to that of water (η = 0.89 cP) or DMSO (η = 1.96 cP).

The use of less aqueous solvent systems for the detection of fluorescamine derivatives has been considered previously. The isoleucine derivative exhibits a higher fluorescence intensity in ethanol—water mixtures than in pure water [8], but the observed increment is greater in DMSO—water mixtures. Mixed acetone—water solvents also improve the fluorescence intensities (compared to pure water) for some derivatives [9], but the effect on other derivatives is small or even negative (see Table 1). The present work shows that acetone indeed increases the fluorescence intensity of the tryptophan derivative although this increase is less than that found with DMSO (Table 2).

The increase in luminescence of fluorescamine derivatives in DMSO—water mixtures compared to acetone—water mixtures is probably most useful in the detection of peptides (see Table 1), but the results indicate that the use

TABLE 2

Luminescence of the fluorescamine derivative of tryptophan formed in various solvents and detected in various solvents

Solvent for reagent	Solvent for detection	R.F.I.[a]
Acetone	H_2O	1.00
Acetone	50 % DMSO	2.77
Acetone	50 % Acetone	2.23
DMSO	H_2O	0.81
DMSO	50 % DMSO	2.31
DMSO	50 % Acetone	1.36

[a]The relative fluorescence intensity of the solution compared to a solution prepared from the fluorogenic reagent in acetone and diluted with water. All data from duplicate results.

of DMSO—water solvents should be considered generally to enhance the sensitivity of the assay.

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Short Communication

BORON TRIOXIDE–LITHIUM CARBONATE (10:1) AS A FLUX IN SILICATE ANALYSIS

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The analysis of silicate minerals and rocks for major and many minor elements is very important in geochemistry, petrology and ceramics. The method of decomposition selected depends on the nature of the material, the purpose of the analysis and the analytical procedure to be used. Particularly powerful fluxes are needed to decompose completely some refractory mineral constituents of rocks, such as andalusite ($Al_2O_3 \cdot SiO_2$), kyanite ($Al_2O_3 \cdot SiO_2$), sillimanite ($Al_2O_3 \cdot SiO_2$), corundum (Al_2O_3), tourmaline (borosilicate of Fe, Al, Mg, Cr, Li, K, Na), rutile (TiO_2), garnet ($3(Ca, Fe, Mn, Mg)O \cdot (Al, Fe, Cr, Ti)_3 \cdot 3SiO_2$), staurolite ($HFeAl_5Si_2O_{13}$), zircon ($ZrSiO_4$) and spinel ($MgAl_2O_4$).

The method of decomposition should be reasonably simple and rapid and should not attack the vessel used for treatment. Moreover, the constituent sought should not be lost, nor should the constituent to be determined or any interfering substance be introduced; large amounts of even relatively inert salts are usually undesirable.

The present communication deals with the use of boron trioxide–lithium carbonate in a 10:1 ratio as a flux in silicate analysis. Boron trioxide is well known as a very powerful flux for oxides, silicates and refractory minerals of all kinds [1], and it is excellent for silicate analysis because no cationic species are introduced to the sample solution. Recently, Ohlweiler et al. [2, 3] determined silica in silicates after decomposition by fusion with a mixed flux consisting of boron trioxide and lithium carbonate (10 + 1, w/w), the flux–sample weight ratio being 10:1. The addition of lithium carbonate was necessary to improve the depolymerization of silica. Subsequently, this same flux was applied in the determination of potassium in silicates by atomic-absorption spectrometry [4]. The fusion of silicate rocks and minerals with boron trioxide, either alone or associated with lithium carbonate, offers interesting possibilities, but certain difficulties may be encountered in its application. Means of avoiding these difficulties are discussed below. Various refractory minerals were submitted to boron trioxide–lithium carbonate (10:1) fusion. The behavior of sulfate and fluoride in fusions with boron trioxide or boron trioxide–lithium carbonate (10:1) is described.

Experimental

Reagents and equipment. Boron trioxide and lithium carbonate and all other chemicals used were of reagent-grade purity. The ultrasonic generator was the same as described previously [3].

General procedure. Transfer 0.1000—0.3000 g of the finely powdered sample (<200 mesh) to a 30-ml platinum crucible. Add 1.0—3.0 g of boron trioxide; a flux—sample ratio of 10:1 is generally the most satisfactory. For refractory silicates or to simplify complete decomposition of any silicate sample, also add lithium carbonate (a tenth of the weight of boron trioxide taken). Mix intimately with a short glass rod with rounded ends.

Set the crucible on a silica triangle and heat carefully with a small flame until any water is completely expelled. Then, cover the crucible and heat with a strong oxidizing flame (ca. 1000 °C) for 15—30 min until a clear melt is obtained. Remove the Meker burner and allow the crucible to cool to room temperature; the fused mass forms a transparent glass.

Transfer the main part of the dilute acid prepared for dissolving this glass (e.g. 0.015—0.1 M hydrochloric, nitric or perchloric acid) to a suitable beaker; if titanium must be kept in solution, add 1—2 ml of 30 % hydrogen peroxide. Place the platinum crucible in the solution. Rinse the lid of the crucible with a stream of the dilute acid. Put the beaker in the cavitation bath of the ultrasonic generator; usually about 1 min suffices to detach the glass completely from the crucible. Then, place the beaker on a magnetic stirrer. Place a magnetic bar in the liquid, suspend the crucible in the solution (if necessary), cover the beaker and run the stirrer at a convenient rate until dissolution of the glass is complete. Remove and rinse the crucible with the dilute acid. Transfer the solution to a volumetric flask of suitable capacity and dilute to the mark.

Discussion

Fusion conditions. Silicate materials may be decomposed by fusion with boron trioxide alone or with a mixed (10:1) flux of boron trioxide and lithium carbonate, depending on the nature of the samples and the constituents sought. This mixed flux after fusion has the approximate composition 0.09 Li_2O:1 B_2O_3. Fusions should be done in a platinum crucible over an oxidizing Meker flame until a clear melt is obtained; usually 15—30 min of heating suffices. It is very important to reduce the sample to a fine powder (<200 mesh) and to mix the sample thoroughly with the flux; the melt is very viscous and local concentrations of silica disperse slowly. When the decomposition of the sample is complete, the fused mass solidifies on cooling giving a perfectly transparent glass. Higher temperatures and longer fusion times instead of intimate mixing of sample and flux are not recommended.

Many silicate minerals, e.g. feldspar, are completely decomposed by fusing with boron trioxide alone at about 1000 °C for 15 min. Flux—sample ratios may be varied from 10:3 to 10:1, but the latter is generally more reliable. Lower flux—sample ratios may require higher temperature and longer fusion times. With low flux—sample ratios and short fusion times, the resultant opaque mass may not dissolve completely in dilute acids.

The decomposition of refractory silicates was best accomplished by adding a little lithium carbonate. The sample (0.1 g) was fused with a mixture of boron trioxide (1 g) and lithium carbonate (0.1 g) at about 1000 °C for 30 min. With larger samples, the mixed flux must be increased proportionally. This fusion was shown to be effective for refractory minerals such as andalusite, kianite, sillimanite, tourmaline, garnet, staurolite, spinel, corundum and quartz, the fused samples dissolving completely in mineral acids. Fusion with 1 g of boron trioxide and 0.1 g of lithium carbonate was also effective for 0.050-g samples of zircon, as well as for 0.025-g samples of rutile; lower flux—sample ratios gave opaque melts with incomplete decomposition.

The addition of lithium carbonate in these fusions assists the conversion of silica to monosilicic acid, which is necessary in the determination of silica as 12-molybdosilicic acid [2, 3]. As observed by Maesson and Boumans [5], silicate structures may persist after fusion; even when the mineral decomposition appears complete, fragments of the silicon—oxygen crystal framework remain when the glass has been dissolved in dilute acids.

Treatment after fusion. The fusion product is a mechanically strong glass, that cannot be removed readily from the crucible by dissolution in situ. If the hot crucible (covered to avoid loss by fragmentation of the melt) is cooled suddenly by setting it in a dish of ice water, the fused mass will crack or loosen. However, it is better to put the cooled crucible into the solution chosen to dissolve the cake, and then to detach the glass by ultrasonics; in this way, the glass can be removed rapidly without damage to the platinum vessel.

After being detached from the crucible, the transparent glass may be dissolved in dilute mineral acids; the acid and its concentration are chosen according to the subsequent analytical procedure. There must be enough acid to react stoichiometrically with the lithium content in the flux and provide a suitable excess. Hydrogen peroxide may be necessary to convert any titanium to its peroxy complex, thus ensuring that titanium(IV) does not hydrolyze or precipitate possibly as phosphate [3].

The time needed to dissolve the glass by stirring depends on the amount of the sample, the flux—sample ratio, the concentration and volume of the acid, the temperature, etc. The data presented in Table 1 refer to dissolution of the fusion product of a feldspar sample (without crushing) in 1 l of hydrochloric acid at various concentrations. Dissolution accelerates greatly as the acidity is increased. It is little affected when the volume of acid is

TABLE 1

Dissolution of the fusion product

Sample (g)	Flux		HCl (M)	Dissolution time (min)
	B_2O_3(g)	Li_2CO_3(g)		
0.1	1 +	0.1	0.015	60
			0.025	45
			0.025	35
			0.10	20
0.2	1 +	0.1	0.10	45
0.3			0.10	85
0.3	3 +	0.3	0.10	40

reduced to 200 ml, but becomes slower for larger amounts of sample or when lower flux—sample ratios are used. Dissolution can be hastened by using a pre-heated acid solution, and by maintaining the ultrasonic wave until dissolution is complete.

Elimination of fluoride. Elimination of fluoride in fusion with either boron trioxide alone or boron trioxide and lithium carbonate (10:1) was investigated. First, sodium fluoride (10 mg F^-) was fused with 1 g of boron trioxide in an open platinum crucible at 1000 °C for 30 min. Application of the zirconium—alizarin visual comparison method [6] showed that only 95 % of the fluoride was eliminated, i.e. about 0.5 mg of fluoride was retained in the fusion product. Further tests, in which only 1 mg of fluoride was fused with 1 g of B_2O_3, alone or with 0.1 g of Li_2CO_3 added, in a covered crucible, indicated a fluoride loss of only about 25 %. When 0.1 g of feldspar and 1 mg of fluoride were fused with 1 g of B_2O_3 and 0.1 g of Li_2CO_3, the fluoride loss was about 30 %. Presumably, fluoride volatilizes as boron trifluoride, but those assays prove that some fluoride is firmly retained by the flux.

Elimination of sulfate. The elimination of sulfate was also investigated. Potassium sulfate (50 mg) was fused in an open platinum crucible with 1 g of B_2O_3 at 1000 °C for 45 min; determination of sulfate in the resulting melt, by the barium sulfate turbidimetric method, indicated that about 1 % of the sulfate remained in the flux. When 1 g of B_2O_3 and 0.1 g of Li_2CO_3 were used as flux, about 92 % of the sulfate volatilized. Hence, some sulfate is also firmly retained, especially by the mixed flux.

Conclusion

Boron trioxide is a powerful flux for most silicates, but a mixed flux consisting of boron trioxide and lithium carbonate in a 10:1 ratio is more effective and reliable for refractory silicates and other rock-forming minerals. Higher temperatures or longer fusion times are not required for such materials. The glass produced by fusion is easily detached from the crucible with the aid of ultrasonic waves, and is readily soluble in dilute mineral acids.

The mixed flux introduces only a little lithium to the sample solution. Fusion methods that utilize sodium or potassium salts eliminate the possibility of determining one or other of these elements; lithium, however, is less commonly determined. The mixed flux can be useful in silicate analysis by spectrophotometry, flame photometry and atomic-absorption spectrometry. The fact that no cations, other than lithium, are introduced by reagents, eliminates or diminishes significantly chemical, ionization and matrix interferences for atomic absorption measurements. The addition of lithium could be an advantage in atomic absorption methods, as it could serve as an ionization suppressor or general "buffer".

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Book Reviews

David C. Burrell, *Atomic Spectrometric Analysis of Heavy-Metal Pollutants in Water*, Ann Arbor Science Publishers, Michigan, 1974, xi + 331 pp., price £13.00.

In providing information on the nature, level and methods of determination of toxic heavy metals in water, this book represents a compromise which will be useful to both environmental and analytical chemists. The latter will find the information on the occurrence and nature of these metals in water of considerable interest. The sections on atomic spectrometry, sources and detection systems, sample preparation and atomization, and interferences are similar to those found in general text books on this subject, and apart from the section on sample preparation, they are not specifically related to water analysis. Thus the section on interferences does not discuss particular problems found in either heavy metal or water analysis. Recent developments such as the carbon furnace and filament atomizers are described in more detail than in most recent text books on atomic absorption spectrometry. However, few methods based on these techniques are given, and an optimistic hope for the future use of such methods is not tempered by a realistic appraisal of the matrix problems likely to be found in analysis of sea water. Throughout the book, the relationship and respective advantages of atomic emission, absorption and fluorescence are discussed carefully, and this provides useful reading for anyone considering the employment of such techniques. In the final chapter, methods for the determination of mercury, silver, cadmium, lead, arsenic and selenium are reviewed. No detailed procedures are given so that it is impossible to compare the length, accuracy or precision of the methods discussed but atomic spectrometric methods are put carefully into context and compared with other available techniques such as spectrophotometry and anodic stripping voltammetry.

This book could be criticised for its selectivity and lack of detailed consideration of methods designed for the determination of metals in water. However, it does present a well balanced review of both the requirements of the environmentalist and methods by which analytical information can be obtained, and in this context can be recommended.

J. M. Ottaway

E. Schroll, *Analytische Geochemie Band I: Methodik*, Ferdinand Enke Verlag, Stuttgart, 1975, xii + 292 pp., PVC-kart. DM 59,--.

En relation avec, par exemple, l'étude intensive de notre environnement, les sciences de la terre trouvent aujourd'hui une nouvelle voie de développement. A cette évolution, sont intimement liées nos connaissances actuelles de la chimie en général et des méthodes analytiques en particulier. C'est ce qu'Erich Schroll se propose de nous décrire dans son ouvrage "Géochimie Analytique" en 2 volumes, dont le premier, sorti de presse, est consacré à la méthodologie.

En effet, après une courte introduction, l'auteur aborde les problèmes de l'échantillonnage, de l'homogénéisation et de la préparation des échantillons (125 pages), puis décrit les diverses techniques analytiques (150 pages). Les premières techniques traitées sont celles dites par voie humide (méthodes classiques: gravimétrie et titrimétrie; spectrophotométrie d'absorption moléculaire; méthodes électrométriques; spectrophotométrie de flamme et d'absorption atomique). Dans un second groupe sont classées les techniques permettant des déterminations sur des échantillons sous forme solide (spectroscopie d'émission; spectroscopie de fluorescence X; spectrométrie gamma après activation nucléaire; spectrométrie de masse). Chaque méthode est introduite par un rappel des bases théoriques, auquel fait suite une description de l'appareillage actuellement à disposition, avec ses possibilités et ses limites. Des applications pratiques d'analyses terminent chaque chapitre.

L'auteur ne néglige pas l'importance d'une introduction à l'étude de l'évaluation statistique des résultats obtenus (110 pages). Ce chapitre est, lui aussi, illustré par de nombreux exemples qui permettent aux non initiés de se rendre compte de l'intérêt qu'offre l'interprétation des données dans le cadre particulier de la géochimie.

L'ouvrage se termine par une série de tableaux intéressant quelques propriétés des éléments (masse atomique, rayons atomique et ionique, potentiel d'ionisation et électronégativité), la composition élémentaire de divers milieux (sols, eaux, roches), ainsi que les caractéristiques (dénomination et composition) d'échantillons de roches et de minéraux de référence.

Il ne fait aucun doute que ce premier volume permet à tous ceux qui s'intéressent à la géochimie de faire le bilan des possibilités actuelles de la chimie analytique dans ce domaine.

W. Haerdi

Z. Deyl, K. Macek and J. Janak (Eds.), *Liquid Column Chromatography*, Elsevier Scientific Publishing Company, Amsterdam, 1975, xxii + 1176 pp., price Dfl. 290.00; U.S. $120.95.

This massive book (weight 1.2 kg) is Volume 3 in the Journal of Chromatography Library. All but two of its contributors are Czechoslovakian, yet the English style is so fluent and the text so free from minor errors that this publication must be regarded as a triumph for the translators and editors. A detailed table of contents, and adequate subject and author indexes, are essential for a book of this size; those provided are excellent, and it is easy to find what the book does and does not contain.

The book is divided into four main sections — Theoretical Aspects of Chromatography (7 chapters, 94 pp.); Techniques of Liquid Chromatography (4 chapters, 160 pp.); Practice of Liquid Chromatography (6 chapters, 125 pp.); and Applications (39 chapters, about 700 pp.). The applications range from very short chapters on ethers and peroxides and polysaccharides to a quite lengthy chapter on amino acids; in addition to chapters on other common functional groups, there are chapters on pesticides, dyestuffs, pigments, macromolecules and plastics, cells and sub-cellular particles, isotopes, radioactive compounds, and inorganic, coordination and organometallic compounds.

Although the coverage is wide, the depth of treatment is variable; the chapter on organic phosphorus compounds refers to nothing more recent than 1970, while the chapter on pesticides offers 69 references of which 13 are to work published in 1970, 5 refer to 1971, and one to 1972. About half the chapters include the odd references to papers published in 1973 or 1974, but this book rests largely on the 1969—1972 literature. Perhaps it is unreasonable to expect this time-scale to be improved; translations had to be done, the editors' preface is dated April 1974, and the book appeared in mid-1975. The time-scale problem on large edited volumes is well known.

And what of the price? The cost per page is in line with that of other books published recently, and there is evidence that increased proportions of books in the £45—£55 bracket are on their way. But it is difficult, at best, to envisage that many personal purchases will be made at such prices, and the immediate problem for the reviewer is whether this type of publication — excellent in every respect but inevitably a little outdated — can be recommended for library purchase.

D. M. W. Anderson

T. R. Crompton, *Chemical Analysis of Organometallic Compounds*, Academic Press, London, *Vol. 2*, 1974, ix + 163 pp., price £5.00; *Vol. 3*, 1974, x + 211 pp., price £6.50; *Vol. 4*, 1975, x + 302 pp., price £9.40.

The enormous development of organometallic chemistry over the past 25 years has depended very largely on the application of spectroscopic techniques; where elemental analysis is involved, it has all too often been associated merely with the elements carbon and hydrogen, and even with those the presence of certain metals has created difficulties. More recently it has become clear that the use of infrared and n.m.r. spectroscopy by themselves to characterise compounds may lead to misleadingconclusions; this makes the appearance of the volumes in the series "Chemical Analysis of Organometallic Compounds" timely. Analytical chemistry is a title that can be used to cover almost the whole of structural characterisation, from the most qualitative of tests through quantitative conventional analysis to way-out applications of spectroscopy; the volumes discussed here deal exclusively with quantitative analysis, and almost exclusively with elemental analysis, involving decomposition of the compound concerned. The volumes deal with a wide range of elements: lithium, sodium, potassium, copper, silver, gold, iridium and thallium (Vol. 1, 1973); titanium, zirconium, hafnium, thorium and silicon (Vol. 2, 1974); germanium, tin and lead (Vol. 3, 1974); vanadium, niobium, tantalum, palladium (sic), phosphorus, antimony, bismuth and arsenic (Vol. 4, 1975). Some sections are very long: that on phosphorus occupies 233 pages; others are short: the epitome of these is the section in Vol. 5 on vanadium, niobium, tantalum and palladium, which consists of the single sentence "References to the analytical chemistry of organometallic compounds of elements of this group have not been found". Within the longer sections, the author varies the way in which he presents the material. Some analytical procedures are described with a wealth of experimental detail; others are referred to with a few words and a reference. The choice of methods for detailed description is very much a matter of taste, and in my view the author has done pretty well. For someone who has an unusual complex of tin and wants some suggestions for methods of analysing it by fairly conventional techniques, the appropriate volume (in the case of tin, Vol. 3) would certainly be one of his best starting places.

There are two significant weaknesses in these books. The first is a matter of date. Although Vol. 4 appeared in 1975, there are few references in any of the volumes to material published after 1970. This is not a disaster, but it is a little unfortunate, and to some extent it detracts from the usefulness of the treatment. The other disadvantage is perhaps more serious. There is now a very wide range of methods of elemental analysis involving spectroscopic techniques; X-ray fluorescence, ESCA and so on. Infrared and n.m.r. spectroscopy are used analytically in an enormous variety of ways. There is relatively little space in the volumes here devoted to the use of these techniques. The references that are made to infrared spectroscopy vary immensely in level of sophistication and relevance to analytical chemistry. On the one hand, an analytical procedure is described with reference to a Perkin-Elmer 21 infrared spectrometer; nowadays there must be very few Perkin-Elmer 21's outside a science museum. On the other hand, there is a reference to a study of the vibrational spectra of silyl phosphines that includes suggestions about the low-frequency torsional modes, and these can be of absolutely no interest to the quantitative analyst. The trouble is, of course, that a study of the use of even vibrational spectroscopy in the analysis of organometallic compounds would be a multi-volume work. The author has certainly not been misleading in the title he has chosen, but the odd bits of high-flown infrared spectroscopy jar slightly on the reader. The same is true of some of the brief references to n.m.r. spectroscopy; there seems little reason, for instance, why the ^1H n.m.r. spectrum of butyl lithium should be described in any detail.

The reader, therefore, who wants to know about the relationship between spectroscopy and analysis will not find much to help him here. But a person who wants to know how to try to analyse an organometallic compound by a chemical method will certainly find these volumes most helpful. Their compilation must have been a considerable labour, and I am sure that it has been well worth while.

E. A. V. Ebsworth

L. Fishbein, *Chromatography of Environmental Hazards, Vol. III — Pesticides,* Elsevier, Amsterdam, 1975, xii + 820 pp., price Dfl. 260.00, U.S. $108.50.

This, the third of four volumes dealing with the chromatography of environmental hazards, describes the detection, separation and determination of the most important insecticides, acaricides, herbicides, fungicides and growth-retardants, etc. Perhaps the most important types of compounds involved are chlorinated hydrocarbons, cyclodienes, chlorophenoxyacetic acids, chlorophenols, phosphorothioates, phosphorodithioates, carbamates, ureas, triazines and synergists.

This treatise must be regarded as an essential handbook for all chemists concerned with any aspect of analyses for these classes of compound. There is no doubt that the author is justified in his hope that the book will be welcomed by chemists involved in the areas of biochemistry, biology, genetics, pharmacology, etc. The scope of the book, and its comprehensive nature, make it a piece of work that must have proved to be a colossal challenge to its author; many a fainter heart would have readily refused to contemplate such a task. Each chapter ends with an extensive bibliography, and although the coverage is essentially to 1972, references to work published in 1973 and 1974 are not uncommon, and there are many references to journals which are not normally consulted by chemists.

In every respect, the production of this book leaves nothing to be desired. The era of the £50 textbook is now with us; it is still difficult to accept that many individuals will be prepared to pay such an amount personally, but there is no doubt that this book must be recommended, without reservation, to all chemists concerned with pesticides for acquisition by fair means or foul.

D. M. W. Anderson

Energy Transformation in Biological Systems, Ciba Foundation Symposium 31 (New Series), Associated Scientific Publishers, Amsterdam, 1975, x + 416 pp., price Dfl. 70.00, U.S. $29.25.

This book gives the full text of the twenty papers presented at a Symposium held at the Ciba Foundation, London, in July 1974. The remarks made during the discussions after each paper, and during a general discussion at the end of the meeting, are also recorded. The Symposium was held in tribute to

Fritz Lipmann on his 75th birthday, and was a select gathering of international authorities.

Lipmann's opening paper on "the roots of bioenergetics" gives an excellent historical review of the development of this specialized field of study over the past 50 years. It would be invidious to single out any of the other contributions — all appear to have stimulated considerable discussion, upon which the success of a symposium such as this really depends. This is essentially a book for the specialist; its editors, G. E. W. Wolstenholme and D. W. Fitzsimons (whose names are not openly associated with the book), are to be congratulated on an excellent production.

Terence Allen, *Particle Size Measurement, 2nd edn.*, Chapman and Hall, London, 1975, xviii + 454 pp., price £8.50.

The expansion in the knowledge and technique of particle size measurement since the first edition of this book was written in 1968 is reflected in the increased size of the present edition. The coverage is comprehensive, dealing with sampling of powders, dusty gases and the atmosphere, with the basic concepts of particle dimensions, and with sieving and microscopy. The interactions of particles and fluids in a gravitational field, and the dispersion of powders is also discussed. Both incremental and cumulative sedimentation methods of size analysis are described, followed by centrifugal, Coulter counter, scattering, permeability and gas diffusion, gas adsorption, and other methods. Finally, methods of determining pore size distribution are considered. Two appendices give the suppliers (including addresses) of the apparatus described in the text. There is an author index and a (brief) subject index.

The book is well produced and illustrated. The much expanded section on sampling will be valuable to all analysts, and the whole text will be a standard reference work on particle size measurement for the next few years.

Jacques Oudar, *Physics and Chemistry of Surfaces*, Blackie and Son, Glasgow, 1975, xii + 130 pp., price £6.55.

In recent years, the use of physical methods such as ion and field microscopy and electron spectroscopy, has contributed to a new depth of understanding of processes that occur at surfaces. This translation of Professor Oudar's *La Chimie des Surfaces* (1973) provides an excellent survey of recent ideas on gas—solid interfaces. Different aspects of the chemisorption of gases on metals are discussed in 9 chapters; 7 chapters are devoted to the oxidation of metals and alloys. The level of treatment is suitable for undergraduates, but this book can also be recommended to more advanced workers with interests in surface science and catalysis.

M. J. Frazer and R. J. Sleet, *Resource Book on Chemical Education in the United Kingdom,* Heyden and Son, London, 1975, x + 155 pp., price £3.30.

This book provides a guide to chemical education in the United Kingdom. Chapter I gives details of the organizations and institutions concerned with chemical education; address, structure, functions, publications, courses and conferences are listed. Subsequent chapters cover the organization of secondary and tertiary education; new science curricula; teaching, learning and assessment; educational and statistical terminology; the literature on chemical education; and an annotated bibliography. The emphasis is entirely on chemical education, which, distressingly, appears to have little to do with chemistry.

A. Meixner, *Chemisch Farbreaktionen von Pilzen.* J. Cramer, Lehre, Germany, 1975, 286 pp., price DM 29.50.

This paperback describes the chemical colour reactions of fungi of the classes *Ascomycetes* and *Basidiomycetes* with reagents such as α-naphthol, guaiacol tincture and iron sulphate. The bulk of the text (220 pp.) consists of tabulated data on the reactions listed by groups, orders and families.

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AUTHOR INDEX

ANALYTICA CHIMICA ACTA, VOL. 84 (1976)

SUBJECT INDEX

CHROMATOGRAPHY OF ENVIRONMENTAL HAZARDS

by **LAWRENCE FISHBEIN**, Chief, Analytical Division, National Center for Toxicological Research, Jefferson, Arkansas, U.S.A.

To cope with the uparalleled need to determine the parameters of environmental abuse, this four-volume work is designed to provide the analytical chemist with a practical text as well as a literature source of selected descriptive chromatographic procedures. Additional priority is given to those methods that may be utilized in a general sense, beyond the analysis of a specific toxicant **per se.** Toxicants such as pesticides, drugs, food and feed additives, and industrial chemicals are considered within the broader framework of their methods of preparation, areas of utility, biochemistry, metabolism and toxicity, and are thus of importance to additional investigation into other areas such as toxicology, pharmacology, biology, genetics and environmental medicine and health.

Volume 1: Carcinogens, Mutagens and Teratogens

1972. 507 pages. US $ 56.25/Dfl. 135.00. ISBN 0-444-40948-3

This volume centers on toxicants of carcinogenic, mutagenic and teratogenic environmental significance with particular focus on those which are pesticides, food and feed additives, drugs and alkylating agents of industrial utility.

Volume 2: Metals, Gaseous and Industrial Pollutants

1973. 649 pages. US $ 62.50/Dfl. 150.00. ISBN 0-444-41059-7

The primary object of this book is to present a survey of the main features of selected chromatographic procedures involved in the detection, separation and determination of the principal metal, gaseous and industrial chemical hazards encountered in the environment. The use of chromatography in environmental studies has many advantages - choice of a given chromatographic method to suit a particular problem; the speed at which separations and detection can be made; the very high sensitivity of instruments which allow the detection of very small amounts of samples. All of these ensure that chromatography has a principal role to play in determining environmental pollutants.

Volume 3: Pesticides

1975. about 840 pages. US $ 108.50/Dfl. 260.00. ISBN 0-444-41185-5

The unique feature of this book is the blending of relevant information regarding the synthesis, areas of utility, degradation and metabolic fate of pesticide toxicants, thus presenting as thorough and cohesive a picture as possible of the specific environmental hazard.

Volume 4: Drugs

1976. In preparation

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NEW IN CATALYSIS

CATALYSIS: HETEROGENEOUS AND HOMOGENEOUS

edited by B. DELMON and G. JANNES

1975. 584 pages. US $ 45.95/Dfl. 110.00. ISBN 0-444-41346-4

This book constitutes the Proceedings of the International Symposium on the relations between heterogeneous and homogeneous catalytic phenomena, held in Brussels on October 23-25, 1974.

The following topics were discussed in 28 contributed papers:

- Heterogeneous catalytic phenomena which exhibit some fundamental aspects of homogeneous catalysis; effects of modifying substances and selectivity promoters in heterogeneous catalysis; effects of carriers, when interpreted by fundamental concepts of homogeneous catalysis.
- Catalytic systems in which an attempt has been made to heterogenize coordination complexes. The corresponding papers give information on the progressive modification of the coordination and activity of the complexes.
- Similitude of mechanisms and precursors in homogeneous and heterogeneous catalysis.

In addition to the contributed papers 10 invited lectures or reviews are presented.

REACTION KINETICS AND CATALYSIS LETTERS

Editors: G.K. BORESKOV and F. NAGY
Associate Editor: L.I. SAMÁNDI
1976. 2 volumes in 8 issues. Subscription price: US $ 103.95/Dfl. 260.00 including postage.

This journal was established by the USSR and Hungarian Academies of Science on the realisation that a medium was urgently needed for the rapid publication of new results in the fields of Kinetics and Catalysis. The profusion of scientific papers originating from researchers in various parts of the world makes literature searches a formidable task. Specialised journals serve the purpose of concentrating information concerned with a specific group of subjects, whereas media for rapid communication efficiently reduce the time for the flow of information between research workers. REACTION KINETICS AND CATALYSIS LETTERS aims at assisting scientists of all countries in both respects, by ensuring rapid publication of original work in a specialised journal. Papers are, of course, accepted from all over the world, but a point of special interest is the inclusion of much new work from the USSR which hitherto became accessible only after great delay. Some of these papers will appear in Russian, but will be accompanied by an English summary.

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