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CHROMATOGRAPHY OF ENVIRONMENTAL HAZARDS

Volume III: Pesticides

by **LAWRENCE FISHBEIN,** Chemistry Division, National Center for Toxicological Research, Jefferson, Adjunct Professor of Chemistry, University of Arkansas, Little Rock, Arkansas, U.S.A.

1975. 830 pages. US $108.50/Dfl. 260.00. ISBN 0-444-41158-5

Pesticides represent a major area of increasing environmental concern both in terms of their potential ubiquity as well as toxicity. The main objective of this third volume in the series Chromatography of Environmental Hazards is to provide the analytical chemist with a practical text as well as a literature reference source of selected descriptive chromatographic procedures. Information is provided wherever possible concerning the basic equipment, operating parameters, sensitivity, and interferences encountered in the analysis of a particular pesticide and/or group of related contaminants.
The unique feature of the 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.

CONTENTS: Introduction. DDT and metabolites. Cyclodienes: Dieldrin, Aldrin and Endrin. Chlordane, Heptachlor and Heptachlor epoxide. Miscellaneous organochlorine pesticides Perthane, Methoxychlor, Endosulfan and Toxaphene. Benzene hexachloride and hexachlorobenzene. Multiple organochlorine analyses. 2,4-D and its esters. Pentachlorophenol. Miscellaneous herbicides and acaricides (bipyridylium salts, Dinoseb, Trifluralin and Cycocel). Parathion, Methyl Parathion and Malathion. Bidrin, Azodrin, Diazinon, Dursban and Dasanit. Disyston, Dimethoate, Phorate. Multiple organophosphorus pesticide analysis. Carbamates. Ureas. Triazines. Pesticidal synergists. Index.

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EXTRACTION CHROMATOGRAPHY

edited by **T. BRAUN,** Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary, and **G. GHERSINI,** Centro Informazioni Studi Esperienze, Segrate-Milano, Italy

JOURNAL OF CHROMATOGRAPHY LIBRARY, Vol. 2

1975. 584 pages. US $54.25/Dfl. 130.00. ISBN 0-444-99878-0

The purpose of this book is to provide analytical chemists and radiochemists, especially those interested in separations, with a broad survey of the role that extraction chromatography can and should play in chemical analysis.

This volume is the result of the collective work of many specialists, each responsible for a chapter in which a definite aspect of column extraction chromatography is thoroughly presented and discussed. Subjects presented include the basic and technical aspects of the method, the organic stationary phases and supports, the separation of elements with particular reference to radiochemical problems, the separation of lanthanides, actinides and fission products, radiotoxicological separations and the preconcentration of trace elements in various materials prior to their determination.

The book should prove invaluable to chemists working in various fields, as well as to students, physicists and research workers in biology and medicine.

CONTENTS: Theoretical aspects of extraction chromatography *(S. Siekierski).* Correlation between extraction chromatography and liquid-liquid extraction *(I. Akaza).* Techniques in column extraction chromatography *(P. Markl, E.R. Schmid).* Stationary phases in extraction chromatography *(G. Ghersini).* Inert supports in column extraction chromatography *(G.S. Katykhin).* Extraction chromatography of metallic and non-metallic ions *(I. Stronski).* Extraction chromatography of actinides *(W. Müller).* Extraction chromatography of lanthanides *(S. Siekierski, I. Fidelis).* Extraction chromatography of fission products *(M. Bonnevie-Svedsen, K. Joon).* Use of extraction chromatography in radiotoxicology *(C. Testa).* Chelating agents as stationary phase in extraction chromatography *(F. Sebesta).* Use of extraction chromatography for trace metal preconcentration and separation *(I.P. Alimarin, T.A. Bolshova).* Use of cellular plastics in extraction chromatography *(T. Braun, A.B. Farag).* Laminar techniques as an aid in planning column extraction chromatographic separations *(G. Ghersini, E. Cerrai).* Bibliography of extraction chromatography *(W. Drent, H. Eschrich).* Author index. Subject index.

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Review

POLYMER CHARACTERIZATION BY THERMAL EVOLUTION TECHNIQUES

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(Received 9th June 1975)

SUMMARY

Thermal evolution techniques continuously monitor materials thermally evolved from a sample on controlled heating. Either stepwise detection of such volatiles as a function of temperature or time, or quantitative measurement and identification of these materials provides very useful information. Transducers include vacuum gauges, electrochemical devices, thermal conductivity and flame ionization detectors, etc. These techniques have shown promise in studies of thermal stability and degradation mechanism, analysis of trace impurities and additives, and elucidation of polymer structures. Other applications are in the areas of vapor pressure measurement and toxicity studies of constituents in polymer systems.

Thermal methods of analysis are becoming increasingly important for polymer characterization, mainly because they are relatively immune to the difficulties associated with the non-volatile and insoluble nature of high polymers. Techniques such as differential thermal analysis (d.t.a.), differential scanning calorimetry (d.s.c.), thermogravimetry (t.g.), thermomechanical analysis (t.m.a.), and electrothermal analysis (e.t.a.) are frequently employed to study polymer samples as received without further preparation. During the past several years, another group of thermal techniques has been established on the basis of detection and analysis of materials thermally evolved from the sample upon controlled heating. These techniques are summarized in Table 1. Volatiles from a well-controlled furnace, a differential thermal analyzer, a thermogravimetric analyzer, etc., are monitored by any one of the evolved gas detectors (e.g.d.) based on thermal conductivity, flame ionization, pressure, volume, density, radioactivity, or electrochemical and photometric behavior. If desirable, evolved gas analysis (e.g.a.) can be performed on the gaseous products either directly from the source of heating or through the detector to an analyzer such as a gas chromatograph, an infrared spectrophotometer, a mass spectrometer, or any other suitable instrument.

In this paper, well established thermal evolution techniques such as d.t.a.

TABLE 1

Thermal evolution techniques

	E.g.d.	E.g.a
Furnace	Thermal conductivity	G.c.
[(T.e.a.)	Flame ionization	I.r.
D.t.a.	Pressure change	M.s.
T.g.	Volume change	Uv—vis.
—	Gas density	Chemical
—	Electrochemical	—
—	Photometric	—
—	Radioactivity	—

and t.g. are not discussed, but only those defined in Fig. 1. The sample is heated in a furnace controlled by a temperature programmer, and thermally evolved volatiles are swept by an inert carrier gas into a detector. Thus, the amount of volatiles is continuously and automatically recorded as a function of temperature. The plot of detector output vs. temperature is equivalent to a weight loss scan obtained by a thermobalance. For convenience of discussion, this family of techniques is named Thermal Evolution Analysis (t.e.a.) to distinguish it from e.g.d. coupled with d.t.a., t.g., etc. E.g.a. then includes all techniques which use an analyzer to identify the effluents from t.e.a., d.t.a., etc. Combinations of d.t.a./d.s.c. and t.g. with e.g.d. or e.g.a. have been extensively reviewed by various authors including Mitchell and Chiu [1], Murphy [2], Wendlandt [3], Daniels [4], Garn [5], Kenyon [6], and Lodding [7]. It must be emphasized that t.e.a. is not just a heating device to produce volatiles, but rather an analytical tool to provide qualitative and quantitative information on the sample. Examples to illustrate important features of t.e.a. are given below.

TECHNIQUES BASED ON PRESSURE CHANGES

Even though the use of thermal conductivity detectors was probably the earliest demonstration of the applicability of a thermal evolution technique to practical chemical problems [8], vacuum gauges were successfully employed by McNeil for studies of polymer degradations [9, 10]. As shown

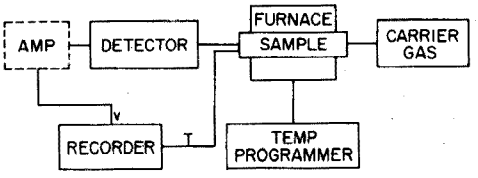

Fig. 1. Definition of thermal evolution analysis.

in the layout of the apparatus used by McNeil (Fig. 2), the sample is placed in a Pyrex glass degradation tube, A, and continuously heated at a programmed rate in a continuously evacuated system. As the sample degrades to produce volatile materials, a small pressure exists between the hot sample chamber and the cold traps some distance away. The pressure change corresponding to the rate of degradation of the sample is measured continuously by Pirani gauges located at E, F and G. The thermogram, showing the rate of volatilization as a function of temperature measured at B, is very similar to a derivative t.g. scan, and provides similar information. However, this technique has the selectivity to distinguish between products condensable and non-condensable at a certain trap temperature. Also, the products are readily recovered for other analyses. Materials condensed by a cold water jacket, C, provide a cold ring fraction. For complementary results, a pressure gauge has been coupled to t.g. [11—13] or d.t.a. [14].

Figure 3 shows the use of this technique to study the effect of molecular weight on thermal stability of poly(methyl methacrylate) (PMMA) prepared by a free-radical mechanism [15]. Evolution peaks below 200 °C are attributed to trapped volatiles released when the polymer softens. The two major depolymerization peaks indicate different mechanisms of initiation of chain depolymerization process. At the first peak between 220° and 300 °C, the rate of degradation is lower and the peak temperature is higher for samples of higher initial molecular weight. At the second peak between 320° and 450 °C, the rate of degradation is higher for samples of higher molecular weight, while the peak temperature is lower. These observations are consistent with the accepted view that the first stage of the degradation of PMMA is chain end-initiated and the second is initiated by random chain scissions. This is further supported by the fact that samples prepared by an anionic mechanism do not show the first stage of degradation because of the apparent lack of unstable chain ends present in the free radical samples.

A t.e.a. method based on a simple thermocouple vacuum gauge was used to study the degradation of ethylene—acrylic acid copolymers [16]. When

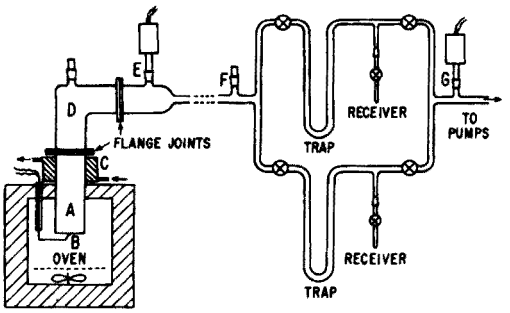

Fig. 2. Evolved gas detection using vacuum gauges [10].

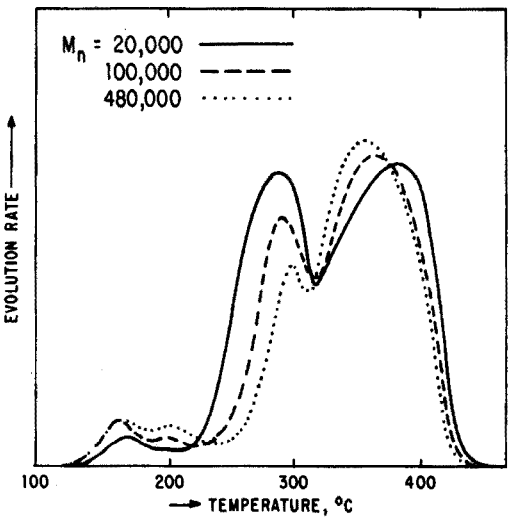

Fig. 3. Thermal degradation of poly(methyl methacrylate) [15].

the copolymer is modified by 20 % conversion to the sodium salt, the thermogram shows an additional evolution peak below 200 °C. Mass spectrometric analysis of the gases evolved during this decomposition stage shows water, carbon dioxide, and other hydrocarbon fragments. This early decomposition peak was correlated with the extent of salt modification.

McNeil [17] has suggested that considerably more information may be obtained in thermal evolution measurements in which differential condensation of products is carried out as shown in Fig. 4. Several cold traps, each at a different temperature, are placed before the Pirani gauges, A, B, C and D. The gauge response then depends on the relative volatility of the products passing through each trap. Another gauge, E, is placed after the main trap at —196 °C to register the presence of any non-condensable gases. The outputs from the Pirani gauges are fed to a multipoint recorder. X and Y are sample collection points. This modification makes it possible

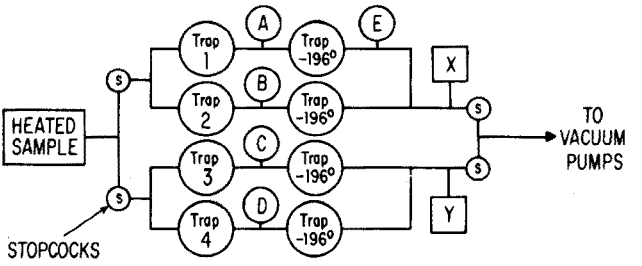

Fig. 4. Differential condensation—thermal evolution system [17].

to obtain information on the nature of the products and also on compositional changes of the products on heating without isolation and subsequent analysis. Products of different volatilities can be separated and collected.

Figure 5 shows an example of the use of thermal evolution plus differential condensation to study the thermal degradation of poly(butyl methacrylates) with only structural differences [18]. The thermal evolution curves are clearly different for different structures, tert-, iso-, n-, and sec-, as shown by the steps of decomposition and the temperatures for reactions to occur. In addition, evolution curves obtained at various condensation temperatures provide information on product composition changes. For instance, as shown in Fig. 5 (a), poly(tert-butyl methacrylate) decomposes

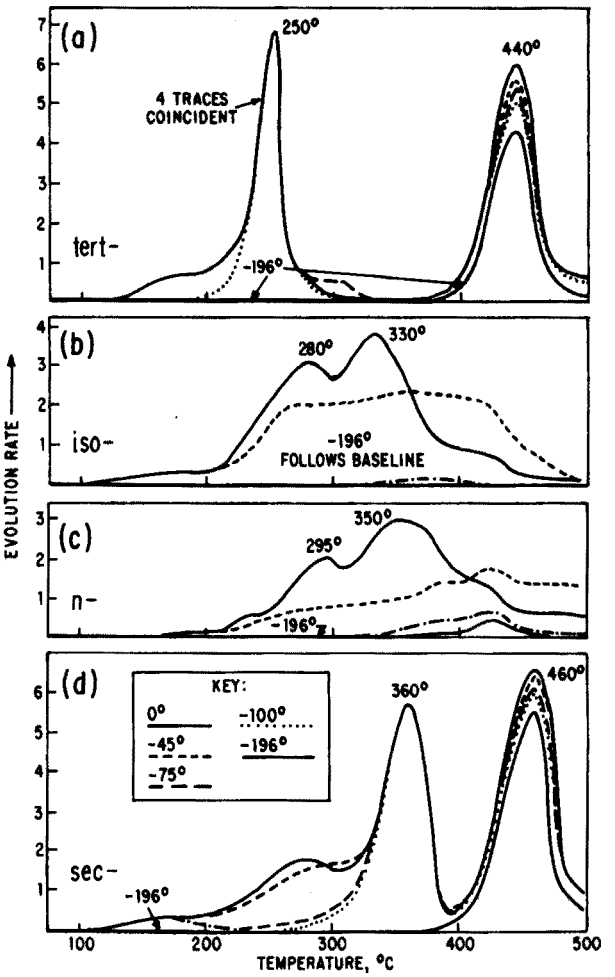

Fig. 5. Thermal degradation of poly(butyl methacrylates) [18].

in three stages. The 440 °C-peak involves a complex mixture of products, including non-condensable gases even at −196 °C, which would reflect a random scission to produce small molecules. The 250 °C-peak is quite different; the products are volatile at −100 °C, but condensed at −196 °C, indicating substances of molecular weight less than 60. The first stage overlaps with the second, but again shows a different product composition. The materials are condensed at −100 °C, suggesting less volatile substances than the second stage. Further analysis of products at various stages shows monomer at the first stage, isobutene at the second stage, and mainly carbon dioxide at the third stage, in complete agreement with the above observation.

In Figure 5(b), for poly(iso-butyl methacrylate), in spite of the two evolution peaks observed, there is no major change in product composition. All products are essentially condensed at −75 °C. There is a limiting rate effect for the −45 °C-curve. However, the areas under the 0° and the −45 °C-curves are comparable, indicating only one product involved. Infrared analysis of product gases shows only monomer, confirming the above conclusion.

Besides detection of gas evolution by pressure change at constant volume, the change in volume at constant pressure can also monitor thermal decomposition. Recently, Wendlant [19] reported a simple constant pressure-variable volume gas detection apparatus (Fig. 6). The pressure change caused by volatilization activates a relay which controls a motor-driven variable-volume gas syringe. A slidewire in contact with the syringe plunger permits the recording of volume change as a function of sample temperature. Such a system is simple to use and requires little instrumentation. Although no polymer example is given by the author, this technique should be readily adaptable to polymer decomposition studies.

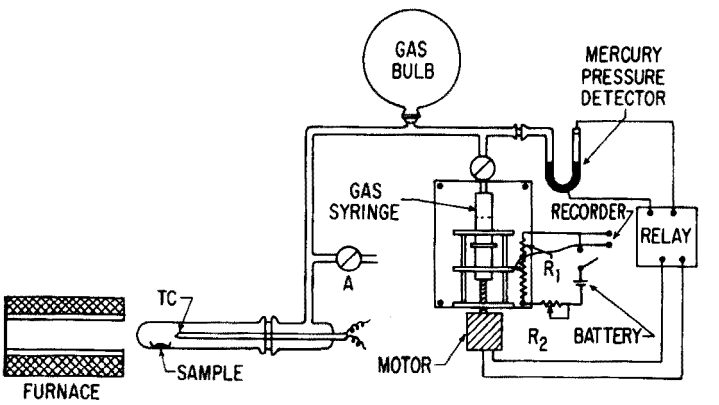

Fig. 6. Evolved gas detection based on volume change [19].

TECHNIQUES BASED ON FLAME IONIZATION

The first commercial thermal evolution analysis equipment was based on a design by Eggertsen et al. [20] with flame ionization detection. It was introduced by Carle Instruments, Inc. (Fullerton, California) [21] and is presently marketed by Du Pont Company (Wilmington, Delaware) [22]. The apparatus is schematically shown in Fig. 7. A sample furnace whose temperature is programmable from ambient to 500 °C is closely coupled to a flame ionization detector (f.i.d.) to prevent precondensation. The sample temperature is read at the tip of the sample probe close to the sample boat. This apparatus has high sensitivity to detect microgram amounts of material. The high-temperature detector arrangement also secures complete recovery of most volatile products. These features make this instrument suitable for determining small amounts of additives or contaminants in polymer systems. For instance, low levels of antioxidants such as 2,6-di-tert-butyl-*p*-cresol in polyethylene have been successfully determined (Fig. 8) [23]; the furnace is maintained at 217 °C, and the sample is inserted to vaporize the antioxidant to completion, the amount of antioxidant being determined from the peak area relative to a known standard sample.

The high sensitivity of f.i.d. has been utilized for vapor pressure measurement below the level of 1 millitorr [24, 25]. A vapor pressure probe is available in the Du Pont 916 TEA apparatus for such a measurement. The sample is mixed with inert granules and placed in the sample chamber. When the sample is heated at a relatively slow heating rate, the carrier gas flowing through the sample chamber and the small opening at the end is nearly saturated with the vapors in equilibrium with the sample. As shown in Fig. 9 [25], the vapor pressure of di-(2-ethylhexyl)phthalate at various temperatures can be calculated directly from the t.e.a. curve once the response factor of the substance has been obtained. This method is rapid, but not as precise as the isothermal method (Fig. 10). In this method, the temperature of the

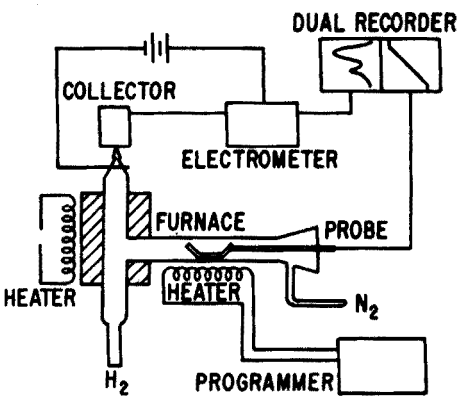

Fig. 7. Thermal evolution analyzer based on flame ionization detection [20].

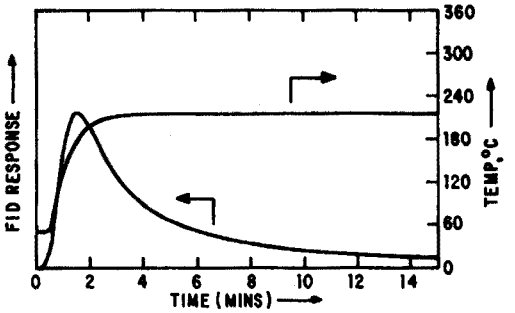

Fig. 8. Thermal evolution analysis of antioxidant in polyethylene [23].

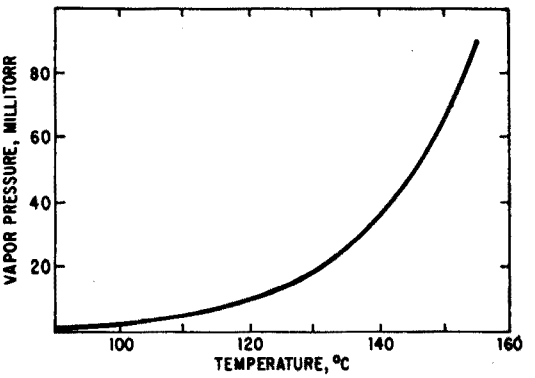

Fig. 9. Vapor pressure of di-(2-ethylhexyl) phthalate determined by t.e.a. [25].

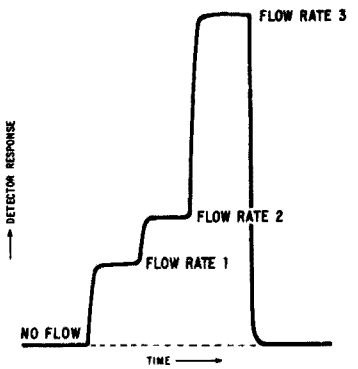

Fig. 10. Stepwise isothermal method for vapor pressure determination.

sample is maintained at the desired value and allowed to equilibrate with no carrier gas flowing through the sample chamber, thus establishing the baseline. Then a certain flow of carrier gas is passed through the sample to produce a step signal, the magnitude of which is proportional to the vapor pressure of the sample at that temperature. In order to determine whether saturation has actually been achieved, successively higher flow rates are applied to produce correspondingly larger signal steps. A precise proportionality between the detector signal and the flow rate indicates saturation of the carrier gas by the sample. This technique has been used to obtain vapor pressure data for a plasticizer, dimethyl phthalate [25]; the results are in Fig. 11, compared with literature values.

Most laboratories possess gas chromatographs equipped with either flame ionization or thermal conductivity detectors. These instruments can be readily adapted to perform thermal evolution analysis. A heating system (e.g. Fig. 12) is very simple to build and convenient to use. It consists of a stainless steel block with cavities to contain two cartridge heaters and two thermocouple wells, one for temperature control and another for sample temperature recording. The sample is placed in the sample chamber through an access manhole. The carrier gas inlet is connected to the g.c. injection port, while the outlet is connected to the inlet of either a flame ionization or thermal conductivity detector. Heating is controlled by a temperature programmer or simply a powerstat. A modified design [26] (Fig. 13) permits

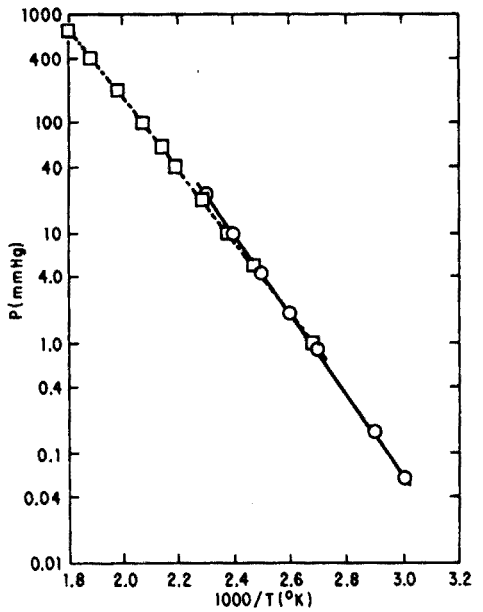

Fig. 11. Vapor pressure of dimethyl phthalate determined by t.e.a. [25]. (□) From Merck Index. (○) By t.e.a.

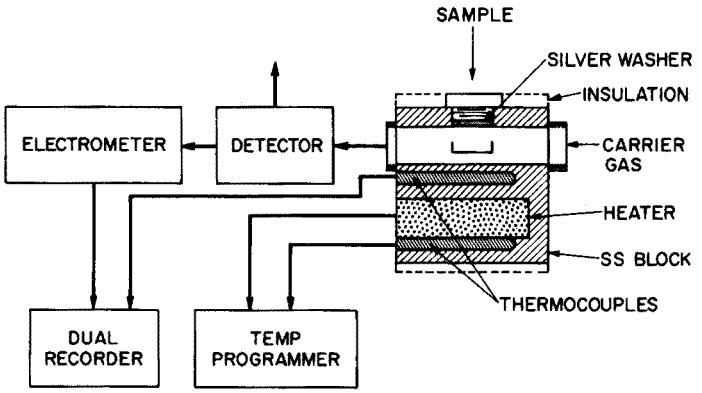

Fig. 12. Schematic diagram of thermal evolution analysis apparatus.

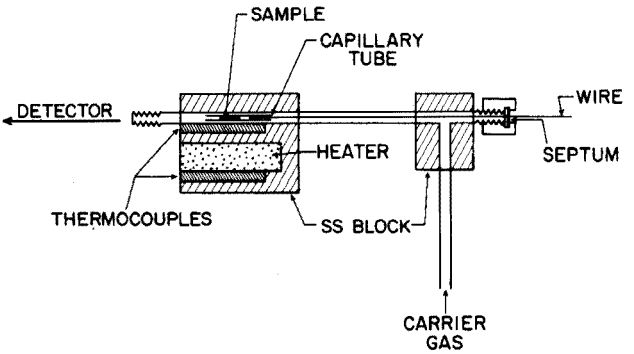

Fig. 13. Thermal evolution analysis apparatus for both isothermal and programmed heating.

the sample to be placed in a cold zone before introduction into the hot chamber maintained at a preset temperature.

TECHNIQUES BASED ON THERMAL CONDUCTIVITY

The two above-described heating systems can be used with either a f.i.d. or a thermal conductivity detector (t.c.d.). The f.i.d. has greater sensitivity for organic materials and a more stable baseline. But the t.c.d. detects water, carbon dioxide, etc., and also permits collection of g.c. effluents for further analyses.

Mass spectrometric thermal analysis, in use for many years [27, 28], employs a mass spectrometer to analyze volatile products from a sample heated at a constant rate, but the evolution of the products is not recorded.

Figure 14 shows a combined t.e.a.-mass spectrometry system which is very useful in polymer degradation studies [29]. The sample, s, is heated in

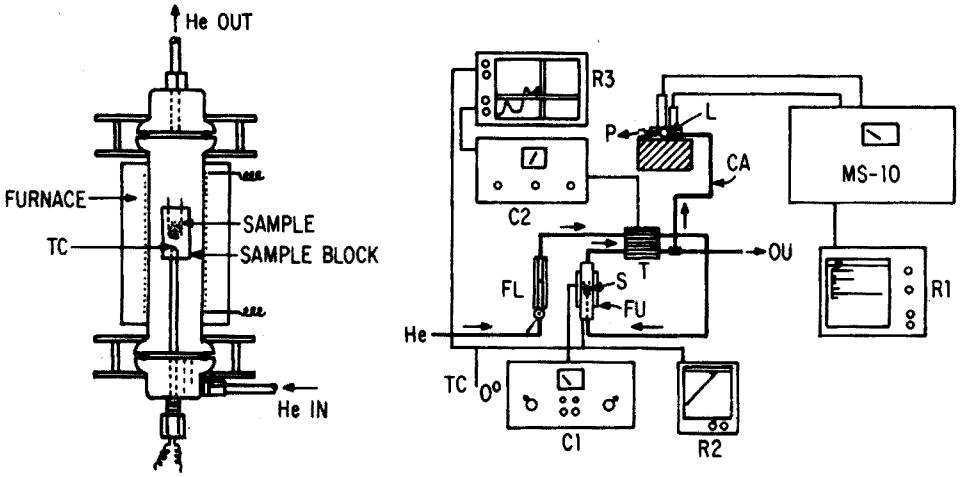

Fig. 14. A combined thermal evolution and mass spectrometric analysis system [29].

the pyrolysis chamber, Fu, shown in the left diagram, the temperature of which is controlled by a programmer, C_1, and recorded on recorders R_2 and R_3. The evolved products are detected by a thermal conductivity cell, T, and pass through a capillary tubing, CA, to the mass spectrometer (MS-10) inlet system containing a molecular leak, L. Thus a portion of the products is introduced to the mass spectrometer while the remainder is pumped out by a mechanical pump at P. The thermal evolution curve is generated from the thermal conductivity cell through a bridge circuit, C_2, and displayed on the X—Y recorder, R_3 and the MS-10 spectra are shown on recorder, R_1.

Identification of the evolved products is highly desirable. However, the cost of a mass spectrometer is prohibitively high for routine combination with t.e.a. in most laboratories. Recently, a relatively inexpensive t.e.a.—g.c. instrument was introduced by Chromalytics Corporation [30] for identification of thermal effluents and is now marketed by Spex Industries (Metuchen, New Jersey). The operating principle of this instrument is illustrated at the top of Fig. 15. The evolved gases flow through two rotary valves nos. 1 and 3 to a t.c.d., and are condensed in a suitable trap such as a Porapak tube. For g.c. analysis of products up to a certain stage of decomposition, the trap is heated rapidly, and the trapped materials are back-flushed into the g.c. column for separation and identification on proper turning of the rotary valve no. 2. In this particular instrument, the reference side of the thermal conductivity detector is also used to monitor the g.c. effluents. Other analyzers, such as an i.r. spectrophotometer, can be connected to the outlet of the detector, and the attachment of an additional f.i.d. is optional.

The features of such a t.e.a.—g.c. technique are illustrated by the analysis of poly(vinyl chloride)—poly(vinyl acetate) systems. The t.e.a. scans of a physical blend of 87:13 PVC:PVAc, and 87:13 VC/VAc copolymer, along

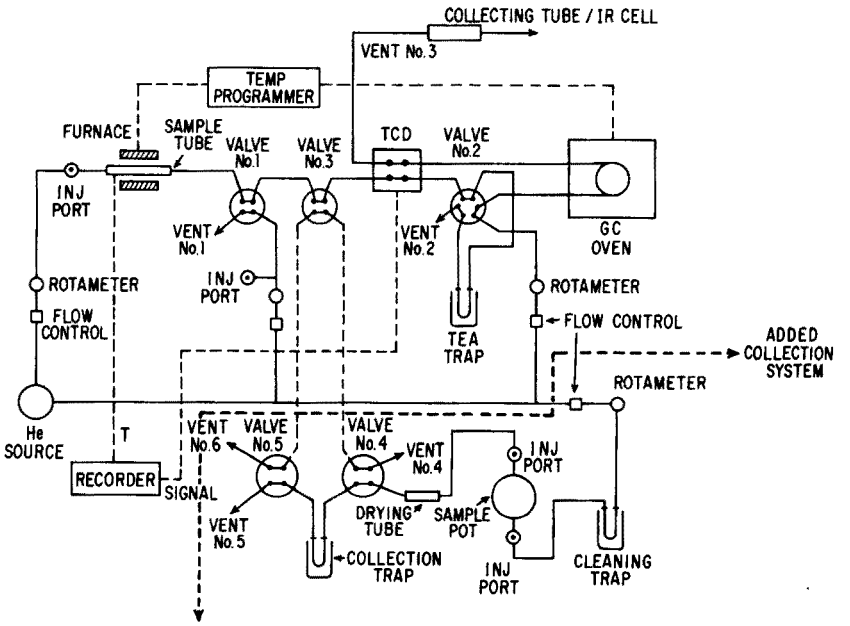

Fig. 15. Thermal evolution—gas chromatography system.

with the two homopolymers are shown in Fig. 16. Obviously, the patterns of the evolution peaks can distinguish some but not all of the four polymers. However, if the evolved products are trapped out at successively higher temperatures in the first major decomposition region, and analyzed by g.c., all four polymers are readily identified as shown by the bar graphs in Fig. 17. PVC and PVAc are identified by their release of HCl or acetic acid (HOAc), respectively, as the main product up to ca. 400 °C. For the physical blend, HCl is the dominating product at the beginning of the decomposition, and then HOAc is produced in increasing amounts with temperature, until both HCl and HOAc are completely evolved and only hydrocarbons are detectable. This is in great contrast to the case of the copolymer, where the ratio of HCl to HOAc produced at various temperatures remains essentially constant. The ability to distinguish polymer blends from copolymers is very important because it is difficult to do so by most spectroscopic methods.

A collection system can be added to this instrument to allow determination of trace odorous materials in polymers. The connection of this system to the original apparatus, as done in this laboratory, is shown in Fig. 15 at the bottom of the diagram. Kilogram amounts of polymer sample are placed in a 4-l or larger glass pot and swept through by helium to a Porapak collection trap for a certain period of time. The collection trap is connected to the t.e.a. instrument through rotary valve no. 3. By proper manipulating of valves 3, 4, and 5, the volatiles can be transferred from the collection

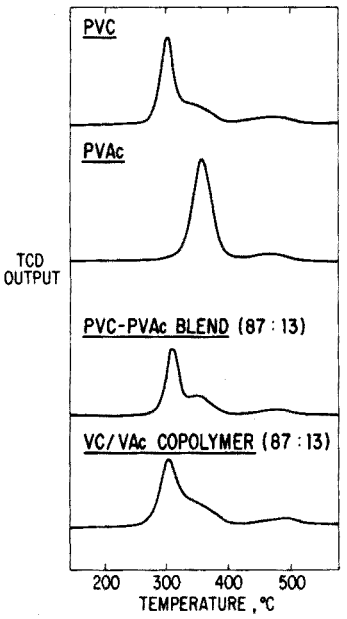

Fig. 16. Thermal evolution analysis of poly(vinyl chloride)—poly(vinyl acetate) blends and copolymers. Heating rate, 20 °C min^{-1}; helium flow, 16 ml min^{-1}; detector current, 150 mA; sample size, 1.5 mg.

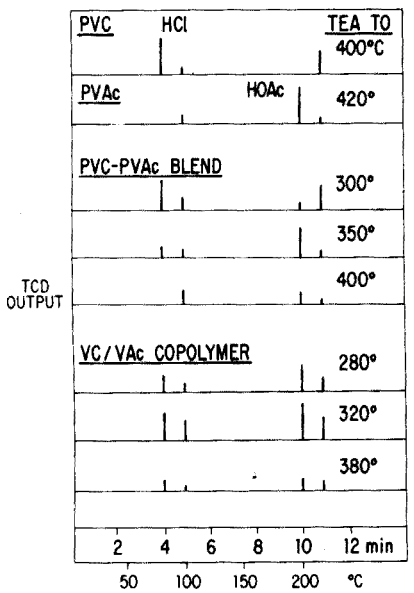

Fig. 17. Gas chromatograms of t.e.a. effluents. 5 ft. x 1/8-o.d. stainless steel column, 80/100-mesh Chromosorb 101; heating rate, 20 °C min^{-1}; helium flow, 16 ml min^{-1}; detector current, 150 mA.

trap to the t.e.a. trap. After this has been done, the volatiles are separated and analyzed by g.c. with the normal procedure. If necessary, further identification of g.c. effluents by i.r. spectrometry can be undertaken. Thus, the t.e.a.—g.c. capability can be utilized to analyze microgram amounts of materials collected from kilogram quantities of sample.

The collection efficiency of this arrangement has been studied for substances of a wide variety of volatility and polarity including n-hexane, styrene, methyl methacrylate, and methacrylic acid. The results are shown in Fig. 18 with the % recovery plotted vs. the total volume of gas swept through the sample pot (gas flow rate times the total sweeping time). The sample is injected at the port under the pot, and collected in the trap at room temperature. At a flow rate of 200 ml min^{-1}, a recovery of more than 95 % is obtained for all the materials after 2—3 h. By this technique, ca. 10 p.p.b. of styrene but negligible acrylonitrile was found in the headspace for a typical ABS resin (Fig. 19). An interesting observation was made when this technique was used to monitor the volatile monomer content in a commercial sample of polymethyl methacrylate. The resin was left in the pot in a static atmosphere for a varying number of days to allow the residual monomer to permeate throughout the headspace. After each equilibration period, the pot was swept with helium to measure the monomer content. The monomer level was found to increase steadily to a constant value of 20 p.p.b. of the resin after a two week period (Fig. 20). This residual monomer did not reappear after the resin was placed in a vacuum oven at

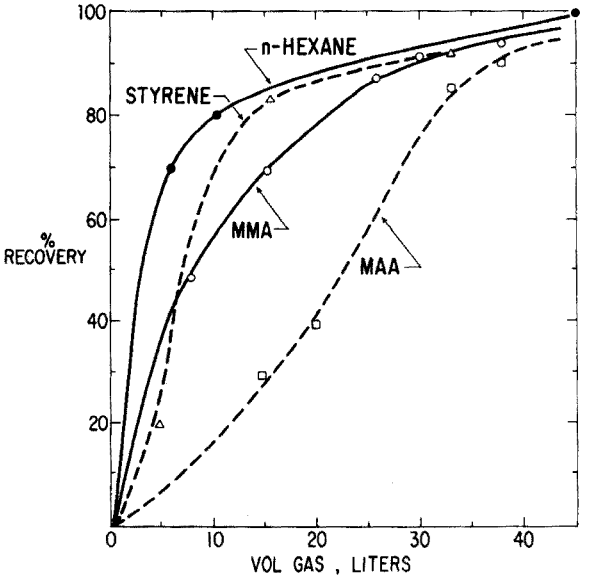

Fig. 18. Collection efficiency.

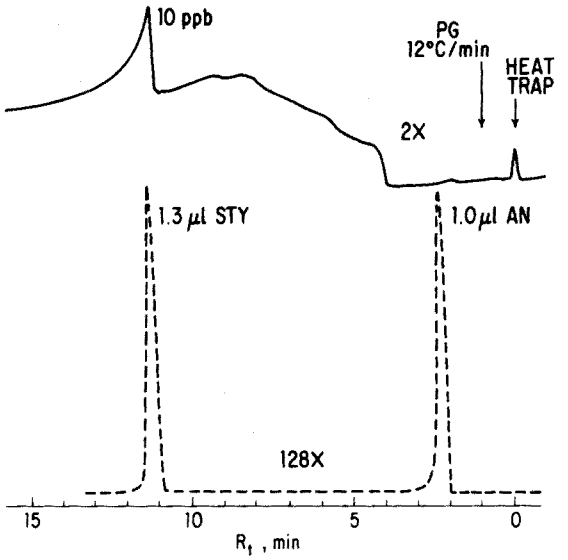

Fig. 19. T.e.a.—g.c. analysis of volatiles collected from an ABS resin. 1.5-kg sample for 1.5 h at 250 ml He min^{-1}. 6 ft × 1/8-in. o.d. stainless steel column, 10 % DC-410 on Chromosorb W, 80/100-mesh; heating rate, 12 °C min^{-1}; helium flow, 16 ml min^{-1}; detector current, 150 mA.

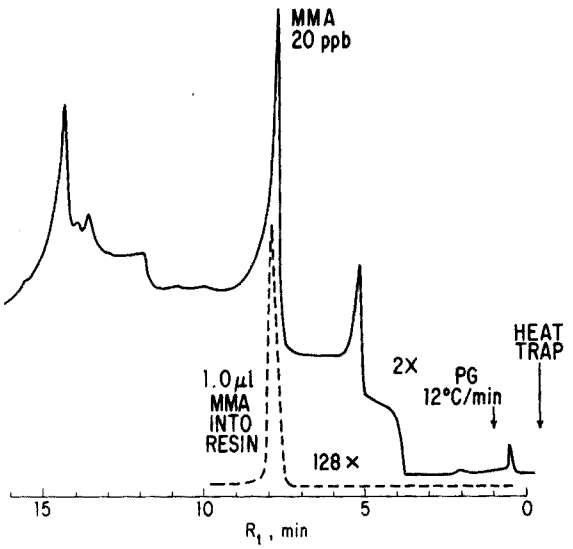

Fig. 20. T.e.a.—g.c. analysis of volatiles collected from an acrylic resin. 2-kg sample for 2.5 h at 250 ml He min^{-1}. G.c. conditions as in Fig. 19.

80 °C for one week. Thus, the monomer in the headspace seemed to be in equilibrium with its solution in the resin and not regenerated from the polymer.

Technique based on other transducers

Besides the above three types of detectors most commonly used, there are other detectors each showing unusual applications. Of particular interest is the use of chemical or electrochemical means to monitor the evolution of a specific component. The technique is both selective and precise. Automatic titrators have been coupled to t.g. for such measurements [31, 32]. A thermal evolution device in place of a thermobalance is perhaps simpler in operation and less expensive in instrumentation. Figure 21 shows such a technique with an ion-selective electrode as the detecting device to monitor evolution of hydrogen fluoride [33]. A carrier gas is passed through a molecular sieve drying tube and over heated copper gauze to remove oxygen before entering a pyrolysis tube made of calcium fluoride. The sample is contained in a platinum or calcium fluoride boat. The effluent gas is passed into a 10^{-5} M solution of sodium fluoride made up in 0.1 M ammonium acetate contained in a polyethylene beaker. An Orion fluoride electrode and a calomel reference electrode used to measure the concentration of fluoride ion are connected to a direct reading pH meter, which in turn is connected to an X—Y recorder. The thermogram — essentially pF vs. temperature — is easily transposed to a plot of yield of available HF or F vs. temperature from the calibration curve of the fluoride electrode and the weight of the sample.

Figure 22 shows results of three hydrofluoroethylene polymers degraded in nitrogen and in air. Also included are plots of total weight loss curves and yield of fluoride as a percentage of weight loss curves. In nitrogen the yields of fluoride from poly(vinyl fluoride) and poly(vinylidene fluoride) are

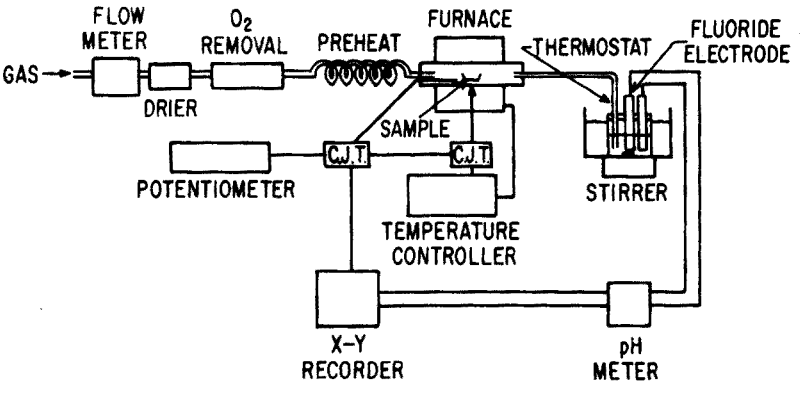

Fig. 21. Thermal evolution analysis with an ion-selective electrode [33].

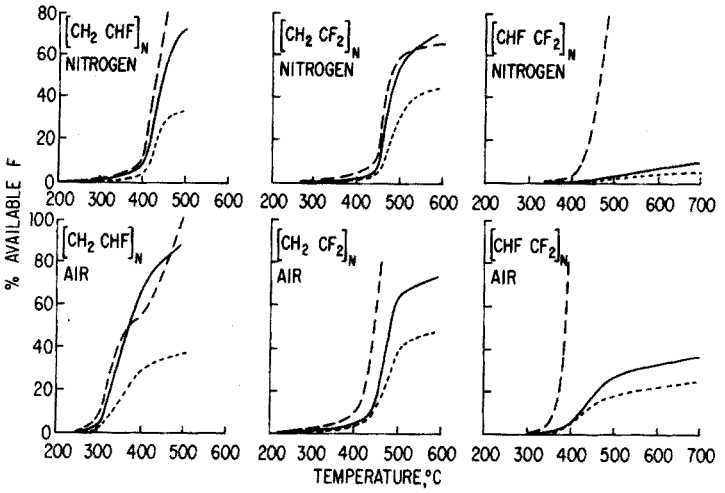

Fig. 22. Thermal degradation of hydrofluoroethylene polymers [33]. (—) Fluoride yield. (— — —) Total weight loss. (-----) Fluoride yield as % of weight loss.

similar, but that from polytrifluoroethylene is much smaller. In air, the yield of fluoride for all three polymers is larger, but still polytrifluoroethylene produces the least amount of hydrogen fluoride. Evidently, the elimination of hydrogen fluoride plays a major role in the degradation of poly(vinyl fluoride) and poly(vinylidine fluoride) but not polytrifluoroethylene.

Other detectors such as gas density balance [34], photocells for light scattering [35], and radioactivity [36—38], etc., have been demonstrated as powerful tools for monitoring thermal evolution and should be potentially useful for polymer degradation studies.

CONCLUSION

It is clear that thermal evolution analysis can establish itself as an excellent tool for polymer studies complementary to the well-known thermal techniques such as d.t.a. and t.g. Its applications include thermal degradation studies, determination of additives and contaminants, polymer composition and structure identifications. With small variations, the apparatus can also be used for vapor pressure measurements, and for determination of odorous materials in polymer systems.

The coupling of g.c. to t.e.a. for the identification of t.e.a. effluents is practicable and useful. This area of coupling other analyzers to a suitable thermal evolution analyzer for effluent identification certainly has great potential in terms of application and instrumental development. D.t.a. has been successfully coupled with thermal conductivity [39—42], photometry [43], mass spectrometry [44—53], and gas chromatography [54, 55]. Even more useful is the combination of t.g. with i.r. [56], g.c. [57—59], m.s.

[60—63], g.c.—i.r. [64], and g.c.—m.s. [65—66]. More specific purposes are served by coupling t.g. to a photometer for measuring smoke generation [67] and ignition temperature [68]. Recently, Kiran and Gillham [69] coupled molecular weight chromatography to t.e.a. for identification of decomposition products of polymers. One can certainly visualize further progress being made in the broad field of coupling t.e.a. to a wide variety of analytical tools such as i.r., m.s. and other specific instruments for dedicated applications.

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THE DEVELOPMENT OF A FULLY COMPUTERIZED SYSTEM FOR SAMPLED D.C. POLAROGRAPHY WITH STANDARD INTERFACING

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SUMMARY

A complete system, based on the online PDP-11 computer (Digital Equipment Corporation) was developed for computerized sampled d.c. polarography with direct digital control. The system includes compensation of ohmic cell resistance and processing of the polarographic data. The accuracy of the system in the determination of the various polarographic parameters is: diffusion current ± 2 %, half-wave potential ± 2 mV, and slope of the log plot ± 2 mV.

Process computers have been used to control [1, 2] and evaluate [3] stationary electrode polarography, and the idea of programming a digital online computer to perform sampled d.c.-polarography is not new [4]. However, no reports about this subject have appeared in the literature, and important questions with regard to the accuracy and sensitivity that can be obtained have remained unanswered. This investigation was started to answer these questions, and to evaluate different methods of processing polarographic data with respect to speed, accuracy and the amount of information extracted from the data. Multiparametric curve-fitting methods were chosen for the data processing, as these methods are also suitable for polarographic waves which have the diffusion plateau obscured, a rather common situation in polarographic analysis which greatly limits the possibilities of conventional polarography. Finally this study was also undertaken to obtain a rough estimate of the total effort in the development of a fully computerized analytical method.

EXPERIMENTAL

Chemicals

Cadmium chloride (Analar), potassium chloride (Merck, reagent grade) and mercury (DRIJFHOUT, Polarographic grade) were used as received. Tetraethylammonium perchlorate (TEAP; Eastman) was recrystallized from ethanol (Merck, reagent grade) and dried in vacuo at 40 °C.

Apparatus

A Radiometer PO4 polarograph, equipped with a Radiometer DLT1 droplife timer, was used in the experiment for comparison purposes; it was adapted to three-electrode operation with a Sargent model A *iR* compensator. The characteristics of the dropping mercury electrode used were (at open circuit) in 1 M KCl: m = 3.98 mg s^{-1} t = 2.39 s. In the double-walled thermostatted (20.00 ± 0.05 °C) polarographic cell, a saturated calomel reference electrode was used with a mercury pool at the bottom of the vessel as auxiliary electrode.

The "computer polarograph" consisted of the Radiometer droplife timer and a digital online computer (PDP11/20, Digital Equipment Corporation) with the following standard accessories: teletype ASR 33; Dectape unit TU 56; Analog to Digital conversion subsystem ADO1 (2 channels in use), resolution 10 bits + sign, ranges ± 2.50 V, ± 5.00 V, ± 10.00 V; Digital to Analog conversion subsystem AA-11-D (4 channels in use), resolution 11 bits + sign, range ± 10 V, 10 mA.

The memory size was 8 K words (16 bits). The D/A conversion subsystem AA-11-D can provide ± 10 V at 10 mA, so it is possible to drive the polarographic cell directly from this source. Furthermore a + 10 V signal from this D/A converter can also directly drive the synchronization input of the droplife timer.

The polarographic cell used with this equipment was of the same type as that used for the Radiometer PO4 experiments. The characteristics of the dropping mercury electrode used with this "computer polarograph" were as follows: m = 1.29 mg s^{-1}, t = 5.40 s in 1 M KCl, and m = 1.30 mg s^{-1}, t = 5.72 s in 0.1 M TEAP—50 % ethanol. A saturated calomel electrode or a silver/silver chloride electrode of the double junction type (Ingold 373-90-NS-M5) served as reference electrode; the inner compartment of the latter was filled with saturated potassium chloride, while the outer compartment was filled with 0.1 M TEAP in 50 % ethanol. A diagram of the complete equipment for computerized sampled d.c. polarography is given in Fig. 1.

Polarographic procedure

The sample was placed in the cell, with mercury as auxiliary electrode. The solution was deoxygenated for 15 min with nitrogen purified by passing it over copper heated to 350 °C. The polarographic curve was then recorded. Cadmium samples in 1 M potassium chloride as supporting electrolyte were prepared from a stock solution of cadmium chloride standardized against EDTA with xylenol orange as indicator. Potassium samples in 0.1 M TEAP supporting electrolyte were prepared from a stock solution made from a weighed amount of dried potassium chloride.

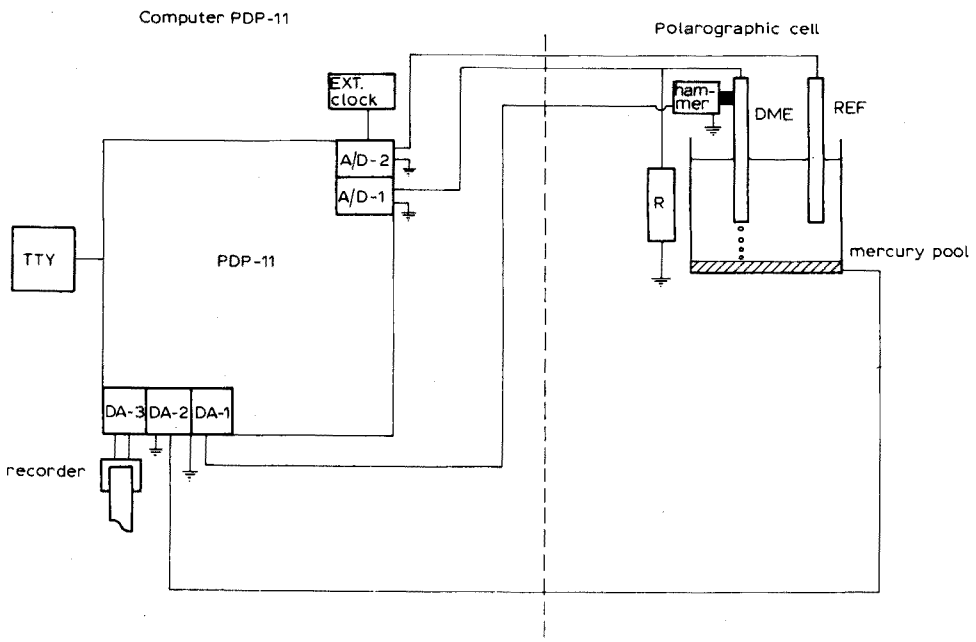

Fig. 1. The "computer polarograph".

Computer programs

Program for digital control of polarography

In carrying out the polarographic experiment, the computer has to perform the following functions:

1. maintain the potential of the dropping mercury electrode (DME) at a set point value versus the reference electrode by changing the potential of the auxiliary electrode (mercury pool);
2. change this set point value of the potential of the DME linearly with time;
3. measure and store the cell current with a relative accuracy $\leqslant 0.1$ % of its full scale value;
4. synchronize the measurement of cell current with the mercury drop life; and
5. dislodge the mercury drop at fixed intervals.

Furthermore, in order to obtain the optimal conditions, the operator must be able to choose the drop life time, the potential from which the scan starts, the direction of the scan (i.e. cathodic or anodic), the potential at which the scan stops, the scan rate, the sensitivity of the current measurement, and the amplification in the ohmic cell resistance compensation circuit.

For the convenience of the operator, it is also desirable to have the following facilities: (a) a display of the recorded polarogram on an

oscilloscope; (b) the possibility of obtaining a hard copy of the polarogram on a chart recorder; and (c) the possibility of repeated recording of the polarographic curve for the same sample.

A flow chart of the computer program that meets all these requirements is given in Fig. 2. The symbols used for the various parameters in the program are listed in Table 1.

The PDP-11/20 online computer features interrupt facilities at different priorities. Real-time operations are programmed with the use of these interrupt facilities for a line frequency clock and separate external clock for the A/D conversion. At the right moments these clocks cause an interrupt, i.e. they interrupt the normal flow in program execution, start the execution of a specific service routine, and when this service routine has been completed, resume normal program execution.

The program starts with a conversational part in which the parameters set by the operator are input to the computer via the teletype. Then a waitloop follows where the computer waits for the start command. After the start command has been received, the values of SCANPO and CURREN are set. Then the line clock (50 Hz) is started and the A/D converter is activated. From this point every time that a pulse of the external clock is encountered, the A/D converter measures the potential between the DME and the reference electrode. With these values the adjustment of the potential of the auxiliary electrode is calculated: PROPOR × (SCANPO − POTDME + POTREF). The calculated adjustment is applied to DA channel 2. If more

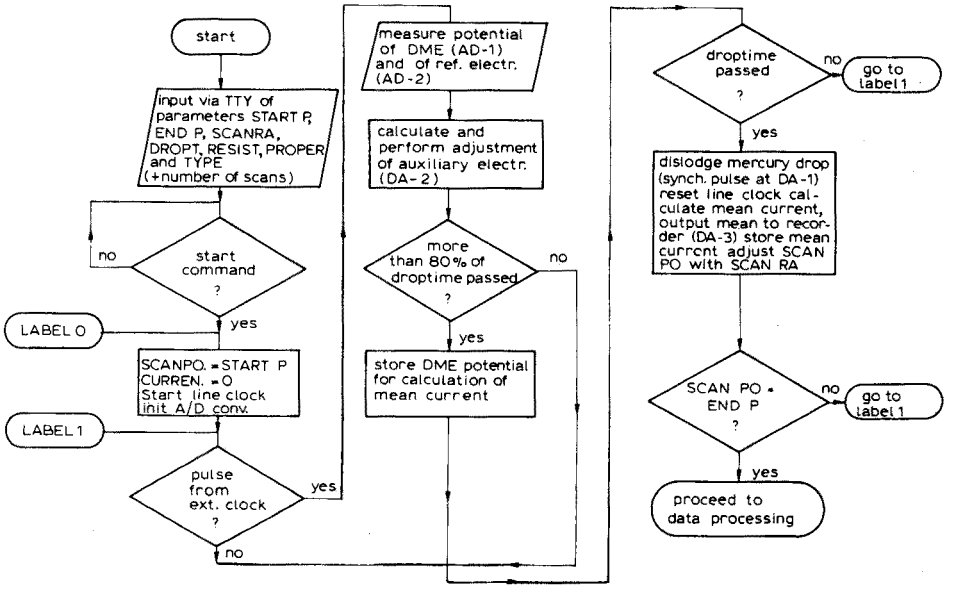

Fig. 2. Flow diagram of program for digital control of polarography.

TABLE 1

Symbols used in flow chart of computer programs

CURREN	: measured cell current
DA	: Digital to Analog Converter
DROPT	: mercury drop time
ENDP	: potential of end of scan
NOPOL	: number of polarograms to be recorded
PROPOR	: amplification factor in iR compensation circuit (can be < 1)
RESIST	: value of current measuring resistor
SCANRA	: increment or decrement of potential of DME per drop time
SCANPO	: value of potential of DME versus reference electrode
STARTP	: potential of start of scan
POTDME	: potential of dropping mercury electrode
POTREF	: potential of reference electrode
TYPE	: Type of measurement, viz. P = single scan, V = single scan + data processing, S = multiple scan + data processing for each scan
$E_{\frac{1}{2}}$	: halfwave potential
i_d	: diffusion limiting current

than 80 % of the drop time has elapsed, the value POTDME is stored for later calculation of the mean current during the last 20 % of drop life. Line clock pulses are counted to determine the stage of the drop life. When the drop time is complete the mercury drop is dislodged by a synchronization pulse of DA-1. The line clock counter is reset and the mean value of the current during the last 20 % of drop life is calculated. This value of the mean current is output to a chart recorder at DA-3, and is also stored in the computer memory. Then the value of SCANPO is adjusted with SCANRA. Finally a check is made that the end of the scan has been reached. If this test is successful, the program proceeds to the data-processing part; if not, the computer must wait for a new pulse of the external clock.

Program for processing polarographic data

Especially when polarography is used not only for analytical purposes, but also to elucidate electrode processes, the handling of the polarographic data should include calculation of the half-wave potential and the slope of the log plot, as well as calculation of the limiting current, and digital filtering of the signal to reduce noise. A simple but effective way of filtering the polarographic signal digitally is the method given by Savitzky and Golay [5].

If the theoretical equation describing the experiment is known, curve-fitting methods can provide the values of the parameters which determine the result. Most polarographic waves are described by the equation [6]

$$E = E_{\frac{1}{2}} - \frac{RT}{\alpha nF} \ln\left(\frac{i}{i_d - i}\right) \qquad (1)$$

which can be rewritten as [7]

$$i = i_d/\{\exp[(E - E_{\frac{1}{2}})/S] + 1\} \quad (2)$$

where $S = RT/\alpha nF$.

It should be noted that the program which utilizes this equation can be applied only to the polarography of substances which have a reduction product that is either soluble in mercury or in the medium.

For curve fitting based on eqn. (2), the rigorous least-squares method given by Wentworth [8] for three parameters was chosen, mainly because of its computational speed; this method requires reasonable initial estimates of the parameters wanted. The initial estimate of the diffusion current can be found from the difference in the currents at two points, one before and one after the rising part of the polarographic wave. An initial estimate of the half-wave potential of a polarographic wave can easily be found from the zero crossing point in the second derivative of the polarographic curve. Equation (2) applies only to the points of the rising part of the polarographic wave, so that it is necessary to determine which points belong to that part. This can be accomplished by means of the first derivative of the polarographic curve: when this first derivative exceeds a certain threshold value the corresponding points in the polarographic curve are on the rising part of a wave. The first and second derivatives of the polarographic curve can be calculated by a procedure similar to that used for the smoothing [5]. A flow chart of the complete program for the processing of the polarographic data is given in Fig. 3. The program operates on data stored in the computer memory by the program for digital control of polarography described in the previous section. Throughout the program, standard computational DEC subroutines are used.

RESULTS

The programs were written in DEC PAL-11A assembly language. The total memory size needed to accommodate the complete set of programs is about 15 K words (16 bits) including the memory space reserved for storage of the data. If only 8 K memory is available, a magnetic tape unit can be used to store the complete set of programs, and the appropriate programs are brought into the memory as required. Data-processing programs are not required while the experiment is running, whereas the digital-control program can be removed from the memory during data processing. Development of programs, debugging and experimental testing of the complete system took about 600 man-hours, of which 300 were spent at the computer. The program that controls the experiment has the following features:

1. the potential at which the scan starts and ends can be set to any integral value in the range ± 5000 mV;
2. the scan rate can be adjusted in 1-mV steps down to ± 1 mV per drop time;
3. the lowest drop time is 1 s, and this can be increased by 1-s increments;
4. the cell current is measured during the last 20 % of the drop life;

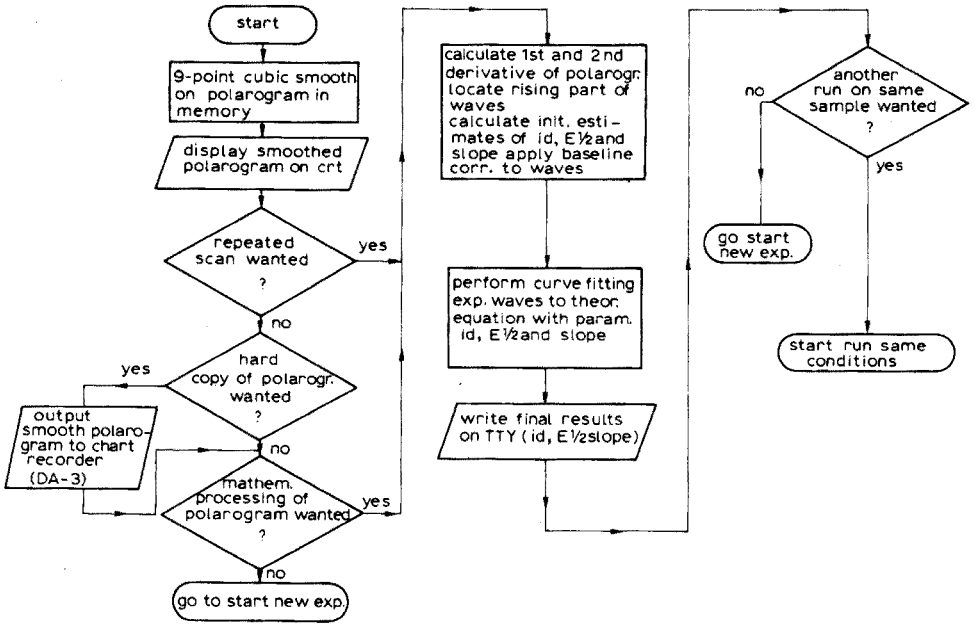

Fig. 3. Flow chart of program for processing polarographic data.

5. the ramp voltage increment (scan rate) is synchronized with the drop fall;
6. the polarographic curve can be recorded (strip chart) during the experiment;
7. the smoothed polarographic curve can be shown on the chart recorder after display on an oscilloscope;
8. three-electrode operation provides for iR-compensation;
9. repeated scans and data processing on the same sample are possible without operator intervention.

The sensitivity of the current measurement is not under computer control, but can be changed by changing the measuring resistance R (Fig. 1).

The data-processing program produces for each wave in the polarographic curve: (a) current versus voltage values for all points on the rising part of the wave; and (b) values for the limiting current, half-wave potential and slope of the log plot. Baseline correction for the waves is done by extrapolating a least-squares line drawn through 20 points, starting 40 points before the polarographic wave, from the starting potential side. For anodic scans, calculations are adjusted appropriately.

Initially, the brute-force multiparametric curve-fitting method of Meites [7] was used in the calculations, but for waves with about 30 points the computer time needed exceeds 20 min. With the Wentworth method [8] computer time for the processing of one polarographic wave with 30

points, is about 1 min and proportionately less for waves with fewer points (higher scan rate).

The results for the reduction of cadmium in 1 M potassium chloride as supporting electrolyte by computerized sampled d.c. polarography are given in Table 2. The experimental conditions were: starting potential, −0.300 V; final potential, −0.750 V; scan rate 0.004 V/2 s; drop time, 2 s; measuring resistance value, 80.000 Ω. For comparison, Table 2 also shows the results of similar experiments run on a commercial polarograph; in this case the $E_{\frac{1}{2}}$ values and diffusion currents were determined graphically on the recorder paper.

Figure 4 shows the polarographic wave recorded by the "computer polarograph" for the reduction of potassium ion in 0.1 M tetraethylammonium perchlorate in 50 % ethanol as supporting electrolyte. The conditions were: starting potential, −1.500 V; final potential, −2.052 V; scan rate, 0.006 V s^{-1}; drop time, 1 s; measuring resistance, 80.000 Ω. No diffusion current plateau

TABLE 2

Sampled d.c. polarography of cadmium(II) in 1 M KCl by the computerized method and by the Radiometer PO4 method

Concn. ($\cdot 10^{-4}$ M)	Computerized method				PO4 method (2-s drop time)		
	i_d (μA)	$E_{\frac{1}{2}}$ (V)	Slope (mV)	I_d[a]	i_d (μA)	$E_{\frac{1}{2}}$ (V)	I_d[a]
2.026	1.183	−0.6440	27.55	3.81	2.80	−0.635	4.27
2.026	1.206	−0.6440	29.96	3.89	2.72	−0.640	4.14
2.026	1.215	−0.6444	29.27	3.91	2.66	−0.635	4.05
3.039	1.766	−0.6436	28.61	3.79	3.96	−0.640	4.02
3.039	1.790	−0.6443	28.95	3.84	4.00	−0.640	4.06
3.039	1.761	−0.6444	28.54	3.78	—	—	—
4.052	2.452	−0.6427	29.53	3.95	5.30	−0.635	4.04
4.052	2.410	−0.6429	29.57	3.88	5.20	−0.635	3.96
4.052	2.418	−0.6434	28.98	3.90	—	—	—
5.065	2.984	−0.6445	28.15	3.85	6.64	−0.640	4.05
5.065	3.029	−0.6449	29.64	3.90	—	—	—
5.065	2.989	−0.6437	29.04	3.85	—	—	—
6.078	3.654	−0.6450	29.11	3.92	8.00	−0.645	4.06
6.078	3.602	−0.6449	28.49	3.87	7.94	−0.640	4.03
6.078	3.590	−0.6448	29.39	3.86	7.92	−0.635	4.02
8.104	4.796	−0.6417	28.93	3.86	10.56	−0.640	4.02
8.104	4.825	−0.6414	29.60	3.89	10.32	−0.640	3.93
8.104	4.807	−0.6417	29.04	3.92	10.16	−0.640	3.87
10.130	5.990	−0.6422	29.14	3.86	13.20	−0.640	4.02
10.130	5.960	−0.6420	28.75	3.84	12.94	−0.635	3.94
10.130	6.014	−0.6419	29.48	3.88	13.22	−0.635	4.06
Mean		−0.643	29.0	3.87		−0.638	4.03
s		0.001	0.5	0.04		0.003	0.09

[a] in μA. $mMol^{-1}.1.mg^{-2/3}.s^{\frac{1}{2}}$, calculated for mean current during whole drop life.

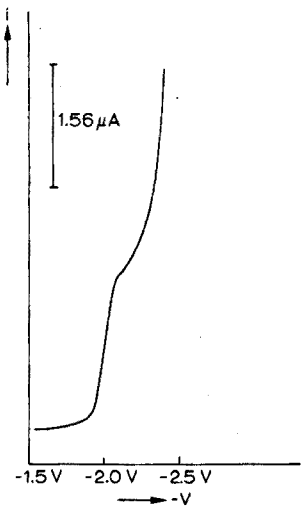

Fig. 4. Sampled d.c. polarogram for $8 \cdot 10^{-4}$ M K^+ in 0.1 M TEAP—50 % ethanol.

TABLE 3

Computerized sampled d.c. polarography of potassium(I) in 0.1 M TEAP in 50 % ethanol, with 1-s drop time

Concn (10^{-4} M)	i_d (μA)	$E_{\frac{1}{2}}$ [a] (V)	Slope (mV)	I_d [b]
3.00	0.769	−1.9574	58.7	1.87
3.00	0.760	−1.9573	55.2	1.84
4.00	1.005	−1.9603	56.7	1.83
4.00	1.060	−1.9625	61.6	1.93
4.00	1.009	−1.9598	57.5	1.84
4.00	1.030	−1.9621	58.7	1.87
5.00	1.231	−1.9629	59.2	1.79
5.00	1.245	−1.9615	58.9	1.81
5.00	1.240	−1.9618	59.0	1.80
5.00	1.254	−1.9619	59.1	1.83
5.00	1.264	−1.9615	60.0	1.84
6.00	1.547	−1.9640	60.7	1.88
6.00	1 556	−1.9652	61.9	1.89
6.00	1.538	−1.9643	59.3	1.87
8.00	1.982	−1.9639	61.1	1.80
8.00	1.979	−1.9653	60.9	1.80
Mean		−1.962	59.3	1.84
s		0.002	1.8	0.04

[a] Versus Ag/AgCl (saturated KCl).

[b] in $\mu A.mMol^{-1}.1.mg^{-2/3}.s^{\frac{1}{2}}$, calculated for mean current during whole drop life.

can be observed, but the data-processing program is still successful as indicated by the results in Table 3.

CONCLUSIONS

The results prove that even in unfavourable cases such as the determination of potassium, the accuracy of the computerized sampled d.c. polarography is ± 2 % for the diffusion current constant, ± 2 mV for the half-wave potential and ± 2 mV for the slope of the log plot. These errors compare favourably with the conventional method. Moreover, considerable time can be saved by processing the experimental data by computer. Diffusion current, half-wave potential and slope of the log plot are obtained within 1 min of finishing the experiment.

The use of Assembly language in the development of the programs for the data processing proved to be uneconomical. About one half of the development time was used in writing and debugging these programs. Partly this can be accounted for as follows: Initially a Basic program written by Meites [7] was used for the multiparametric curve-fitting, but execution of this program on the PDP-11 was very slow (> 60 min for waves with 30 points); the use of assembly language reduced the time considerably, but not enough to be of real practical value. Only with the Wentworth approach [8] programmed in assembly language, could data-processing times of 1 min be achieved.

It is estimated that the total effort for the development of the computerized sampled d.c. polarography system could have been reduced by 40 % by the use of fortran in the data-processing programs. The use of assembly language is only recommended where short execution times are mandatory.

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SOME INTERFERENCES IN ALTERNATING CURRENT, DIFFERENTIAL PULSE AND OTHER POLAROGRAPHIC METHODS

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SUMMARY

The influence of a preceding electrode process in the analytical use of a.c., differential pulse and other polarographic methods is discussed. Coupled chemical reactions, such as found with the Cr(III)/Fe(III) system, cause considerable interference in all the techniques examined, interference is readily recognized by a shift in peak potential and a change in the wave shape on addition of increasing concentrations of the more positively reduced species. With other systems, a depolarizer more negatively reduced than another can be determined over a wide range of conditions with three-electrode instrumentation. *IR*-drop problems with two-electrode systems place considerable restrictions on their use. With Zn/Cu and Cd/Cu and other systems, reliable determinations were possible only when the concentration of the more positively reduced species was less than 10^{-2} M.

Modern polarographic methods are used extensively to determine simultaneously two or more electroactive species which have well separated $E_{1/2}$ values, and have considerable advantages over conventional d.c. polarography for this purpose [1]. In such determinations, it has been assumed that electrode processes in multi-component systems operate independently of each other and that the more positively reduced species do not interfere. Indeed, it has been stated that a thousand-fold or greater concentrations of species reduced at positive potentials can be tolerated in pulse and a.c. methods [1].

There can be no question that polarographic waves formed in the presence of large concentrations of more positively reduced species can be readily measured. However, that the electrode processes are identical in the presence and absence of large concentrations of such species is less certain. With conventional a.c. polarographic instrumentation, some earlier results [2, 3] indicated that considerable problems can be expected in this kind of measurement. These measurements were made without a three-electrode potentiostat system, and *iR* drop and other instrumental difficulties prevented a clear distinction between chemical interferences and instrumental artefacts. However, Yamaoka [4] unambiguously demonstrated that the a.c. polarographic wave height of one reducible entity can be influenced by the presence of another,

and Smith et al. [5—7] have substantiated these findings by extensive theoretical calculations. They also suggested that such effects could occur in pulse polarography and other modern polarographic methods. These results suggest that the electrode processes used for a.c. polarographic multicomponent assay procedures should at least be reversible in the d.c. sense. However, few experimental data are available on this vital facet of a.c. polarography. No data have been reported for pulse and other techniques.

Obviously if this kind of interference occurs in all polarographic methods, the implications are considerable. In the present paper, the influence of preceding electrode processes is described for a variety of polarographic methods, and the possible analytical difficulties are assessed.

EXPERIMENTAL

Polarographic curves were recorded with either a Princeton Applied Research Electrochemistry System Model 170 or Polarographic Analyzer Model 174 modified to perform second-harmonic a.c. and other techniques as described elsewhere [8, 9]. Unless otherwise specified, a three-electrode format was used for all measurements with Ag/AgCl as the reference electrode and platinum wire as the auxiliary electrode.

All solutions of metal ions were prepared from their nitrate salts (A.R. grade). Solutions were thermostated (25 ± 0.1 °C) and degassed with argon before the curves were recorded.

INTERFERENCES IN DIFFERENT REACTION SYSTEMS

Homogeneous redox reactions

The presence of a more positive electrode process might influence the reduction pathway of another electroactive species in several ways. As a first example, analytical data where a homogeneous redox reaction causes difficulties, are presented. This is the mechanistic scheme :

$$A + e \rightleftharpoons B \text{ (electrode reaction)}$$

$$C + e \rightleftharpoons D \text{ (electrode reaction)}$$

$$A + D \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + B \text{ (homogeneous redox reaction)}$$

theoretically considered by Smith et al. [5]. The example chosen is the reduction of chromium(III) in 1.0 M $NaClO_4$/0.024 M $HClO_4$ in the presence of iron(III). The reduction of chromium(III) in the medium is irreversible, and the redox reaction : $Fe^{3+} + Cr^{2+} \rightarrow Fe^{2+} + Cr^{3+}$ is known to be fast [10] and to enhance the a.c. polarographic wave height for chromium [4, 7]. The iron(III) reduction occurs at a potential more positive than the oxidation of mercury and the reduction of chromium(III) at about –0.9V vs. Ag/AgCl.

In the present study, the techniques of fundamental and second harmonic a.c. polarography, and linear-sweep d.c., normal and differential pulse polarography and a.c. and pulse voltammetry with the sweep rate synchronized with the DME were employed. On each occasion a considerable enhancement of the peak current (or equivalent parameter proportional to concentration in analytical work) and a negative shift in wave position of the chromium(III) reduction wave occurred on addition of iron(III). Typical data for fundamental harmonic a.c. polarography and differential pulse polarography are contained in Table 1.

From Table 1 and other data obtained, the determination of chromium in the presence of iron(III) would clearly be prone to considerable interference, for all the polarographic methods examined. To check the proposed mechanism all the experiments were repeated, with addition of iron(II) instead of iron(III); as expected the chromium peak height was not affected, which proves that the interference originates from the more positively reduced iron(III). In complex analytical mixtures, the method of standard addition rather than reference to a calibration curve is frequently recommended. Figure 1 shows that for all iron(III) concentrations, peak heights for chromium(III) under both a.c. and differential pulse conditions are linear functions of concentration. This is a prerequisite for using the method of standard additions and it would appear that the method of standard additions must be recommended for determining species in the presence of coupled homogeneous chemical reactions. Obviously, if the wave position or wave shape of polarographic curves of standards prepared for calibration purposes differs from the unknown solutions, results should be queried. Interference from a homogeneous chemical reaction of the kind considered above can be detected by the negative shift of $E_{1/2}$ concomitant with the iron(III) interference.

TABLE 1

Influence of iron(III) on the polarographic reduction of chromium(III) (Medium = 1 M $NaClO_4$/0.024 M $HClO_4$. [Cr(III)] = $1.0 \cdot 10^{-3}$ M. For a.c. measurements the applied potential was 10 mV at 200 Hz. Differential pulse amplitude = 50 mV. Drop time = 2 s.)

Technique	[Fe(III)] M	Peak height μA	Peak potential V vs. Ag/AgCl	Half width mV
A.c.	0	0.35	−0.930	182
	$1.90 \cdot 10^{-3}$	0.90	−0.950	170
	$4.10 \cdot 10^{-3}$	1.28	−0.955	170
	$6.75 \cdot 10^{-3}$	1.70	−0.965	168
	$9.38 \cdot 10^{-3}$	1.88	−0.985	168
	$1.54 \cdot 10^{-2}$	2.10	−0.995	168
Differential pulse	0	6.16	−0.895	—
	$2.10 \cdot 10^{-3}$	9.70	−0.925	—
	$1.35 \cdot 10^{-2}$	10.50	−0.965	—
	$2.74 \cdot 10^{-2}$	11.30	−0.985	—

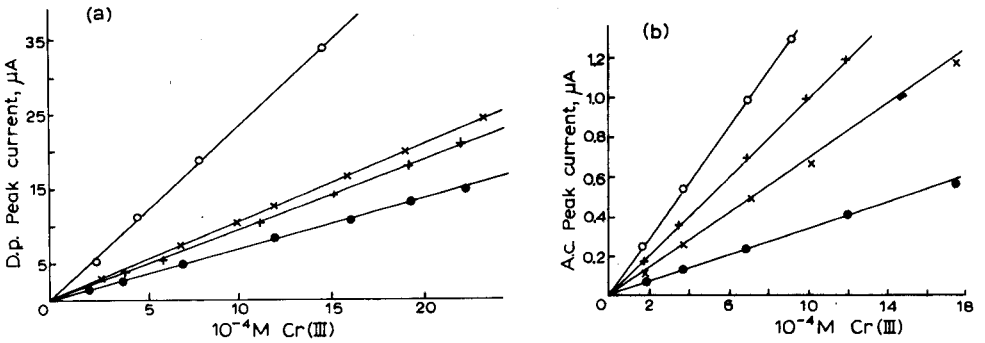

Fig. 1. Dependence of peak current on concentration for the reduction of chromium(III) in the presence of iron(III). Medium = 1.0 M $NaClO_4$/0.024 M $HClO_4$. (a) Differential pulse method. Pulse amplitude = 50 mV. [Fe(III)]: (•) 0 M; (+) $2 \cdot 10^{-3}$ M; (x) $3 \cdot 10^{-3}$ M; (○) $5 \cdot 10^{-2}$ M. (b) A.c. method. Amplitude = 10 mV at 200 Hz. [Fe(III)]: (•) 0 M; (x) $1 \cdot 10^{-3}$ M; (+) $2 \cdot 10^{-3}$ M; (○) $5 \cdot 10^{-3}$ M.

Amalgam-forming systems

In inverse polarography or stripping analysis, intermetallic interferences have been well documented [10—12]. For example, several reports [13—15] deal with copper—zinc intermetallic formation. Polarographic determinations of metals involving amalgam formation are amongst the commonest in the literature, yet it has nearly always been assumed that a preceding electrode process has no effect on another. However, for zinc determinations in the presence of copper [16], it seems possible that at high copper concentrations and at the potentials for the Zn(II)/Zn(Hg) couple, reduction of zinc could effectively be occurring at a dropping copper amalgam electrode; based on knowledge gained from stripping analysis this could lead to interference. Bauer et al. [17, 18] have shown that at high concentrations, copper gives rise to unusual resistance-controlled currents and maxima over a wide potential range in several media. Reduction of another species in the presence of a resistance-controlled current could also cause interference.

With up to 10^{-3} M concentrations of copper, the zinc wave in 0.5 M $NaClO_4$ was unaffected (Table 2). However, in the presence of copper concentrations around 10^{-2} M all a.c., pulse and derivative techniques gave enhanced peak currents for the reduction of zinc. Figure 2 summarizes some data for the determination of zinc in the absence and presence of 10^{-2} M copper(II). The enhancement is not nearly as large as for the previously considered homogeneous chemical reaction, but it is still significant. Unlike the iron(III)/chromium(III) system, the interference does not occur at all copper concentrations examined.

Table 3 gives some data for the reduction of cadmium in the presence of copper. For concentrations of copper up to 10^{-2} M, the cadmium peak height in all methods studied was independent of copper concentration.

TABLE 2

Measurement of the Zn(II)/Zn electrode process in the presence of increasing concentrations of the more positively reduced copper(II) (Medium = 0.5 M $NaClO_4$; [Zn(II)] = $1.00 \cdot 10^{-3}$ M; a.c. potential = 10 mV; a.c. frequency = 100 Hz; $E_{1/2}$ (Cu(II)/Cu) = 0.055 V vs. Ag/AgCl. All $E_{1/2}$ and E_p values are given vs. Ag/AgCl)

[Cu(II)] M	D.c. tast					D.c. deriv. tast					A.c.				
	2-electrode[a]			3-electrode[b]		2-electrode[c]			3-electrode[d]		2-electrode[e]			3-electrode[f]	
	$-E_{1/2}$ V	i_d μA	$\Delta E_{1/2}$ mV	$-E_{1/2}$ V	i_d μA	$-E_p$ V	i_p μA	ΔE_p mV	$-E_p$ V	i_p μA	$-E_p$ V	$i_p \sim$ μA ~	ΔE_p mV	$-E_p$ V	$i_p \sim$ μA ~
0.000	0.975	2.00	0	0.967	2.00	0.978	2.15	0	0.975	2.15	0.961	1.25	0	0.960	2.12
0.003	1.000	2.00	25	0.969	2.00	1.000	2.15	22	0.975	2.16	0.985	1.25	24	0.957	2.12
0.005	1.018	2.02	43	0.968	2.00	1.018	2.17	40	0.976	2.15	1.003	1.25	42	0.962	2.12
0.008	1.039	2.04	64	0.968	2.02	1.042	2.18	64	0.974	2.18	1.023	1.26	62	0.960	2.14
0.010	1.051	2.04	76	0.967	2.04	1.051	2.20	73	0.975	2.18	1.031	1.28	70	0.961	2.16
0.017	1.098	2.06	123	0.967	2.06	1.100	2.20	122	0.975	2.20	1.080	1.30	119	0.963	2.18

[a]($E_{1/4} - E_{3/4}$) = 38 mV, [b]($E_{1/4} - E_{3/4}$) = 33 mV, [c]Half width = 55 mV, [d]Half width = 60 mV, [e]Half width = 105 mV, [f]Half width = 68 mV.

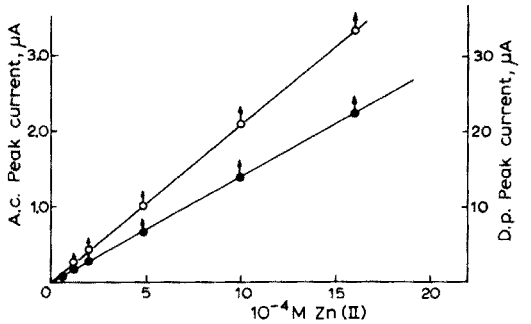

Fig. 2. Dependence of a.c. and differential pulse peak current on concentration for the reduction of zinc in the presence and absence of copper. (•) a.c., (○) differential pulse. Points marked are in the absence of copper. Arrows indicate increase in peak current on addition of $2 \cdot 10^{-2}$ M copper.

At very high concentrations, slight enhancements were observed; for example, the peak current in a.c. 3-electrode polarograms under the conditions specified in Table 3, increased only from 10.0 μA to 10.8 μA, as the copper concentration increased from $1.65 \cdot 10^{-3}$ M to 10^{-1} M. This result agrees with previously obtained d.c. data [19].

Other systems

Tables 4 and 5 show data obtained for other systems involving, respectively, an amalgam system with a soluble system at a more positive potential, and a soluble system with amalgam systems at a more positive potential. These systems are characterized by marginal increases in peak currents at very high concentrations and a slight negative shift in peak potential.

INSTRUMENTAL PROBLEMS

In the presence of high concentrations of a more positively reduced species, large d.c. currents flow through the cell in a.c. and pulse experiments. These are now shown to be the cause of the large negative shifts in the peak potential with two-electrode polarographs, and probably of the small negative shifts observed at high concentrations of more positively reduced species even with a three-electrode potentiostat.

The d.c. electrode process

In d.c. polarography, a preceding or more positive electrode process causes a d.c. current i_B, with limiting or diffusion current $(i_d)_B$, to flow through the polarographic cell. At more negative potentials where the second electrode process occurs, an additional current i_A, with limiting value $(i_d)_A$, is superimposed on the current $(i_d)_B$. Thus, the total current flowing through the cell, i_T, at potential C, will be given by

TABLE 3

Measurement of the Cd(II)/Cd electrode process in the presence of increasing concentration of the more positively reduced copper(II) (Medium 0.5 M $NaClO_4$; [Cd(II)] = $1.30 \cdot 10^{-3}$ M; a.c. potential = 10 mV; frequency = 80 Hz. All $E_{1/2}$ and E_p values are given vs. Ag/AgCl.)

[Cu(II)] M	D.c. tast					D.c. deriv. tast					A.c.				
	2-electrode[a]			3-electrode[b]		2-electrode[c]			3-electrode[d]		2-electrode[e]			3-electrode[f]	
	$-E_{1/2}$ V	i_d μA	$\Delta E_{1/2}$ mV	$-E_{1/2}$ V	i_d μA	$-E_p$ V	i_p μA	ΔE_p mV	$-E_p$ V	i_p μA	$-E_p$ V	$i_p \sim$ μA ~	ΔE_p mV	$-E_p$ V	$i_p \sim$ μA ~
0	0.543	2.15	0	0.543	2.15	0.547	2.45	0	0.545	2.60	0.550	5.50	0	0.545	10.0
$1.65 \cdot 10^{-3}$	0.566	2.15	13	0.543	2.15	0.560	2.45	13	0.546	2.60	0.563	5.45	13	0.547	10.0
$3.22 \cdot 10^{-3}$	0.571	2.10	28	0.543	2.15	0.575	2.40	25	0.546	2.60	0.576	5.45	26	0.546	10.0
$6.35 \cdot 10^{-3}$	0.588	2.15	45	0.543	2.15	0.590	2.45	43	0.546	2.60	0.573	5.50	43	0.547	10.0
$7.46 \cdot 10^{-3}$	0.606	2.20	53	0.546	2.15	0.605	2.50	58	0.547	2.60	0.605	5.50	55	0.547	10.0

[a]($E_{1/2} - E_{3/4}$) = 32 mV, [b]($E_{1/4} - E_{3/4}$) = 27 mV, [c]Half-width = 50 mV, [d]Half width = 45 mV, [e]Half-width = 70 mV, [f]Half width = 47 mV.

TABLE 4

Measurement of the Cd(II)/Cd electrode process in the presence of the more positively reduced uranium(VI)
(Medium = 1 M $NaClO_4$; [Cd(II)] = $2.0 \cdot 10^{-4}$ M; a.c. potential = 10 mV at 200 Hz. Differential pulse amplitude = 50 mV. Drop time = 2 s.)

Technique	[U(VI)] M	Peak height μA	Peak potential V vs. Ag/AgCl
A.c.	0	5.35	−0.523
	$2.82 \cdot 10^{-3}$	5.35	−0.523
	$4.92 \cdot 10^{-3}$	5.35	−0.525
	$8.68 \cdot 10^{-3}$	5.35	−0.528
	$1.09 \cdot 10^{-2}$	5.35	−0.530
	$1.31 \cdot 10^{-2}$	5.40	−0.530
	$1.46 \cdot 10^{-2}$	5.40	−0.532
	$1.86 \cdot 10^{-2}$	5.50	−0.532
	$2.12 \cdot 10^{-2}$	5.50	−0.535
Differential pulse	0	11.40	−0.520
	$1.64 \cdot 10^{-2}$	11.60	−0.525
	$3.50 \cdot 10^{-2}$	12.00	−0.530

TABLE 5

Measurement of the Cr(III)/Cr(II) electrode process in the presence of the more positively reduced lead(II)
(Medium = 1 M $NaClO_4$; [Cr(III)] = $1.0 \cdot 10^{-3}$ M; a.c. potential = 10 mV at 200 Hz. Differential pulse amplitude = 50 mV. Drop time = 2 s.)

[Pb(II)] M	A.c.		Differential pulse	
	Peak height μA	Peak potential V. vs. Ag/AgCl	Peak height μA	Peak potential V. vs. Ag/AgCl
0	0.35	−0.930	5.10	−0.895
$6.87 \cdot 10^{-3}$	0.35	−0.940	5.10	−0.895
$2.79 \cdot 10^{-2}$	0.35	−0.950	5.05	−0.900
$2.98 \cdot 10^{-2}$	0.35	−0.950	5.05	−0.900
$3.40 \cdot 10^{-2}$	0.40	−0.950	5.25	−0.915

$$i_T = (i_d)_B + (i_d)_A \quad (1)$$

If both electrode processes are diffusion-controlled, then according to the Ilkovic equation,

$$i_T = k_B C_B + k_A C_A \quad (2)$$

where k_A and k_B are constants. Thus, if the concentration of the more positively reduced species C_B is considerably greater than that of the species being determined, C_A, i.e. $(i_d)_B \gg (i_d)_A$, then

$$i_T \approx (i_d)_B \quad (3)$$

which is the condition applying in much of this work.

It will now be assumed that the more positive electrode process, B, does not alter the nature of the electrode process being measured, A, by, e.g., a coupled chemical reaction, and that the only possible influence from electrode process B on electrode process A arises from the current $(i_d)_B$ flowing through the cell. The current $(i_d)_B$, flowing through a cell of resistance, R, will induce an ohmic potential drop of $(i_d)_B R$ at all potentials on wave A as shown in Fig. 3. It should be noted that neither the shape of the wave nor the limiting current $(i_d)_A$ should be altered by this ohmic loss. Electrode process B will thus cause the measured or apparent half-wave potential of A, to shift in the negative direction by $(i_d)_B R$ volt. Thus measurement of the difference of the half-wave potential of A in the absence of B and at various concentrations (currents) of B, should be given by

$$(\Delta E_{1/2})_A = (i_d)_B R \tag{4}$$

Equation (4) indicates that a plot of $(\Delta E_{1/2})_A$ versus $(i_d)_B$ should be a straight line of slope R. Alternatively, if electrode process B is diffusion-controlled, a plot of $(\Delta E_{1/2})_A$ versus C_B should be a straight line.

Similarly, if a three-electrode polarograph is used to measure the $E_{1/2}$ value, then

$$(\Delta E_{1/2})_A = (i_d)_B R_{\text{uncomp.}} \tag{5}$$

where R is the uncompensated resistance. Thus a negative shift in $E_{1/2}$ can be observed at large values of $(i_d)_B$. Some representative data to test these equations are included in Tables 2 and 3 along with the three-electrode results. It can be seen that with two-electrode Tast d.c. polarography, the $E_{1/2}$ values for both cadmium(II) and zinc(II) do become more negative with increasing concentrations of copper. Furthermore, Tables 2 and 3 show that the $(E_{1/4} - E_{3/4})$ values of the waves do not alter, i.e. the shapes of the d.c. waves are unaltered by the presence of the more positively reduced copper(II) species. With the 2-electrode format, plots of $\Delta E_{1/2}$ against copper(II)

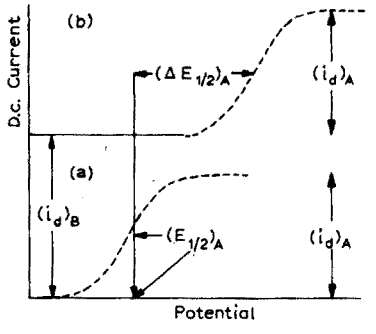

Fig. 3. Influence of the iR drop from the preceding electrode process. (a) In the absence of electrode process B. (b) In the presence of electrode process B.

concentration in the range $0—16 \cdot 10^{-3}$ M, and against $(i_d)_{Cu}$ in the range 0—20 μA showed the same rectilinear relationships for both the zinc and cadmium systems, which indicates that Ohm's Law is obeyed. From the former plot, the cell resistance was found to be $(4.0 \pm 0.1) \cdot 10^{-3}$ Ω, so that a means of measuring cell resistance is available.

The a.c. electrode process

With a.c. polarography, a small a.c. potential is superimposed on the d.c. potential and an alternating current as well as a direct current flows across the polarographic cell at potentials around $E_{1/2}$. The d.c. current is filtered from the a.c. current, and the readout of an a.c. polarographic curve therefore consists of a plot of a.c. current versus d.c. potential.

The shape of a reversible a.c. wave is the same as the derivative of the reversible d.c. wave, and for this type of electrode process the alternating current has decayed to an extremely small value relative to the maximum or peak current, at potentials 200—300 mV removed from $E_{1/2}$ (Fig. 4). Thus, even if the concentration of B is much greater than that of A, the alternating current from B is so small at the potentials where A is electroactive, that it can be neglected, as can its influence in terms of ohmic losses.

The direct current from electrode process B, even though electronically filtered out from the readout and not observed, still flows across the cell during the a.c. experiment and can influence the more negative electrode process.

If it is assumed that the same direct current flows through the cell during an a.c. experiment, as in the d.c. case, then the total current is given by

$$i_T = (i_{dc}) + (i_{ac} \sim) \qquad (6)$$

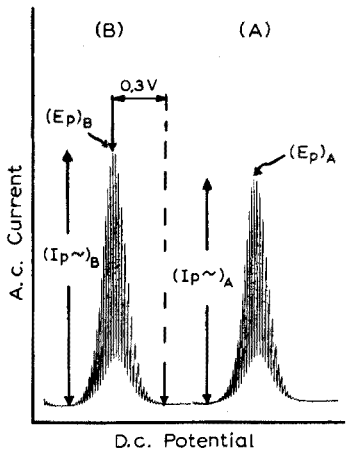

Fig. 4. A.c. polarogram of the two-electrode processes considered.

where at $E_{½}$ for electrode process A, $i_{dc} = (i_d)_B + (i_d/2)_A$ and $i_{ac} = (i\sim)_B + (i\sim)_A$.

As discussed earlier, at potential $(E_{½})_A$, $(i\sim)_B$ can be considered negligible; $(i\sim)_A$ is a function of potential. For example, with a reversible a.c. electrode process, the simplest case to consider, $(E_p)_A$ is equal to $(E_{½})_A$ and the value of $(i\sim)_A$ is $(i_p\sim)_A$. Thus at $(E_{½})_A$, $i_{ac} = (i\sim)_A$, or for the particular case where the a.c. electrode process is reversible, $i_{ac} = (i_p\sim)_A$.

If it is valid to treat the influence of the preceding electrode process as arising solely from the direct current, and to treat the alternating and direct currents mathematically as separate, non-interacting components of the current network, then the sole effect from the more positive electrode process should be to shift the a.c. wave to a more negative potential. The shape of the a.c. wave should remain unaltered. In addition, this requires that the shift in E_p on addition of increasing concentrations (direct currents) of the more positive depolarizer should be given by

$$(\Delta E_p)_A = (i_d)_B R \tag{7}$$

and that

$$(\Delta E_p)_A = (\Delta E_{½})_A \tag{8}$$

Tables 2 and 3 and the data from the plots of $(\Delta E_p)_A$ vs. [Cu] and $(i_d)_{Cu}$ show that all the above equations adequately describe the data for the same systems as considered with d.c. polarography.

With a two-electrode arrangement and with high concentrations of depolarizer at the 10^{-3} M level producing high currents (see Tables 2 and 3), the influence of resistance on the alternating current is obvious from the considerable decrease in measured $(i_p\sim)_A$ values and broader a.c. wave obtained, compared with the three-electrode arrangement. When lower concentrations of cadmium(II) and zinc(II) (ca. 10^{-4} M) were used, so that resistance effects were negligible in that two-electrode and three-electrode polarograms were indistinguishable in the absence of copper(II), the addition of the same copper(II) concentrations as in Tables 2 and 3 gave shifts in $(E_p)_A$ identical to those reported in these Tables. The result proved conclusively that direct currents associated with the electrode processes do not interact with the alternating current, and can be treated quite separately in considering resistance effects.

Pulse polarography

The same kinds of d.c. effects operate in pulse polarography as in d.c. and a.c. polarography, and discussion with respect to other techniques is not required.

The present work suggests that, in the absence of chemical interference, a depolarizer reduced more negatively than another depolarizer can be determined over a wide range of conditions with three-electrode instrumentation, but not with two-electrode instrumentation.

The possibility of the preceding electrode process causing interference, other than by *iR* drop, is always present — as illustrated by the Fe(III)/Cr(II) system. This type of interference via coupled chemical reaction is readily recognized by a shift in peak potential and probably a change in shape and peak height of the a.c. or pulse polarograms on addition of increasing concentrations of the more positively reduced species. When more than 10^{-2} M copper(II) is added to cadmium or zinc solutions, a slight change in the cadmium(II) and zinc(II) electrode processes is in fact evident. Similar results were found with other systems. The interference appears to have a different origin from the Fe(III)/Cr(III) case. The cause of the interference of extremely high copper(II) concentrations is unknown, although it might be attributed to an amalgam effect. Any further speculation on its origin from the data obtained in this work is unwarranted, as it occurs under conditions where changes in viscosity or ionic strength could occur, and non-diffusion-controlled conditions are operative. However, it does seem that concentrations of a species causing a preceding electrode process must be maintained below about 10^{-2} M in polarography.

The changes in wave shape found when the non *iR*-compensated Metrohm AC polarograph was used [2] must be due to instrumental artefacts absent in the solid-state electronics used in the PAR equipment. There are many circuitry differences between the Metrohm and PAR instrumentation, and the distortion with Metrohm instrumentation could have many causes, though the most probable is incomplete filtering of extremely high direct currents. Certainly under normal operating conditions and with low direct currents, no distortions of shape were encountered with Metrohm instrumentation. Alternatively particular phase shifts may be introduced with high d.c. currents.

In conclusion, it seems that three-electrode *iR*-compensated instrumentation is necessary for simple, convenient multi-element polarographic analysis and that careful checks must always be carried out. Only if this procedure is adopted can all the claims regarding the advantages of modern methods over d.c. polarography, with respect to determining a species reduced at more negative potentials than another depolarizer [1], be fulfilled.

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THE DETERMINATION OF BOUND NITROGEN IN URANIUM HEXAFLUORIDE WITH AN AMMONIA ELECTRODE*

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SUMMARY

Uranium hexafluoride reacts with nitrosyl fluoride (NOF), nitryl fluoride (NO_2F), and nitrogen oxides to form solid compounds such as nitrosyl heptafluorouranate ($NOUF_7$) and nitryl heptafluorouranate (NO_2UF_7). Since these compounds are undesirable impurities in uranium hexafluoride, a method has been developed for the determination of these nitrogen oxyfluorides in uranium hexafluoride. Uranium hexafluoride is hydrolyzed in a potassium permanganate solution which converts the uranium hexafluoride to uranyl fluoride and the nitrogen oxyfluorides to nitric acid. The nitrate is reduced with aluminum powder to ammonia, which is then measured with an ammonia electrode in a basic solution. The method is relatively interference-free because the electrode is a gas-sensing device. The detection limit is 0.8 μg bound N/g U, and the precision at 3 μg bound N/g U is ± 16 %.

In the production of uranium hexafluoride by the direct fluorination of uranium oxides (UO_3 or U_3O_8) [1], the presence of trace quantities of nitrates can lead to the formation of compounds such as nitrosyl and nitryl hexafluorouranates and heptafluorouranates ($NO_x UF_y$, where $x = 1$ or 2 and $y = 6$ or 7). These compounds are solids at 25 °C and have very low vapor pressures; however, at slightly elevated temperatures, the heptafluorouranates dissociate to nitrosyl fluoride (NOF) or nitryl fluoride (NO_2F) and uranium hexafluoride with significant dissociation pressures [2—4]. NOF and NO_2F can recombine over a wide temperature range with the uranium hexafluoride and other gaseous fluorides such as CrO_2F_2, MoF_6, and PF_5 to form solids which are undesirable impurities. Consequently, an analytical method was needed to determine trace quantities of bound nitrogen in uranium hexafluoride.

The hydrolysis reactions and products of the N—O—U—F compounds must be considered in the choice of an analytical method. Hydrolysis of the nitrosyl and nitryl hexafluorouranates and heptafluorouranates with water yields the same nitrogen compounds obtained on the hydrolysis of NOF and

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NO_2F, i.e., NO, HNO_2 and HNO_3 [2, 5, 6]. Because of the slight solubility of NO, partial loss of nitrogen can occur during hydrolysis. To prevent this loss N—O—U—F compounds are hydrolyzed in a cold acidic solution of potassium permanganate which oxidizes nitric oxide and nitrous acid to nitric acid [7].

Several analytical methods are available for determining trace amounts of nitrate, but large amounts of UO_2F_2 interfere in nearly all of them [7]. Initially, two methods, one involving the Devarda metal reduction—distillation [8] and the other colorimetry with chromotropic acid [9, 10], were investigated but neither was satisfactory because excessive variations in the blanks affected the analytical precision at low nitrogen concentrations. Subsequently, a method was developed for the determination of bound nitrogen in uranium hexafluoride as ammonia with an ammonia electrode. The method is based on the reduction of nitrate to ammonia with aluminum powder in an HCl—UO_2F_2 solution, and direct measurement of the ammonia in a basic solution with an ammonia-specific electrode. This method offers several advantages: (1) the addition of minimum amounts of reagents in the reduction step results in a low nitrogen blank; (2) the aluminum reduction system is versatile, and several reductions can be made simultaneously with very little operator attention; (3) the nitrogen concentrations can vary widely; and (4) the analysis with the electrode is relatively interference-free, and the measurement can be made directly in the original solution. The precision of the method is ± 16 % at 3 μg bound N/g U, and the detection limit is 0.8 μg bound N/g U.

EXPERIMENTAL

Apparatus

An Orion Ammonia Electrode Model 95-10 was used with a Corning Model 12 pH Meter and a Heath—Schlumberger Model SR-255 Recorder.

Reagents

An internal fill solution of 0.01 M NH_4Cl and 1.0 M KCl was used instead of internal fill solution supplied with the ammonia electrode in order to match the osmolar strength of the test solutions. Aluminium powder (dust) and sodium fluoride (heated for 16 h at 850 °C) were used for the reduction. The sodium fluoride was added to fluoride-free samples. All other chemicals used were reagent grade.

Procedure

Pipet a sample of UO_2F_2 solution containing 350—500 mg U into a 125-ml Erlenmeyer flask. Adjust the volume to 17 ml with deionized water and add 2 ml of 12 M HCl. Using a magnetic stirrer, stir the solution slowly,

and add 0.3 g of aluminum dust. Cap the flask with a vented stopper, and continue stirring until hydrogen evolution stops. Then add 1 ml of 12 M HCl, and continue stirring until the aluminum dust dissolves (about 45 min for reduction). Adjust the volume to 92 ml with deionized water, and stir the solution. Add 8 ml of 10 M NaOH and transfer the solution to a 150-ml beaker. Immerse the ammonia electrode into the solution and cover the beaker to prevent ammonia loss or contamination. Stir the solution slowly while the electrode voltage is monitored with a strip chart recorder to determine when the voltage stabilizes (i.e., less than 0.1 mV change min^{-1}). Record the voltage reading to 0.1 mV. Pipet a known quantity of nitrogen (about twice the amount of nitrogen as expected in the sample) as an NH_4Cl solution into the sample, and record the new voltage reading in the same manner. Calculate the nitrogen concentration of the original sample using a standard additions table provided with the electrode or by the usual standard additions formula. Alternatively prepare a calibration on a daily basis to determine the nitrogen concentration directly from the originally observed potential. A reagent blank should be carried through the entire procedure.

RESULTS AND DISCUSSION

Formation and hydrolysis of the N—O—U—F compounds

Uranium hexafluoride reacts readily with the nitrogen oxides (NO and NO_2) and nitrogen oxyfluorides (NOF and NO_2F) to form solid compounds such as nitrosyl and nitryl hexafluorouranates and heptafluorouranates [2, 3]. These compounds hydrolyze easily in water to form nitric acid, nitrous acid, and nitric oxide. Typical formation of N—O—U—F compounds and hydrolysis reactions are given below; the asterisked equations are proposed hydrolysis reactions.

$$NO + UF_6 \rightarrow NOUF_6 \quad (1)$$

$$6\,NOUF_6 + 10\,H_2O \rightarrow 3\,UF_4 + 3\,UO_2F_2 + 4\,NO + 2\,HNO_3 + 18\,HF \quad (2)$$

$$NO_2 + UF_6 \rightarrow NO_2UF_6 \quad (3)$$

$$2\,NO_2UF_6 + 4\,H_2O \rightarrow UF_4 + UO_2F_2 + 2\,HNO_3 + 6\,HF \quad (4)$$

$$NOF + UF_6 \rightarrow NOUF_7 \quad (5)$$

$$3\,NOUF_7 + 8\,H_2O \rightarrow 3\,UO_2F_2 + 2\,NO + HNO_3 + 15\,HF^* \quad (6)$$

$$NO_2F + UF_6 \rightarrow NO_2UF_7 \quad (7)$$

$$2\,NO_2UF_7 + 6\,H_2O \rightarrow 2\,UO_2F_2 + 2\,HNO_3 + 10\,HF^* \quad (8)$$

The hydrolysis reactions of the nitrosyl and nitryl hexafluorouranates have been established, while the hydrolysis reactions of the heptafluorouranates have not been well defined [11]. Structural studies of the heptafluorouranates indicate the presence of both an ionic ($NO_x^+ \cdot UF_7^-$) and a lattice ($NO_xF \cdot UF_6$) form. The hydrolysis reactions of the lattice form should be similar to the hydrolysis of NOF and NO_2F; therefore, the hydrolysis products of the heptafluorouranates are assumed to be NO, HNO_2, and HNO_3 [3, 5, 6].

In the hydrolysis of the N—O—U—F compounds, nitric oxide is formed directly or by the decomposition of nitrous acid in hydrofluoric acid solutions. Because of the slight solubility of nitric oxide, nitrogen losses could occur. To prevent this loss, the N—O—U—F compounds are hydrolyzed in a closed container with a cold potassium permanganate solution which oxidizes nitric oxide and nitrous acid to more stable nitric acid.

Reduction of nitrate to ammonia

Two reduction techniques for the conversion of nitrate to ammonia in UO_2F_2 solutions were evaluated. One was the reduction with Devarda's metal in an alkaline solution from which the ammonia is distilled. The other was the reduction with aluminum powder in a strongly acidic UO_2F_2 solution in which the ammonia is converted to ammonium ion. The reduction with aluminum metal eliminates the need for distillation and requires less time and control than the Devarda's metal—alkaline solution reduction. Reagent blanks are also much lower with the aluminum powder reduction, and the blanks become very significant in low-level nitrogen determinations. Therefore, the aluminum powder technique was chosen as the method of reduction.

The reduction efficiency depends on the generation of hydrogen and contact time. Acid fluoride ion concentration and surface area control the dissolution rate of the aluminum powder and thereby the generation rate of hydrogen. The effect of the amount of aluminum powder and fluoride ion on reduction efficiency is shown in Fig. 1. Aluminum powder with a surface area of about 0.7 $m^2\ g^{-1}$ is satisfactory in a solution that contains 1.2 M HCl and 0.6 M fluoride. As the original acid is consumed, more acid is required to dissolve the aluminum powder completely. The dissolution rate must be controlled to allow intimate contact of the hydrogen with the liquid. If the acid concentration is too great, the aluminum powder dissolves too rapidly and reduction efficiency decreases. The amount of the uranyl ion also affects the reduction efficiency because aluminum is consumed to reduce U(VI) to U(IV). It was found that 0.5 g of aluminum is sufficient to reduce 100 μg N to ammonia in the presence of 1.0 g of uranium (VI). The reduction efficiency is 92 % for the recommended procedure.

Electrode operation and measurement

The ammonia electrode is relatively interference-free, and ammonia can be determined directly in a basic solution of UO_2F_2. The response time of the electrode depends on the ammonia concentration and condition of the membrane. The response is faster as the ammonia concentration increases and electrode voltage stabilizes in about 10 min at the 20 p.p.b. nitrogen level. Response time is also a function of membrane age, and in this application a membrane was found to operate satisfactorily for 1—2 weeks. A typical calibration curve (Fig. 2) shows that the response to the concentration of ammonia is identical for sodium hydroxide solutions whether or not UO_2F_2 was originally present. The dashed line shows a calibration without correction for the residual blank. With the residual blank added, the electrode response is linear down to about 30 p.p.b. nitrogen.

The partial pressure of the dissolved ammonia is a function of the ionic strength of the test solution and temperature; thus, variations in these conditions will affect the electrode response. Adequate control of the temperature can

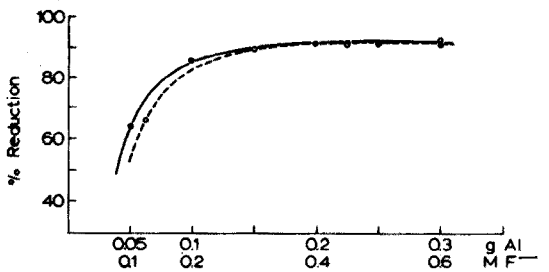

Fig. 1. Effect of aluminum powder and fluoride ion on the reduction of nitrate ion. Reduction conditions: 20 ml volume, 1.2 M HCl, 45-min stirring. (○) 0.25 g Al. (●) 0.6 M fluoride.

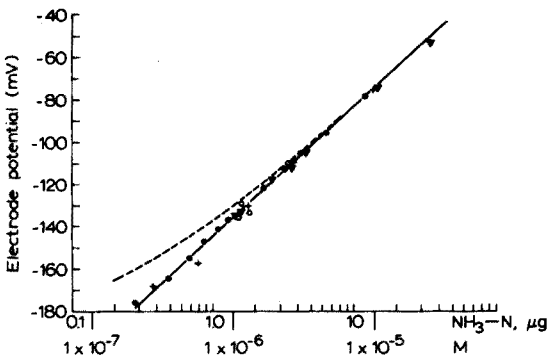

Fig. 2. Calibration curves for the ammonia electrode. Solutions: (•) H_2O—NaOH. (×) H_2O—NaOH + H_2O_2. (▲) UO_2F_2—NaOH. (○) UO_2F_2—NaOH + H_2O_2. (----) Uncorrected. (——) Corrected for N blank. (Note: H_2O_2 was added to keep uranium in solution.)

be achieved by allowing samples and the electrode to reach ambient temperature. Since the partial pressure of the dissolved ammonia is also a function of ionic strength, calibration should be made with standards that match the ionic strength of the test solutions. If the ionic strengths of the test solutions vary, the standard additions method should be used.

A second source of error arises if the osmolar strength of the test solution is considerably greater than that of the internal electrolyte. In this situation, water vapor can diffuse from the electrode through the membrane and change the ammonia concentrations of the very small working volume (10^{-2}—10^{-3} ml) in the electrode. This change will cause electrode instability and drift [12]. Ideally, the osmolar strength of the test solution should match that of the internal electrolyte. The osmolar strength of the test solutions is about 2 M while the commercial internal electrolyte has a osmolar strength of only 0.2 M. To reduce the differential, the internal electrolyte solution was replaced with a solution of higher osmolar strength instead of diluting the test solutions which would raise the detection level. A comparison of the response of the electrode was made with different internal electrolytes. The calibration curves (Fig. 3) show that the three internal electrolytes give identical ammonia response except that electrode potentials shift. The commercial fill solution can be salted with either KCl or NaCl; however, above 0.6 M NaCl solutions begin to crystallize. A 0.01 M NH_4Cl—1.0 M KCl internal electrolyte operates very satisfactorily.

Analytical precision and comparative analysis

In the determination of nitrogen at low levels, the amount of nitrogen in the reagent blank and the accuracy with which it is known are extremely important. The blank should be very low, because it determines the detection level in the test solution; thus, the use of reagents with very low ammonia and

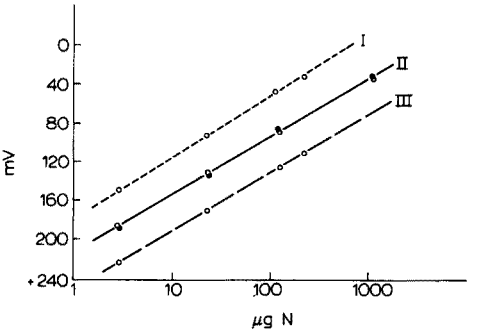

Fig. 3. Comparison of calibration curves with internal fill solutions of varying molar strengths. I, Commercial internal fill solution (0.01 M NH_4Cl—0.2 M NaCl); test solution, 0.8 M NaOH—0.1 M Al—0.13 M F^-. II, Internal fill solution, 0.01 M NH_4Cl—1 M KCl; test solution, (○) As I, (●) As I + 0.015 M UO_2F_2. III, Internal fill solution, 0.01 M NH_4Cl—0.6 M NaCl; test solution, as for I.

reducible nitrogen concentrations is essential. The analytical precision for a typical reagent blank and a series of UO_2F_2 solutions spiked with nitrogen as nitrate ion is given in Table 1.

The results of a series of comparative analyses on UF_6 known to contain $NOUF_7$ and NO_2UF_7 are given in Table 2. Three UO_2F_2 solutions containing very small quantities of nitrogen were analyzed by three methods, and these results are also presented in Table 2.

This procedure has also been adapted for the determination of nitrogen as nitrite or nitrate in other uranium compounds and in environmental samples.

TABLE 1

Precision of Analysis

	No. of detn.	μg N		s_r
		Added	Found	
Reagent—Reduction Blank 350—700 mg U as UO_2F_2	8	—	1.5 ± 0.16	10
UO_2F_2 solutions spiked with NO_3^- and reduced, and nitrogen above blank determined	18	0.50	0.44	29
	16	1.00	0.95	16
	6	2.26	2.30	8.6
	6	11.30	11.70	6.3

TABLE 2

Comparative results

Sample type	Method, μg N/g U found		
	Al-reduction NH_3 electrode	Devarda metal reduction-distillation	Chromotropic acid
UF_6—$NOUF_7$	888	874	—
UF_6—NO_2UF_7	129	129	—
UF_6—NO_2UF_7	40	50	—
UO_2F_2	2.2	2.5	2.2
UO_2F_2	2.0	1.1	1.6
UO_2F_2	1.7	2.1	2.4

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NON-DISPERSIVE ATOMIC-FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF MERCURY AND ITS APPLICATION TO FISH SAMPLES

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SUMMARY

A simple non-dispersive atomic-fluorescence spectrometer is described for the assay of mercury in solution at the $\mu g\ l^{-1}$ level; it has also been applied to fish samples at the $mg\ kg^{-1}$ level. After destruction of the fish sample, the mercury is reduced by tin(II) chloride and released from solution by a stream of argon which crosses the beam of a mercury lamp. The fluorescence signal is detected directly by a solar-blind phototube without the need for monochromators or filters. One analysis requires less than 40 min. The results correlate well with those from atomic-absorption spectrometry and neutron-activation analysis.

Many publications [1, 2] deal with mercury pollution problems and several analytical methods are available for this metal, e.g.: atomic-absorption spectrometry (a.a.s.) [3—6], neutron-activation analysis (n.a.a.) [7], u.v. spectrometry [8] and atomic-fluorescence spectrometry (a.f.s.) [9—13].

For the analysis of traces of a few elements, a.f.s. is regarded as being more sensitive than a.a.s. [14, 15] but recent developments in a.a.s., particularly those concerning flameless techniques, may improve the limits by a factor of 10—1,000 for most elements. Although the possibilities of a.f.s. are, therefore, limited in relation to a.a.s., a.f.s. is still an attractive method when the fluorescence signal contains no background but only the lines of the element to be determined. This allows maximum amplification and, consequently, very low detection limits to be attained.

In common with other investigators [16], attempts were made to modify the a.a.s. technique to allow fluorescence measurements of mercury but this resulted in low sensitivities. As a.f.s. clearly required specific modifications, a new set-up, resulting in a versatile atomic-fluorescence spectrometer permitting easy optimization of the technique, was devized. This paper describes the experimental procedure and the evaluation of the method with standard mercury solutions; the results of a.f.s. are compared with those obtained by a.a.s. and n.a.a. Applications to fish samples, including a rapid method for sample destruction are also discussed.

Principle of the method

A small amount of a solution of a mercury salt is introduced into an atomization flask where the ionic mercury is reduced to atomic mercury by tin(II) chloride; it is then quickly carried by a stream of argon through a glass tube, the open end of which is located close to the beam of a mercury lamp. There, a fluorescence signal is instantaneously generated; it contains no background but only mercury lines, so that a monochromator or filters need not be used. The open end of the glass tube from which the mercury atoms are emitted is located just above the aperture of the solar blind phototube, which directly detects both the 184.96-nm resonance line and the 253.65-nm inter-combination line. The height of the recorded peak is a measure of the mercury content. This technique is called non-dispersive atomic-fluorescence spectrometry [13, 18—20].

EXPERIMENTAL

Equipment

The apparatus is depicted in Fig. 1; Figs. 2 and 3 show the light-source assembly and the atomization flask.

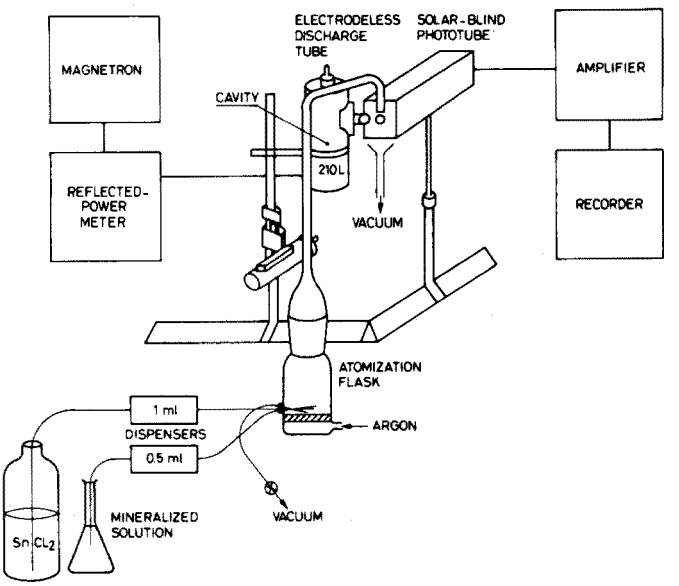

Fig. 1. Atomic fluorescence spectrometer.

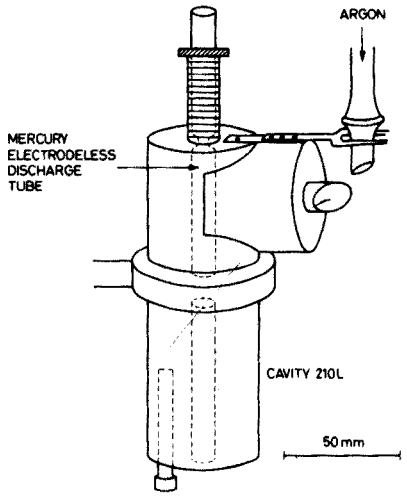

Fig. 2. Light-source assembly.

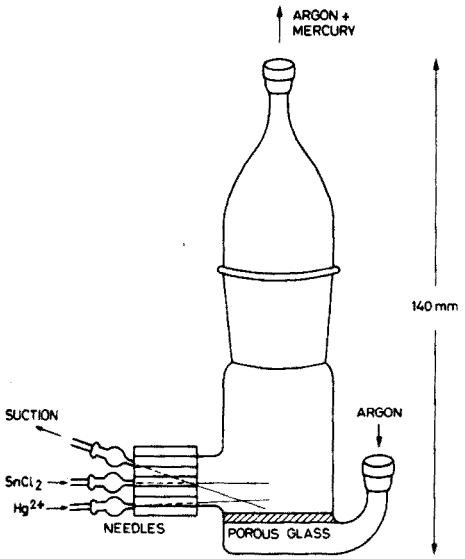

Fig. 3. Atomization flask.

The specifications of the equipment are as follows.

Light source

A mercury electrodeless discharge tube of length 3.5 cm, internal diameter 0.8 cm, mercury weight 5 mg, argon pressure 270 Pa ($\hat{=}$ 2 torr), is excited in a 210 L ($\frac{3}{4}$-wave) type cavity. The microwave generator is a Magnetron 200 (Electro-Medical Supplies Ltd.) of frequency 2.4 GHz, power range 0–200 W, power used 25 W, reflected power 7 W.

Atomization flask

This was designed and constructed in our laboratory. The dispensers are 0.5 and 1 ml (Mecolab). The argon flow is 300 1 h^{-1}.

Detector

A solar-blind phototube EMI type 9616 QA is used with an Oltronix A (2.5 K-10 HR, 0—2500 V, cathode voltage 1000 V) power supply.

Amplifier

This is a current—tension converter (10 V μA^{-1}, linearity $< 10^{-3}$).

Recorder

Philips PM8 100 potentiometric recorder, chart speed 5 cm min^{-1}, input 50 mV.

The apparatus is located in a room illuminated by sodium light.

PROCEDURE

The sample injection procedure, automated by means of two dispensers, comprises successively: injection of 1 ml of tin(II) chloride solution (20 g of tin(II) chloride in 100 ml of 10 % (v/v) nitric acid containing 2 drops of antifoam silicone emulsion); injection of 0.5 ml of mercury (II) solution; and removal of the reagents by suction.

EVALUATION OF THE ATOMIC FLUORESCENCE SPECTROMETER

The equipment is calibrated daily with standard solutions of mercury(II) sulphate (corresponding to a mercury concentration of 1—100 $\mu g\ l^{-1}$) freshly prepared by dilution of stock solution (1 $g\ l^{-1}$, calculated on mercury) in 10 % (v/v) nitric acid containing 1 drop of a saturated solution of potassium permanganate. A plot of the peak height versus the mercury content is linear up to at least 50 $\mu g\ l^{-1}$.

When another mercury(II) solution is analysed, the peak height becomes satisfactorily constant after only a few (5—7) conditioning cycles. Injection of a 10 $\mu g\ l^{-1}$ standard solution ($\hat{=}$ 5 ng mercury) in 75 successive cycles gave a relative standard deviation of 3.3 %. Because the method is fairly rapid, three successive peaks are determined and the mean is taken as the analytical result. The relative standard deviation then drops to 2.2 % (25 mean values). For another 15-cycle sequence with a 1 $\mu g\ l^{-1}$ solution, this deviation was 2.2 % and this reduced to 1 % when 3 peaks were averaged. Figure 4 shows a typical recording of atomic fluorescence signals. Since the fluorescence signal is not biased by background signals, the detection limit of the apparatus is limited only by the mercury content of the reagents. Injection of 0.1 $\mu g\ l^{-1}$ solution ($\hat{=}$ 0.05 ng mercury) generates a signal twice as high as that of a blank determination. Although the equip-

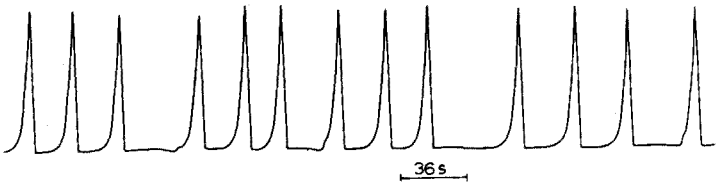

Fig. 4. Typical recordings of atomic-fluorescence signals.

ment permits a larger signal amplification, for practical reasons this concentration is considered to be the detection limit.

ASSAY OF MERCURY IN FISH SAMPLES

Apparatus and materials

The major problem connected with the determination of mercury in fish samples is the destruction of the organic matter and the oxidation of the mercury without loss by volatilization. The destruction method of Cumont [4] was performed in a conical flask (200 ml) provided with a highly efficient condenser (length 50 cm) connected to a cryostat kept at −20 °C. The reagents are added dropwise to the conical flask from a lateral funnel whilst the flask contents are heated and continuously stirred magnetically. Before each experiment, all glassware is cleaned with nitric acid (10 %, v/v) and thoroughly rinsed with twice-distilled water.

The following analytical-grade reagents were used: vanadium pentoxide; nitric acid (65 %, specific gravity 1.40); nitric acid (10 %, v/v); sulphuric acid (95—97 %, sp. gr. 1.84) and hydrogen peroxide (30 %).

As sample material fish flesh is preferred to homogenized samples because the temperature rise during homogenization may cause loss of mercury. This may also occur when the sample is too large and an excess of nitrous oxide vapours escapes from the condenser. The optimum sample weight is about 1 g; a mercury content of 1 mg kg^{-1} gives after destruction a solution containing 10 $\mu g\, l^{-1}$ of mercury. A completely dry sample leads to vigorous destruction which also causes mercury losses, and 1 ml of water should therefore be added before the addition of reagents.

Destruction procedure

Introduce successively into the conical flask 100 mg of vanadium pentoxide and 1 g of sample; then, while stirring, add 3 ml of nitric acid (65 %) dropwise followed by 6 ml of sulphuric acid. It is usually necessary to initiate the reaction by gentle heating, but this must be done carefully to avoid the formation and escape of an excess of nitrous oxide vapours. Continue the reaction for about 5 min, and then cool the solution to room

temperature. Then, add 10 ml of water carefully followed by dropwise addition, while stirring, of hydrogen peroxide until the nitrous oxide vapours have completely disappeared (2 ml are generally sufficient) leaving a brown solution. Wash the condenser with 50 ml of nitric acid (10 %) and disconnect the cryostat. Heat the solution gently again to destroy completely the excess of hydrogen peroxide, which results in a green solution. Then cool the whole apparatus to room temperature and rinse again with twice-distilled water. After removing the condenser from the conical flask, transfer the contents quantitatively to a 100-ml measuring flask, and dilute to the mark with twice-distilled water. This mineralized solution is then introduced into the atomization flask as described above.

The destruction of 1 g of fish takes about 20 min and the solution remains stable for many days.

Results and discussion

To determine the precision of the method when applied to fish, 13 analyses of a sample of non-homogenized fresh tuna flesh were made on different days. The arithmetic mean of the results (each result representing the mean of three recorded peaks) was 0.81 mg kg^{-1} with a relative standard deviation of 10.8 %.

The recovery of mercury from the destruction procedure including the mineralization step was assessed by determining the mercury content of four samples (about 100 mg) of refined fish oil to which dimethyl-mercury had been added (9.86 mg kg^{-1}).(It had been verified previously that the fish oil contained no mercury.) The recoveries (%) were: 88.1, 88.2, 81.3 and 82.8. When 1 ml of a mercury(II) sulphate solution in 10 % nitric acid (1 mg kg^{-1}) was analysed in duplicate the recoveries were 92 and 91 %.

Table 1 shows other analytical data on tuna flesh indicating that homogenization without temperature control tends to reduce the mercury content but further experimental evidence is required to substantiate this effect.

TABLE 1

Mercury content in tuna fish determined by atomic-fluorescence spectrometry

Sample		Mercury content (mg kg^{-1})	
Fresh tuna[a]	flesh only	0.74	0.81
	flesh only, but exposed to air for 24 h	0.73	0.76
	after homogenization (without temp. control)	0.66	0.65
Tinned tuna	flesh only	0.29	

[a]Within the range published in ref. 21.

Comparison with other methods of analysis

Four different fish samples were analysed for their mercury content by neutron-activation analysis, atomic-absorption spectrometry and atomic-fluorescence spectrometry. Table 2 shows that a good correlation was obtained between these methods.

TABLE 2

Mercury content (mg kg^{-1}) of several fish samples analysed by atomic-absorption spectrometry, neutron-activation analysis and atomic-fluorescence spectrometry

	A.a.s.	N.a.a.	A.f.s.
Shrimp (homogenized, *i.e.* flesh + carapace)	0.26	0.22	0.24
Mussel (flesh only)	0.07	0.09	0.09
Eel (flesh only)	0.29	0.37	0.30
Tuna[a] (fresh flesh)	—	1.06	0.91

[a]Within the range published in ref. 21.

CONCLUSION

The simple atomic-fluorescence spectrometer developed has proved to be very sensitive and reliable for the determination of mercury. The detection limit is determined only by the mercury content of the reagents. The spectrometer may be applied to the determination of mercury in fish samples at the $\mu g\ kg^{-1}$ level. The method for the destruction of fish samples is fast, and results in complete ionization of the mercury. Recording of the fluorescence signal requires 10 s and the total time of analysis is less than 40 min. Extension to the determination of mercury in other foodstuffs should be possible.

We thank Mr. J. Siebesma of our Instrumentation Department for assembling the detector and amplifier.

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DETERMINATION OF MANGANESE IN IRON AND STEELS BY U.H.F. PLASMA-TORCH EMISSION SPECTROMETRY

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SUMMARY

The determination of manganese in iron and steels by u.h.f. plasma torch spectrometry is described. The intensity of the Mn II 257.16-nm ion line decreased with increasing concentration of iron, whereas the intensity of the Mn I 403.07-nm atom line increased; only the Mn I 279.48-nm atom line showed constant intensity as the concentration of iron increased. This behavior can be explained in terms of plasma temperature. The effects of acids were examined; the influence of small amounts of diverse elements was depressed by a large amount of iron. A simple and rapid method for the determination of manganese in iron and steels was established, the relative standard deviation being 2.6 % for 0.10 % Mn.

In recent years, many papers on the use of inert-gas plasmas as excitation sources for emission spectrometry have appeared [1—14]. It has been shown [14] that u.h.f. plasma-torch spectrometry is very suitable for the determination of chromium in iron and steels.

The present paper describes the determination of manganese by u.h.f. plasma-torch spectrometry, with special reference to the behaviourof each manganese spectral line, which was the most important factor in avoiding interference from large amounts of iron. A method for the rapid, simple determination of manganese in iron and steels is outlined.

EXPERIMENTAL

Reagents

For the stock standard solution of manganese, manganese metal (99.9 %) was dissolved in hydrochloric acid; the solution was evaporated to eliminate excess of hydrochloric acid, and diluted with distilled water to make a solution containing 10 mg Mn ml^{-1}. This solution was diluted to the required concentration just before use.

All acids and other metals and salts used were of reagent grade.

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Apparatus

The high-frequency plasma-torch spectrometer (2450-MHz discharge) used was a Hitachi u.h.f. plasma-torch spectrometer 300, which is the same as described previously [14].

Argon was used as the plasma gas and as the sheath gas.

Working conditions for the plasma torch

Factors such as the field and anode current, the flow rates of the plasma-forming gas and sheath gas, which fundamentally affect the line intensity of manganese in the u.h.f. plasma torch, were examined in the same manner as for chromium [14]. The relationships between these factors and the line intensity of manganese were almost the same as in the case of chromium. The optimal working conditions for manganese are shown in Table 1. All subsequent experiments were carried out under these conditions.

RESULTS AND DISCUSSION

Selection of spectral lines for manganese and spatial distribution of spectral line intensity in the plasma torch.

As shown in Table 2, several spectral lines of manganese may be used. The Mn II 257.61-nm ion line was more intense than the Mn I 279.48-nm atom line, when the manganese solution was used in the absence of iron (Fig. 1a), but when large amounts of iron were present, the Mn I atom line intensity was enhanced whereas the Mn II ion line intensity decreased (Fig. 1b), the Mn I 279.48-nm line becoming the more sensitive. Obviously the effect of large amounts of coexisting elements had to be examined in order to select the best line for manganese. The intensity of the Mn I 403.676-nm line was weak under these working conditions, but the signal could be increased by increasing the photomultiplier voltage without a corresponding noise increase, because the background intensity at this wavelength and its fluctuation were very low. Though the intensity distribution of chromium in the plasma torch shifted in the presence of a large amount of iron, it did not shift in the case of manganese.

TABLE 1

Working conditions

Frequency	2450 MHz
Flow rate of plasma-forming gas	3.0 1 min^{-1}
Flow rate of plasma-sheath gas	4.0 1 min^{-1}
Field current	360 mA
Anode current	280 mA
Entrance slit width	50 μm
Exit slit width	50 μm

TABLE 2

Comparison of line intensities for manganese (Mn, 0.50 μg ml^{-1})

Wavelength (nm)	Intensity [15]	eV	Plasma-torch intensity
II 257.610	M 1200	4.81	135
II 259.373	M 800	4.77	100
II 260.569	M 500	4.75	75
I 279.482	M 800	4.44	132
I 279.827	M 650	4.43	105
I 280.108	M 480	4.43	70
I 403.676	M 2000	3.08	34
I 403.307	M 1400	3.08	25
I 403.449	M 800	3.08	15

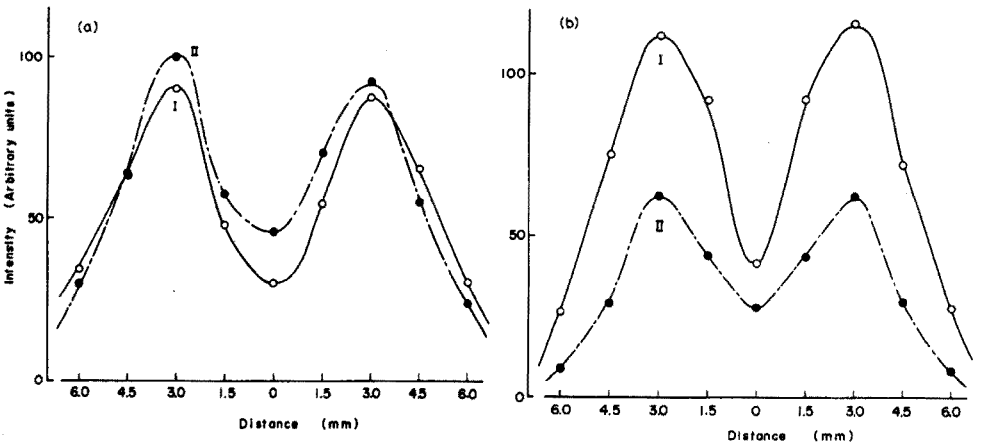

Fig. 1. Projected intensity distribution for atom and ion lines of manganese. (○) I: Mn I 279.48 nm. (●) II: Mn II 257.61 nm. (a) 0.60 μg Mn ml^{-1} in distilled water. (b) 1.0 μg Mn ml^{-1} in 3M HCl containing 2.0 mg Fe ml^{-1}.

Effect of acids

The effects of common acids used for dissolving samples, such as hydrochloric, nitric and sulfuric acids, were similar to those in the case of chromium, i.e. the line intensity decreased significantly with increasing concentration of acid, but it remained approximately constant in the concentration range 2.0—4.5 M for hydrochloric and nitric acids; sulfuric acid had a large effect and was considered unsuitable for use.

The effects of hydrochloric acid on the atom and ion lines of manganese were also examined for solutions containing 1.0 μg Mn ml^{-1}. The atom lines were less affected than the ion line (Fig. 2), and there was no shift in the

intensity distribution (Fig. 3). The line intensities in Fig. 2 were normalized to the same initial (no HCl) value.

Effect of diverse elements

The effects of the elements usually found in iron and steels were examined by adding chromium, copper, cobalt, etc. in the 5—50 μg ml^{-1} concentration range. As shown in Fig. 4, there were two patterns of interference. Elements showing pattern A, such as Al, As, Mo, Sb, Ti, V and Zn, slightly decreased the intensity of manganese lines (Mn I 279.48 nm, Mn I 403.07 nm, Mn II

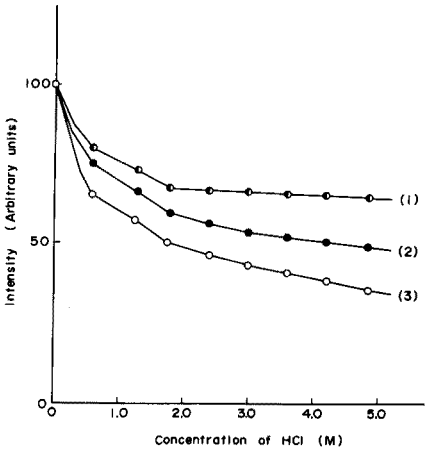

Fig. 2. Effect of hydrochloric acid on intensity of manganese lines. 1 μg Mn ml^{-1} (excitation potential). (1) Mn I 403.07 nm. (2) Mn I 279.48 nm. (3) Mn II 257.61 nm.

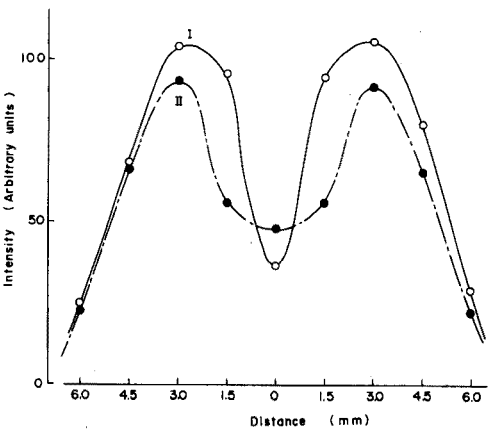

Fig. 3. Projected intensity distribution for atom and ion lines of manganese. 1.0 μg Mn ml^{-1} in 3 M HCl. (○) I: Mn I 279.48 nm. (●) II: Mn II 257.61 nm.

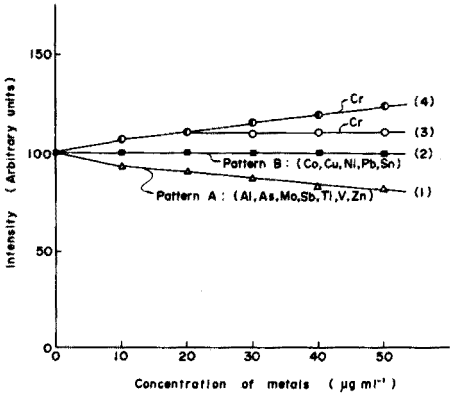

Fig. 4. Effect of other elements on manganese spectral line intensities. 0.5 μg Mn ml^{-1} in distilled water. (1), (2): Mn I 279.48 nm, Mn I 403.07 nm and Mn II 257.61 nm. (3): Mn I 279.48 nm. (4): Mn I 403.07 nm.

257.61 nm) with increasing concentration of the element. Elements showing pattern B, such as Co, Cu, Ni, Sb and Sn, did not affect the intensities of these lines as their concentration increased. Each element showing pattern A or B had essentially identical effects. In contrast, increasing amounts of chromium increased the atom line intensity of manganese (Mn I 279.48 nm, Mn I 403.07 nm) but did not affect the ion line intensity (Mn II 257.61 nm).

The effect of a large amount of iron on the atom and ion lines of manganese was then examined. The intensity of the Mn I 403.07-nm atom line increased with an increase in iron concentration, but the intensity of the Mn II 257.61-nm ion line decreased with an increase in iron concentration, and the Mn I 279.48 nm atom line showed constant intensity in the concentration ranges 2.0—10.0 and 40—100 mg Fe l^{-1} in 3 M hydrochloric acid (Fig. 5).

In order to investigate the cause of these effects, the temperature of the plasma-torch at the position of 3 mm from the center of the torch was measured by the two-line method with copper spectral lines based on the data given in NBS Monograph 53. The physical constants used were as follows: for the Cu I 521.820-nm (6.19 eV) 515.324-nm (6.19 eV), and 510.554-nm (3.82 eV) lines, the Ag values were 5.8, 4.7 and $0.051 \cdot 10^{-8}$ s^{-1}, respectively. The temperature of the plasma torch changed from 5500 K for distilled water to 5300 K for a solution containing 2 mg Fe ml^{-1} in 3 M HCl. These results indicate that the decrease in intensity of the Mn II 257.61-nm ion line (ionization potential 7.43 eV) was caused by the increase in the atomic state of manganese in the plasma torch because of the decrease in temperature when much iron was present. The Mn I 403.07-nm atom line has a low excitation energy (3.08 eV), and is enhanced by the decreased temperature of the torch. The Mn 279.48-nm atom line has a higher

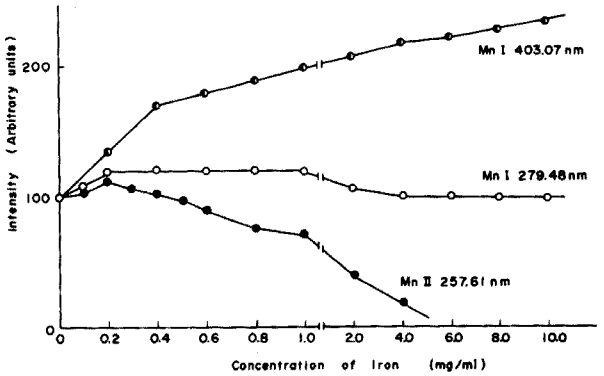

Fig. 5. Effect of iron on manganese spectral line intensities. 1.0 μg Mn ml^{-1}, 3 M HCl.

excitation energy (4.44 eV), so that its intensity decreases slightly with the decrease in temperature of the torch. It seems probable that a balance is obtained in the intensity of the Mn 279.48-nm atom line between the increase in the atomic state of manganese and the decrease in the temperature of the plasma.

It was reported earlier [14] for chromium determinations that a large amount of iron prevented interference from small amounts of coexisting elements. In this study of manganese, a large amount of iron also prevented interference of elements such as Al, As, Mo, etc. It was shown, for the determination of 1.0 μg Mn ml^{-1} in the presence of 0.5 mg Fe ml^{-1} in 3 M hydrochloric acid, that concentrations of 5 mg ml^{-1} of As, Co, Cu, Cr, Mo, Ni, Pb, Sb, Sn, V and Zn, and 1 mg ml^{-1} of Al, Sb, Si and Ti did not interfere.

Calibration curves

Calibration curves for manganese, prepared in the presence of iron (0.1—1.0 mg ml^{-1}) in 3 M hydrochloric acid under the recommended conditions (Table 1), were found to be linear over the range of 0.05—50 μg Mn ml^{-1}, when measurements were made at the 279.48-nm line.

Analytical procedure and results

Based on these results, the following analytical procedure for manganese in iron and steels was established.

An accurately weighed sample (0.05—0.1 g) was dissolved in 10 ml of 6 M hydrochloric acid and a small amount of nitric acid by heating. The solution was evaporated to dryness, the residue was dissolved in 20 ml of 3 M hydrochloric acid and the solution was transferred to a 100-ml volumetric flask and diluted with 3 M hydrochloric acid to the mark.

TABLE 3

Analytical results and precision for manganese in iron and steels by plasma-torch spectrometry

Sample		Mn (%) found	Certificate value	s_r (%)
J.S.I.S.[a]	156-2	0.099[b]	0.10	2.6
J.S.I.S.	157-2	0.610	0.61	—
J.S.I.S.	158-2	1.01	1.02	—

[a] J.S.I.S.: Japanese Standard of Iron and Steel.
[b] Average of 11 determinations (range 0.097—0.106 %).

When large amounts of silicon were present, they were removed by treatment with hydrofluoric acid in a platinum crucible. After filtration of the sample solution and washing with 3 M hydrochloric acid, the residue in the crucible was also dissolved in 3 M hydrochloric acid and then added to the main solution.

The results obtained for the determination of manganese in iron and steels (Table 3) are in satisfactory agreement with the certificate values. A relative standard deviation of 2.6 % for 0.10 % of manganese in iron and steels was obtained.

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THE DETERMINATION OF SOME TOXIC METALS IN HUMAN LIVER AS A GUIDE TO NORMAL LEVELS IN NEW ZEALAND PART I. DETERMINATION OF Bi, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl AND Zn

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SUMMARY

Procedures are described for the determination of bismuth, cadmium, chromium, cobalt, copper, lead, manganese, nickel, silver, thallium and zinc in post-mortem liver samples by atomic absorption spectrometry. The technique involves a simple HCl/HNO_3 digestion at 100 ± 20 °C, gives good recoveries and appears to be applicable to other tissues, and blood. Results of analyses of post-mortem material from eleven subjects with no known exposure to toxic metals, are presented. They are comparable with overseas findings and show no excessive levels.

There is world-wide concern that man's body burden of toxic metals may be increasing because of pollution of both natural and industrial origin. Although New Zealand is not heavily industrialized and there is no evidence of any general metal intoxication problems, there is insufficient information on toxic metals in human tissue to provide an assessment of normal New Zealand levels in relation to overseas levels. This study has been made to establish a base level as a guide to monitoring possible future increases, and to detect any local problem cases or areas.

The samples used were taken from eight subjects whose death was attributed to drug overdose and from three subjects for whom the cause of death was not attributed to drugs or poisons. None of the subjects had any known abnormal exposure to toxic metals. However, it will be shown that in some cases there had been some abnormal exposure. Mercury, arsenic and selenium were not included in this investigation because the analytical procedures used are different, and these elements will be studied separately.

Many authors favour nitric—sulphuric—perchloric acid mixtures to digest the samples. Perchloric acid probably gives the most efficient breakdown of the fat—lipid fraction, but nitric—hydrochloric acid mixtures have the advantage that digestions can be carried out at lower temperatures. Although breakdown of lipids is incomplete, recoveries are not affected. Sulphuric acid was avoided because of matrix interference in the atomic absorption procedure. The simple digestion method at low temperature allows many samples to be processed concurrently with very little attention.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer 403 or 303 Atomic Absorption Spectrophotometer was fitted with Perkin-Elmer or Varian-Techtron hollow-cathode lamps, except for thallium where an Osram arc-discharge lamp was used. A water-cooled, three-slot, Boling burner was used with the air—acetylene and air—propane flames, and a thermostatted high-temperature tantalum burner [1] for the nitrous-oxide acetylene flame. The burner was in the normal position for all analyses except zinc for which it was rotated 90°. In all cases the major analytical line for the particular element was used.

Materials

Glass-distilled water was used throughout. All acids (analytical-grade) were redistilled, the first 200 ml of distillate being discarded.

All glassware and polypropylene were soaked in Decon 90, washed in hot 2 M hydrochloric acid, and finally rinsed copiously with distilled water. Where possible, silica glassware was used, particularly for the digestions.

Scalpel blades were briefly immersed in aqueous 1 % EDTA solution, rinsed in distilled water and oven-dried. Horn spatulas were used.

Stock solutions

Analytical-grade chemicals were used. Stock solutions (1000 μg ml^{-1}) were prepared by dissolving the appropriate amount of cadmium sulphate, potassium dichromate, thallium(I) nitrate, lead nitrate or silver nitrate in distilled water; manganese dioxide or zinc metal in 12 M hydrochloric acid; and nickel, cobalt, bismuth or copper metal in 16 M nitric acid. When diluted to volume each solution contained 1 % (v/v) nitric or hydrochloric acid, depending on the acid used initially. Nitric acid was added to the aqueous solutions to achieve a 1 % concentration; this retarded adsorption of metal on the container wall. Stock solutions prepared in this way proved to be reliable for at least a year. Successive dilutions of the stock solutions were made to obtain working standards of 10 μg ml^{-1}.

Calibration standards

Combination standards containing all the metals were prepared from the 10 μg ml^{-1} working standards as follows:
(1) Co, Cd, Pb, Mn, Tl, Ag, Cr, Bi, Ni, 0.5 μg ml^{-1}; Cu 2.0 μg ml^{-1}; Zn 10.0 μg ml^{-1}; with 1000 μg Na ml^{-1}.
(2) Co, Cd, Pb, Mn, Tl, Ag, Cr, Bi, Ni, 1.0 μg ml^{-1}; Cu 4.0 μg ml^{-1}; Zn 20.0 μg ml^{-1}; with 1000 μg Na ml^{-1}.

These standards contained the same concentrations of nitric and hydrochloric acids as the samples. The sodium (as Analar sodium chloride) was added to the standards to duplicate the large amount of sodium naturally present in liver.

All calibration graphs were linear in the required ranges, except for zinc where the graph was not linear at high absorbance levels. This difficulty was overcome by diluting the solutions appropriately.

When the absorption of the pure analyte solution was compared to that of the same analyte solution containing all of the remaining ten metals, no inter-element interferences were observed.

Sample preparation

All samples were stored frozen in clear polythene bags. The tissue was sliced thinly from the still frozen liver with a scalpel. Duplicate 30-g samples were spread on large petri dishes, and oven-dried at 100 ± 5 °C overnight. The samples were then carefully chipped off the dish, weighed into a digestion flask, and 25 ml of a (1 + 1) mixture of 16 M nitric acid and 12 M hydrochloric acid was added. The samples were digested on an asbestos-covered hot plate at 100 ± 20 °C until only the lipid fraction remained undigested; this fraction formed a clear oily layer above the hot digest, but sank on cooling. After centrifuging, the supernatant liquid was removed, and the remaining lipid was extracted with hot distilled water, cooled and recentrifuged. The supernatant portions were combined, evaporated at 100 ± 20 °C to 25 ml, and then diluted to 50 ml with distilled water, a clear yellow solution being obtained.

All samples and standards were kept in polypropylene containers under refrigeration and brought to room temperature immediately before analysis.

RESULTS AND DISCUSSION

Possible losses of metals by absorption in the lipid fraction were investigated by mineralizing and analysing this fraction; in all cases, the results were equivalent to the blank, indicating that the original digestion was completely adequate.

Recovery experiments (Table 1) were done on six replicate samples of the same liver, which were spiked before digestion, with a solution containing all the metals of interest so that the final concentrations were equivalent to those found in the low calibration standard.

Ten replicate samples from the same liver were analysed for all eleven metals and the standard deviations were calculated (Table 1).

For trace analyses below 250 nm, background absorption from sample matrix interference was corrected by using a non-absorbing line near the analytical line. The determinations of cadmium, copper, chromium, silver, manganese and zinc by atomic absorption appeared free from interference,

TABLE 1

(A) Recovery of eleven elements from liver digestions (B) Average and standard deviation of ten results on unspiked samples of the same liver

(A) Element	Pb	Cd	Co	Zn	Ag	Cu	Bi	Mn	Tl	Cr	Ni
Amount added $\mu g\ ml^{-1}$ digest	0.5	0.5	0.5	10.0	0.5	2.0	0.5	0.5	0.5	0.5	0.5
Recovery range %	78—104	95—120	99—102	93—104	99—101	99—102	94—105	88—107	99—100	105—111	99—103
Average recovery %	92	107	100	98	100	100	99	98	100	108	101
(B) Average for unspiked digests ($\mu g\ g^{-1}$)	9.1	13.0	<0.5	159	<0.4	27.3	0.3	4.3	0.4	0.1	0.5
s ($\mu g\ g^{-1}$)	0.5	0.5	0.5	10.1	0.1	1.3	0.1	0.5	0.5	0.1	0.5

while some background was experienced with lead, bismuth, nickel, cobalt and thallium.

With the exception of cadmium, the concentrations of metals in the solutions obtained from processed tissue samples changed negligibly over a period of six weeks. Presumably cadmium is adsorbed on the polypropylene container, and a 25 % loss was experienced over a period of three weeks. However, analysis of the solutions with as little delay as possible overcame this difficulty.

The results of analyses of eleven liver samples are given in Table 2. Samples of tissue taken across the liver gave very constant analyses within experimental limits of error for all metals. The ages of subjects from whom post-mortem liver samples were taken ranged from 11 to 52 years with an average age of 39 years. Levels of metals present showed no obvious correlation with age. In some cases there had been some abnormal exposure to toxic metals. This is reflected in the distribution ranges and should be considered when evaluating the results. An earlier investigation into levels of metals in human liver by spectrographic analysis of ashed samples [2] showed relative proportions of the elements very similar to those reported in this study.

For toxicological purposes it is suggested that the mean levels reported in Table 2 be regarded as normal levels for human liver samples in New Zealand. Since recoveries of metals from spiked solutions ranged from 92 to 108 %, it was considered unnecessary to adjust the values given in Table 2.

While the levels of thallium, cobalt, chromium and silver found are very little more than the detection limits for these metals, documented cases of poisoning attributed to these metals show levels well above the detection

TABLE 2

Levels of toxic metals in post-mortem livers expressed as $\mu g\ g^{-1}$ dried tissue

Metal	Mean	Range	s	Literature values		
				Normal range	Mean	Toxic level
Pb	4.13	1.6—9.1	2.24	1.6—10.9[a] [3]		70.2—310[a] [3]
Cd	4.50	1.0—26.7	4.35	7.8—10.9[a] [4]	10.5 ± 10.1 [5]	624[a] [4] 20 [6]
Mn	4.53	2.8—6.9	1.25			
Cr	1.08	<0.1—4.5	1.69			
Cu	24.62	8.0—35.3	9.98	9.2—46.8 [7]	29.8 ± 11.4 [5]	>250 [8]
Bi	0.2	<0.1—0.9	0.26			
Ni	0.68	<0.5—1.8	0.49			
Tl	0.47	<0.4—0.9	0.13			18.6 [9]
Zn	194	57—312	92	41.7—298 [7]	326 ± 154 [5]	
Ag	0.34	0.1—0.7	0.19			
Co	0.59	<0.5—1.0	0.16	0.3—0.5 [10]		

[a]Corrected from "wet" tissue figure to dry tissue; factor = 3.90.

limits of this method, and positive diagnoses are therefore possible.

The mean and range of copper concentration is similar to that obtained by McKenzie [5]. However, there is no apparent reason for the significantly higher zinc and cadmium levels found by the same investigator.

Arsenic, mercury and selenium analyses on liver samples from the same eleven subjects are being performed by different procedures and will be the subject of a separate publication.

Levels of cadmium, lead, copper, zinc and cobalt in samples of human liver taken from normal post-mortems in New Zealand are consistent with overseas findings and give no indication of excessive intake.

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RÖNTGENSPEKTROMETRISCHE BESTIMMUNG VON BLEI IN AUTOMATENSTAHL
TEIL II. SULFAT-VERFAHREN

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ZUSAMMENFASSUNG

Es wird eine Methode zur röntgenspektrometrischen Bestimmung von 0,02—0,5 % Pb in Automatenstählen beschrieben. In der Probelösung wird das Blei als Sulfat mit Bariumsulfat als Spurenfänger ausgefällt und der getrocknete und fixierte Niederschlag für die Messung im Röntgenspektrometer verwendet. Die Methode weist eine Reproduzierbarkeit und Genauigkeit von $s = \pm 0{,}002$ % Pb auf. Der Zeitbedarf beträgt für eine Einzelbestimmung $\sim$32 min und für eine Serie von 20 Proben $\sim$ 120 min.

SUMMARY

A method is described for the x-ray spectrometric determination of 0.02—0.5% Pb in free-cutting steels. Lead in the sample solution is precipitated as sulphate with barium sulphate as collector, and the dried fixed precipitate is used for the x-ray spectrometric measurement. The method shows a reproducibility (s) of ±0.002 % Pb. The time required is ca. 32 min for one determination and ca. 120 min for a series of 20 samples.

Im vorangegangenen Teil I [1] wurde eine röntgenspektrometrische Methode (Brikett-Verfahren) für die Bestimmung von Blei in Automatenstahl beschrieben, bei der ein Stahlspäne-Brikett für die Messung verwendet wird and die als einfaches und rationelles Verfahren in der Produktions- und Qualitätskontrolle eingesetzt werden kann. Gegenüber der früher mitgeteilten photometrischen Methode [2—5] ist das Brikett-Verfahren [1] vorteilhafter wegen des geringeren Arbeits- und Zeitaufwandes.

Mit dem Brikett-Verfahren [1] erzielt man zufriedenstellende Analysenergebnisse, wenn die Arbeitsbedingungen genau eingehalten werden. Vor allem muss die Spanqualität (Form, Feinheit) stets gleich sein, da sie das Analysenergebnis entscheidend beeinflusst. Häutig werden aber von anderen Werksabteilungen Stahlproben in Spanform an das Laboratorium eingesandt, die sehr ungleichmässige Späne aufweisen. Deshalb war die Ausarbeitung einer für diese inhomogenen Proben geeigneten röntgenspektrometrischen Methode notwendig, da ungleichmässige Späneproben beim Brikett-Verfahren sehr grosse Analysenfehler bis zu 100 rel. % verursachen.

In der vorhergehenden Mitteilung [1] wurden die verschiedenen Möglichkeiten für eine Homogenisierung der Stahlproben erörtert. Dort wurde bereits erläutert, dass die zweckmässigste Methode zur Homogenisierung inhomogener Stahlspäneproben darin besteht, das Probematerial in Säure aufzulösen. Das Ziel der Versuche war daher, die Vorteile dieser Homogenisierung mit jenen der röntgenspektrometrischen Endbestimmung zu verbinden. Die auf dieser Grundlage ausgearbeitete Methode ist nachfolgend beschrieben.

Zuerst wurde nach einer Methode gesucht, mit der neben Blei auch die übrigen in Stahl interessierenden Elemente gleichzeitig in einem Arbeitsgang bestimmt werden können. Hierzu wurde die Stahlprobe in Säure gelöst, die Probelösung in Schälchen verschiedener Ausführung eingedampft und der Eindampfrückstand für die Messung im Röntgenspektrometer verwendet. Die zahlreichen Versuche führten jedoch zu wenig befriedigenden Ergebnissen.

Deshalb wurde die zweite Möglichkeit gewählt, das Blei von den übrigen Bestandteilen abzutrennen und anschliessend der Messung zuzuführen. Von den verschiedenen Isolierungsmethoden erschien die Fällung als Bleisulfat am zweckmässigsten. Für eine quantitative Abscheidung des Bleisulfats ist normalerweise eine Standzeit von $\sim$15 h erforderlich. Da aber für die oben geschilderten Routineanalysen ein Schnellverfahren notwendig ist, wurde versucht, zur Abkürzung der Standzeit Bariumsulfat als Spurenfänger zu verwenden. In mehreren Versuchsreihen wurden die günstigsten Arbeitsbedingungen der Fällung ermittelt, deren wichtigste Ergebnisse in Tabelle 1 zusammengestellt sind.

Aus Tabelle 1 ist ersichtlich, dass der Bleiverlust mit steigender Menge an zugesetztem Bariumchlorid abnimmt und die Fällung des Bleisulfats mit 5—8 ml Bariumchloridlösung praktisch quantitativ ist. Hier muss aber gleichzeitig berücksichtigt werden, dass die Blei-Messwerte mit steigender Menge an Bariumsulfat im Niederschlag abnehmen infolge der Absorberwirkung des

TABELLE 1

Einfluss der Bariumchloridmenge und der Standzeit der Fällung (Versuchsbedingungen: nach der Arbeitsvorschrift. Vorgelegt: 0,250 % Pb im Stahl)

$BaCl_2$-Lösung[a] zugesetzt (ml)	% Pb gefunden[b]		Standzeit (min)	% Pb	
	Im Niederschlag[b]	Im Filtrat[b]		Gefunden[b]	Abweichung[b]
0,0	0,001	0,249	—	0,248	—0,002
1,0	0,244	0,006	5	0,250	0,000
2,0	0,245	0,005	10	0,252	+0,002
3,0	0,246	0,004	30	0,249	—0,001
4,0	0,248	0,002	90	0,248	—0,002
5,0	0,249	0,001	18 (h)	0,252	+0,002
6,0	0,249	0,001			
7,0	0,2492	0,0008			
8,0	0,250	0,000			

[a]Wässrige 5 %ige Lösung.
[b]Bezogen auf die Stahlprobe.

Bariums. So ist der Blei-Messwert mit 8 ml Bariumchloridlösung um 21 % niedriger als jener mit 5 ml Bariumchloridlösung. Deshalb sollte die zugesetzte Menge an Bariumchlorid möglichst niedrig sein. Aus den Versuchen geht weiterhin hervor, dass die in der Kälte durchgeführte Fällung praktisch ohne Standzeit bereits quantitativ ist. Als optimale Fällungsbedingungen wurden gewählt: 5 ml Bariumchloridlösung und 3 min Standzeit.

Für die Fixierung des $PbSO_4/BaSO_4$-Niederschlages auf dem Rundfilter wird dieses mit dem wasserlöslichen Lack Plextol B 500 besprüht, der sich aufgrund zahlreicher Versuche als am zweckmässigsten erwies [6]. Nach dem Trocknen haftet der Lack Plextol B 500 sehr fest auf der Unterlage und damit auch das mit diesem besprühte Filter. Aus diesem Grunde werden die besprühten Filter zum Trocknen auf silikonisiertes Papier gelegt, von dem sie nachher leicht abgenommen werden können.

EXPERIMENTELLER TEIL

Apparatur

Mehrkanalröntgenspektrometer 72000 von Applied Research Laboratories (Ecublens, Schweiz) mit angeschlossenem Digitalrechner Mincal 4 N (Dietz, Mülheim).

Messbedingungen

Pt/Rh-Röhre, 50 kV, 50 mA; gekrümmter (r = 11″) LiF-Kristall; Linie Pb $L\alpha_1$, 1,175 Å; Messzeit: 20 s; Probe gedreht.

Reagentien

Bariumchloridlösung. 5,0 g $BaCl_2 \cdot H_2O$ werden in Wasser gelöst und auf 100 ml aufgefüllt.

Plextol-Lösung. Man mischt 2 Volumteile Plextol B 500 (50%ige wässrige Akrylharzdispersion, von Röhm GmbH, Darmstadt) mit 1 Volumteil Wasser.

Ausführung

Für die Filtration verwendet man ein Filtrationsgerät [2] (z.B. Sartorius-Membranfilter GmbH, Göttingen), in das ein dichtes Rundfilter plan eingespannt ist.

Das Probematerial (2,0 g) wird in einem 250 ml-Becherglas mit 30 ml Mischsäure [300 ml $HClO_4$ (1,53) + 300 ml HCl (1,19) + 400 ml Wasser] unter Erwärmen gelöst, mit 100 ml Wasser verdünnt und die kalte Lösung unter Umschwenken der Reihenfolge nach mit 5,0 ml Bariumchlorid-Lösung und 1,0 ml H_2SO_4 (1 + 1) versetzt. Nach einer Standzeit von 3 min

wird der $PbSO_4/BaSO_4$-Niederschlag über ein dichtes Filter (55 mm Durchmesser, Schleicher & Schüll Nr. 585) mit dem Filtrationsgerät abfiltriert und mit kaltem Wasser einmal nachgewaschen. Man entnimmt das Rundfilter mit Niederschlag (Niederschlagsdurchmesser 40 mm) aus dem Filtrationsgerät, legt es auf eine Papierunterlage und besprüht es mit Hilfe einer Spritzpistole mit Plextol-Lösung. Anschliessend legt man das besprühte Rundfilter auf ein silikonisiertes Papier (z.B. Anticoll-Silicon-Papier KV 75 weiss, von W. Jackstädt & Co., 56 Wuppertal—Elberfeld), trocknet ∿ 10 min bei 105 °C im Trockenschrank und bewahrt das Filter in einem Exsikkator oder in einem verschlossenen Behälter bis zur Messung auf. Für die Messung wird das Filter im Probenhalter mit einer Platte aus Reinaluminium unterlegt, die Probe dann in das Röntgenspektrometer eingefahren, die Pb-Strahlung doppelt gemessen und der Mittelwert für die Auswertung verwendet. Vom Messwert zieht man den Reagentienblindwert ab, den man täglich mit Vorprobenstahl nach der Arbeitsvorschrift herstellt. Die Auswertung erfolgt mittels Eichkurve oder Eichkurventabelle.

Die Eichkurve wird nach der Arbeitsvorschrift unter Verwendung von bleifreiem Vorprobenstahl unter Zusatz von Blei-Standardlösung aufgestellt. Die tägliche Justierung (Kalibrierung) des Blei-Messkanals des Röntgenspektrometers erfolgt am zweckmässigsten mit zwei Normalproben (z.B. mit 0,100 % Pb und 0,300 % Pb), die mit bleifreiem Stahl und Blei-Standardlösung hergestellt und nach der Arbeitsvorschrift behandelt werden.

ERGEBNISSE UND DISKUSSION

Die Eichkurve ist leicht gekrümmt (s. Tabelle 2), weshalb die Auswertung mit Hilfe der Eichkurve oder einer Eichkurventabelle durchgeführt werden muss.

Die beschriebene Methode eignet sich zur Bestimmung von 0,02—0,5 % Pb in unlegiertem und niedrig legiertem Automatenstahl. Das Verfahren weist mit synthetischen Probelösungen eine Reproduzierbarkeit und Genauigkeit von $s = \pm 0{,}002$ % Pb auf. Bei der Beurteilung der Analysenergebnisse ist allerdings zu berücksichtigen, dass eine ungleichmässige Verteilung des Bleies im Stahl die Analysenstreuung verschlechtern kann. Der Zeitaufwand für eine Einzelbestimmung beträgt ∿32 min (Einwaage bis getrockneter Niederschlag ∿30 min, Doppelmessung mit Auswertung ∿ 105 s), der sich

TABELLE 2

Messwerte der Eichkurven

% Pb	0,050	0,100	0,200	0,300	0,400	0,500
Messwert (mV)						
Eichkurve 1	1210	2280	4240	5980	7600	—
Eichkurve 2	780	1500	2830	4040	5170	6120

jedoch durch Serienarbeit reduzieren lässt. Für die Analyse einer Serie von 20 Proben benötigt man ∿120 min, so dass hier auf eine Probe ein Zeitaufwand von 6 min entfällt. Die Bestimmungsgrenze [2] ($L_Q = 10\ \sigma$) des Verfahrens liegt unter den gewählten Arbeitsbedingungen bei L_Q = 0,02 % Pb, lässt sich aber bei Bedarf noch erheblich senken.

Im Vergleich zur photometrischen Methode [2—5] weist das Sulfat-Verfahren folgende Vorteile auf: einen geringeren Zeitaufwand, eine bessere bis gleiche Reproduzierbarkeit und Genauigkeit, vor allem aber infolge seiner einfacheren Durchführung weniger Fehlerquellen und eine grössere Sicherheit. Gegenüber dem röntgenspektrometrischen Brikett-Verfahren [1] hat das Sulfat-Verfahren an Vorteilen eine höhere Reproduzierbarkeit, Genauigkeit und Sicherheit, als Nachteil einen höheren Zeitaufwand, der aber bei Serienarbeit nicht erheblich ist. Die einfache Durchführung des Sulfat-Verfahrens ermöglicht es, den nasschemischen Teil der Methode, d.h.von der Einwaage bis zum fixierten getrockneten Niederschlag, von ungelernten Hilfskräften durchführen zu lassen. Lediglich die anschliessende röntgenspektrometrische Messung und Auswertung wird von qualifizierten Kräften durchgeführt. Wegen der genannten Vorteile wird das beschriebene Sulfat-Verfahren zur Zeit ausschliesslich anstelle der photometrischen Methode [2—5] und des Brikett-Verfahrens [1] verwendet.

Die Methode wird in unserem Laboratorium seit über einem Jahr mit befriedigendem Erfolg eingesetzt, wobei täglich etwa 100—200 Bleibestimmungen durchgeführt werden.

Herrn H. Siffrin danke ich für die sorgfältige Durchführung der zahlreichen Versuche bei der Ausarbeitung des Analysenverfahrens.

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THE DETERMINATION OF IODIDE IN SEA WATER BY NEUTRON ACTIVATION ANALYSIS

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SUMMARY

A simple and sensitive method for the determination of iodide in sea water by neutron activation analysis has been developed. Iodide is separated from most other anions by passing sea water through a strongly basic anion-exchange column, recovered by elution with 2 M sodium nitrate, and concentrated from the eluate by precipitation as palladium(II) iodide in the presence of excess of palladium(II) with elemental palladium as carrier; elemental palladium is generated by reduction of some of the palladium(II) with thiosulfate. The precipitate is separated from the supernatant liquid by filtration. Checks on the efficiency of separation by means of added ^{125}I showed recoveries of 100 ± 3 %. The filter paper containing the precipitate is pressed into a pellet for neutron activation analysis by irradiation for 5 min at a flux of $4 \cdot 10^{12}$ n cm^{-2} s^{-1} and counting the ^{128}I 442.7-keV photopeak.

Iodine occurs in the ocean predominantly as dissolved iodate and iodide [1, 2]. A minute amount of organic iodine may also be present [3]. Iodide, the thermodynamically unstable species in oxygenated waters, ranges in concentration from 0.25 μM (near shore surface waters) to below the detection limit (deep ocean). The high concentrations of iodide in surface waters may constitute 50 % of the total iodine concentration (ca. 0.5 μM). Iodide is believed to be produced by the biologically mediated reduction of iodate [4], and thus plays a significant role in the geochemical cycling of iodine in the oceans. Moreover, a study of the iodine distribution in the oceans may give clues to the effects of biological activities on the redox chemistry of multi-oxidation-state elements in the marine environment, and yield information concerning the effective redox potential of sea water as suggested by Liss et al. [5].

The distribution of iodate in sea water [6] has been studied. This paper describes a simple and sensitive method for the determination of iodide. A literature review showed that various titrimetric [7—10], photometric [8—15] and polarographic [16] methods have been proposed for the determination of iodide in sea water. Many of these procedures require tedious initial oxidation, concentration and separation steps, and stringent

control of experimental conditions, and the iodide concentration is calculated frequently from the difference between the iodate and total iodine concentrations. Consequently, any organic iodine will be included in the iodide fraction. The only known direct method is that of Sugawara et al. [11], or its modified versions [9, 12]; iodide is first concentrated from sea water by precipitating mixed silver halides which are treated with bromine water to oxidize iodide to iodate; the excess bromine and hypobromite are carefully removed and the iodate is determined by iodometric titration. This method is time-consuming and considerable manipulative skill is required to remove the bromine compounds quantitatively.

The nuclear characteristics of iodine make it particularly favorable for neutron activation analysis (n.a.a.); it occurs as the mono-isotopic ^{127}I with a rather large (n, γ) cross-section of 5.6 barns. Bombardment with thermal neutrons gives ^{128}I, which has a half-life of 25 min and undergoes β-decay, emitting γ-rays with energies of 442.7 keV, 526.3 keV and 743.5 keV with relative intensities of 100:9:1 [17], and β-particles with energies of 1.13 meV, 1.67 MeV and 2.12 MeV and relative intensities of 2:16:76 [18]. N.a.a. has been used to determine the total iodine content of biological [19—22], industrial [23, 24] and some meteorological materials [25—27]; all these methods involve a post-irradiational separation of iodine from the sample matrix, and because of the short half-life of ^{128}I, their usefulness is reduced.

In the present application to the determination of iodide in sea water, post-irradition chemical manipulations of the samples have been eliminated in favor of a simple pre-irradiation separation step; the simplicity and higher sensitivity yield distinct advantages over the existing methods. The procedure involves a separation of iodide from iodate, other halides, and most other anions by passing the sample of sea water through an ion-exchange column containing AG 1-X8 resin in the nitrate form. Iodide is retained in the column and is recovered by eluting with 2 M sodium nitrate. The iodide is precipitated selectively from the eluate as palladium(II) iodide in the presence of excess of palladium(II); elemental palladium, produced by reducing some of the excess of palladium(II) with sodium thiosulfate, is used as a carrier. The precipitate is filtered and analyzed by n.a.a.

EXPERIMENTAL

Reagents

All reagents were analytical reagent grade. Sodium nitrate solution (2 M). The reagent should be recrystallized until free from iodine. Sodium thiosulfate solution (1.5 mM). Dissolve 0.37 g of sodium thiosulfate pentahydrate and 0.1 g of sodium carbonate in freshly boiled, distilled water to make 1 l. Standard palladium solution (1 mg Pd^{2+} ml^{-1}). Dissolve 0.67 g of ammonium chloropalladite in about 150 ml of distilled water. Add 41.7 ml of 12 M hydrochloric acid and dilute to 250 ml. Standard rubidium sulfate solution

(1000 p.p.m. Rb^+). Dissolve 0.78 g of rubidium sulfate in distilled water and dilute to 500 ml. Standard potassium iodate solution (10 μg I/100 μl). Dissolve 0.1687 g of potassium iodate in distilled water and dilute to 1 l. Bio-Rad AG 1-X8 resin, 100—200 mesh, chloride form.

Preparation of the ion-exchange column

Transfer about 100 g of the AG 1-X8 resin to an Erlenmeyer flask. Add 150 ml of (1 + 4) hydrochloric acid. Swirl the mixture vigorously. Allow the resin to settle and decant the supernatant liquid. Repeat this procedure with 150 ml of distilled water, then 150 ml of 0.5 M sodium hydroxide solution and then with 150 ml of distilled water again. Repeat this cycle three times. Wash the resin once with 150 ml of 2 M sodium nitrate and store it in 2 M sodium nitrate overnight. Pack the resin into glass columns, of i.d. 1 cm and length 11—12 cm.

Flux monitor

Pipette 100 μl of the standard rubidium sulfate solution onto a Nudepore filter (0.45-μm, 47-mm diam.). Dry the filter under an infrared lamp. Press the filter into a pellet (ca. 8 mm diam.) in a stainless steel press as described by Spencer et al. [28]. One of these pellets accompanies each sample or standard throughout the irradiation and counting procedure.

Standard

Pipette 100 μl of the standard potassium iodate solution onto a Nudepore filter (0.45-μm, 47-mm diam.). Dry, and treat the standard exactly as for a sample pellet.

Procedure

Pass 250 ml of sea water sample through the ion-exchange column at 2 ml min^{-1} (controlled by a peristaltic pump). Wash the column with ca. 5 ml of distilled water. Discard the eluate. Elute the column with 2 M sodium nitrate solution at the same rate. Discard the first 30 ml of the eluate. Collect the next 80 ml in a 125-ml Erlenmeyer flask. Add 1 ml of the standard palladium solution and 2.5 ml of 1.5 mM sodium thiosulfate. Swirl the mixture vigorously. After 5 min, place the flask in a water bath at 80 °C for 30 min, then allow the mixture to cool. Collect the precipitate by filtering the mixture through a Nudepore filter (0.45-μm, 47-mm diam.). Wash the filter with distilled water, and then dry it in a desiccator for at least 2 h. Press the filter into a pellet.

Irradiate the pellet and a rubidium flux monitor for 5 min in a thermal neutron flux of ca. $4 \cdot 10^{12}$ n cm^{-2} s^{-1}. Let the pellets cool for 30 min. Count

both pellets for 800 s on a Ge(Li) detector coupled with a pulse-height analyzer.

RESULTS AND DISCUSSION

Strongly basic anion-exchange columns, such as AG 1-X8, separate chloride, bromide and iodide from each other efficiently [29—31]. The affinities of various anions for the resin are in the order [32]: $I^- >$ phenolate $> HSO_4^- > ClO_3^- > NO_3^- > Br^- > CN^- > HSO_3^- > NO_2^- > Cl^- > HCO_3^- > IO_3^- > HCOO^- > Ac^- > OH^- > F^-$. Thus, when sea water is passed through the resin in the nitrate form, few anions other than iodide will be retained.

The behavior of iodide during column loading and elution was studied with an iodide-selective electrode and by the radioactive isotope ^{125}I. Figure 1 summarizes the behavior of the halides during the loading and the elution of the column. The electrode potential produced by each halide at the concentration used in the experiment differs. Bromide and chloride give a positive electrode potential; 10^{-6} M iodide or above gives a negative electrode potential, and therefore the peaks in the elution diagram can be identified. The identity of the iodide peak was confirmed by radioisotopic studies. As reported previously [29—31], chloride and bromide are eluted earlier than iodide but with the resin in the nitrate form, a large portion of the chloride and bromide is not retained in the loading process. The changes in total

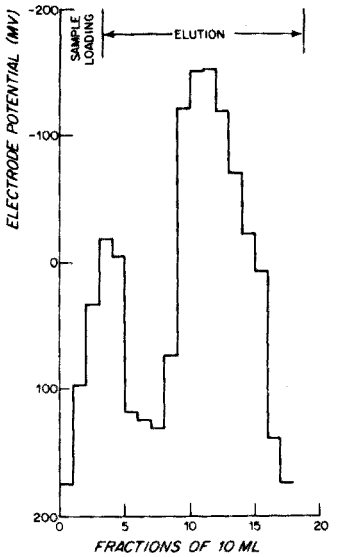

Fig. 1. The loading and elution behavior of halides as determined by an iodide electrode. The sample is a mixture of 25 ml of sea water and 5.3 ml of 1 mM NaI. The flow rate is 0.5 ml min^{-1}.

halide concentration during the loading of 250 ml of sea water onto the column, and the subsequent elution, were followed by potentiometric titration of fractions of the eluate with silver nitrate, the iodide electrode being used to detect the end-point. The results, summarized in Fig. 2 show that most of the chloride and bromide escapes from the column before elution. The residual amount is eluted after passing 20 ml of 2 M sodium nitrate through the column.

The elution behavior of iodide was also studied with ^{125}I, which has a half-life of 60 d and emits γ-rays of 35—27 keV. Figure 3 summarizes the results: the major portion of the activity is confined to fractions 6—10; quantitative recovery is ensured by collecting fractions 4—11.

The ion-exchange capacity of the column for iodide is shown in Fig. 4. After passing 1 l of sea water (four times the sample size) through the column, its capacity has not been reached and break-through does not occur.

Palladium(II) is a well known selective precipitant for iodide [33, 34] in the presence of bromide and chloride. However, in producing elemental palladium as the co-precipitant, care must be taken to control the amount of reducing agent used. Excess of thiosulfate slowly reduces palladium(II) iodide, and poor and variable yields result. Thus, an excess of palladium(II), as evident from the persistence of a slight straw yellow color in the supernatant liquid, should always be maintained. The elemental palladium thus produced forms large spongy clumps and is ideal for separation by filtration.

The recovery given by this procedure was tested (Table 1) by comparing the activities of added radiotracer in sample pellets and in standards. The standard is prepared by adding carrier iodide to the same amount of tracer and then precipitating the iodide with excess of palladium(II). The three samples gave activities that were indistinguishable within the counting and

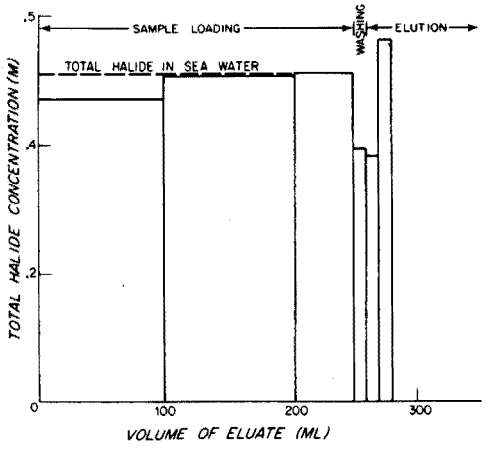

Fig. 2. Changes in the concentration of total halide in the eluate during loading and elution of 250 ml of sea water.

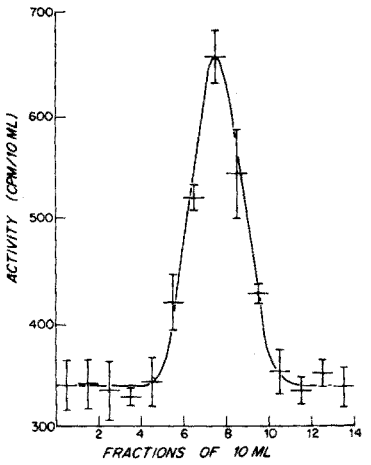

Fig. 3. The elution behavior of iodide from 250 ml of sea water. Error bars show 1 s.d. calculated from three 1-min counts.

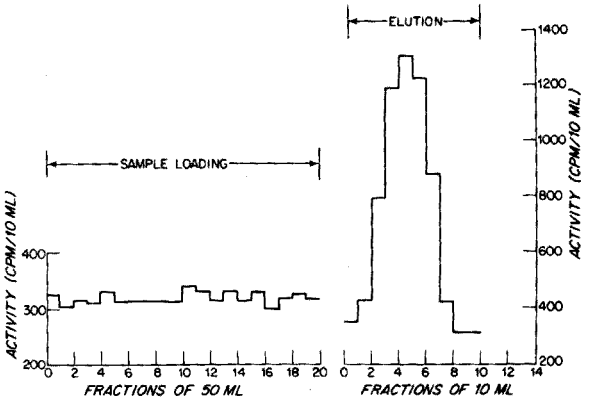

Fig. 4. Test of the ion-exchange capacity of the column during loading and elution of 1 l of sea water.

handling uncertainties, from the standards.

Since palladium is used as the precipitant and one of its stable isotopes (^{108}Pd) has a large thermal neutron cross-section of 12 barns, dead-time can present a serious counting problem. Natural palladium contains 26.7 % of ^{108}Pd. During neutron activation, ^{108}Pd is transformed to ^{109m}Pd or ^{109}Pd. ^{109m}Pd decays to ^{109}Pd with a half-life of 4.75 min by emitting 188.9-keV γ-rays [17], ^{109}Pd in turn decays to ^{109}Ag with a half-life of 13.5 h via β-decay and emits 88-keV and 311.5-keV γ-rays in the process. The amount of palladium in the precipitate has therefore been limited to the least amount that can be easily handled. A relatively long cooling period of 30 min is

TABLE 1

Check of recovery of added radiotracer from sea water

	Activity (c.p.m.)[a]	Mean	s (1 σ)
Woods Hole surface water	1. 2010, 2059, 2012	2027	28
	2. 1979, 1951, 2072	2001	63
	3. 2001, 1990, 2008	2000	9
Mean of 3 samples		2009	37
Standards	1. 2045, 1980, 1968	1998	41
	2. 1929, 1942, 1918	1930	12
	3. 1918, 1932, 1970	1940	27
Mean of 3 standards		1956	41
% Recovery		103 %	

[a]The figures for each sample represent three consecutive counts for 1 min.

used. In addition, pellets containing a rubidium standard for each sample or iodide standard are used as a dead-time and neutron flux monitor.

Figure 5 shows the γ-ray spectra of a blank filter, a standard iodate—iodine sample and a surface water sample from Woods Hole. The major γ-peaks are identified on the spectra. The region around the iodine 442.7-keV γ-peak is expanded in Fig. 6. The blank is insignificant and for all practical purposes can be ignored. In the sample, the peak shows no shoulder, suggesting no spectral interferences within the resolution of the detector (2.5 keV FWHM for ^{60}Co 1.33-MeV γ-rays). The ratios of the photopeaks at 442.7 keV, 526.3 keV and 743.5 keV in the standard and the sea water sample are 100 : 7.4 : 0.7 and 100 : 7.6 : 0.5, respectively. They agree with each other well, which further suggests that there are no spectral interferences.

The iodide concentrations in three subsamples from one sample of surface water collected near Woods Hole were determined by this method. The average concentration was 0.123 μM and the standard deviation was 0.006 μM. This precision is better or similar to that of the methods presently available.

Figure 7 shows a profile of dissolved iodide from near surface waters in the Equatorial Atlantic. The absolute concentrations agree well with others reported in the literature [1, 2]. Since concentrations as low as 0.006 μM can be detected, it appears that there is no serious contamination problem during the pre-irradiation manipulations. The smoothness of the profile is as expected and gives some confidence in the reliability of the method. The three data points from 400 m to 750 m have an average concentration of 0.007 μM. This sensitivity far exceeds those of methods reported previously.

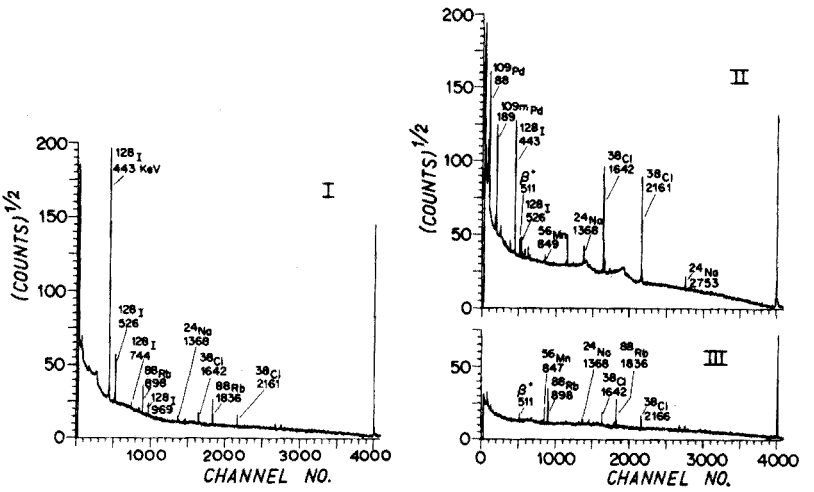

Fig. 5. The γ-ray spectra of a standard iodate—iodine sample (I), a Woods Hole surface water sample (II) and a blank filter (III). Energies of major γ-peaks are given in keV.

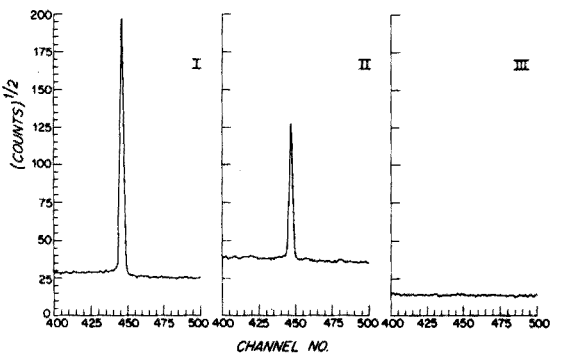

Fig. 6. The region around 442.7 keV of the γ-ray spectra of a standard iodate—iodine sample (I), a Woods Hole surface water sample (II) and a blank filter (III).

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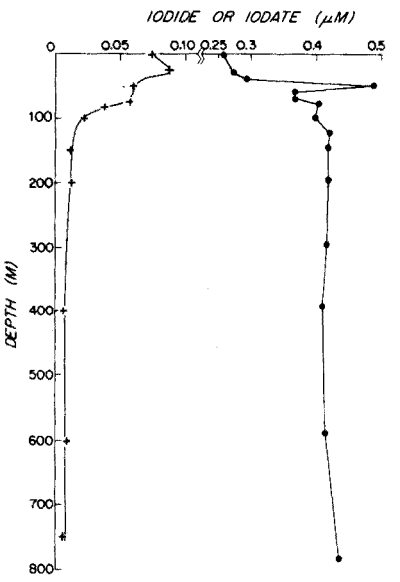

Fig. 7. Iodide (+) and iodate (·) profiles at 00°01'N and 09°58'W. Error bars in iodide profile represent 5 % uncertainty.

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ADSORPTION CHARACTERISTICS OF RADIONUCLIDES ON NICKEL HEXACYANOFERRATE(II)

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SUMMARY

The composition of nickel hexacyanoferrate(II) complexes depends on the ratios of sodium hexacyanoferrate(II) and nickel nitrate solutions mixed. The adsorption behavior of nickel hexacyanoferrate(II) is described; acid treatment of $Ni_2Fe(CN)_6$ accelerates the adsorption rate of cesium, but does not increase the adsorption capacity. The Ni—Cs exchange ratios of $Ni_2Fe(CN)_6$ are discussed. In concentrated salt solutions, the distribution coefficients of ^{59}Fe, ^{60}Co, ^{65}Zn, ^{137}Cs, ^{95}Zr and ^{144}Ce are determined together with those of ^{85}Sr and ^{106}Ru. A simple determination of ^{137}Cs in sea water containing ^{59}Fe, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{144}Ce, ^{85}Sr and ^{106}Ru is described.

Nickel hexacyanoferrate(II) is a valuable adsorbent for radionuclides, especially ^{137}Cs; [1—8] its chemical properties and adsorption characteristics have been thoroughly investigated [9—14]. A study of the adsorption characteristics of several metal hexacyanoferrates showed that the composition and ion-exchange behavior of zinc hexacyanoferrate(II) depended on the mixing ratio of the starting materials [16]. In order to confirm that metal hexacyanoferrates(II) gave such effects, analogues of nickel hexacyanoferrate(II) were prepared by mixing different ratios of nickel nitrate and sodium hexacyanoferrate(II); analysis of these analogues showed their composition to be either $Ni_2Fe(CN)_6$ or $Na_2NiFe(CN)_6$.

The present paper reports the following studies: (1) the relationship between the ratios of nickel nitrate and sodium hexacyanoferrate(II) taken; (2) relative adsorption rates of cesium from aqueous solutions with or without the addition of nitric acid; (3) the atomic ratio of adsorbed cesium to released nickel; (4) the distribution coefficients for radionuclides in concentrated salt solutions; (5) the determination of ^{137}Cs in sea water containing ^{59}Fe, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{144}Ce, ^{85}Sr etc.

EXPERIMENTAL

Preparation of nickel hexacyanoferrate(II) analogues

All reagents were of analytical grade. The nickel hexacyanoferrate(II) analogues were prepared by mixing 0.1 M sodium hexacyanoferrate(II) (200—300 ml) and 0.1 M nickel nitrate in the ratios 1:10, 1:3, 1:2, 1:1 and 1:0.1. The green slurries, obtained by adding both these solutions dropwise to a beaker for 30 min while stirring, were heated with stirring on a boiling water bath for 2 h, allowed to stand for 24 h, filtered or centrifuged, washed thoroughly, and dried at room temperature. Slurries other than from the 1:10 ratio were finely dispersed, and were centrifuged for 15 min at 15000 *g* rather than filtered. The precipitates labelled with ^{22}Na were prepared by the same procedure.

Relative adsorption rate and batch distribution coefficient

The relative adsorption rates for cesium were determined by mixing 0.1 g of the nickel hexacyanoferrate(II) analogues with 5 ml of a cesium chloride solution labelled with ^{137}Cs (0.01 μCi ml^{-1}) followed by centrifugation at 8000 *g* for 1 min. The radioactivity of the supernatant solution was measured by a well-type scintillation counter. Distribution coefficients, K_d, (ml g^{-1}), for the radionuclides were determined by equilibrating 0.1 g of the analogues with 5 ml of an aqueous solution containing the radionuclides, followed by the same treatment as described for the determination of the relative adsorption rates.

Ni—Cs exchange ratio

Exchanges of Ni—Cs were studied by shaking 5 g of the nickel hexacyanoferrate(II) with 100 ml of the ^{137}Cs-labelled cesium chloride solution. After equilibrium had been attained, the mixture was centrifuged and cesium or nickel in the supernates was determined by radioactivity measurement or by EDTA titration, respectively. The Ni—Cs exchange ratio was calculated from the ratio of the amounts of cesium adsorbed to those of nickel released. The amounts of nickel released into the aqueous phase, and the amount of cesium taken up, were obtained by the ^{137}Cs decrease and the nickel increase in the aqueous phase, respectively.

Determination of nickel, hexacyanoferrate(II), and sodium

The nickel hexacyanoferrate(II) (or ^{22}Na-labelled $Na_2NiFe(CN)_6$) was destroyed by heating with concentrated sulfuric acid and evaporation to dryness, followed by the addition of 12 M hydrochloric acid. A large proportion of the iron in this hydrochloric acid solution (8 M) was extracted

with isopropyl ether saturated with 8 M hydrochloric acid. The hydrochloric acid solution was passed through a Dowex 1-X8 column, and the nickel (or sodium) and the iron were separated by the method of Kraus and Moore [15]. The nickel or the hexacyanoferrate(II) were determined titrimetrically; the sodium was determined by the ^{22}Na activity.

Column studies

After cutting off the tip of a conventional glass column (1.2 × 30 cm), the remaining portion of the column was connected to a polyethylene test tube (1.3 × 10 cm) with a hole (diameter 4 mm, plugged with glass wool) at the bottom. Nickel hexacyanoferrate(II) (20—30 mesh) was slurried with 0.1 M nitric acid and poured into this tube to make a column (1.3 × 3 cm). To sea water (1 l with sufficient nitric acid to give 0.1 M) spiked with several radionuclides (ca. 0.1 μCi each), 1.825 g of *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (DCyTA) was added to make 10^{-2} M DCyTA in the sea water. The pH was then adjusted to 4 with 10 % sodium hydroxide, and the solution was passed through the column at a flow rate of 1 l h^{-1}. The polyethylene tube was disconnected from the glass column and wrapped in a vinyl bag, and the radioactivity was measured with a well-type NaI(Tl) detector coupled to a 400-channel pulse height analyzer.

RESULTS AND DISCUSSION

Possible differences in the stoichiometric composition of the resulting hexacyanoferrate(II) analogues were checked by varying the ratios of 0.1 M sodium hexacyanoferrate(II) and 0.1 M nickel nitrate. Analysis showed that the compositions resulting from the 1:10, 1:3, 1:2 and 1:1 ratios are best represented as $Ni_2Fe(CN)_6$; and that of the 1:0.1 ratio as $Na_2NiFe(CN)_6$.

The relative adsorption rates of cesium on $Ni_2Fe(CN)_6$ were determined by varying the shaking time in batch experiments. The adsorption rate in 0.1 M nitric acid was faster than that in aqueous solution (Fig. 1). For this reason, most of the adsorption experiments with metal hexacyanoferrates were carried out in acidic rather than in aqueous solution. $Ni_2Fe(CN)_6$ was allowed to stand for 1 d in 1 M nitric acid, filtered, washed thoroughly with water, and air-dried at room temperature. The adsorption rate for cesium of this treated $Ni_2Fe(CN)_6$ was determined in aqueous solution; the treatment accelerated the adsorption rate to that in 0.1 M nitric acid; $Ni_2Fe(CN)_6$ was therefore used after acid treatment. The acid treatment accelerated the adsorption rate of cesium, but did not increase the adsorption capacity.

In solutions of 10^{-1}, 10^{-2} or 10^{-3} M cesium chloride, the exchange of nickel in the $Ni_2Fe(CN)_6$ for cesium was determined by batch experiments (Table 1); the atomic ratios of the adsorbed cesium to the released nickel were found to be 14, 9 or 8, respectively. For ion-exchange adsorption, the ratio of adsorbed cesium to released nickel should be 2. The adsorption

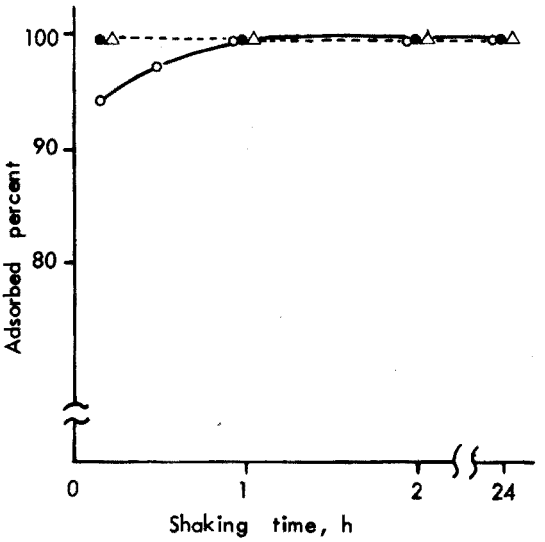

Fig. 1. Relative adsorption rate of cesium on $Ni_2Fe(CN)_6$. (•) 0.01 M $CsNO_3$ in 0.1 M HNO_3. (△) 0.01 M $CsNO_3$ in aqueous solution; $Ni_2Fe(CN)_6$ was treated previously with 1 M HNO_3. (○), 0.01 M $CsNO_3$ in aqueous solution.

TABLE 1

Ratio of cesium adsorbed to nickel released

Solution	Cs adsorbed (mmole)	Ni released (mmole)	Ratio Cs/Ni
10^{-1} M CsCl	$9.9 \cdot 10^{-1}$	$7.0 \cdot 10^{-2}$	14
10^{-2} M CsCl	$9.9 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$	9
10^{-3} M CsCl	$9.9 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	8

observed may therefore involve a retention other than an ion-exchange; such retention of cesium has also been observed in adsorption by zinc hexacyanoferrate(II) analogues [16].

Distribution coefficients of $Ni_2Fe(CN)_6$ for radionuclides in concentrated salt solutions

Table 2 shows the variation in distribution coefficients for ^{59}Fe(III), ^{60}Co, ^{65}Zn, ^{137}Cs, and ^{95}Zr(IV), on the addition of concentrated salts to the nitric acic solutions. The K_d values decrease to some extent with increasing concentration of nitric acid, and decrease markedly on addition of the salts. With ^{144}Ce, ^{85}Sr, and ^{106}Ru [added as $RuCl_{3.4}$, $RuNOCl_3$, $RuNO(NO_3)_3$ or $RuNO(NO_2)_4$], the distribution coefficients are less than 10 for all the conditions mentioned in the Table.

TABLE 2

Variation in distribution coefficients for radionuclides in nitric acid solutions on addition of salts

Nuclides	0.1 M HNO_3				4 M HNO_3
	0	0.5 M NH_4NO_3	0.5 M NaCl	Sea water	0
^{59}Fe	$1 \cdot 10^3$	$1 \cdot 10^2$	$9 \cdot 10$	$5 \cdot 10^2$	$7 \cdot 10$
^{60}Co	$4 \cdot 10$	— [a]	— [a]	— [a]	$2 \cdot 10^2$
^{65}Zn	$4 \cdot 10^3$	— [a]	$3 \cdot 10$	$8 \cdot 10^2$	$2 \cdot 10^2$
^{137}Cs	$4 \cdot 10^4$	$7 \cdot 10^3$	$5 \cdot 10^4$	$1 \cdot 10^4$	$2 \cdot 10^4$ [b]
^{95}Zr	$1 \cdot 10^2$	$7 \cdot 10$	$2 \cdot 10$	— [a]	— [a]

[a] Distribution coefficients of below 10.
[b] When 4 M NH_4NO_3 was also present, the K_d value was $7 \cdot 10^2$ for ^{137}Cs but was below 10 in all other cases.

In the case of sea water, K_d values for ^{59}Fe, ^{65}Zn and ^{137}Cs are considerably higher than those for ^{60}Co, ^{95}Zr, ^{144}Ce, ^{85}Sr and ^{106}Ru. The values for these radionuclides in sea water are nearly equal to those in 0.5 M sodium chloride. The concentration of sodium chloride in sea water is about 0.5 M [17].

Addition of DCyTA to sea water containing several radionuclides

Table 2 shows that the simultaneous determination of the radionuclides in concentrated salt solutions is feasible by means of column chromatographic adsorption combined with γ-spectrometry. The selective adsorption of ^{137}Cs in the presence of the radionuclides provides a simple technique for routine analysis. Accordingly, the possibility of selective adsorption of ^{137}Cs from sea water containing several radionuclides was determined after the addition of DCyTA, which serves as a chelating agent for various radionuclides; the addition of DCyTA may preclude the rapid dissolution of $Ni_2Fe(CN)_6$ as a result of the slow complex formation of DCyTA with nickel ions from $Ni_2Fe(CN)_6$.

To determine the optimum concentration of DCyTA to be added to sea water, the K_d values for several radionuclides were determined by varying the concentration of DCyTA in the sea water (adjusted to 0.1 M in hydrochloric acid); after adding a given quantity of DCyTA, 10 % sodium hydroxide solution was added to give pH4, and the resulting solution was used for batch experiments. Table 3 shows that the K_d values for ^{59}Fe, ^{60}Co and ^{65}Zn in the sea water decrease significantly on the addition of DCyTA; 10^{-2} M DCyTA in sea water is the most appropriate concentration for the selective adsorption of ^{137}Cs. The variation in K_d values for ^{137}Cs was subsequently determined by batch experiments in 10^{-2} M DCyTA in sea water. The K_d value is $1 \cdot 10^4$ after 10 min and then remains unchanged at $2 \cdot 10^4$ for shaking times of 20—60 min. This suggests that the $Ni_2Fe(CN)_6$ is not dissolved appreciably

TABLE 3

Variation in distribution coefficients of radionuclides in sea water on addition of DCyTA

Radionuclides[a]	DCyTA added (M)		
	10^{-2}	10^{-3}	10^{-4}
^{65}Zn	— [b]	$1 \cdot 10$	$7 \cdot 10^2$
^{137}Cs	$2 \cdot 10^4$	$3 \cdot 10^4$	$4 \cdot 10^4$
^{95}Zr	$1 \cdot 10$	$3 \cdot 10$	$8 \cdot 10$
^{144}Ce	$7 \cdot 10$	$2 \cdot 10^4$	$2 \cdot 10^4$
^{106}Ru[c]	$5 \cdot 10$	$1 \cdot 10^2$	$1 \cdot 10^2$

[a] For ^{59}Fe, ^{60}Co and ^{85}Sr, the distribution coefficients were below 10 for all conditions tested.
[b] Distribution coefficients of below 10.
[c] Added as $RuNO(NO_3)_2$.

and that the combination of $Ni_2Fe(CN)_6$ and 10^{-2} M DCyTA is suitable for the adsorption of ^{137}Cs from sea water.

Determination of ^{137}Cs in sea water containing several radionuclides

As described above, ^{137}Cs spiked in 10^{-2} M DCyTA-sea water was adsorbed quantitatively on $Ni_2Fe(CN)_6$ with low contamination from ^{95}Zr, ^{144}Ce and ^{106}Ru. The addition of DCyTA decreased the contamination of ^{59}Fe, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{144}Ce and ^{106}Ru. The combination of $Ni_2Fe(CN)_6$ and 10^{-2} M DCyTA in sea water was used for column studies. To 1 l of sea water (adjusted to 0.1 M in hydrochloric acid) containing ^{137}Cs, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{144}Ce, ^{85}Sr and ^{106}Ru was added 1.825 g of DCyTA to give a 10^{-2} M solution. The resulting solution was adjusted to pH 4 with 10 % sodium hydroxide solution and passed through the $Ni_2Fe(CN)_6$ column, and the radioactivity of ^{137}Cs retained in the column was determined with a well-type NaI(Tl) detector coupled to a 400-channel pulse-height analyzer. The amounts of ^{137}Cs detected (cpm measured/cpm added) in measurements of different aliquots of the sea water containing ^{59}Fe, ^{60}Co and ^{65}Zn were 90, 81, 77, 80, and 73. In the presence of ^{59}Fe, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{144}Ce, ^{85}Sr and ^{106}Ru, 94, 89, 82, 90, and 85 % of ^{137}Cs was detected. About 2 h was adequate for the complete analysis. The proposed method is therefore useful for the simple determination of ^{137}Cs in 1 l of sea water containing ^{59}Fe, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{144}Ce, ^{85}Sr and ^{106}Ru.

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THE USE OF DIFFERENTIAL SCANNING CALORIMETRY TO IDENTIFY METHAQUALONE SAMPLES: FORENSIC APPLICATIONS

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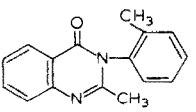
SUMMARY

The d.s.c. curves of commercial samples of methaqualone—Quāālude (U.S.A.), Quāālude (Mexico), Sopar, Mandrax and Parest — are presented. Similar d.s.c. curves were found for Quāālude (U.S.A.), Quāālude (Mexico), and Mandrax, while Sopar and Parest exhibited different types of curves. New and old formulations of the Quāālude (U.S.A.) brand could be differentiated by differences in the tablet filler and binder. Unfortunately, d.s.c. could not be used to determine the country of origin of the drug, although it was useful to characterize it. The technique can be used to identify samples of 0.15 mg or less.

Methaqualone, 2-methyl-3-*o*-tolyl-4-(3*H*)-quinazolinone, is a sedative and



hypnotic drug chemically unrelated to other sedative-hypnotics. Its mechanism of action is not very well known but it has antitussive and anti-spasmodic activity in experimental animals and is metabolized by the liver and excreted in the urine and feces. The compound has become the "drug of choice" among those who have previously abused barbiturates or are starting to use depressants. The United States government reclassified methaqualone as a Schedule Two drug in 1973 making it more difficult to obtain and possess the substance. Consequently, large quantities of the drug have been illegally smuggled into the United States from Mexico where it is available in the form of white tablets marked "Mandrax" or "Rorer-714".

This investigation was carried out to determine whether or not the thermal analysis technique of differential scanning calorimetry (d.s.c.) could be used to identify the various manufacturers of commercial methaqualone preparations and perhaps the country of origin. Differential

scanning calorimetry has previously been applied to studies of the thermal properties of analgesics [1], antacids [2] and vitamin preparations [3]. This technique, along with thermogravimetry (t.g.), has proved to be a valuable tool for the qualitative identification of these preparations, especially in forensic science applications.

EXPERIMENTAL

Thermal analysis equipment

A DuPont Model 990 DSC cell and console was used. Samples ranged from 0.15 to 3.6 mg and were analyzed at a heating rate of 10 °C min^{-1} in a dynamic nitrogen atmosphere. Duplicate and in some cases triplicate runs were made on each sample.

Methaqualone samples

The trade names of the methaqualone preparations and their manufacturer are given in Table 1. All the samples studied were obtained from drug seizures by the Houston Police Department over a two-year period, and came from containers retaining their respective factory seals with proper labels. All the samples were analyzed by other procedures before being studied by d.s.c. Most of the preparations were in tablet form and were methaqualone with the exception of the Parest brand which came in a capsule form and

TABLE 1

Trade names and manufacturers of methaqualone samples

Trade name	Markings (code)	Weight of compound (mg)	Country of mfg.	Manufacturer
Quāālude	RORER 714	300	Mexico	Rorer de Mexico, S.A. de C.V.
Quāālude	RORER 714	300	U.S.A.	Rorer Inc., Fort Washington, Pa.
	RORER 712	150	U.S.A.	
	RORER	300	U.S.A.	
	WHR	150	U.S.A.	
Mandrax	MANDRAX	300	Mexico	Grupo Roussel, S.A.
Sopar	A/S	300	U.S.A.	Arnar-Stone Labs. Mount Prospect, Ill.
	A/S	150	U.S.A.	
Parest	PD-574	400	U.S.A.	Parke-Davis and Co. Detroit, Mich.
	PD-572	200	U.S.A.	

consisted of methaqualone hydrochloride. The initial d.s.c. samples studied were of the tablet material which came from the surface and center portions of the tablet; with capsules, one sample was taken from the open end and the other from the center. D.s.c. curves were also obtained of pure methaqualone extracted from the tablets and capsules.

Extraction procedure

About 0.5 mg of a tablet or capsule was crushed to a fine powder and dissolved in 50 ml of 0.3 M sulfuric acid. The solution was filtered and extracted with 100 ml of chloroform in a separatory funnel. The aqueous solution was separated, neutralized, made basic with Na_2CO_3 and then re-extracted with 100 ml of chloroform. The chloroform fraction was separated and evaporated to dryness on a steam bath, and the residue dissolved in a small quantity of methanol. Crystals of the pure methaqualone precipitated on cooling this solution to 0 °C for 24 h.

RESULTS AND DISCUSSION

The d.s.c. curves of samples from the 300-mg tablets from different sources are shown in Fig. 1. The 150-mg tablets exhibited similar curves and are not given here.

The curves for the first three samples were almost identical, while the

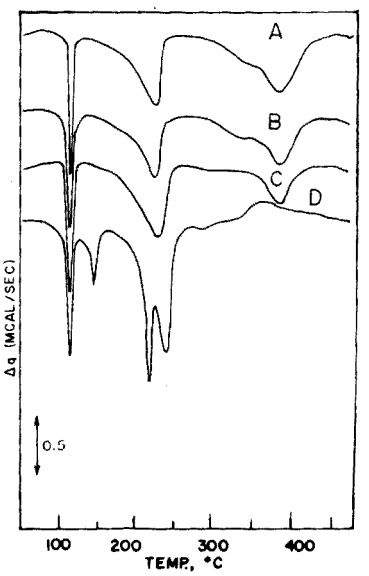


Fig. 1. D.s.c. curves of methaqualone. A, Mandrax. B, Quaalude (Mexico). C, Quaalude Rorer 714 (U.S.A.). D, Sopar. Sample sizes were 3.2—3.6 mg.

fourth possessed an entirely different curve, indicating a different composition in the filler or binder material. As can be seen in curves A—C, all three contained a narrow endothermic peak with a ΔT_{min} of 115 °C, a broad endothermic peak with a ΔT_{min} of about 210 °C, and then another broad peak or peaks with a ΔT_{min} of about 375 °C. The first endothermic peak is due to the fusion of the methaqualone (mp 114 °C [4]), the second is caused by its subsequent vaporization and/or decomposition, while the third region in the curve is due to the decomposition of the filler or binder material.

The effect of methaqualone composition in the different samples appeared only in the Parest brand (Fig. 2). Parest contains methaqualone hydrochloride and would be expected to exhibit a different d.s.c. curve from those samples containing pure methaqualone. The curves for the 400-mg tablet differed from those of the 200-mg capsule, indicating perhaps a different binder or filler material. Material from the 400-mg tablet had a more crystalline appearance.

The d.s.c. curves of the "new" and "old" tablet forms of the Quaalude (U.S.A.) brand are presented in Fig. 3. Before 1973 the Rorer Company apparently not only changed the tablet size and markings but also the filler and binder materials. Only samples from the 300-mg tablets are illustrated; the 150-mg tablets gave similar curves. It is interesting to note that the curve obtained from the Sopar brand (Fig. 1/D) is similar to that obtained from the "old" brand of Quaalude. These similarities are more evident by the two curves shown in Fig. 4; evidently the fillers and binders used by

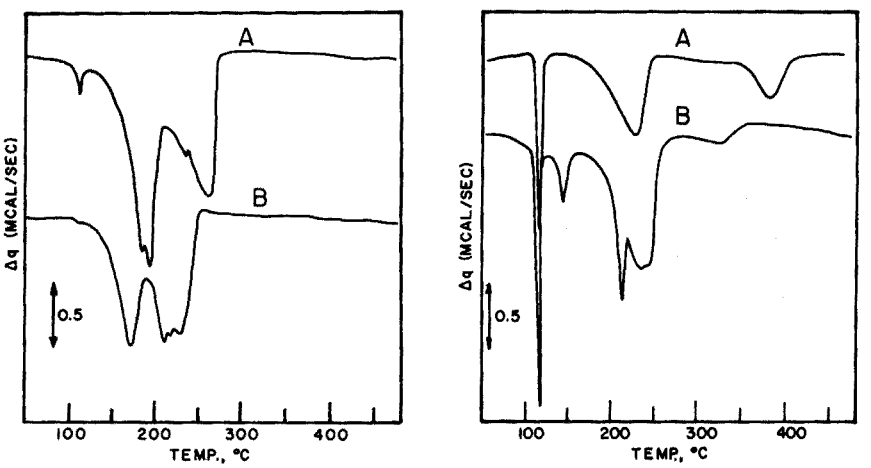


Fig. 2. D.s.c. curves of Parest. A, Sample from 400-mg tablet. B, Sample from 200-mg capsule. Sample size used was 3.2 mg.

Fig. 3. D.s.c. curves of Quaalude (U.S.A.). A, Rorer 714 (new). B, Rorer (old). Sample sizes used were 3.2—3.3 mg.

the two manufacturers were similar at one time.

The d.s.c. curves of pure methaqualone, as extracted from the Quaalude, Mandrax and Parest tablets, are shown in Fig. 5. When the recommended extraction procedure was used, the compounds all gave similar d.s.c. curves, indicating complete removal of the filler and binder materials and the conversion of the methaqualone hydrochloride (Parest) to methaqualone. The characteristic fusion endothermic peak at 115 °C is present as well as the vaporization and/or decomposition curve peaks in the 150—250 °C region.

The potential of d.s.c. to identify trace amounts (< 1 mg) of methaqualone is illustrated in Fig. 6. When the methaqualone was extracted from Quaalude and Parest, a d.s.c. curve was obtained from only 0.15 mg of sample. This could be useful when only trace amounts of the drug are available, such as the material found on syringes, protective needle caps, spoons or empty tablet or capsule containers. Even smaller samples than this could perhaps be identified.

CONCLUSIONS

Unfortunately, the technique of d.s.c. cannot be used to establish unequivocally the country of manufacture of the methaqualone. Samples obtained from Quaalude, whether manufactured by Rorer Inc. (U.S.A.) or Rorer de Mexico, gave similar d.s.c. curves. Apparently, the same filler or

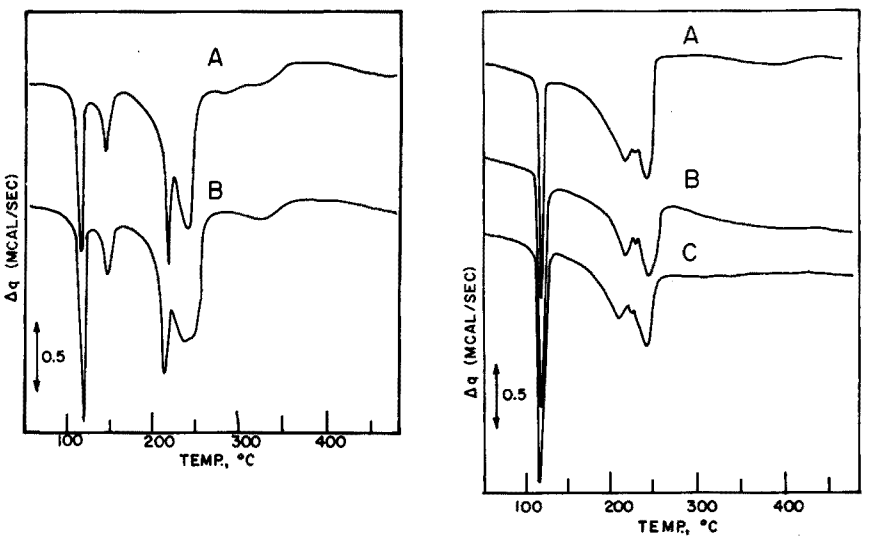


Fig. 4. D.s.c. curves of Sopar (curve A) and the old-style 300-mg tablet of Quaalude (U.S.A.) (curve B). Sample size used was 3.3 mg.

Fig. 5. D.s.c. curves of pure methaqualone extracted from commercial tablets. A, Mandrax. B, Parest. C, Quaalude. Sample sizes were 1.5—1.6 mg.

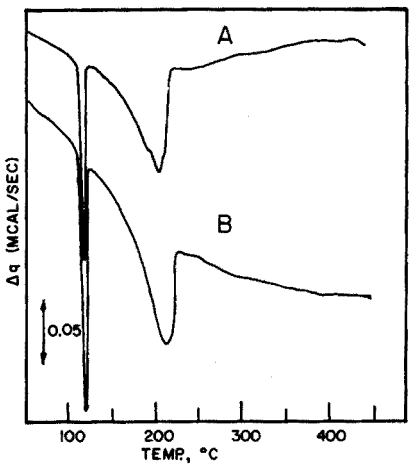


Fig. 6. D.s.c. curves of 0.15-mg samples of (A) Quāālude and (B) Parest. Samples were pure methaqualone extracted from commercial preparations.

binder materials must be used in their manufacture. There was a difference between the d.s.c. curves for the Quāālude from the old and new tablets, which was attributed to differences in filler or binder materials. It was possible, however, to distinguish between Quāālude, Sopar, and Parest although it should be noted that the old Quāālude tablet gave a curve similar to Sopar. It is possible to identify Parest because of its different composition (methaqualone hydrochloride). Trace amounts of methaqualone ($\sim$0.1 mg) can easily be identified by the d.s.c. technique.

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SIMULTANEOUS MICRODETERMINATION OF WATER AND OXYGEN IN METAL HALIDES BY REDUCTIVE FUSION IN AN INERT GAS

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SUMMARY

The carrier-gas technique has been used for the simultaneous determination of water and oxygen impurities in metal halides. In a hot carbon crucible these impurities are converted to hydrogen and carbon monoxide, which are separated on a MS 5A column and determined with a zirconia solid electrolyte detector with a coupled feedback circuit. The measuring range is 1—1000 p.p.m. in samples of 1—20 mg.

Metal halides are used as additives in high-pressure discharge lamps. The quality of these lamps is strongly influenced by water and oxygen impurities in the metal halides [1—3]. This requires the availability of reliable analytical equipment for the determination of the impurity level (range 1—1000 p.p.m. in a 10-mg sample).

The determination of water or oxygen in inorganic salts by the carrier-gas technique is well known. Oxygen has been determined by fusion of the sample in a reactive crucible (carbon) and the evolved carbon monoxide has been measured conductimetrically [4], manometrically [5], or by thermal conductivity [6]. Water has been determined by heating the sample in an inert crucible (platinum or fused silica) and the evolved water vapour determined with an electrolytical hygrometer [4, 7, 8], by thermal conductivity [9], or with the Karl Fischer method [10]. The determination of water in inorganic salts by reductive fusion in a carbon crucible has not been described previously.

This investigation deals with the simultaneous determination of water and oxygen by reductive fusion. A solid electrolyte galvanic cell has been used as a detector for the evolved gases.

Principle of operation

In the hot carbon crucible, water is converted to equal amounts of hydrogen and carbon monoxide, while oxygen is converted to carbon monoxide. These two gases are transported by the carrier gas to the detector after separation on a gas-chromatographic column. The detector consists of a

solid-electrolyte, high-temperature galvanic cell, in which hydrogen and carbon monoxide are oxidized at the platinum electrodes; the oxygen required is delivered automatically by an electronic feedback system. The flow-sensitive detector requires that the determination be carried out at a constant carrier gas flow and at a constant high temperature of the carbon crucible.

The various components of the apparatus are so arranged that the fusion furnace forms an integral part of the gas-chromatographic system [11] (Fig. 1). In this way, impurities present in the carrier gas, or resulting from system degassing, do not contribute to the measurement of the blank value, as in the earlier methods of freezing-out the evolved gases. The intrinsic impurity level produces a steady detector-signal of the order of 1 vol. p.p.m. of reducing gases, and the hydrogen and carbon monoxide evolved are determined above this baseline. The sensitivity required could be obtained only with this technique; the freezing-out method proved inadequate.

EXPERIMENTAL

Instrumentation

The gas-chromatographic system (Fig. 1) consisted of three main parts: the inlet system with fusion furnace, the gas-chromatographic column and the detector. Impurities in the helium carrier gas were reduced with an Oxisorb-purifier (Messer Griesheim). The flow (30 ml min^{-1}) was adjusted with a Brooks flow controller type 8744.

The fusion furnace (Fig. 2) consisted of a water-cooled quartz cell with an inductively heated carbon crucible (8-mm diameter, 20-mm high) supported on a tungsten rod, containing a tin bath. The operating temperature of the crucible (1500 °C) was measured with an optical pyrometer. The operating pressure in the quartz cell was ca. 2 atm. Above the quartz cell was placed an O-ring valve with a hole for introducing the sample into the crucible (Fig. 2). A six-armed glass sample holder was coupled to this O-ring valve; this holder

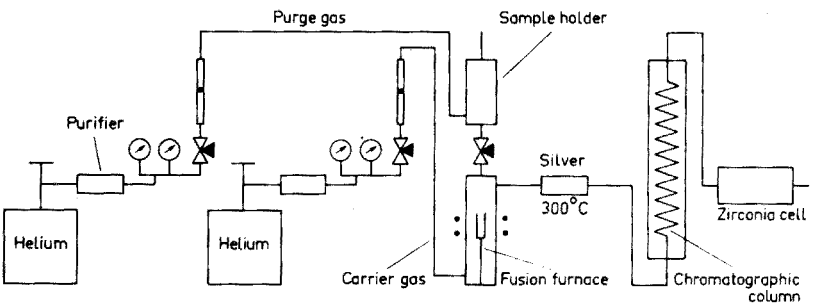

Fig. 1. Block diagram of the gas-chromatographic system.

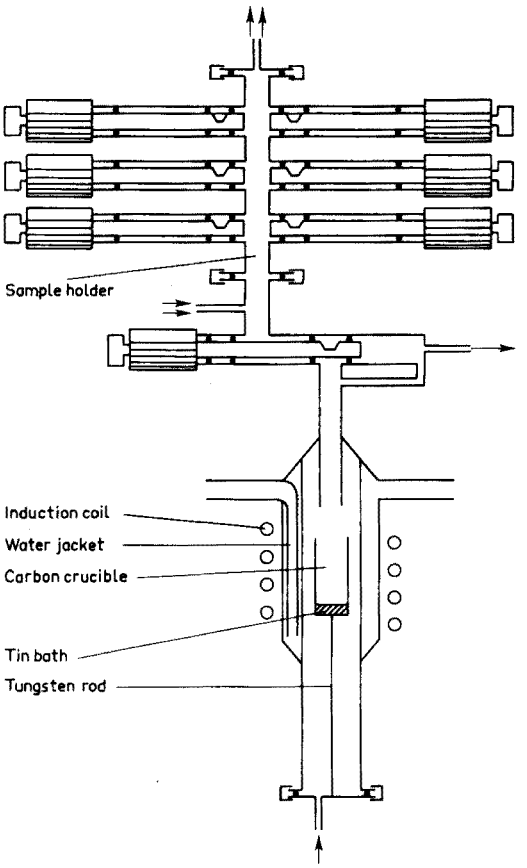

Fig. 2. Detailed construction of the furnace and inlet section. The single arrows indicate the path of the helium carrier gas and the double arrows the path of the purge gas.

was used to transport the samples from the glove box to the apparatus.

Between the quartz cell and the gas-chromatographic column, a pyrex tube packed with shredded silver foil at 300 °C, was placed to remove free halogens, in order to protect the hot electrodes in the detector. The gas-chromatographic column was a 1.0-m 1/8-in. o.d. stainless steel tube packed with 30—50-mesh molecular sieve 5A, and was maintained at 30 °C by passing a direct current along the tube. The detector was a calcium-stabilized zirconia galvanic cell [12—15] (Philips type PW9620), equipped with an electronic feedback circuit [15—17]. The signal-output was fed to a recorder and an electronic integrator.

Procedure

The carbon crucible was kept at the operating temperature (1500 °C) for ca. 20 min until a low and constant zero level of the detector was obtained. This temperature was maintained throughout the analysis of many samples.

The samples were prepared in a glove box. Powders were packed in tin foil (30-μm thick). The sample was introduced into the hot crucible, after the sample holder had been purged with helium for ca. 15 min. After the hydrogen and carbon monoxide peaks appeared on the recorder, the next sample could be introduced. The time required for one sample determination was ca. 10 min.

The quartz cell was periodically cleaned to remove the salts deposited on the glass wall. The formation of these deposits near the O-ring valve caused a certain stiffness in the operation of the valve. Depending on the sample weight, 40—60 samples could be analyzed successively.

The Faradaic efficiency of the zirconia cell was checked with known amounts of barium chloride hydrate (1—100 μg). These samples were obtained by injection of a dilute solution in water into small tin cups with a microsyringe; the cups were then placed in a desiccator for three days, beside an open boat filled with water-free barium chloride [18].

RESULTS AND DISCUSSION

Table 1 shows the water and oxygen contents of some commercially available anhydrous metal halides. Some of these salts were also subjected to an extra dehydration process.

The limit of detection for the water and oxygen determination in compact samples (without tin foil) is reached when the base-line fluctuations are of the same order as the amplitude of the hydrogen and carbon monoxide signal. These fluctuations are caused by variations in temperature of the different hot parts, by the electrical interference of the induction heating, and by noise from the electronic feedback circuit. This limit was found to correspond to 10^{-8} g of water or oxygen, which allows the detection of 1 p.p.m. in a 10-mg sample. For powder samples the limit of detection is established by the hydrogen and oxygen contents of the tin foil (ca. 4 p.p.m. hydrogen; ca. 40 p.p.m. oxygen). With ca. 30 mg of tin, this limit is 10^{-6} g. With tin capsules extruded from tin granules it is possible to improve the limit of detection to 10^{-7} g.

The upper limit for the determination is controlled by two different effects: that of the sample weight and that of the limited oxygen delivery in the detector. Experiments with different sample weights of one material showed that complete conversion of the water and oxygen in the carbon crucible is influenced by the sample weight; above 20—30 mg, the conversion becomes incomplete in the range below 1000 p.p.m. water or oxygen. A possible explanation is as follows: after the sample has been dropped into

TABLE 1

Water and oxygen contents of anhydrous metal halides

Sample	Delivery, dehydrating process	H_2O (p.p.m.)	O_2 (p.p.m.)
NiCl flakes[a]	Packed under argon	⩾ 1000	—
	Sublimed in vacuum	⩽ 100	150
LiI pellet[b]	Sealed glass ampoule	270	320
TlI flakes[c]	Not specially packed	⩾ 1000	—
	Sublimed in vacuum	⩽ 100	⩽ 100
NaI pellet[b]	Sealed glass ampoule	15	⩽ 5
NaI crystal[d]	Not specially packed	60	⩽ 5
NaI flakes[c]	Not specially packed	620	115
HgI_2 pellet[b]	Sealed glass ampoule	14	15
HgI_2 flakes[e]	Not specially packed	120	⩽ 100
$HgCl_2$ pellet[b]	Sealed glass ampoule	160	84
NaI-TlI-InI pellet[b]	Sealed glass ampoule	33	10

[a]Ventron, U.S.A.
[b]Anderson, U.S.A.
[c]Merck, Germany.
[d]Harshaw, U.S.A.
[e]U.C.B., Belgium.

the hot crucible, a gaseous cloud of sample material is generated; if the volume of this cloud exceeds the volume of the crucible (ca. 1 ml) the conversion becomes incomplete, because the time is too short for complete reaction with the wall of the crucible. This dependence suggests that the tin bath (with some reactive carbon in solution) is not essential here. Generally a tin bath is used as the medium for the complete conversion of oxygen in non-volatile samples, such as refractory materials.

An upper limit for the determination is also set by the maximum rate of oxygen delivery of the zirconia cell. More than 10^{-4} g of water or oxygen causes overloading of the cell; this was found in tests with known amounts of barium chloride hydrate.

The standard deviation of the determination in compact samples is about 10 % below 100 p.p.m. and 5 % above. The accuracy of the determination in powder samples is limited mainly by the spread in the hydrogen (4 ± 1 p.p.m.) and oxygen (40 ± 6 p.p.m.) contents of the tin foil. In such cases, the standard deviation is about 20 % in the region below 100 p.p.m.

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A MECHANISM FOR THE HEAT-INDUCED FLUORESCENCE OF COUMAPHOS AND RELATED COMPOUNDS AND THE IDENTIFICATION OF THEIR METABOLITES IN WATER

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(Received 28th April 1975)

SUMMARY

A simple method is proposed for the identification and determination of Potasan in technical coumaphos. The major fluorescent products of coumaphos and Potasan, after heat treatment on t.l.c., are identified as chlorferone and 4-methylumbelliferone, respectively, by i.r., m.s., t.l.c. and fluorescence spectral data. In water, coumaphos degrades into Coroxon, the oxygen analog, and chlorferone, the hydrolysis product. These three compounds can be determined simultaneously on the same chromatogram after extraction from water.

A new technique [1] for the detection of some organophosphorus insecticides, e.g. coumaphos, on silica-gel thin-layer chromatograms (t.l.c.) has recently been described. Fluorescence is produced by heating the chromatogram at an optimum temperature for a definite time; a few nanograms of coumaphos can be detected [2]. The detection technique, which has been applied successfully for coumaphos in lake and sewage water [3] and to the determination of coumaphos and its oxygen analog, Coroxon, in eggs [4], is interesting because the fluorescence originates from the pesticide, and not from a spray reagent [5—8] or a labelling compound [9].

The mechanism by which the fluorescence of coumaphos is obtained by heating has not been explained previously. Mallet and Brun [3] observed that the compound yielded several fluorescent species on pyrolysis and established the presence of Potasan, an impurity resulting from the synthesis of coumaphos, in the original formulation. Zakrevsky and Mallet [4] showed that coumaphos, and its oxygen analog, gave species that fluoresced at the same wavelength after heating. This permitted the simultaneous determination of both compounds in eggs.

This study was undertaken in order to identify the major fluorescent species obtained on t.l.c. after the pyrolysis of coumaphos and Potasan, and to study the degradation of both compounds in water with the expectation that common degradation products could be identified and determined simultaneously.

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EXPERIMENTAL

Chemicals and apparatus

The solvents used were either Spectranalyzed or Pesticide grade (Fisher Scientific Co.). Coumaphos (O,O-diethyl-O-(3-chloro-4-methyl-7-coumarinyl)-phosphorothioate), Coroxon (O,O-diethyl-O-(3-chloro-4-methyl-7-coumarinyl)phosphate), chlorferone (3-chloro-4-methyl-7-hydroxycoumarin) and Potasan (O,O-diethyl-O-(4-methyl-7-coumarinyl)phosphothioate) were obtained (the first three as analytical standards) from Chemagro Corp., Kansas City, and 4-methylumbelliferone (4-methyl-7-hydroxycoumarin) from Fisher Scientific Co.

Silica Gel H and extraction thimbles (Brinkmann Instruments) were required. T.l.c. plates (20 × 20 cm) were coated with a 250-μm layer in the usual way [2].

Fluorescence spectra were recorded with a Farrand uv—vis Chromatogram Analyzer equipped with motorized monochromators. Excitation filter 7-60 was used at all times; emission filter 3-75 was used for coumaphos and filter 3-73 for Potasan. A Hitachi Perkin-Elmer RM-50 mass spectrometer, a Perkin-Elmer 467 infrared spectrophotometer and a Turner Model 111 fluorimeter with t.l.c. attachment (filters 7-60 and 2A for excitation and emission, respectively) were used.

Analysis of technical coumaphos for Potasan

A sample (10 μg) of coumaphos was spotted on a t.l.c. plate along with appropriate standards of Potasan, and the plate was developed with chloroform. After the solvent front had migrated 10 cm, the plate was dried in air, and then heated in an oven at 200 °C for 20 min. After cooling, the plate was scanned with the photofluorometer; the concentration of Potasan was calculated from the calibration curve.

Identification of the major fluorescent product of coumaphos and Potasan

To obtain a sufficient quantity of material for further analysis, a solution (1000 p.p.m.) of coumaphos was applied to a silica-gel t.l.c. plate as close parallel bands and the plate was heated at 200 °C for 20 min. The adsorbent was collected with a glass vacuum apparatus and extracted with methanol by stirring for 3 h.

The extract was concentrated, applied as a band on a chromatographic plate, and developed in hexane:acetone (1:1). The major fluorescent product was then removed from the layer and extracted as before. The sample was used for mass spectral and infrared analysis. The fluorescence spectra were recorded directly on a thin-layer chromatogram.

The same procedure was utilized for Potasan except that extraction was

with acetone, and the plate was developed with carbon tetrachloride:methanol (100:7).

Extraction of coumaphos and related compounds from water

A sample of water (500 ml) was extracted with chloroform (3 × 75 ml), shaking each time for 3 min. The chloroform extract was dried for 2 min with 10 g of anhydrous sodium sulphate and decanted in a 500-ml round-bottomed flask. The extract was then evaporated to 10—20 μl in the usual way [3]. The concentrate was spotted on a t.l.c. plate with a syringe.

RESULTS AND DISCUSSION

Coumaphos is usually formulated as a 25 % wettable powder, Co—Ral, which is utilized mainly as a parasiticide on cattle. The technical material contains [10] at least seven impurities of which Potasan, the unchlorinated analog, is the most important. Wasleski separated [10] Potasan from coumaphos by t.l.c., and determinations were made colorimetrically after extraction of the particular spot from the silica-gel layer; this procedure is tedious, time-consuming, and lacking in sensitivity.

A typical chromatogram of technical coumaphos, observed under u.v. light, is shown in Fig. 1. The spots appear faintly mauve (non-fluorescent) on a

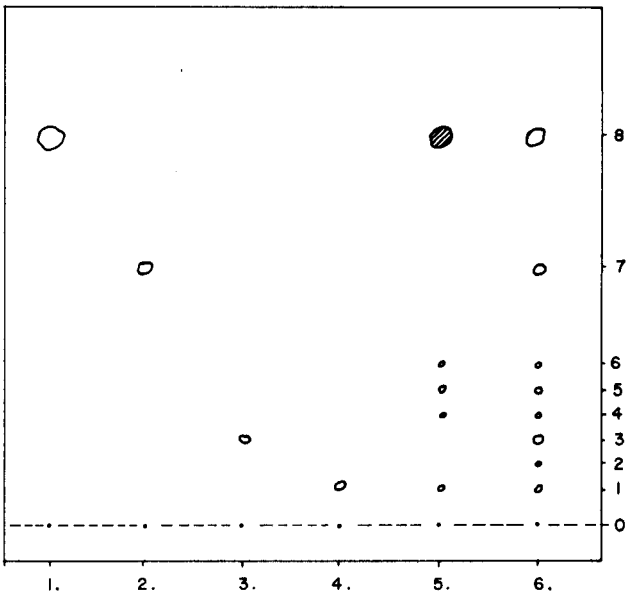


Fig. 1. Thin-layer chromatogram of technical coumaphos. 1, Coumaphos. 2, Potasan. 3, Coroxon. 4, Chlorferone. 5, Technical coumaphos (under u.v.). 6, Technical coumaphos (under u.v. after heat treatment).

dark background with the exception of 5.1 which is blue fluorescent. When the chromatogram is heated, more fluorescent spots appear. The presence of Potasan (6.7) and Coroxon (6.3) are easily recognized after the heat treatment although only 10 μg of technical coumaphos has been chromatographed. A small amount of chlorferone (6.1), the hydrolysis product of coumaphos, is also detected; this compound is naturally fluorescent (see 5.1). No attempt was made to identify the other impurities.

By applying appropriate standards the concentration of Potasan in this sample of technical coumaphos was found to be 4.3 %. The whole procedure takes ca. 1 h and is much simpler than that of Wasleski [10].

The species responsible for the fluorescence of coumaphos, Potasan and Coroxon after heating is of interest; t.l.c. experiments indicate that chlorferone is the major fluorescent species for both coumaphos and Coroxon, while 4-methylumbelliferone is the major species responsible for the fluorescence of Potasan (Fig. 2). Chlorferone and 4-methylumbelliferone are the expected hydrolysis products of coumaphos and Potasan, respectively [10]. Mass and i.r. spectra were obtained for spots 5.2 and 6.2; the spectra of both compounds were identical. By analogy it was concluded that

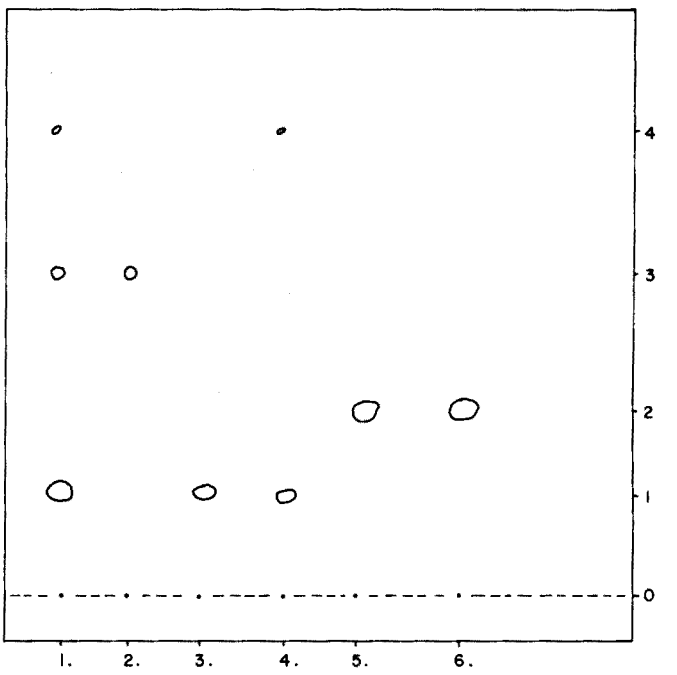
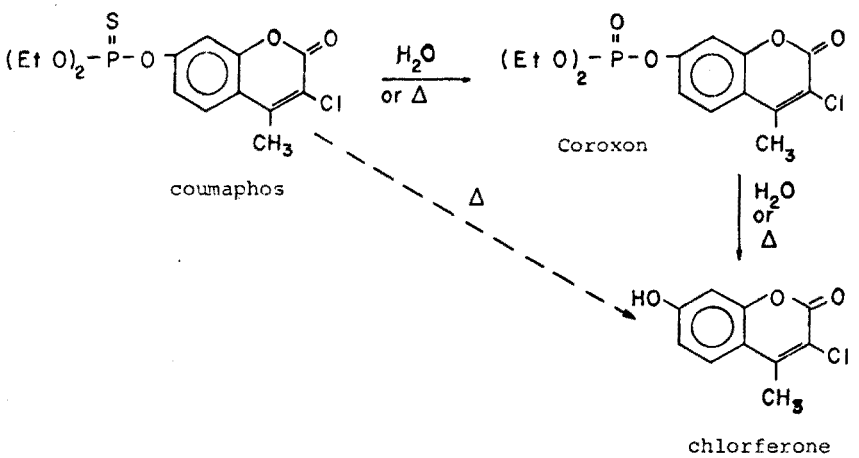


Fig. 2. Chromatogram of coumaphos, Coroxon, Potasan, chlorferone and 4-methylumbelliferone. 1, Coumaphos heat-treated before development. 2, Coumaphos heat-treated after development. 3, Chlorferone reference. 4, Coroxon heat-treated before development. 5, Potasan heat-treated before development. 6, 4-methylumbelliferone reference.

chlorferone is the product that fluoresces when coumaphos is heat-treated. Both coumaphos and Coroxon give unidentified spots (1.4 and 4.4) after heat treatment. Spot 1.3 was identified as undecomposed coumaphos (see 2.3) which becomes fluorescent after the second heat treatment. For excitation at 345—350 nm, identical emission spectral data at 430 nm were obtained for coumaphos (heated), Coroxon (heated) and chlorferone (unheated); likewise, the emission data obtained for Potasan and 4-methylumbelliferone at 450 nm were identical. The fluorescence spectra of chlorferone and 4-methylumbelliferone in the emission mode are sufficiently different to characterize these compounds in the presence of each other.

When coumaphos (10 p.p.b.) was extracted from distilled water after 2 h, the three distinct blue fluorescent spots observed after development and subsequent heat treatment (see Fig. 3) were identified as coumaphos (1.3), Coroxon (1.2), and chlorferone (1.1). An analytical standard of coumaphos, which gives only one spot on t.l.c., was added to the water. The results indicated that coumaphos is oxidized to Coroxon, which is then hydrolyzed to chlorferone (see below). A similar mechanism is expected upon heat



treatment of coumaphos, although direct conversion to chlorferone may occur. Strong heating can also cause chlorferone or 4-methylumbelliferone to decompose further into fluorescent compounds, but this effect is minimal under the conditions used here.

The authors thank the "Conseil de Recherches" of this University for financial support.

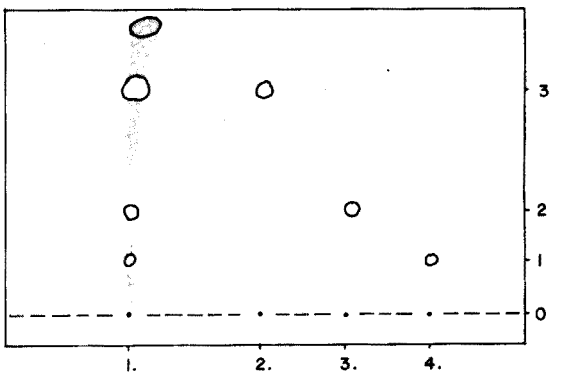


Fig. 3. Chromatogram of coumaphos extracted from water. 1, Sample extract of coumaphos in water. 2, Coumaphos standard. 3, Coroxon standard. 4, Chlorferone standard.

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SPECTROPHOTOMETRIC STUDY OF THE RUTHENIUM(III, II)—2,2′,2″-TERPYRIDINE SYSTEM*

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SUMMARY

Ruthenium(III) reacts with 2,2′,2″-terpyridine in aqueous solution at pH 3.0—4.5, when heated at 85 °C for 2 min, giving a green cationic complex with an absorbance maximum at 690 nm. The color is stable for at least 25 h. The system conforms to Beer's law. The optimal range for measurement (1.00-cm optical path) is 2—10 p.p.m. Ru; the molar absorptivity is $8.3 \cdot 10^3$. Ruthenium(II) reacts with terpyridine at pH 5.5 to develop an amber cationic complex (absorption maximum at 475 nm) on heating at 95 °C for 45 min. The color is apparently stable indefinitely. The system conforms to Beer's law; the optimal range is 1—5 p.p.m. Ru; the molar absorptivity is $1.45 \cdot 10^4$ l mol^{-1} cm^{-1}. Common anions do not interfere; separation as RuO_4 is necessary when iron and a few other transition cations are present. The green complex, a strong oxidant, is converted to the ruthenium(II) complex by oxidation of water, slowly at room temperature, or more quickly by longer heating and/or higher temperature, and by increase of pH. The Ru(II) complex can be converted to the Ru(III) complex by strong oxidants such as Ce(IV). In the amber complex, the reaction ratio is 1 Ru : 2 terpyridine, in which the ligand is tridentate, whereas in the green complex the reaction ratio is 1 Ru : 3 terpyridine, the latter acting only as a bidentate ligand. Short gentle warming of a mixture of ruthenium(III) and terpyridine first produces a transient unidentified blue-colored species (absorbance at 790 nm).

Preeminent in the field of analytical reagents are certain heterocyclic nitrogen compounds containing the =N—C(=)—C(=)—N= group (often called the "ferroin" group, or the "iron(II) methine chromophore"), which are notable for formation of highly colored water-soluble chelate complexes with iron(II) and a few other transition elements. The best known examples are 1,10-phenanthroline and 2,2′-bipyridine and their various substitution products, which have been widely used for spectrophotometric determination of iron(II); the complexes can be reversibly oxidized to iron(III) complexes, giving rise to a broad range of high potential redox indicators. The outstanding work of G. F. Smith [1, 2] and his colleagues has been a significant contribution in the practical applications and theoretical considerations

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related to their reactions. Another type of compound giving similar reactions with iron(II) contains the functional group =N—C(=)—C(=)—N=C—C(=)—N=, called by Smith the "terroin" group. Examples are 2,2′,2″-terpyridine [3, 4] (hereafter simply terpyridine, or trpy), pyridyl-substituted triazines [5, 6] and pyrazines [7], and a variety of Schiff's bases [8].

As would be expected from the periodic system positions of iron and ruthenium, ruthenium(II) often reacts with the same ligands as iron (II), giving highly colored chelates that can be utilized spectrophotometrically or as redox indicators. Burstall [9] prepared a series of ruthenium(II)—bipyridine salts, which were bright red, water-soluble, and more stable than the corresponding iron(II) complex salts. Stiegman et al. [10] recommended ruthenium tris(2,2′bipyridine) dichloride as a redox indicator of high potential (1.33 V), stable even in strong acid solution; Schilt [11] found the potential of the corresponding sulfate, in 1 M sulfuric acid, to be 1.236 V. The ruthenium(II)-bipyridine complex has also been used as a fluorescent indicator [12]; the ruthenium(III) complex does not fluoresce. Morgan and Burstall [3] prepared 2,2′,2″-terpyridine and made an extensive study of its complex metal salts [4], including the very stable $[Ru(trpy)_2]Cl_2 \cdot 4H_2O$. Terpyridine and bipyridine were used by Moss and Mellon [13] for the determination of iron; the iron—terpyridine complex was also studied by Brandt and Wright [14]. Dwyer and Gyarfas [15] reported the potential of the ruthenium(III, II)—terpyridine complex, in 0.1 M acid, to be 1.281 V.

2,4,6-Tris(2′-pyridyl)-s-triazine (TPTZ) and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT), both of which contain the terroin functional group, are color reagents for iron [5, 6], and for ruthenium [16, 17]; TPTZ is also useful for the determination of cobalt [18].

The phenanthroline, bipyridine, and terpyridine complexes of ruthenium have been the subjects of several studies involving electrochemistry, fluorescence, chemiluminescence, and electro-generated chemiluminescence [19—21], and also rate and spectral studies involving electron transfer between complexes of divalent and tervalent transition metals [22, 23]. Apparently 1,10-phenanthroline is the only one of these reagents that has been reported for the spectrophotometric determination of ruthenium [24].

Aqueous solutions of ruthenium(II)—terpyridine complex are yellow to amber, depending on concentration, with an absorbance maximum at 475 nm, and a molar absorptivity about 10^4; oxidation to the ruthenium(III)—terpyridine complex gives a green solution. Dwyer and Gyarfas [15] noted the instability of the green terpyridine complexes of iron(III), ruthenium(III), and osmium(III), and that their salts had not been prepared. Lytle and Hercules [19] found that the ruthenium(III) complexes could not be isolated as dry solid salts from aqueous solution.

In a study of the ruthenium—terpyridine system, Ciantelli et al. [20] state that the intensely colored ruthenium complex "can be used for the spectrophotometric determination of the element", but there seems to be no report that this actually has been done.

In much of the published work involving ruthenium(III) complexes with organic ligands, the complex species has been formed in solution by oxidation of the ruthenium(II) complex with strong oxidants such as cerium(IV), or lead dioxide in sulfuric acid medium, rather than being formed directly from ruthenium(III) solution, readily prepared from $RuCl_3 \cdot 6H_2O$. Preliminary experiments showed that the green solution containing the ruthenium(III)—terpyridine complex was easily formed by heating a solution of the reactants at pH 3—5. Therefore, it seemed appropriate to make a thorough study of terpyridine as a reagent for the spectrophotometric determination of ruthenium, based on the green solution produced directly in ruthenium(III) solution, and also based upon the amber solution formed with ruthenium(II) obtained by reduction of ruthenium(III).

EXPERIMENTAL

Apparatus

A Cary Model 14 spectrophotometer was used for absorbance scanning. Precision absorbance measurements at fixed wavelength were made with a Beckman Model DU quartz spectrophotometer. Matched 1.00-cm silica cells were used. A Beckman Century SS pH meter, with combination calomel and glass electrode, was used for pH measurements. Class A tolerance volumetric ware was used for critical transfers and dilutions.

Reagents

Standard ruthenium solutions

Ruthenium(III) stock solution was prepared from $RuCl_3 \cdot 6H_2O$ (A. D. Mackay, Inc.), and standardized by reduction of aliquots, finally weighing as metal [16]. A measured volume of this solution was reduced with iron-free hydroxyammonium chloride, by heating at 50—60 °C for several hours, while progressively increasing the pH by addition of small increments of sodium hydroxide, until the solution was neutral. Dilution to known volume gave a standard solution of ruthenium(II) [17, 20]. Solutions of lower concentration of either standard were prepared, as needed, by dilution.

2,2',2''-Terpyridine

This (G. Frederick Smith Chemical Co.) was used as received to prepare a 0.50 % (w/v) solution in 95 % ethanol.

Buffers

Acetate buffers of total concentration 1 M were prepared from appropriate amounts of acetic acid and sodium acetate, to give a pH range of 3.5—6.

Other reagents

Common laboratory chemicals were ACS reagent grade. For interference tests, cations were used as nitrates or chlorides, and anions as sodium or potassium salts; the other platinum elements were from standard solutions prepared in previous investigations.

Recommended procedures

Ruthenium(III)

Into a 10-ml volumetric flask measure enough solution to give a final ruthenium(III) concentration of 2—10 p.p.m. Add 1.0 ml of 0.50 % terpyridine reagent, adjust the pH to 3.5 (pH meter) by addition of dilute sodium hydroxide, and dilute to volume with distilled water. Heat in a water bath at 85 °C for 2 min to develop the green color. Cool to room temperature, replace any solvent lost by evaporation, and measure the absorbance at 690 nm against a water blank. (A reagent blank has negligible absorbance at this wavelength.)

Ruthenium(II)

Into a 10-ml volumetric flask measure enough solution to give a final ruthenium(II) concentration of 1—5 p.p.m. Add 1.0 ml of 0.50 % terpyridine reagent and 1.0 ml of pH 5.5 acetate buffer. Dilute to the mark with distilled water, and heat the mixture in a 95 °C water bath for 45 min to develop the amber color; cool to room temperature, replace any solvent lost by evaporation, and measure the absorbance at 475 nm against a water blank.

Calibration, range and sensitivity

Both color systems conform to Beer's law. The optimum range and sensitivity for each oxidation state are as follows:

	Ru(III)	Ru(II)
Optimum range for 1.00-cm path, p.p.m.	2—10	1—5
Specific absorptivity, p.p.m.$^{-1}$ cm^{-1}	0.083	0.145
Molar absorptivity, ϵ, l mol^{-1} cm^{-1}	$8.3 \cdot 10^3$	$1.45 \cdot 10^4$
Sandell sensitivity, ng cm^{-2}	12.0	6.9

Precision

Ten samples of ruthenium(III) at 6.0 p.p.m., and ten samples of ruthenium(II) at 4.0 p.p.m., were developed and measured according to the recommended procedures, with the following results:

	Ru(III)	Ru(II)
Average absorbance	0.500	0.580
Range	0.498—0.501	0.578—0.583
Standard deviation	0.001	0.002

STUDY OF VARIABLES

Tests for the study of variables were made on solutions with a final concentration of 6.0 p.p.m. ruthenium(III) or 4.0 p.p.m. ruthenium(II); these concentrations are near the middle of the respective optimum concentration ranges. Other conditions were as given in the recommended procedure, except for the variable being studied.

Effect of reagent concentration

The volume of 0.50 % terpyridine reagent was varied from 0.2 to 1.6 ml. Full color development required a minimum of 0.8 ml; 1.0 ml was chosen as a more convenient volume for routine use. This amount of terpyridine provides a very large ligand-to-metal molar ratio even for the largest amounts of ruthenium.

Effect of development time and temperature; stability

Ruthenium(III)

The green color of the complex developed very slowly at room temperature. Full color was developed by heating at 85 °C for 2 min; heating for more than 5 min caused a decrease in the 690-nm absorbance, fading of the green color, and, after 30—75 min, the appearance of the characteristic amber color of the ruthenium(II)—terpyridine complex. Full color could also be developed by heating the solution just to boiling, but absorbance precision was then poorer by this method. Spectral scans of 6.0 p.p.m. solutions made by the latter method (Fig. 1) showed a progressive decrease in the 690-nm absorbance band and an increase in the 475-nm band, the

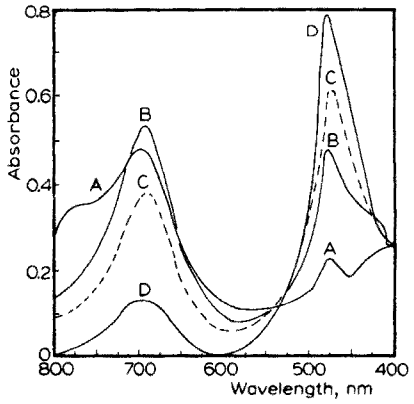

Fig. 1. Effect of time at boiling temperature. (A) 0 min. (B) 5 min. (C) 30 min. (D) 75 min. Ruthenium concentration, 6.0 p.p.m.

longer the high temperature development. Samples developed by the recommended procedure were stable for at least 25 h; over a period of several days the 690-nm absorbance gradually decreased as the ruthenium(III) complex converted to the ruthenium(II) complex. In order to test for possible photochemical reaction a developed sample was divided into two parts, one being stored in the dark and the other in ordinary room illumination. After 5 days both solutions had developed some absorbance at 475 nm, but more so in the solution that was exposed to room light.

Ruthenium(II)

With other parameters constant, the heating time at 95 °C was varied. Maximum absorbance was attained in 30 min; additional heating time was without further effect. Samples developed by the usual procedure showed no change in absorbance in 40 h, and apparently are stable indefinitely.

Effect of pH

Ruthenium(III)

Samples were prepared by the usual procedure, except that the pH was varied by addition of hydrochloric acid or sodium hydroxide. Constant and maximum absorbance (at 690 nm) was attained in solutions of pH 3.0—4.5. Solutions of pH above 4.5 showed progressively lower absorbance at 690 nm, and development of increasing absorbance at 475 nm, because of conversion to the ruthenium(II) complex. The spectral changes are shown in Fig. 2.

Ruthenium(II)

With increasing pH from 1.3 to 4.0, samples showed a sharp increase in the 475-nm absorbance, which attained a maximum at about pH 5.5, with no further change up to at least pH 8.1.

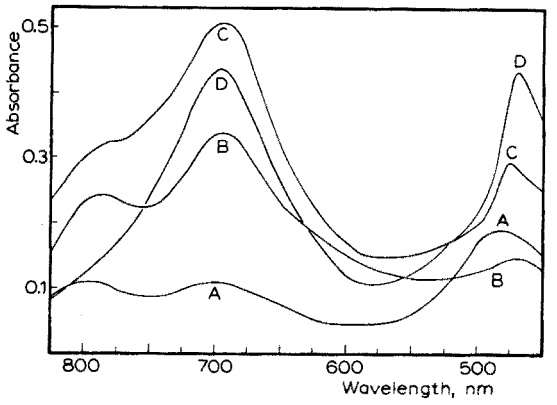

Fig. 2. Effect of pH. (A) pH 1.6. (B) pH 2.4. (C) pH 4.6. (D) pH 4.8.

Effect of foreign ions

Varying amounts of foreign ions were taken with a fixed amount of ruthenium, and the color was measured as usual. The tolerance for a foreign ion was taken as the largest amount that gave an absorbance differing by no more than 0.01 from that produced by the ruthenium alone. Table 1 gives the results for both ruthenium(III) and ruthenium(II). For analysis of samples containing significant amounts of interfering substances, ruthenium can be separated by the conventional distillation method as ruthenium tetroxide.

STUDY OF REACTION AND PRODUCTS

Continuous variations method [25, 26]

Typical data are shown in Fig. 3. Extrapolation of the plot for ruthenium(III) (curve A) gives an intersection at 0.25 mole fraction of ruthenium, corresponding to the composition $[Ru(trpy)_3]^{3+}$ for the green complex. The extrapolated plot of curve B intersects at 0.33 mole fraction of ruthenium, indicating the composition $[Ru(trpy)_2]^{2+}$ for the amber complex. From these plots the formation constants of the complexes are estimated [27] to be ca. $7 \cdot 10^{13}$ and $2 \cdot 10^{11}$, respectively; taking into account the different stoichiometries of the complexes, the ruthenium(II) complex is somewhat more stable than the ruthenium(III) complex.

TABLE 1

Effect of foreign ions

Foreign ion	Tolerance (p.p.m.)		Foreign ion	Tolerance (p.p.m.)	
	Ru(III)	Ru(II)		Ru(III)	Ru(II)
Rh(III)	5	10	Au(III)	4	25
Pd(II)	6	2	Na(I), K(I)	> 2800	> 2400
Os(IV)	12	28	Br^-, NO_3^-	> 2800	> 2400
Ir(IV)	0.4	40	I^-	400	> 2400
Pt(IV)	6	15	F^-	130	700
Fe(III)	2	Nil	SO_4^{2-}	60	1200
Fe(II)	2	Nil	PO_4^{3-}	50	300
Co(II)	6	10	Acetate	100	
Ni(II)	4	8	Tartrate		50
Zn(II)	8	8	Citrate	Nil	100
Cu(II)	6	10	EDTA	Nil	50

Mole ratio method [28]

Typical plots are shown in Fig. 4. In curve A the slope changes at mole ratio trpy/Ru of 3:1, while in curve B the break occurs at 2:1, confirming the stoichiometry of the complexes found by the continuous variations method. Estimation of the formation constant [27] of the ruthenium(II)—terpyridine complex from curve B gives the value $1.3 \cdot 10^{11}$, in good agreement with the value estimated from the continuous variations plot. The

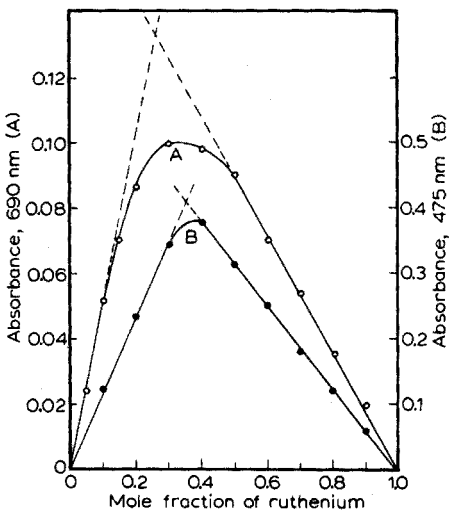

Fig. 3. Continuous variations plot. (A) Ruthenium(III) + terpyridine = $2.0 \cdot 10^{-4}$ M. (B) Ruthenium(II) + terpyridine = $1.0 \cdot 10^{-4}$ M.

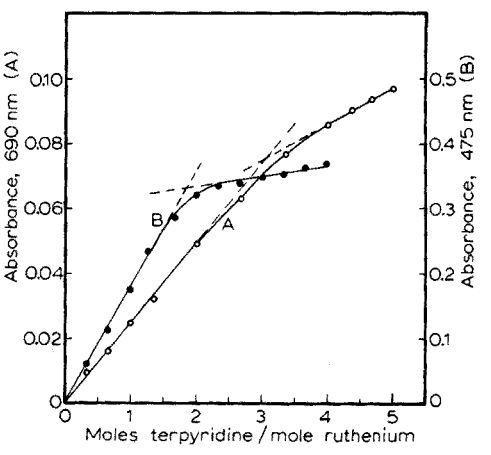

Fig. 4. Mole ratio plot. Ruthenium concentration, $3.0 \cdot 10^{-5}$ M. (A) Ru(III). (B) Ru(II).

small change of slope of curve A around the 3 : 1 mole ratio precludes estimation of the formation constant of the ruthenium(III)—terpyridine complex, but is consistent with the above result by Job's method.

Ion exchange tests

Neither the green complex nor the amber complex was retained by Amberlite IRA-400 anion-exchange resin, but both complexes were retained by Bio-Rad AG50W-X12 cation-exchange resin; the complexes are cationic, $[Ru(trpy)_3]^{3+}$ and $[Ru(trpy)_2]^{2+}$.

Extraction tests

Neither the green nor the amber solute species was extractable into any of the following organic liquids: amyl acetate, amyl alcohol, benzene, carbon tetrachloride, ether, nitrobenzene, 2-octanol.

Isolation of complex salts

Ruthenium(III)

By use of much higher concentrations of reactants (0.5 g each of $RuCl_3 \cdot 6H_2O$ and terpyridine per 75 ml of solution), attempts were made to isolate the ruthenium(III)—terpyridine complex as the perchlorate, iodide, acetate, and picrate. In each case, heating the solution resulted in a green precipitate, but this always decomposed to a dark gray solid during washing and/or attempts at drying even at room temperature or with volatile organic solvents. Previous workers [11, 19] have noted similar problems.

Ruthenium(II)

Ruthenium trichloride hexahydrate, 0.5 g, dissolved in about 75 ml of 0.02 M hydrochloric acid, was added to 0.5 g of terpyridine in 50 ml of 95 % ethanol, and the mixture was heated to near boiling for 15—20 min, during which time the pH was gradually increased to about 5.5 by addition of sodium hydroxide. The solution was evaporated to about half its original volume, then cooled. Addition of a saturated solution of sodium perchlorate caused formation of a red-brown precipitate. After an hour, the precipitate was filtered off, and washed several times with distilled water. The solid was dissolved in acetone, and insoluble material was filtered off, and the filtrate was evaporated to dryness. The solid was washed repeatedly with ether, then air-dried. A sample of the solid, dissolved in 10 % ethanol and buffered at pH 5.5, had an absorption spectrum identical with solution samples prepared by the recommended procedure. The salt was analyzed for ruthenium by the spectrophotometric method presented here, and for other elements by Galbraith Laboratories (Knoxville, Tenn.).

Calculated for $[Ru(C_{15}H_{11}N_3)_2](ClO_4)_2$, 13.18 % Ru, 47.0 % C, 2.90 % H, 11.0 % N, 9.25 % Cl; found, 13.25 % Ru, 46.7 % C, 2.99 % H, 10.7 % N, 9.27 % Cl.

DISCUSSION

Various literature reports have commented on the instability of the terpyridine complex of ruthenium(III), and of other trivalent cations, notably iron and osmium. In their study, Morgan and Burstall [3] noted the remarkable stability of bis-terpyridine ruthenium(II) chloride, but make no reference to the ruthenium(III) complex. Dwyer and Gyarfas [15] observed that the green tervalent complexes $[M(trpy)_2]^{3+}$ (M = Fe, Ru, Os) were less stable than the corresponding bipyridine complexes.

The green solution containing the ruthenium(III)—terpyridine complex was found here to be sufficiently stable that no special precautions were required in using this system for spectrophotometric determination of ruthenium. On long standing at room temperature the green color gradually gave way to the amber color of the ruthenium(II) complex, the solution ultimately having the same absorption spectrum as one prepared directly from ruthenium(II). The same change was promoted by heating for a longer time and/or at a higher temperature, or by increasing the pH to above 5.5. The color change could be reversed by oxidation with cerium(IV), but could not be reversed by decreasing the pH.

In a study of the ruthenium—terpyridine system, Ciantelli et al. [20] made spectrophotometric measurements only of the ruthenium(II) complex, and confirmed the 1 : 2 ratio for the ruthenium(II)—terpyridine complex, as would be expected from the 6-coordinate property of ruthenium, the terpyridine acting as a tridentate ligand. We have found the same stoichiometry for the complex by the mole ratio and continuous variations methods. The composition was also established by elemental analysis of the perchlorate salt isolated from solution. Dwyer and Gyarfas [15] state that the green crystalline perchlorate, formed by oxidation of the bivalent complex, "underwent reduction during filtration and washing." However, the reduction product is not the red ruthenium(II)—terpyridine salt; in our experiments the green salt decomposed to a dark gray residue. By the mole ratio and the continuous variations methods the metal to ligand ratio in the green complex was found to be 1 : 3, and not 1 : 2 as has been generally considered, perhaps by analogy to complexes of iron and of ruthenium with 1,10-phenanthroline and with bipyridine, in which the metal to ligand ratio is the same for both the +2 and the +3 cations. In the green ruthenium(III) complex, which has moderate stability only at low pH, one nitrogen atom of the terpyridine is prevented from coordination with the ruthenium, so that the ligand acts only as a bidentate coordinator. From the change in absorbance of the ruthenium(II)—terpyridine complex with change in pH, Ciantelli et al. [20] proposed the formation of a protonated complex at low pH:

$$x\,H^+ + Ru(trpy)_2^{2+} \rightleftharpoons [Ru(trpy)_2H_x]^{(2+x)+}$$

without any departure from the 1 : 2 ratio of metal to ligand.

Brandt and Wright [14] showed terpyridine to be a diacid base and found a composite acid dissociation value $pK_{1,2} = 7.1$. Martin and Lissfelt [29] determined the separate step values to be $pK_1 = 2.64$ and $pK_2 = 4.33$ (combined, $pK_{1,2} = 7.0$). In a study of the ultraviolet spectra of terpyridine at various pH values in aqueous solution, Nakamoto [30] concluded that in basic solution and in organic solvents, the terpyridine molecule is *trans—trans*, in acidic solution the *cis—cis* form predominates, and at intermediate pH values the *cis—trans* form is present. The highest conjugate acid that could be isolated, starting with the free base, was the dihydrochloride, and in solution only two protons could be added per molecule of base, even in 5 M sulfuric acid. Nakamoto determined the stepwise pK_a values for the dication to be 2.59 and 4.16, respectively. The central ring in terpyridine acquires increased aromatic character because of the pyridine rings at the 2- and 6-positions [31]. From the above considerations it may be reasoned that in the green ruthenium(III) complex, coordination occurs only from the two terminal pyridine nitrogen atoms, and that under the required conditions (low pH) terpyridine acts as a bidentate ligand because of its conformation, and not because of "blocking" of the central nitrogen by protonation.

The spontaneous conversion of the ruthenium(III)—terpyridine complex to the ruthenium(II) complex is favored by increased pH and by high temperature and/or longer time. A question of interest is then the identity of the reducing agent and its oxidation product. It has been observed [21] that ruthenium(III)—bipyridine (in acetonitrile) is bright green and is unstable in air overnight, but stable for several days under vacuum; after exposure to laboratory air it converts to the orange ruthenium(II)—bipyridyl. The reduction potentials of the phenanthroline, bipyridine, and terpyridine ruthenium(III, II) complex couples are all nearly the same, namely 1.2—1.3 V; i.e., the ruthenium(III)—terpyridine complex is a quite strong oxidizing agent [22]. Indeed, most of the M(III) complexes of these ligands are usually prepared in solution by oxidation of the M(II) complexes by very strong oxidants. Fink et al. [32] state that "Ter reduces Fe(III) to form Fe(II)—$(terpyridine)_2^{2+}$," citing as reference a paper by Reiff et al. [33], but apparently misinterpreting the latter's statement that "Direct addition of terpyridine to Fe(III) salts results in rapid reduction and formation of $[Fe(terpy)_2]^{2+}$." It is highly unlikely that Fe(III) or even Ru(III) could oxidize terpyridine, which is a very inactive substance, being stable in hot concentrated mineral acids [2], and very resistant to oxidation even by acid or alkaline permanganate [3]. Nord and Wernberg [34] studied the reduction of iron(III)—bipyridine and —phenanthroline complexes by hydroxyl ion, in the reaction:

$$4\,FeL_3^{3+} + 4\,OH^- \rightarrow 4\,FeL_3^{2+} + O_2 + 2\,H_2O$$

Potentials of the iron(III, II) complexes of phenanthroline, bipyridine, and terpyridine, at about 1.0 V, are even lower than the potentials of the corresponding ruthenium(III, II) systems [15], so it is reasonable to expect ruthenium(III)—terpyridine to oxidize water even in slightly acidic solution.

Addition of terpyridine to ruthenium(III) solution at low pH always produced at first a blue or bluish-green color which quite rapidly changed to green. The blue component usually showed on the recorded spectra as a broad shoulder at about 790 nm (see Figs. 1 and 2) on the side of the absorption band of the green complex (690 nm). By gently warming the reactants and then quenching the mixture in ice water and immediately recording absorbance vs. wavelength, spectra were obtained in which the absorbance at 790 nm was much greater than that at 690 nm, the latter appearing as a shoulder on the side of the strong 790-nm band; but the reproducibility at 790 nm was very poor. The lifetime of the blue component decreased with increase in time or temperature of heating during development, and with increase in pH of the solution, and simultaneously there was an increase in absorbance at 475 nm without any appreciable change in absorbance at 690 nm. No literature reference has been found to absorption in the 790 nm region by the ruthenium—terpyridine system, and no method has been found, so far, for stabilizing the blue component in order to study it for possible identification. Based on the spectral changes described above, one could speculate that it might be ruthenium(III) bis-terpyridine complex, which is rapidly converted to ruthenium(II) bis-terpyridine complex. Another possibility is the formation of a ruthenium(III) complex analogous to the binuclear oxy-bridged complexes of iron(III) with terpyridine [33], 1,10-phenanthroline, and bipyridine [35—37].

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SYNTHESES OF AZO DYES CONTAINING 4,5-DIPHENYLIMIDAZOLE AND THEIR EVALUATION AS ANALYTICAL REAGENTS

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SUMMARY

Eight azo dyes containing the 4,5-diphenylimidazole group have been synthesized, and their potential for determinations of metals has been studied spectrophotometrically. Of these reagents, the pyridylazo and quinolylazo derivatives are suitable as chromogenic reagents, the best being 2-(quinolylazo)-4,5-diphenylimidazole (QAI), which reacts with several metal ions. The copper and mercury complexes of QAI show molar absorptivities of the order of 80 000 l mol^{-1} cm^{-1}.

In a search for new sensitive and selective reagents, studies of some azo compounds containing various heterocycles have been made [1—12]. Of these, 4-(2-pyridylazo)-1, 3-diaminobenzene (4-(2-pyridylazo)-*m*-phenylene-diamine, PADAB) [5, 8] and 5-(2-pyridylazo)-2,4-diaminotoluene (PADAT) [7] and their analogs possess good selectivity and high sensitivity for cobalt and palladium. [4]. Another of these compounds, 2-(2-pyridylazo)-5-dimethyl-aminophenol (DMPAP) [6] and its analogs possess very high sensitivity for copper, nickel, zinc and cadmium; although their selectivities are not so good, the molar absorptivity of the 5-Br-DMPAP—cadmium complex in 3-methyl-1-butanol [13] is $1.41 \cdot 10^5$ l mol^{-1} cm^{-1}.

Although the analytical application of pyridylazo compounds has been extensive, investigations of imidazolylazo compounds are few [14, 15]. Imidazole has two nitrogen atoms, respectively of the pyridine and pyrrole type; high reactivity with metals is expected because of the strong basicity of the pyridine-type nitrogen in comparison with pyridine itself. In addition, various analogs can be prepared because coupling at the 2-position is easily achieved in comparison with pyridine. This paper reports the preparation of eight azo derivatives of 4,5-diphenylimidazole, and the reaction of these reagents with some metal ions in aqueous solution; the quinolylazo compound is a very sensitive chromogenic reagent for copper and mercury.

EXPERIMENTAL

Preparation of reagents

The reagents were prepared by coupling 4,5-diphenylimidazole with the appropriate diazotate in alkaline pyridine or alcoholic solution. The diazotate was prepared by the appropriate method for each amine.

(1) 2-(Benzeneazo)-4,5-diphenylimidazole (BAI)

A diazonium solution was prepared by taking 0.93 g of aniline in 2 ml of 12 M hydrochloric acid plus 10 ml of water, and adding sodium nitrite solution dropwise until iodo-starch paper changed to blue at 0—5 °C. 4,5-Diphenylimidazole (2.2 g) was dissolved in 200 ml of pyridine, and 50 ml of 10 % sodium hydroxide and 50 ml of 10 % sodium carbonate were added; the diazonium solution prepared above was then added dropwise for coupling. The mixture was allowed to stand overnight, and concentrated (rotatory evaporator). The precipitate was filtered off, and recrystallized twice, as the acetate salt, and finally recrystallized from (1 + 1) aqueous ethanol.

Analysis, $C_{21}H_{16}N_4$ requires: 77.7 % C, 4.9 % H, 17.3 % N; found 77.8 % C, 5.0 % H, 16.7 % N. Reddish-yellow needles (m.p. 222 °C).

(2) 2-[(2-Sulfophenyl)azo]-4,5-diphenylimidazole (SAI)

This was prepared by treating 1 g of 2-aminobenzene sulfonic acid with 4,5-diphenylimidazole in the above manner. The crude precipitate was dissolved in hot sodium hydroxide solution, and insoluble material was filtered off; pale red crystals were obtained from the cold solution.

Analysis. $C_{21}H_{15}N_4SO_3Na \cdot 2\,NaOH$ requires: 49.8 %C, 3.4 %H, 11.1 %N; found 49.8 %C, 3.4 %H, 11.0 %N. m.p. > 300 °C.

(3) 2[(2-Hydroxyphenyl)azo]-4,5-diphenylimidazole(HAI)

This was prepared by treating *o*-aminophenol with 4,5-diphenylimidazole in the above manner. The precipitated crude material was crystallized as the acetate salt; the crystals were dissolved in hot sodium hydroxide solution and filtered. The filtrate was neutralized with hydrochloric acid and the neutral salt obtained was finally recrystallized from (1 + 1) aqueous ethanol.

Analysis. $C_{21}H_{16}N_4O$ requires: 74.1 %C, 4.7 %H, 16.4 %N; found 74.2 %C, 4.7 %H, 14.0 %N. Orange needles (m.p. 243 °C).

(4) 2-[(2-Carboxyphenyl)azo]-4,5-diphenylimidazole(CAI)

This was prepared by treating *o*-aminobenzoic acid with 4,5-diphenylimidazole in the manner described for HAI.

Analysis. $C_{22}H_{16}N_4O_2$ requires: 71.2 %C, 4.4 %H, 15.2 %N; found 72.5 %C, 4.4 %H, 15.0 %N. Red needles (m.p. 235 °C).

(5) 2-[(2-Arsonophenyl)azo]-4,5-diphenylimidazole(AAI)

This was prepared by treating *o*-aminophenylarsonic acid with 4,5-diphenylimidazole in the manner described for HAI.

Analysis. $C_{21}H_{17}N_4O_2As$ requires: 58.3 %C, 3.9 %H, 12.9 %N; found 58.2 %C, 4.1 %H, 11.2 %N. Yellowish orange needles (m.p. > 300 °C).

(6) 2-(8-Quinolylazo)-4,5-diphenylimidazole(QAI)

This was prepared by treating 8-aminoquinoline with 4,5-diphenylimidazole in the manner described for BAI.

Analysis. $C_{24}H_{17}N_5$ requires: 76.5 %C, 4.8 %H, 18.6 %N; found 76.5 %C, 4.8 %H, 18.6 %N. Reddish brown powder (m.p. 202 °C).

(7) 2-(2-Thiazolylazo)-4,5-diphenylimidazole(TAI)

Sodium nitrite (0.7 g) was dissolved in 18 M sulfuric acid; after cooling in ice, 10 ml of acetic acid—propionic acid mixture (17 ml of acetic acid plus 3 ml of propionic acid), was added, followed by solid 2-aminothiazole (1 g). 4,5-Diphenylimidazole (2.2 g) was dissolved in 300 ml of ethanol, and 100 ml of 10 % sodium hydroxide solution and 100 ml of 10 % sodium carbonate solution were added. The diazonium salt was added dropwise to this solution at 0—5 °C with stirring. The mixture was allowed to stand overnight and concentrated (rotatory evaporator). The crude material was recrystallized twice as the acetate salt. After neutralization by sodium hydroxide, the product was finally recrystallized from (1 + 1) aqueous ethanol.

Analysis. $C_{18}H_{13}N_5S$ requires: 65.2 %C, 3.9 %H, 21.1 %N; found 64.8 %C, 3.8 %H, 21.0 %N. Reddish brown powder (m.p. 240 °C).

(8) 2-(2-Pyridylazo)-4,5-diphenylimidazole(PAI)

Sodium metal (1.5 g) was dissolved in 50 ml of ethanol; 2-aminopyridine (2 g) in 100 ml of ether was added and the mixture was refluxed for 30 min. Then 3 ml of isopentyl nitrite was added and reflux was continued for an additional 8 h. 4,5-Diphenylimidazole (4.4 g) was dissolved in the diazonium solution at 0—5 °C, and carbon dioxide was passed through the solution with stirring for 5 h. The mixture was allowed to stand overnight. Water was added to the mixture, and the crude precipitate was filtered off, recrystallized as the acetate salt, and finally recrystallized from (1+ 1) aqueous ethanol.

Analysis. $C_{20}H_{15}N_5$ requires: 73.8 %C, 4.6 %H, 21.5 %N; found 74.2 %C, 4.7 %H, 19.7 %N. Orange needles (m.p. 249 °C).

Reagents

Standard metal solutions. The high-purity metal (99.99 %) was dissolved in nitric acid (1+ 1) or hydrochloric acid (1+ 1), and 10 ml of perchloric acid was added. The mixture was evaporated until fumes of perchloric acid

appeared. After cooling, the solution was diluted to 500 ml with distilled water and a 10^{-2} M solution was finally prepared.

Buffer solutions. 0.2 M Acetic acid—0.2 M sodium acetate, 0.2 M ammonia—0.2 M ammonium chloride, and dilute hydrochloric acid were used for pH adjustment.

10^{-3} M Reagent solutions. Ethanolic aqueous solutions, prepared from pure materials, were stable for several months if stored in amber bottles.

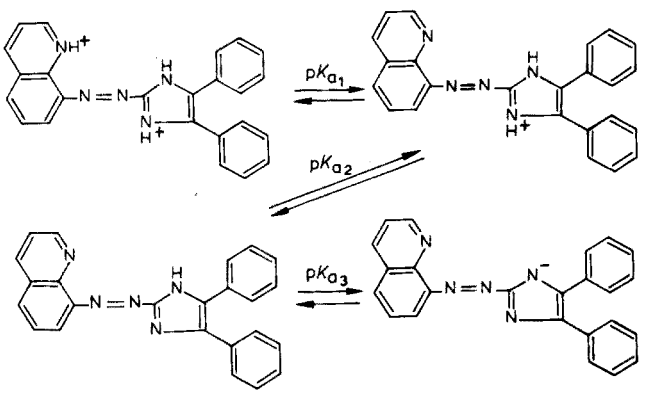
Organic solvents were purified by the usual methods. The other reagents were made from high purity materials or from purified reagents, and solutions were prepared with redistilled water.

Apparatus

Elemental analyses were obtained with a Model MT-2 Yanagimoto CHN analyser. Absorbance curves were obtained with a Model 323 Hitachi spectrophotometer with 1-cm cells, and a Hitachi G-3 infrared spectrophotometer and a Hitachi—Horiba type M-5 pH meter were used.

Acid-dissociation behaviour

The reagents except SAI are sparingly soluble in water (Table 1), but soluble in organic solvents. The equilibria are marked by isosbestic points on the absorption spectra of each reagent (Fig. 1). Figure 2 shows the plots of pH vs. log $[H_2 R^+]/[HR]$ or $[HR]/[R^-]$ for the calculation of the disssociation constants. The pK_a values obtained by the spectrophotometric method are listed in Table 2. For example, the dissociation equilibrium of QAI may be formulated as follows



The optical characteristics of the dissociated forms, including the isosbestic points, are listed in Table 3.

TABLE 1

Solubility of reagents and colour in solution

Reagents	$CHCl_3$		C_2H_5OH		H_2O		1 M HCl		1 M NaOH	
	Soly.[a]	Col.[b]	Soly.	Col.	Soly.	Col.	Soly.	Col.	Soly.	Col.
BAI	++	y	++	y	—		+	y	+	y
SAI	+	y	++	y—o	++	y—o	+	y—o	+	o
HAI	++	y—o	++	y—o	—		—		++	r—o
CAI	+	o	++	y—o	—		+	y	++	y—o
AAI	+	y—o	++	y—o	—		++	y—o	++	r—o
QAI	++	r—o	++	o	—		++	o	+	r—o
TAI	++	r	++	o	—		++	r	++	p—r
PAI	++	y—o	++	y—o	—		++	r	++	p—r

[a] ++ Very good, + good, — not soluble.
[b] y = Yellowish, r = reddish, p = purplish, o = orange.

Colour reactions with metals

The chelate compounds were easily prepared by adding a few drops of a solution of the reagent in alcohol to a solution of a heavy metal. Generally, the solutions containing metal ions showed a red or purple colour under suitable conditions. The colour reactions with some metals at the optimal pH values are listed in Table 4. Although BAI and SAI are fairly selective reagents, the i.r. sensitivity is not good. Most of the reagents react well with cadmium, cobalt, copper, nickel, zinc, manganese and mercury.

The complexes of these reagents with metals are insoluble in water but soluble in organic solvents. The absorption spectra in aqueous 50 % (v/v) ethanolic solution were studied. Although the wavelength shifts on chelation of TAI and PAI are moderate (70—80 nm), those for QAI and HAI are large (110—120 nm). The absorption maxima and molar absorptivities of

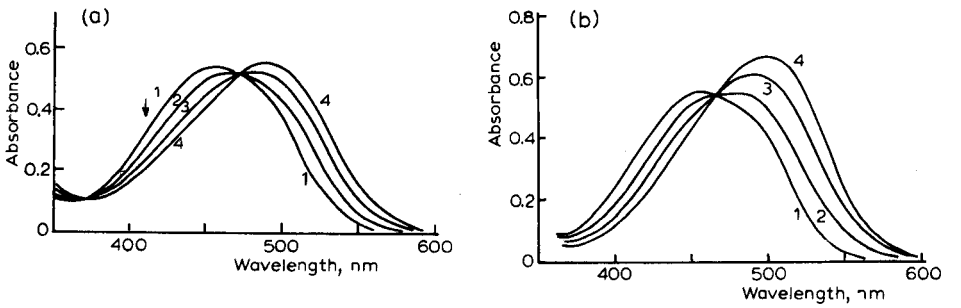


Fig. 1. Absorption spectra of QAI in alcoholic (35 % v/v) aqueous solution. $2.5 \cdot 10^{-5}$ M, μ = 0.1, 1-cm cell. (a) (1) pH 5.0, (2) pH 4.0, (3) pH 3.5, (4) pH 2.8. (b) (1) pH 8.00, (2) pH 10.44, (3) pH 11.06, (4) pH 12.05.

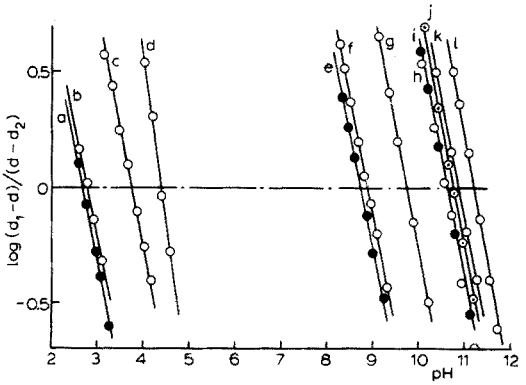


Fig. 2. Plots of log $(d_1-d)/(d-d_2)$ vs. pH for the determination of pK_a. (a) PAI, (b) HAI, (c) QAI, (d) AAI, (e) HAI, (f) TAI, (g) PAI, (h) SAI, (i) BAI, (j) QAI, (k) CAI, (l) AAI.

TABLE 2

Acid dissociation constants of reagents in 35 % (v/v) ethanolic solution (μ = 0.1 KCl, 25 °C)

Reagents	pK_{a2}	pK_{a3}	Reagents	pK_{a2}	pK_{a3}
BAI		10.5	AAI	4.4	11.2
SAI		10.6	QAI	3.7	10.7
HAI	2.7	8.7	TAI		8.9
CAI	3.8	10.8	PAI	2.7	9.7

TABLE 3

Absorption maxima, molar absorptivities and isosbestic points of reagents[a]

Reagents	H_2R^+		HR		R^-	
	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
BAI	—	—	417	2.28 (431)	468	2.9
SAI	—	—	430	1.88 (438)	475	2.3
HAI	474	2.18 (489)	462	2.51 (491)	516	2.14
CAI	424	2.38 (465)	426	2.16 (440)	465	2.72
AAI	456	2.32 (441)	430	2.24 (431)	472	2.88
QAI	495	2.24 (473)	456	2.24 (467)	500	2.70
TAI	—	—	494	2.64 (487)	524	3.94
PAI	514	2.16 (474)	438	2.34 (447)	486	3.36

[a] λ_{max} and isosbestic points (in parentheses) are given in nm. Molar absorptivities (ϵ) are given as $\cdot 10^4$ l mol^{-1} cm^{-1}.

TABLE 4

Colour reactions with various metal ions[a]

Reagent	Ag	Bi	Be	Cd	Co	Cu	Cr	Ga	Fe	Hg	Mn	Mg	Ni	Pb	Ti	V	W	Zn	Zr	Tl	Th	U	Ir	Ru	Sc	Os	Pt	Rh	Au	Pd	Y	Lu	Tm	Gd
BAI				—	—	—				—			—					—		—										—				
SAI				+		+	++			—	—		+					+		—										—				
HAI	++	+	—	++	++	++	—	++	+	+	++	—	++	++	—	++	+	++	+	+	—	—	—	—	—	+	—	—	—	—	+	—	+	+
CAI	—	—		—	++	++		+	+	—	+	—	+			+		+		+										+	—	—	—	—
AAI	—	—		—	—	++		—		—	+	—	+		—	—		—		++										+				
QAI		+		++	++	++		++	—	++	++	+	++	+	—			++		++	—	—								+				
TAI	+	—	—	+	++	++			—	+	++		++		—			++		+										+	—	—	—	—
PAI	++	++		+	++	++				++	+		++		+	—		+		—				—					—	++				

[a] ++ very good, + good, — not good.

TABLE 5

Absorption maxima and molar absorptivities (ϵ) of some metal complexes in 50 % (v/v) ethanol

Reagent		Cu			Ni			Zn			Hg		
	λ_{max}	λ_{max}	ϵ	$\Delta\lambda$[a]	λ_{max}	ϵ	$\Delta\lambda$	λ_{max}	ϵ	$\Delta\lambda$	λ_{max}	ϵ	$\Delta\lambda$
BAI	414	502	4.4	88	493	5.1	79	500	1.9	86	505	3.2	91
SAI	428	524	2.8	96	514	4.4	86	520	1.4	92	500	0.6	72
HAI	470	598	3.0	128	590	2.7	120	580	2.5	110	570	1.9	100
CAI	422	538	3.8	116	512	6.6	90	514	4.5	92	495	1.0	73
AAI	444	520	3.4	86	510	5.3	76	502	2.1	68	500	0.9	66
QAI	456	566	8.3	110	572	6.1	116	570	8.4	114	562	6.8	106
TAI	500	576	3.6	76	576	4.8	76	572	2.0	72	630	1.9	130
PAI	438	512	6.0	74	516	6.4	78	516	2.8	78	526	3.7	88

[a] $\Delta\lambda = \lambda_{max}$ complex—λ_{max} reagent ($\Delta\lambda$ and λ_{max} in nm). ϵ is given as $\cdot 10^4$ l mol^{-1} cm^{-1}.

each chelate with copper, nickel, zinc and mercury are shown in Table 5. Among these reagents QAI would be expected to be the best chromogenic reagent for copper, zinc and mercury. The absorbance curves of the reagent and its copper complex in chloroform are shown in Fig. 3; the absorbance of the reagent is small at the wavelength maximum of its copper complex.

To evaluate optimal pH values for the determination of metals, the effects of pH on the chloroform extraction were studied with the results shown in Fig. 4(a). Since SAI, CAI and AAI do not give complexes soluble in chloroform, their complexes were studied 50 % (v/v) ethanolic solution as shown in Fig. 4(b). Of these reagents, QAI formed a very stable complex over a wide pH range. The absorption maxima, analytical conditions, and molar absorptivities of the different copper complexes are shown in Table 6.

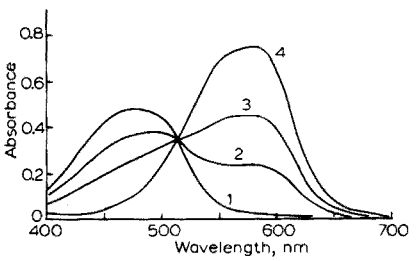


Fig. 3. Absorption spectra of the QAI—copper complex in chloroform, pH 5.0, (1) QAI $2 \cdot 10^{-5}$ M, (2) plus $0.25 \cdot 10^{-5}$ M copper, (3) plus $0.5 \cdot 10^{-5}$ M copper, (4) plus $1 \cdot 10^{-5}$ M copper.

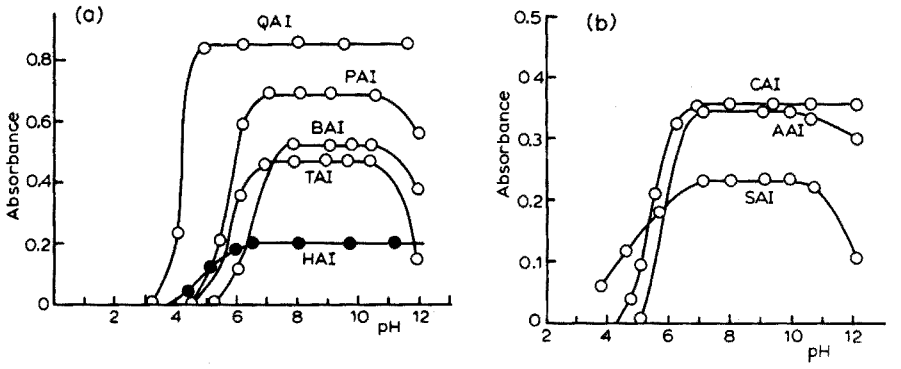


Fig. 4. Optimal pH values for copper determinations. (a) For chloroform extraction. (b) In 50 % ethanolic solution.

Nature of the copper complex

The empirical formula of the coloured complex was determined by the spectrophotometric method at the optimal pH and wavelength. The curves indicated the formation of a 1:2(Cu:R) complex with excess of both reagent and metal (Fig. 5).

The chromogenic reaction of QAI, as a bidentate ligand, with copper ions is assumed to involve coordination predominantly of the quinolyl nitrogen and the azo group nitrogen at about pH 2. Above pH 2.5. the imidazole nitrogen may be coordinated to the metal instead of the quinoline nitrogen.

TABLE 6

The optimal pH values, absorption maxima and molar absorptivities of the copper complexes

Reagents	Solvents	Optimal pH	λ_{max} (nm)	ϵ ($\cdot 10^4$ l mol^{-1} cm^{-1})	Sensitivity (μg cm^{-2})
BAI	$CHCl_3$	8—10	520	5.2	0.0012
SAI	50 % (v/v)				
	C_2H_5OH	8—10	525	2.8	0.0023
HAI	$CHCl_3$	7—12	600	2.0	0.0032
CAI	50 % (v/v)				
	C_2H_5OH	7—12	540	3.6	0.0018
AAI	50 % (v/v)				
	C_2H_5OH	7—10	530	3.3	0.0019
QAI	$CHCl_3$	5—12	580	8.2	0.0008
TAI	$CHCl_3$	7—10	570	4.8	0.0013
PAI	$CHCl_3$	7.5—10.5	520	6.9	0.0009

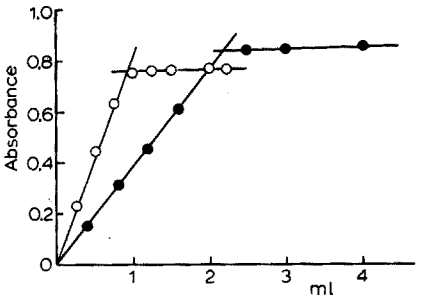


Fig. 5. Composition of copper complex. (-o-) Copper ($1 \cdot 10^{-4}$ M) added to 2 ml of $1 \cdot 10^{-4}$ M QAI. (-•-) QAI ($1 \cdot 10^{-4}$ M) added to 1 ml of $1 \cdot 10^{-4}$ M copper(II). pH 5.0 at 580 nm.

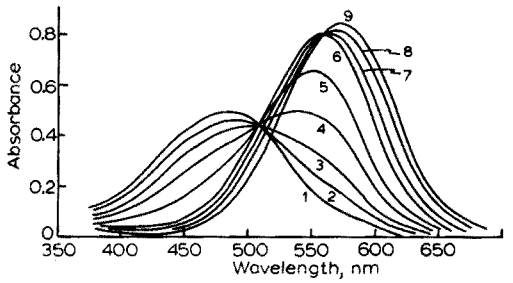


Fig. 6. Effect of pH on absorption spectra of QAI—copper complexes, in 35 % (v/v) alcoholic solution. QAI $2.5 \cdot 10^{-5}$ M, Copper $2.5 \cdot 10^{-4}$ M, μ = 0.1 KNO_3. pH (1) $-H_0$ 0.19, (2) 0.03, (3) 0.10, (4) 0.29, (5) 0.61, (6) 2.23, (7) 3.00, (8) 3.62, (9) 4.04.

Figure 6 shows the absorption spectra of copper-QAI complexes at various pH values. QAI forms two complexes with copper.

Work on solvent extraction and the analytical application of QAI for the determination of copper and mercury is now in progress.

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THE CLUSTER ANALYSIS TECHNIQUE OF PATTERN RECOGNITION: APPLICATION TO THE TRACE METAL COMPOSITION OF CARDIOVASCULAR TISSUES

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SUMMARY

Application of the statistical method of cluster analysis as a pattern recognition technique was investigated by classification of cardiovascular tissues on the basis of their trace metal composition. The distribution patterns of 13 trace metals among 17 tissues of the heart and its appended blood vessels were determined. Cluster analysis of the data resulted in ready differentiation of tissues derived from ordinary and specialized myocardium from those of blood vessels and heart valves. Further similarities and differences among the 17 tissues were identified by comparing the patterns generated when different numbers of groups (i.e., 3, 4, 5, 6, and 7 groups) were designated. It is suggested that cluster analysis may provide a generally useful tool in the interpretation of data from multi-phasic laboratory testing procedures.

Research on trace metals has been stimulated in recent years by the increasing awareness of the wide variety of biological effects mediated by trace metals and by the availability of analytical techniques sensitive in the range of p.p.m. and less. In many studies it is desirable to determine several trace metals simultaneously thus producing profiles of trace metal composition. Such studies commonly generate large amounts of numerical data that need to be manipulated to allow quantitative comparison among the objects studied. In our studies emission spectrometric procedures have been employed for the simultaneous determination of up to 17 elements in biological specimens [1—5]. Recently, to facilitate the handling of extensive sets of analytical data, statistical methods of pattern recognition have been exploited [6, 7]. Such statistical procedures offer the promise of ready quantitative comparisons of trace metal profiles of different objects, and indeed should

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prove useful in a wide variety of analytical studies. The results of applying the pattern recognition technique of cluster analysis to the trace metal composition of cardiovascular tissues are discussed in this paper. The method generates visual patterns that allow ready appreciation of the various profiles.

The anatomic sites sampled were distributed throughout the heart and appended blood vessels. They are listed, with the abbreviations used subsequently, in Table 1. They include arterial (aorta and main pulmonary artery), venous (right superior vena cava) and valvular (tricuspid, mitral, pulmonary and aortic valves) tissue, together with an extensive series of samples of ordinary and specialized myocardium (right atrium, left atrial appendage, free walls of right and left ventricles, papillary muscle of left ventricle, interventricular septum, crista supraventricularis, sinus node, atrioventricular node and His bundle, and left bundle branch).

The thirteen trace metals determined include four essential trace metals (copper, manganese, molybdenum and zinc) and nine with, at present, no known essential function (chromium, nickel, cesium, barium, strontium, cadmium, aluminum, tin and lead).

EXPERIMENTAL

Eleven pig hearts from mature animals of either sex were dissected into pieces representing seventeen anatomic sites (Table 1). Details of the dissection, including the precautions observed to avoid contamination of the samples from extraneous sources of trace metals, and preparation of the specimens for spectrometric analysis have been reported [3].

A direct-reading emission spectrometer (Jarrell-Ash, Model 66,000) with a 10-A d.c. arc as the means of excitation was used. The instrument was calibrated daily for the thirteen elements over the range 1—250 μg per 100 g (1 μg % = 0.01 p.p.m.) and the concentration of each metal was computed as described elsewhere [3, 4].

Statistical cluster analysis of the data was carried out on an IBM 370/155

TABLE 1

Anatomic sites sampled and their abbreviations

Site	Abbrev.	Site	Abbrev.
Main pulmonary artery	MPA	Crista supraventricularis	CR
Aorta	AO	Left bundle branch	LBB
Mitral valve	MV	Atrio-ventricular node and His bundle	AVN + B
Tricuspid valve	TV	Left ventricular-papillary muscle	LV—PM
Aortic valve	AV	Right ventricle (free wall)	RV
Pulmonary valve	PV	Left ventricle (free wall)	LV
Right superior vena cava	RSVC	Interventricular septum	IVS
Right atrium	RA	Left atrial appendage	LAA
Sinus node	SN		

computer [8]. Each tissue site was described by the geometric mean of eleven determinations, whose values have appeared elsewhere [4]. In the cluster analysis, linear combinations of the means of the 13 trace metal concentrations of each tissue were formed by an iterative procedure to separate the 17 tissues in the best way into a specified number of groups or clusters. The criterion for the best partition was a maximum value for a transformed Wilks parameter, i.e., the likelihood ratio criterion [9]. The cluster patterns created in this way for 3, 4, 5, 6 and 7 groups of tissues were determined, and were displayed as a two-dimensional plot created by the linear indices that best separate the tissues into the required number of groups. Each tissue site was plotted according to its coefficients in these two indices, EV-1 and EV-2. Tissues in the same group will have similar values for these coefficients, while those outside that group will have quite different values. Coefficients that are considerably different for each group result in a well-differentiated clustering pattern. For descriptive purposes only, tissues that fall into a particular group are enclosed by a broken line in the EV-1—EV-2 plots. Tissues included in any given group are not significantly different from each other, but are significantly different from all other tissues outside the group.

RESULTS AND DISCUSSION

The results of the cluster analysis for 3, 4, 5, 6 and 7 groups of tissues are shown in Figs. 1—5, respectively.

When only three groups were specified (Fig. 1), the 10 tissues derived from the ordinary and specialized myocardium were almost completely differentiated from those derived from the blood vessels and heart valves. Only one of these latter tissues, the main pulmonary artery (MPA) remained

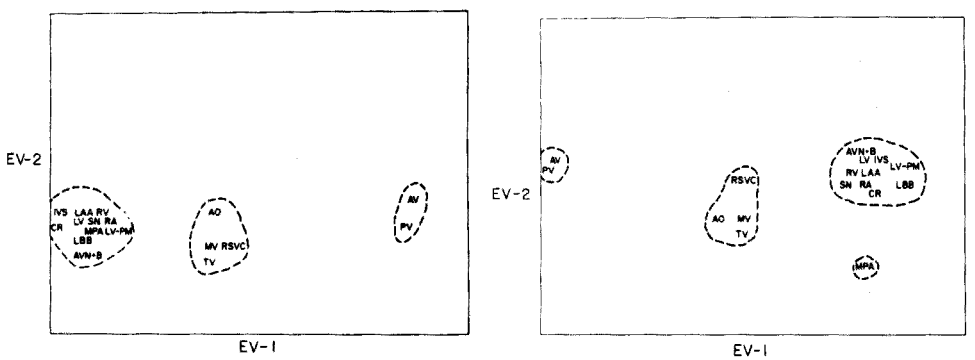

Fig. 1. Tissue groups created by the three-group cluster analysis plotted according to their coefficients (EV-1, EV-2) in the linear indices constructed to create the cluster.

Fig. 2. Tissue groups created by the four-group cluster analysis plotted as in Fig. 1.

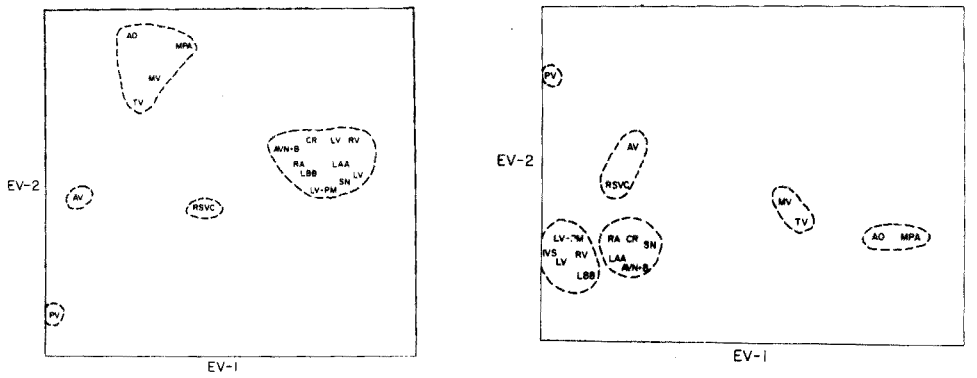

Fig. 3. Tissue groups created by the five-group cluster analysis plotted as in Fig. 1.

Fig. 4. Tissue groups created by the six-group cluster analysis plotted as in Fig. 1.

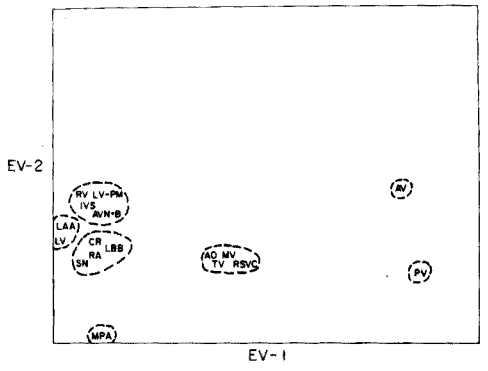

Fig. 5. Tissue groups created by the seven-group cluster analysis plotted as in Fig. 1.

with the myocardium samples. The three clusters were well differentiated in only one dimension, namely, EV-1. Differentiation in the second dimension, EV-2, was more apparent in the cluster pattern created when four groups were specified (Fig. 2). In this pattern, the main pulmonary artery appeared separately from the large myocardium cluster and formed a single cluster of one tissue. The other two groups of two and four tissues respectively remained unchanged from the three-group cluster of Fig. 1.

In the five-group analysis (Fig. 3), the group of ten myocardium tissues remained intact. Some changes occurred in the other groups, namely, the separation of the aortic (AV) and pulmonary (PV) valves into two groups of one tissue each, and the interchange of the main pulmonary artery (MPA) and right superior vena cava (RSVC) with respect to the group containing aorta (AO), the mitral (MV) and tricuspid (TV) valves.

In the six-group analysis (Fig. 4) the cluster of four tissues consisting of

aorta (AO), main pulmonary artery (MPA), mitral valve (MV) and tricuspid valve (TV) separated into two groups of two tissues each: MV, TV; and AO, MPA. The pulmonary valve (PV) remained a unique tissue. However, the aortic valve (AV) and the right superior vena cava (RSVC) which in the five-group analysis of Fig. 3 constituted two groups of one tissue each, were now clustered together. The number of groups specified (six) was now sufficiently great that the tissues of the myocardium separated into two groups which nonetheless appeared quite close together in the EV-1—EV-2 plot.

The final cluster pattern determined was that for seven groups (Fig. 5). Further fractionation of the group of myocardium tissues occurred, but, as in the preceding analysis, the groups formed remained close together. Although the pulmonary valve (PV) remains as a unique tissue, the six other valvular and blood vessel tissues underwent some rearrangements.

The results presented in Figs. 1—5 indicate that while the details of the pattern created by cluster analysis depend at least in part on the number of groups specified, the basic pattern remains relatively stable as the number of groups change. Consequently, the dominant features of the similarities and differences among the 17 tissues can be readily determined by comparing the patterns generated for various numbers of groups. Thus, for example, the tissues derived from ordinary and specialized myocardium are well distinguished from those derived from blood vessels and heart valves, even when only three groups are specified. This distinction is quickly established and maintained. Only when six groups are specified do these tissues separate into two groups. As another example, the pulmonary valve appears to be the tissue that is best distinguished on the basis of the concentrations of 13 trace metals. Thus, the pulmonary valve clusters in a group of two tissues (with the aortic valve, AV) in the three- and four-group analysis, and appears as a single tissue distinct from all others in the analysis for five, six and seven groups.

The number of groups specified in the cluster analysis should not be unreasonably small, or unreasonably large, for the number of objects being clustered. Such extreme conditions can be expected to provide little useful information on diagnostic patterns within the data. Within the range considered in this study, namely 3, 4, 5, 6 and 7 groups, each clustering pattern provides comparative information about the tissues. Comparison among the clustering patterns themselves provides ancillary information useful in further elucidation of similarities and differences among the tissues.

As with other techniques of pattern recognition [5, 6], cluster analysis facilitates the handling of considerable amounts of analytical data generated in profile studies of this kind. Analysis of 17 specimens from 11 hearts for 13 trace metals generated 2431 analytical results. This technique provides a quantitative means of recognizing trends or patterns within the data, which are then summarized in a simple two-dimensional plot. Although this report used data relating to the particular problem of the trace metal

levels in various anatomic sites within the cardiovascular system, the general procedure outlined should be useful in any study that employs analytical techniques that provide a battery of data to be compared. In addition to research applications, pattern recognition techniques when coupled with the automated multiple testing capabilities of modern clinical laboratories may provide a powerful new approach to the diagnosis of disease.

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EXTRACTION OF TRACE AMOUNTS OF NIOBIUM(V) BY AMINE OXIDES AND ITS SEPARATION FROM TANTALUM(V) AND ZIRCONIUM(IV)

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SUMMARY

The use of 4-(5-nonyl)pyridine oxide and trioctylamine oxide for the extraction of niobium(V) from different mineral acid solutions is described. The influence of the concentration of the solvents, acids and salting-out agents is discussed. Separations of niobium(V) from tantalum(V) and zirconium(IV) have been achieved.

The extraction of tungsten(VI) [1] and uranium(VI) [2] from mineral acid solutions by N-oxides of 4-(5-nonyl)-pyridine and trioctylamine has been investigated. A summary of the extraction data of uranium, thorium and some fission products, including niobium, by these amine oxides has been reported [3]. In addition, Torgov et al. [4] have published data for the niobium-nitric acid-2-(nonyl)pyridine oxide extraction system.

This paper reports the use of 4-(5-nonyl)pyridine oxide and trioctylamine oxide as solvents for niobium from different mineral acid solutions. The effects of salting-out agents have been investigated, and possible mechanisms of extraction are suggested. Separation factors of various metals with respect to niobium have been estimated, and separation from tantalum(V) and zirconium(IV) has been carried out. Many methods for the separation of niobium from tantalum(V) and zirconium(IV) make use of hydrofluoric and hydrochloric acid solutions [5]. In the present work, a preferable separation has been achieved from nitric acid solutions.

EXPERIMENTAL

4-(5-Nonyl)pyridine oxide [$C_9H_{19}NO$; NPyOx] and trioctylamine oxide [$(C_8H_{17})_3NO$; TOAO] were purified as reported previously [1]. The diluent used was xylene. Carrier-free ^{95}Nb was obtained from the Radiochemical Centre, Amersham, as oxalate complexes in oxalic acid. The complexes were

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destroyed by evaporation, three times, with 16 M nitric acid and 30 % hydrogen peroxide; the residue was taken up in a mixture of hydrochloric and nitric acid and evaporated to dryness, followed by repeated evaporation (ten times) with nitric, hydrochloric or sulphuric acid to achieve conversion to the respective forms. The other radioisotopes used were either obtained from the Radiochemical Centre, Amersham, or were prepared locally by (n, γ) reaction in the research reactor (PARR) of this Institute or by separation of daughter nuclides from the parents without a carrier.

The distribution ratio, D, defined for a given nuclide as the ratio of the radioactivity of the nuclide in the upper phase to that in the lower phase of two essentially immiscible liquid layers was determined as in previous studies [1—3].

RESULTS AND DISCUSSION

The extraction of niobium by 0.1 M 4-(5-nonyl)pyridine oxide in xylene from aqueous mineral acid solutions is shown in Fig. 1(a). In the nitric acid system the extraction of niobium increases as the acidity increases. The increase in distribution coefficient up to 3 M nitric acid is much less pronounced than that at higher acidities. The anomalously high extraction of niobium from high nitric acid concentrations was also given by 2-(n-nonyl)-pyridine oxide [6]. The extraction at low acidities is probably of a complex of the type $Nb(OH)_n(NO_3)_m \cdot x(NPyOx)$, where $n + m = 5$. The extraction of a similar type of complex has been suggested for the Pa—HNO_3—TBP system

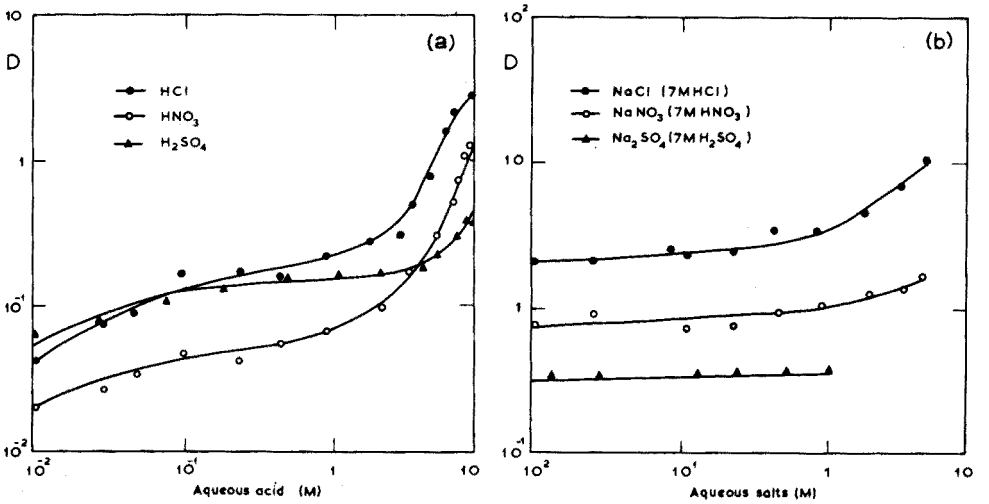

Fig. 1. Variation of distribution coefficient of niobium(V) for extraction with 0.1 M 4-nonylpyridine oxide in xylene. (a) Variation with acidity of aqueous phase: (•) HCl; (○) HNO_3; (▲) H_2SO_4. (b) Variation with salt concentration in 7 M acid media: (•) NaCl (HCl); (○) $NaNO_3$ (HNO_3); (▲) Na_2SO_4 (H_2SO_4).

[7, 8]. The extraction of niobium at high acidities may be due to the acid form of the anionic species $(Nb(OH)_3(NO_3)_3)^-$. The extraction of such species has been postulated by Hardy and Scargill [9].

In hydrochloric acid media the extraction is practically independent of acidity in the range 0.1—2.5 M but increases at high acidity, probably because of extraction of chloro-niobium complexes [6, 9, 10].

The extraction of niobium from sulphuric acid media (Fig. 1(a)), increases less than with the other acids at high acidities. Extraction of niobium from sulphuric acid solution by tri-n-butyl phosphate [11] has been reported. The increase in the extraction of niobium at high acidities can be attributed to the formation of sulphate complexes; for polyions are unlikely to be present at the niobium concentrations used (ca. 10^{-8} M).

As shown in Fig. 1(b), the extraction of niobium increases when sodium chloride and sodium nitrate are added to the corresponding strongly acidic solutions, the increase being more pronounced in the chloride system; a similar salting-out effect was observed in the extraction of niobium with tri-n-butyl phosphate from hydrochloric acid media on addition of calcium chloride [12]. The increase in extraction is influenced not only by the quantity of added neutral salts but also by the acidity of solution.

Figure 2 shows the logarithmic dependence of the distribution coefficients on the pyridine oxide concentration in the organic phase, from solutions of nitric, hydrochloric and sulphuric acids. In the 7 M nitric acid system, a slope of 1.7 is obtained, indicating that the extracted complex requires approximately two molecules of the amine oxide. In the 7 M hydrochloric acid system, the corresponding slope is 2.7. The niobium complex extracted is probably either

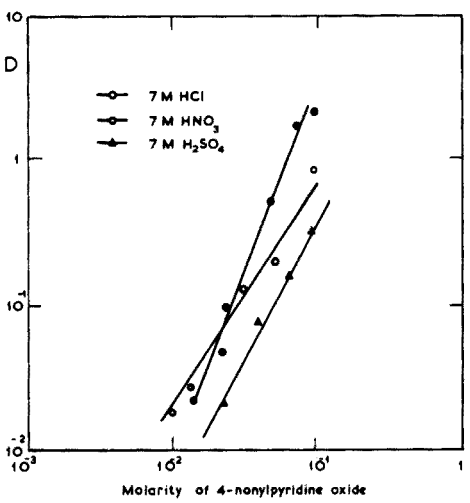

Fig. 2. Variation of distribution coefficient of niobium(V) with concentration of 4-nonylpyridine oxide from 7 M acid solutions. (●) HCl, (○) HNO_3 and (▲) H_2SO_4.

$HNbOCl_4$ or H_2NbOCl_5, coordinated with approximately three molecules of the amine oxide. A similar conclusion was reported by Startsev and Krylov [13] for the TBP—HCl system. In the 7 M sulphuric acid media the slope is 1.9, indicating that niobium is probably extracted as $HNbO(SO_4)_2.2NPyOx$, analogously to the TBP systems.

The extraction of niobium with 0.1 M trioctylamine oxide in xylene was also studied as a function of nitric, hydrochloric and sulphuric acid concentrations. Figure 3(a) shows that, at low acidities, niobium is extracted partially from all the acids studied. Since niobium(V) forms oxyanions in solution at high pH [12], the extraction from weakly acidic solutions may involve protonated oxyanions, which are extractable from solutions of high pH by trialkylphosphine oxide [14]. In hydrochloric acid systems the extraction from concentrated solutions apparently involves anionic chloro complexes of niobium, such as are extracted by amine hydrochlorides [6, 15, 16]. In nitric acid solutions above 0.5 M, anomalous enhancement of extraction is observed. In view of the complicated chemistry of niobium and the contradictory data regarding the state of niobium in nitric acid solutions, it is difficult to predict the nature of the extractable niobium species. The extraction of niobium from media above 0.5 M sulphuric acid is probably

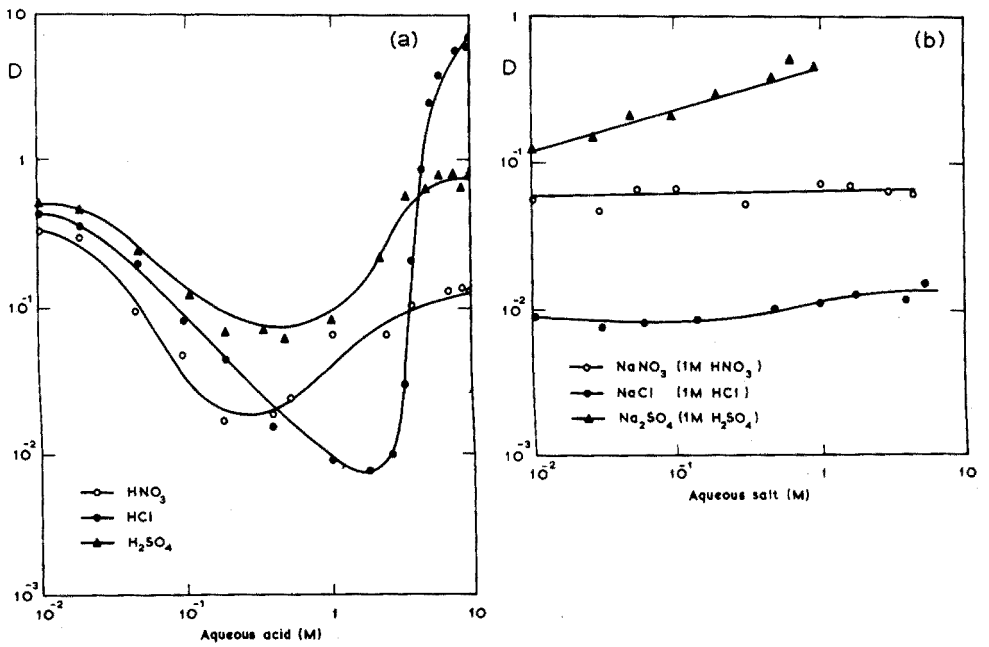

Fig. 3. Variation of distribution coefficient of niobium(V) for extraction of 0.1 M trioctylamine oxide in xylene. (a) Variation with acidity of aqueous phase: (•) HCl; (○) HNO_3; (▲) H_2SO_4. (b) Variation with salt concentration in 1 M acid media: (•) NaCl (HCl); (○) $NaNO_3(HNO_3)$; (▲) Na_2SO_4 (H_2SO_4).

due to anionic complexes [17] which can be extracted with long-chain amines [18, 19].

Unlike the NPyOx system, the extraction isotherms given by TOAO decrease with increasing acidities and have a minimum in the 0.1—2 M acid range. This is probably due to the stronger coextraction of the acids by the more polar TOAO. The extraction of neutral niobium complexes takes place at low acidities, at high acidities the stability of the $(TOAOH)^+$ ion gives rise to results similar to those obtained with trioctylamine.

The extraction of niobium with 0.1 M trioctylamine oxide in xylene as a function of aqueous salt concentration from 1 M acid solutions is shown in Fig. 3(b). In the sulphate system, the addition of sulphate ions causes increased extraction. The addition of chloride to 1 M hydrochloric acid solutions appears to have a salting-out effect; this suggests that the extractable chlorocomplexes are formed only when the concentration of both chloride and hydrogen ions is increased simultaneously. A similar inference has been reported [20]. The addition of nitrate ions to 1 M nitric acid has little effect on the extraction.

In a 5 M sulphuric acid system, the log—log plot of the distribution coefficient versus the amine oxide concentration, was a straight line with a slope of about unity. This indicates that niobium species of the type $NbO(SO_4)_2^-$ are extracted, in agreement with the observed metal—extractant ratio of 1:1. A slope of about one was also obtained for the log—log plot for extractions from 6 M hydrochloric acid with different concentrations of the amine oxide. The extracted species of niobium is probably $Nb(OH)_2Cl_4^-$ [9, 10].

The selectivity towards several metal ions of the extraction separation of niobium with 0.1 M NPyOx or 0.1 M TOAO in xylene from 10 M nitric acid or 7 M hydrochloric acid solutions, respectively, was studied. Table 1 presents separation factors of various metal ions with respect to niobium. 4-(5-Nonyl)-pyridine oxide can be used successfully for the separation of trace amounts of niobium and tantalum; 4-(5-nonyl)pyridine extracts niobium(V) when the acidity is high (10 M) and tantalum(V) when the acidity of the aqueous phase is low (up to 0.1 M). The separations of tantalum and niobium from each other with 10 M nitric acid and 0.1 M nitric acid were checked by γ-spectroscopy. The results are illustrated in Figs. 4 and 5.

Table 1 also shows that niobium can also be separated from zirconium in 7 M HCl media. This was tested by separating a ^{95}Zr—^{95}Nb mixture into two fractions by extracting with 0.1 M TOAO in xylene from7 M HCl (3—4 cycles) and washing the combined organic extracts once with stripped aqueous phase. To identify ^{95}Zr and ^{95}Nb in these fractions, the maximum β-energy of the fraction activity was determined with a set of aluminium absorbers. Suitable aliquots of organic and aqueous phases were evaporated to dryness and the β-energy was measured by plotting absorber thickness versus activity (counts per unit time); the values obtained were in reasonable agreement with the accepted values. Table 1 shows that niobium at 7 M hydrochloric acid can also be separated from thorium and rare earth elements.

TABLE 1

Separation factors for various metal ions in 0.1 M NPyOx/xylene and 0.1 M TOAO/xylene systems from 10 M nitric acid and 7 M hydrochloric acid, respectively

Ion	Concn. mol l^{-1}	Separation factor D_{Nb}/D_M	
		NPyOx	TOAO
^{99m}Tc(VII)	C.f.[a]	40	—
^{233}U(VI)	10^{-3}	17	0.6
^{187}W(VI)	10^{-7}	5	6
^{182}Ta(V)	10^{-9}	$0.75 \cdot 10^3$	$3 \cdot 10^2$
^{95}Zr(IV)	10^{-8}	$4 \cdot 10^{-2}$	$3 \cdot 10^3$
^{234}Th(IV)	C.f.[a]	1.5	$2 \cdot 10^4$
^{144}Ce(IV)	10^{-8}	1.7	60
^{55}Fe(III)	10^{-5}	$2 \cdot 10^3$	—
^{90}Y(III)	C.f.[a]	$> 10^3$	$> 10^3$
^{144}Ce(III)	10^{-8}	$> 10^3$	$> 10^3$
^{140}La(III)	C.f.[a]	$> 10^3$	$> 10^3$
^{90}Sr(II)	10^{-9}	52	$> 10^3$
^{140}Ba(II)	10^{-9}	$3.50 \cdot 10^3$	—
^{65}Zn(II)	10^{-8}	$5.00 \cdot 10^2$	—
^{60}Co(II)	10^{-9}	$1.05 \cdot 10^3$	—
^{54}Mn(II)	10^{-4}	$0.75 \cdot 10^4$	$> 10^3$
^{137}Cs	10^{-8}	$1.5 \cdot 10^2$	$> 10^5$

[a]C.f. = carrier-free.

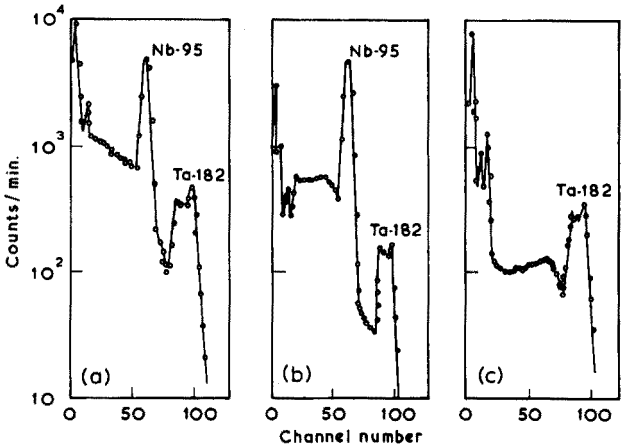

Fig. 4. Separation of tantalum(V) from niobium(V) by 0.1 M 4-nonylpyridine oxide from 0.1 M HNO_3 and their γ-spectra. (a) Aqueous phase before extraction. (b) Aqueous phase after extraction. (c) Amine oxide extract.

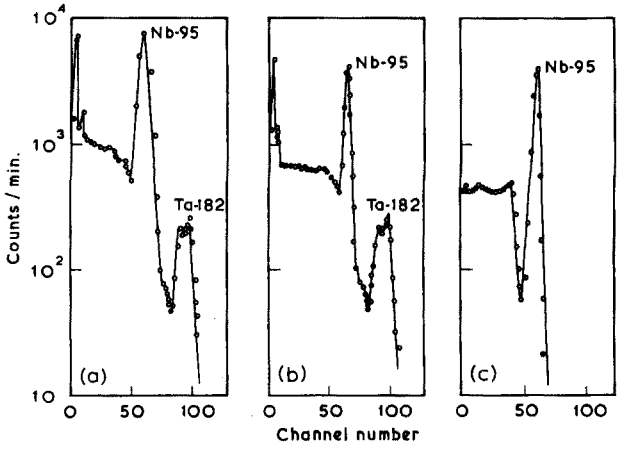

Fig. 5. Separation of niobium(V) from tantalum(V) by 0.1 M 4-nonylpyridine oxide from 10 M HNO_3 and their γ-spectra. (a) Aqueous phase before extraction. (b) Aqueous phase after extraction. (c) Amine oxide extract.

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DI-2-PYRIDYL KETONE THIOSEMICARBAZONE AS AN ANALYTICAL REAGENT

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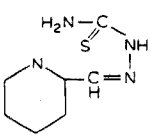
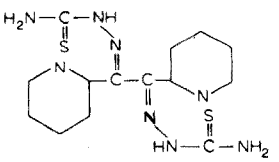
SUMMARY

The synthesis, characteristics and analytical reactions of di-2-pyridyl ketone thiosemicarbazone are described. This compound reacts with iron(II) (λ_{max} = 410 nm, $\epsilon = 9.3 \cdot 10^3$ l mol^{-1} cm^{-1}), nickel(II) (λ_{max} = 395 nm, $\epsilon = 19.6 \cdot 10^3$ l mol^{-1} cm^{-1}), cobalt(II) (λ_{max} = 415 nm, $\epsilon = 1.0 \cdot 10^4$ l mol^{-1} cm^{-1}) and copper(I) (λ_{max} = 395 nm, $\epsilon = 11.3 \cdot 10^3$ l mol^{-1} cm^{-1}). A critical comparison of di-2-pyridyl ketone, picolinaldehyde and bipyridylglyoxal thiosemicarbazones as analytical reagents is given.

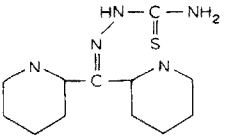
The work described in this paper forms part of a systematic investigation of the use of thiosemicarbazones as analytical reagents. Picolinaldehyde thiosemicarbazone (PAT) [1] has been used in the photometric determination of Co(II) [2]. Fe(II) and (III) [3]. Ni(II) and Cu(I) [4] and their mixtures [5]. Bipyridylglyoxal dithiosemicarbazone (DPGT) [6] — essentially two molecules of PAT — has been applied to the photometric determination of iron(II) and (III) [7], and nickel(II)—cobalt(II) mixtures in catalysts [8].



PAT



DPGT



DPKT

In this paper the synthesis, properties and analytical applications of a new compound, di-2-pyridyl ketone thiosemicarbazone (DPKT) are reported. The spectrophotometric reactions of Co(II), Ni(II), Fe(II) and Cu(I) with DPKT are compared with those of PAT and DPGT.

Azine [9] and oxime [10—13] derivatives of 2-pyridyl ketone have been used previously as analytical reagents.

EXPERIMENTAL

Synthesis of di-2-pyridyl ketone thiosemicarbazone

Di-2-pyridyl ketone (1 g) was dissolved in 10 ml of ethanol, and 0.5 g of thiosemicarbazide in 10 ml of water. The solutions were mixed, 2—3 drops of anhydrous acetic acid were added, and the mixture was refluxed for 2 h. The mixture was then cooled to 0 °C, and the white crystals obtained were recrystallized twice from hot (1 + 1) ethanol—water. (M.p. 200—202 °C. Found: 56.0 %C, 4.3 %H, 27.4 %N, 12.7 %S; calculated for $C_{12}H_{11}N_5S$: 56.0 %C, 4.3 %H, 27.3 %N, 12.45 %S.)

Reagents

All solutions were prepared with analytical-reagent grade chemicals and distilled water.

A 0.1 % (w/v) solution of di-2-pyridyl ketone thiosemicarbazone in ethanol was used. This solution was stable for at least a week.

Standard metal ion solutions were prepared as follows: 1.564 g Fe l^{-1} from ammonium iron(II) sulphate in 1 M sulphuric acid; 1.999 g Ni l^{-1} from nickel(II) sulphate; 5.010 g Co l^{-1} from cobalt(II) sulphate; 3.397 g Cu l^{-1} from copper(II) sulphate. These solutions were standardized by conventional methods, and working solutions (100 μg ml^{-1}) were prepared daily by suitable dilution.

Buffer pH 4.6, was prepared by dissolving 56 g of sodium acetate in water, adding 25 ml of anhydrous acetic acid and diluting to 1 l. Buffer pH 6.6 was prepared by dissolving 13.6 g of potassium hydrogen phosphate and 1.42 g of sodium hydroxide in water and diluting to 1 l.

Apparatus

Unicam SP 800 and SP 600, Coleman 55 (digital) and Beckman DU Spectrophotometers equipped with 1-cm glass or quartz cells, were used, as well as a Radiometer pH meter 29 with glass and calomel electrodes.

General procedure

In 50-ml volumetric flasks, prepare mixtures containing 5 ml of ethanolic 0.1 % DPKT solution, 10 ml of buffer solution, and an appropriate amount of cation solution and dilute to the mark with distilled water. After 30 min, measure absorbance at the appropriate wavelength against a blank solution prepared in the same way but without metal ion. In the case of iron, add 2 ml of fresh 1 % (w/v) ascorbic acid solution.

The molar absorptivities were evaluated statistically from the data for Beer's law.

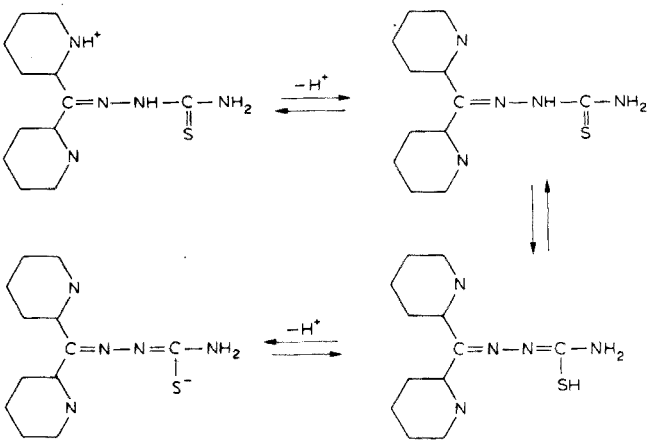
The relative error (p = 0.05) of the photometric method was calculated by measuring the absorbance of eleven samples prepared in the same way, but on different days and with different solutions.

The stoichiometry of the complexes was determined by the continuous variations method.

ANALYTICAL PROPERTIES OF THE REAGENT

The absorption spectrum of DPKT shows an absorbance maximum at 320 nm in neutral solution, but the maximum shifts to about 350 nm in acidic or basic solutions (Fig. 1). There is no absorption above 425 nm (Fig. 2, curve V). DPKT is resistant to hydrolysis in a strongly acidic medium (6 M hydrochloric acid).

The reagent has two pK values (Table 1). These values were obtained by measuring the absorbances of appropriate solutions at 320 nm, 340 nm and 350 nm. The first pK value is due to protonation of a pyridine nitrogen atom, and the second to reaction at the sulphur atom:



SPECTROPHOTOMETRIC STUDY OF REACTIONS WITH CATIONS

Reaction of iron and DPKT

Iron(II) and DPKT immediately form a green complex (λ_{max} = 620 nm; Fig. 2, curve 1). Ascorbic acid ensures that iron remains in the lower oxidation state; in the absence of reducing substances, the iron(II) complex is converted slowly to a yellow iron(III) complex (λ_{max} = 410 nm). Oxidizing agents prevent the green complex formation. The optimal pH range is 2.5—7.5 (Fig. 3, curve I); pH 3 was selected for the photometric study. The complex is stable for at least 2 h. Beer's law is obeyed between 1 and 4 p.p.m. of iron. The molar absorptivity is $9.3 \cdot 10^3$ l mol^{-1} cm^{-1} at 620 nm. The

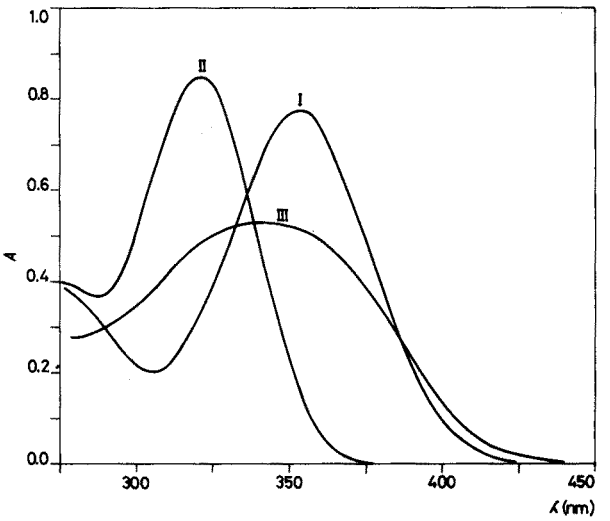


Fig. 1. Absorption spectra of $3.8 \cdot 10^{-5}$ M reagent: I, pH 1.8; II, pH 6.8; III, pH 12.0.

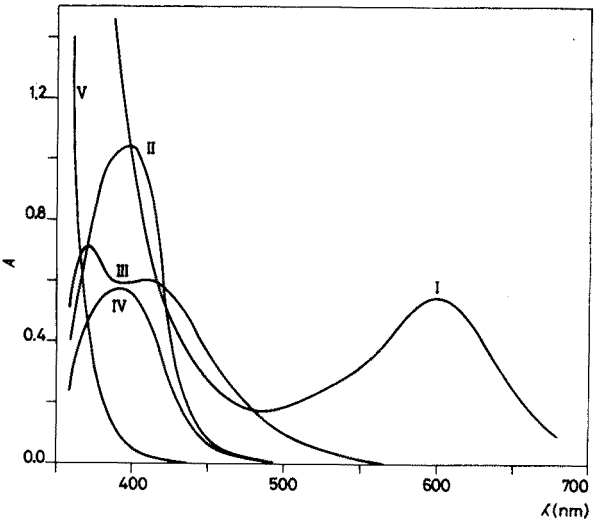


Fig. 2. Absorption spectra of complexes (3 p.p.m. of cation): I, Fe(II); II, Ni(II); III, Co(II); IV, Cu(I); V, $3.8 \cdot 10^{-4}$ M DPKT (reagent blank).

relative error of the method is 0.24 %. The stoichiometric metal:ligand ratio is 1:2 (Fig. 4, curve 1).

TABLE 1

Ionization constants of the thiosemicarbazones

Thiosemicarbazone	pK_1 (pyridine N)	pK_2 (thiol group)
DPKT	3.40	11.25
PAT	4.10	10.50
DPGT	3.80	10.40

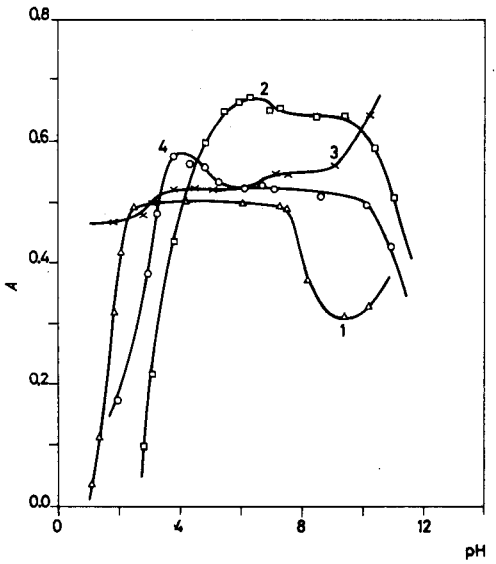


Fig. 3. Influence of pH on the formation of complexes: 1, Fe(II) (λ_{max} = 620 nm, 3 p.p.m.); 2, Ni(II) (λ_{max} = 395 nm, 2 p.p.m.); 3, Co(II) (λ_{max} = 415 nm, 3 p.p.m.); 4, Cu(I) (λ_{max} = 395 nm, 3 p.p.m.).

Reaction of nickel and DPKT

Nickel(II) and DPKT form a yellow complex (λ_{max} = 395 nm, Fig. 2, curve II). Two pH ranges can be used, pH 6.0—6.9 or 7.5—9.5; the former offers greater sensitivity, and pH 6.6 was selected for the further study of the reaction (Fig. 3, curve 2). The absorbance of the complex solutions remains stable for at least 2 h. Beer's law is obeyed between 0.5 and 2.5 p.p.m. of nickel. The molar absorptivity is $19.6 \cdot 10^3$ l mol^{-1} cm^{-1} at 395 nm. The relative error is 0.22 %. The stoichiometric metal:ligand ratio is 1:2 (Fig. 4, curve 2).

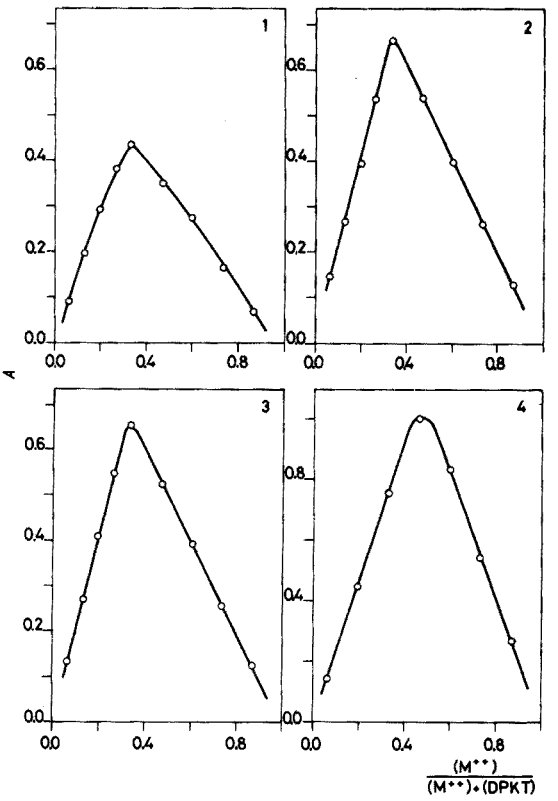


Fig. 4. Composition of the DPKT complexes by the continuous variations method: 1, Fe(II) ($5.6 \cdot 10^{-4}$ M); 2, Ni(II) ($3.4 \cdot 10^{-4}$ M); 3, Co(II) ($6.8 \cdot 10^{-4}$ M); 4, Cu(I) ($6.7 \cdot 10^{-4}$ M).

Reaction of cobalt and DPKT

Cobalt forms an orange complex with DPKT, with an absorption maximum at 415 nm (Fig. 2, curve III). The optimal pH range is 3.8–6.0 (Fig. 3, curve 3), so that an acetate buffer pH 4.6 is satisfactory. The absorbance at 415 nm is stable for at least 2 h. Beer's law is obeyed between 1 and 5 p.p.m. of cobalt. The molar absorptivity at 415 nm is $1.0 \cdot 10^4$ 1 mol^{-1} cm^{-1}. The relative error is 0.24 %. The stoichiometric metal:ligand ratio is 1:2 (Fig. 4, curve 3).

Reaction of copper and DPKT

When dilute copper(II) and DPKT solutions are mixed, a yellow-green compound is formed (λ_{max} = 395 nm, Fig. 2, curve IV). In order to establish the oxidation state of copper, several samples were prepared in the presence of oxidizing and reducing agents. Copper(I) is responsible for the

yellow-green complex, but addition of ascorbic acid is unnecessary because the reagent acts a reducing agent, as frequently happens with other thiosemicarbazones. Two pH ranges can be used, 3.9—4.2 and 5.5—9.0 (Fig. 3, curve 4); buffer solution pH 4.0 was used in the further study. The complex solutions are stable for at least 2 h. Beer's law is obeyed between 1 and 5 p.p.m. of copper. The molar absorptivity at 395 nm is $1.13 \cdot 10^4$ 1 mol^{-1} cm^{-1}. The relative error is 0.22 %. The stoichiometric metal:ligand ratio is 1:1 (Fig. 4, curve 4).

CRITICAL COMPARISON OF DPKT, PAT AND DPGT AS ANALYTICAL REAGENTS

These thiosemicarbazones have similar structures, differing only in the number of pyridine rings and thiosemicarbazone chains. Comparison of their behaviour is therefore of interest.

Characteristics of the reagents

The preparation of DPKT or PAT from the carbonyl compounds and thiosemicarbazide is easy and gives a high yield; the synthesis of DPGT is more difficult.

The absorption spectra of the reagents and their variation with pH are similar. The u.v. absorption spectra of PAT and DPGT at various pH values show isosbestic points at 332 and 329 nm, whereas the DPKT spectra (Fig. 1) do not.

The values of the ionization constants are summarized in Table 1. The deprotonation of a pyridine nitrogen is easier in DPKT than with the other reagents, whereas deprotonation at the sulphur atom is more difficult; the ampholytic form of DPKT exists over a wide pH range in aqueous solution.

The qualitative reactions of 36 ions with these thiosemicarbazones at different pH values are similar. As(III) or (V), Sn(II) or (IV), Al(III), Cr(III), Be(II), UO_2(II), Th(IV), La(III), Ce(III), W(VI), Mo(VI), alkali and alkaline earth metal ions did not react. The most sensitive reactions were shown for Co(II), Cu(I), Ni(II) and Fe(II) or Fe(III). These metal ions formed soluble coloured complexes, that are suitable for the spectrophotometric determination of traces of these metals.

Formation of coloured complexes

The absorption maxima of the iron(II) and nickel(II) complexes with DPKT show small bathocromic shifts (5—10 nm) compared to the PAT and DPGT complexes. The cobalt(II) and copper(I) complexes of DPKT and DPGT have similar λ_{max} values (± 5 nm), but both are higher than the values for the PAT complexes (40—55 nm).

Figure 5 summarizes the optimal pH zones for the formation of the complexes with the three thiosemicarbazones. In all cases, the optimal pH

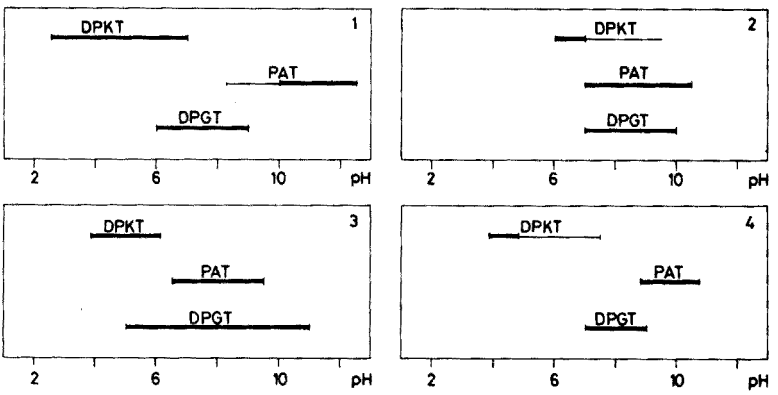


Fig. 5. Optimal pH zones for the metal—DPKT, metal—PAT and metal—DPGT complexes: 1, Fe(II); 2, Ni(II); 3, Co(II); 4, Cu(I).

range of the DPKT complexes lies at more acidic pH values; the interferences of other metal ions in the photometric determination of traces of Fe(II), Ni(II), Co(II) and Cu(I) should therefore be smaller.

The molar absorptivities of the thiosemicarbazone complexes are shown in Fig. 6. The DPKT complexes have the highest values, especially for the nickel complex.

The stoichiometries of the complexes are summarized in Table 2. The metal:ligand ratios are the same for the DPKT and PAT complexes; thus the

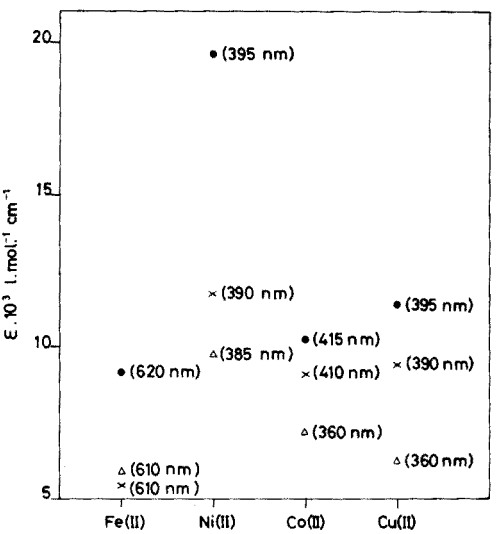


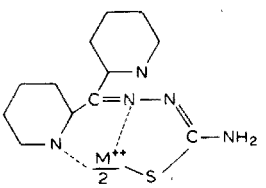
Fig. 6. Molar absorptivity of metal—DPKT, metal—PAT and metal—DPGT complexes at their λ_{max}: (•) DPKT; (×) DPGT; (△) PAT.

TABLE 2

Stoichiometry of the complexes

Thiosemicarbazone	Metal/reagent ratio			
	Fe(II)	Ni(II)	Co(II)	Cu(I)
DPKT	1:2	1:2	1:2	1:1
PAT	1:2	1:2	1:2	1:1
DPGT	1:1	1:1	2:1	2:1

additional pyridine group of DPKT does not participate in the chelate formation. The stoichiometric ratios in the DPGT complexes are different because it contains basically two molecules of PAT. The thiosemicarbazones with other donor groups (e.g. pyridine nitrogen) may act as terdentate and bidentate chelating agents. The structure of the 1:2 octahedral complexes of DPKT with Fe(II), Co(II) and Ni(II) is probably I [14]. Most of the copper complexes with the thiosemicarbazones contain copper(I) [15], so that II seems the most likely structure for the Cu(I)—DPKT complex, with no participation of the pyridine nitrogens.



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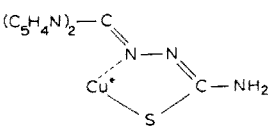

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COMPLEXIMETRIC TITRATION OF ALUMINUM AND ZIRCONIUM IN SILICEOUS MATERIALS AFTER ALKALI FUSION OF SAMPLES

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SUMMARY

Rapid methods for the determination of zirconium and aluminum in siliceous materials are described. Samples are decomposed by sodium carbonate—sodium borate fusion and dissolved in perchloric acid. The zirconium is titrated directly with standard EDTA solution at 90—95 °C in 1 M perchloric acid solution with xylenol orange as the indicator. Aluminum is then complexed by boiling with an excess of EDTA and the free EDTA is back-titrated potentiometrically with standard zinc solution. Interference of titanium in the aluminum determination is prevented by lactic acid masking. The methods have been applied successfully to a wide variety of glass-ceramics, refractories and NBS minerals.

Complexiметric titrations of aluminum and zirconium with (ethylenedinitrilo)tetraacetic acid (EDTA) [1—3] have been widely applied in determining elements in siliceous materials [4, 5]. These procedures, in conjunction with masking or separation techniques for interferences, have gradually replaced the more time-consuming gravimetric methods for routine control analysis. The siliceous materials are usually decomposed with hydrofluoric and perchloric (or sulfuric) acids [5—7]. The acid dissolution is convenient in that the silica is removed as silicon tetrafluoride, but a critical drawback is the presence of residual fluoride, which can cause low bias in the determination of aluminum and zirconium, owing to the formation of stable fluoride complexes. Only by repeated sulfuric or perchloric acid fumings can a fluoride-free solution be obtained [6, 7]. Addition of boric acid or silicic acid to form volatile fluorides, which permits the removal of excess hydrofluoric acid, has been recommended [5, 6].

Over the past several years, a direct alkaline fusion decomposition has been used in this laboratory for the determination of alumina, zirconia and rare earths in glasses, glass-ceramics and refractories, thus eliminating the mineral acid dissolution. The exceptions are fluoride-containing samples, where a hydrofluoric acid dissolution is still employed, but instead of repeated fuming the solution is evaporated to dryness and the residue is ignited to eliminate trace fluoride, before the fusion process. This paper describes rapid procedures for the complexiметric determination of zirconium and aluminum in siliceous materials.

EXPERIMENTAL

Reagents and equipment

Standard zinc solution (0.05 M)

Accurately weigh about 6.5 g of pure zinc, dissolve the metal in ca. 40 ml of 6 M perchloric acid, and dilute to 2 l.

Buffer solution (pH 4.6)

Adjust an aqueous 10 % solution of sodium acetate to pH 4.6 with acetic acid.

Zirconium oxide

Use hafnium-free ZrO_2 (e.g., Carborundum Company) as a primary standard for standardizing the EDTA solution for direct titrations of zirconium.

A Sargent—Welch Model DG recording titrator was employed for all potentiometric titrations of excess of EDTA with standard zinc solution; a mercury ring indicator electrode and a saturated mercury(I) sulfate reference electrode were used.

Procedures

Standardization of EDTA solution

For the determination of aluminum, dilute a suitable aliquot of the 0.05 M EDTA (disodium salt) solution and titrate with standard zinc solution at pH 4.6. For the determination of zirconium, standardize the EDTA solution against an accurately weighed amount of ZrO_2 (ca. 100 mg) by the method give below.

Determination of aluminum in the absence of zirconium

Accurately weigh sufficient ground sample (100—200 mesh) to contain 20—50 mg of Al_2O_3; if possible, the silica level should not exceed 100 mg. Transfer the sample to a 30-ml platinum crucible. Add 10 times the sample weight of Na_2CO_3—$Na_2B_4O_7$ flux (equal amounts of the salts by weight), mix well, cover the crucible and fuse over a gas—air blast burner. Place the platinum crucible in a 250-ml beaker and dissolve the melt in about 50 ml of distilled water and enough perchloric (or sulfuric) acid to make the solution slightly acidic. Magnetic stirring can be used to accelerate the dissolution. Remove the platinum crucible. Add sufficient 0.05 M EDTA solution to complex the aluminum plus 30—50 % in excess. Adjust to pH 4.5—5.0 with 10 M NaOH and add 20 ml of acetate buffer pH 4.6. Boil the solution gently for 30 min, cool to room temperature and add 3 drops of mercury—EDTA indicator solution (Sargent—Welch). Using the autotitrator, titrate the excess of EDTA potentiometrically with standard zinc solution. Run the flux blank and make any necessary correction. For samples

containing up to 8 mg of TiO_2, add 1 ml of lactic acid (Baker Analyzed Reagent; assay > 90 %) to mask the interference before the addition of EDTA. Use pH 5.1—5.3 buffer solution instead of pH 4.6 and titrate the excess of EDTA at a temperature below 10 °C.

Determination of zirconium and aluminum

Accurately weigh sufficient ground sample to give 80—100 mg of ZrO_2 and fuse as described above. The silica level should not exceed 25 mg; if this is not possible, dissolve the sample by H_2SO_4—HF acid mixture in a platinum dish, fume to complete dryness, rinse the sides of the dish with a few ml of concentrated sulfuric acid, repeat the fuming process, ignite the residue, and fuse with the flux. Dissolve the fused melt with 50 ml of 2 M $HClO_4$ and dilute to ca. 100 ml. Add 4—5 drops of aqueous 0.1 % xylenol orange indicator and titrate the zirconium at 90—95 °C with standard EDTA solution; the end-point is taken when the change from purple to yellow remains for 1.5—2 min.

After titration of zirconium, determine the aluminum in the same solution by the procedure given above for aluminum alone.

RESULTS AND DISCUSSION

The major advantages demonstrated by the Na_2CO_3—$Na_2B_4O_7$ fusion over the conventional HF—H_2SO_4 (or $HClO_4$) acid decomposition are that refractory materials are more easily decomposed, and that no fluoride is present (often the cause of low bias in aluminum or zirconium determinations). Moreover, the analysis time can be shortened from the conventional 6 h to less than 2 h. Table 1 shows some results obtained for aluminum in four NBS standards, which contain silica ranging from 44 % to 67 %. Little or no hydrated silica precipitated in any of these samples; any small

TABLE 1

Determination of Al_2O_3 in NBS SRM samples by fusion and EDTA titration

NBS SRM	% Al_2O_3 certified	% Al_2O_3 found	
		Range	Av.
70a Potash Feldspar	17.9	17.9_1—17.7_5	17.8_5 [a]
99a Soda Feldspar	20.5	20.5_2—20.4_4	20.4_8 [a]
97a Flint Clay	38.8	38.7_0—38.9_0	38.8_2 [b]
98a Plastic clay	33.2	33.4_1—33.3_5	33.3_8 [c]

[a] Fe_2O_3 (0.07 %) and TiO_2 (0.01 %) corrected for from certified values.
[b] TiO_2 (1.90 %) masked with lactic acid; Fe_2O_3 (0.45 %) corrected as above.
[c] TiO_2 (1.61 %) masked with lactic acid; Fe_2O_3 (1.34 %) corrected as above.

(2—4 mg) amount of silica that did precipitate did not affect the accuracy of the aluminum results. When sodium carbonate alone was employed as the flux, the precipitation of silica became more pronounced; possibly borate formed weak complexes with monomeric silicic acid and thus prevented its polymerization.

The aluminum procedure was applied to a wide range of complex glasses and glass-ceramics. The use of lactic acid to mask titanium interference [8—10] was satisfactory for samples containing 50 % as much titania as alumina. Slightly higher pH and lower titration temperatures were employed with the masking procedure, to minimize the possibility of the excess of lactic acid competing with EDTA in forming complexes with aluminum. Results obtained by this procedure were in good agreement with values obtained by accepted methods (Table 2).

Electroactive interferences such as Pb, Fe, Cd, etc., can be removed by electrolytic deposition at a mercury pool cathode [13]. However, when the silica levels exceeded 80 mg/100 ml, acute polymerization and precipitation of silica occurred, probably because of the increase in solution temperature during electrolysis. Spectrographic analysis of the precipitate indicated that appreciable aluminum was usually occluded in the precipitate (0.1—1.0 %); however, most of this aluminum was back-extracted into the solution when the solution was boiled with excess of EDTA.

The procedure given for the determination of zirconium and aluminum was developed for zircon refractories. No visible hydrolysis of silica was observed for sample containing as much as 20 % SiO_2. Satisfactory titrations of zirconium were obtained at acidities of 1.0—1.5 M $HClO_4$. When the acidity was below 0.5 M, hydrolysis of zirconium was often observed, and at 2.0 M the end-point became sluggish. Other acids, e.g. nitric or hydrochloric acid, are probably also suitable media for the zirconium titration. However, if the sample solution is to be analyzed for aluminum later, hydrochloric acid must be avoided since chloride interferes with the mercury pM electrode.

The standardization of EDTA solution against pure zirconium dioxide

TABLE 2

Determination of Al_2O_3 in glass-ceramics after masking of titanium

Type of sample	% Al_2O_3	
	Present method	Other method
SiO_2—Al_2O_3—TiO_2 (5 %)—Li_2O	19.6_2 (±0.05)	19.5_3 [a]
SiO_2—Al_2O_3—TiO_2 (4 %)—Li_2O	18.9_5 (±0.02)	18.9_1 [a]
SiO_2—Al_2O_3—Li_2O—TiO_2 (1 %)	19.6_9 (±0.09)	19.8_0 [b]
SiO_2—Al_2O_3—Li_2O—TiO_2 (1 %)	19.5_7 (±0.03)	19.8_8 [b]
SiO_2—Al_2O_3—Li_2O—TiO_2 (1 %)	18.8_5 (±0.07)	18.9_6 [b]

[a] Ti removed by cupferron extraction [11] before titration of Al with EDTA.
[b] Ti determined by Tiron colorimetry [12] and subtracted from Ti + Al titrated by EDTA

was necessary. A relative error of ca. 0.4 % was encountered when zirconium was calculated from the standardization of EDTA against zinc. The titration for zirconium in a 1.0—1.5 M acidic medium is very selective since no other metal except hafnium forms a complex with EDTA at such acidities. Results for refractory samples were in good agreement with values obtained by other methods (Table 3).

The level of silica that could be tolerated in the zirconium procedure was found to be much lower than that for the aluminum procedure (25 mg vs. 100 mg SiO_2 per 100 ml of solution). It might be possible to increase this tolerance by using a back-titration; for most of the occluded ZrO_2 can be redissolved by forming the stable Zr—EDTA complex. However, for the analysis of high-silica materials, the sample is more conveniently treated with $HF—H_2SO_4$ to eliminate the silica, followed by evaporation to dryness, ignition, and fusion. This alternative approach is still faster than the conventional acid decomposition where repeated fuming of sulfuric acid is required to ensure complete elimination of trace fluoride.

TABLE 3

Determination of ZrO_2 and Al_2O_3 in refractories

Type of sample[a]	% ZrO_2		% Al_2O_3[c]	
	Present method	Other method	Present method	Other method
$ZrO_2—SiO_2—Al_2O_3—Na_2O$	71.0 (±0.1)	71.0[b]	10.6 (±0.1)	10.5[d]
$ZrO_2—Al_2O_3—SiO_2—Na_2O$	62.0 (±0.1)	62.1[b]	20.5 (±0.1)	20.7[d]
$ZrO_2—Al_2O_3—SiO_2$	44.3 (±0.1)	44.7[e]	29.8 (±0.3)	29.8[e]

[a]Constituents given in decreasing order of weight percentage.
[b]Gravimetric with bromomandelic acid [14].
[c]Values corrected for Ti and Fe (ca. 0.2—0.3 % TiO_2 + Fe_2O_3).
[d]Al by EDTA titration after separation of Zr with bromomandelic acid [14].
[e]Batched values.

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NIOBIUM(III) AS AN ANALYTICAL REAGENT. PART I. THE TITRIMETRIC DETERMINATION OF IRON, COPPER, THALLIUM, MOLYBDENUM, URANIUM AND VANADIUM

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SUMMARY

Niobium(III) solutions can be used in direct titrations of copper(II), iron(III), thallium(III), molybdenum(VI), vanadium(V) and uranium(VI) in milligram amounts. Phenosafranine is generally satisfactory as the indicator, but potentiometric end-points can also be used. Copper and iron can be determined successively when a mixed indicator containing phenosafranine and methylene blue is used. Thallium(I) and thallium (III) can be determined in mixtures. The niobium (III) solutions are stable for several days under a carbon dioxide atmosphere.

The powerful reducing properties of niobium(III) are obvious from its formal potential, which is ca. —0.280 V vs. S.C.E. in 1.5 M sulphuric acid [1]. Niobium(III) is easily obtained [2] as potassium disulphatoniobate(III) tetrahydrate in a pure state and its solutions in 9 M sulphuric acid are fairly stable in the absence of air. The niobium(III) solution can therefore be employed as an analytical reductant. The present paper reports the titrimetric determinations of copper, iron, thallium, molybdenum, uranium and vanadium with this reagent. The methods are suitable for determining milligram quantities of the metals. The use of the reagent on the macro scale is limited by its low solubility in strong sulphuric acid medium, its instability in dilute acids, and the large changes in the acidity of the titrated solution which can occur when the titrant is used in large volumes. Such difficulties do not arise in determinations on the semimicro scale, and the precision is sufficiently good for the methods to be adopted in routine analytical procedures.

The equivalence points of these titrations can be determined potentiometrically or by using phenosafranine as an internal indicator. In the titration of iron(III), thiocyanate can also serve as the indicator. Mixtures of iron(III) and copper(II) can be determined simultaneously by using a mixed indicator of methylene blue and phenosafranine, the colour transitions being from blue to red-violet for iron(III) and red-violet to colourless for copper(II).

The reactions of niobium(III) with iron(III), copper (II), molybdenum (VI), vanadium(V) and thallium(III) are very fast, so that these metals can be

determined titrimetrically quite easily. Reduction of uranium(VI) is rather slow but potentiometric titrations are feasible. Oxidants such as iodine, cerium(IV), chromium(VI) and manganese(VII) rapidly oxidize niobium(III), but some other oxidants, e.g. rhenium(VII), react very slowly and direct titrimetric methods cannot be applied in the determinations of these ions.

EXPERIMENTAL

Apparatus

An all-glass titration assembly was used. The microburette (graduated to 0.01 ml) was provided with storage for 100 ml of solution in an inert atmosphere. The titration cell was a 100-ml conical flask, and the stopper had holes for two burettes, indicating electrode, salt bridge, and the inlet and outlet for carbon dioxide. A magnetic stirrer was used to stir the solution.

The e.m.f. was measured with an ECIL expanded-scale pH meter between a bright platinum wire and a saturated calomel electrode. A carbon dioxide atmosphere was maintained during the titration and during the storage of the titrant. The volumetric apparatus, including the microburette, were calibrated.

Reagents

Potassium disulphatoniobate(III) was prepared by the method reported earlier [2]. An almost saturated solution in 9 M sulphuric acid was used as the titrant. The solution was standardized by potentiometric titration (or with phenosafranine indicator) against a standard iron(III) solution. Solutions of copper sulphate, thallium sulphate, uranyl acetate, ammonium molybdate and sodium vanadate were standardized by the usual methods [3].

An aqueous 0.02 % (w/v) phenosafranine solution was used as the indicator. The mixed indicator contained 0.02 % (w/v) phenosafranine and 0.05 % (w/v) methylene blue in water.

Stability of the titrant

In order to check the stability of the niobium(III) solution, 1-ml aliquots of the same 10^{-2} M iron(III) solution in 1 M sulphuric acid were titrated occasionally; two drops of phenosafranine served as indicator. The results showed that the solution retained its strength unchanged for 72 h and then oxidized slowly; the titre had decreased by about 2 % after 6 days.

RESULTS

Determination of iron

The determination of small quantities of iron was tested for two minerals, viz. dolomite (Ridsdale 9eG) and manganese ore (Ridsdale 18 cG). The sample was dissolved in (1 + 1) hydrochloric acid and then fumed with a few ml of sulphuric acid. The mixture was diluted to an acid concentration of 1 M, and then boiled to dissolve the salts. The solution was then transferred to the titration vessel. Filtration of insoluble materials like silica was unnecessary. The titration was then completed in an atmosphere of carbon dioxide in presence of two drops of phenosafranine indicator. Initially, the niobium(III) solution was standardized by titrating potentiometrically [1] a standard solution of ammonium disulphatoferrate(III), but later, phenosafranine was used as indicator.

The experimental value for the dolomite was 0.1126 ± 0.0011 % (certificate value 0.112 %) and that for the manganese ore was 0.995 ± 0.012 % (certificate value 1.020 %).

Determination of copper

In the presence of excess of chloride, copper(II) is reduced by niobium(III) to copper(I). For the analyses, 0.5—2.0 ml of standard copper sulphate solutions were transferred to the titration cell with the help of the additional microburette, and 8 ml of 10 M hydrochloric acid and 3 g of potassium chloride were added to the solution, which was then diluted to 20 ml. Air was removed with carbon dioxide, and the titration was carried out to the colourless end-point in the presence of two drops of phenosafranine indicator.

The results are shown in Table 1.

Determination of uranium

Uranium(VI) is reduced by niobium(III) to uranium(IV) and the reaction can be employed in the determination of uranium. The reaction is rather slow, but the equivalence point can be determined potentiometrically provided that the titration is not too rapid. On the addition of one equivalent of the titrant, an ill-defined break is obtained in the titration curve corresponding to the reduction of U(VI) to U(V), but this is not suitable for precise location of the equivalence point. The second inflexion corresponding to U(V) to U(IV), is very sharp and can be utilized without difficulty.

For the determination, 1—2 ml of a solution of uranyl acetate in 2 M acetic acid was added to 20 ml of 1 M sulphuric acid and the titration was carried out as usual under carbon dioxide. The results are shown in Table 1.

TABLE 1

Determination or copper(II), uranium(VI), molybdenum(VI), vanadium(V) and thallium

Metal	Taken as	Taken (mg)	Found[a] (mg)	Deviation (mg)	s (mg)
Cu	Copper sulphate	0.321	0.322	0.001	0.002
		0.514	0.516	0.002	0.003
U	Uranyl acetate	4.422	4.432	0.010	0.003
		1.474	1.483	0.009	0.005
Mo	Ammonium molybdate	1.090	1.102	0.012	0.001
		2.180	2.187	0.007	0.001
V	Sodium vanadate	0.958	0.960	0.002	0.005
		1.816	1.844	0.028	0.008
Tl (I)	Thallium perchlorate	2.244	2.248	0.004	0.028
		1.496	1.503	0.007	0.003
Tl (III)	Thallium perchlorate	2.330	2.335	0.005	0.007
		1.312	1.324	0.012	0.008

[a]Mean of 3—5 determinations.

Determination of molybdenum

Niobium(III) reduces molybdenum(VI) quantitatively to molybdenum(V) in the presence of hydrochloric acid and at temperatures below 20 °C. The end-point is sharp and the equivalence point can be determined precisely by using phenosafranine indicator. A brown precipitate of unknown composition appears if the reaction temperature is higher.

For the determination, 1—2 ml of an aqueous solution of ammonium molybdate was added to 20 ml of 6 M hydrochloric acid in the titration cell, along with two drops of the indicator solution. The temperature was kept below 20 °C and the titration was carried out as usual. The results are shown in Table 1.

Determination of vanadium

Vanadium(V) in sulphuric or hydrochloric acid solution, is reduced to vanadium(IV) and can be determined either potentiometrically or by using phenosafranine indicator. The potentiometric titration shows a sharp inflexion at the equivalence point corresponding to a 1-e change.

For analysis, 1—2 ml of a solution of sodium vanadate in 1 M sulphuric acid was added to 20 ml of 1 M sulphuric acid, and the mixture was titrated as usual in the presence of two drops of phenosafranine indicator. The results are shown in Table 1.

Determination of iron and copper in mixtures

Both iron and copper can be determined in a single titration if two drops of the mixed phenosafranine—methylene blue indicator solution are used. The conditions of titration were exactly similar to those for copper. The colour transitions were easily detectable. The first blue to red-violet transition appeared after iron had been titrated, and the second transition to a colourless solution corresponded to the end-point for copper. The titration of iron had to be done rather slowly in order to achieve a sharp end-point. The results are shown in Table 2.

Determination of thallium

Thallium(III) can be determined successfully by reduction with niobium(III). Thallium(I) can be determined by first oxidizing with bromine water, decomposing the excess of bromine with phenol, and then titrating with niobium(III). It was checked that phenol does not interfere with the niobium(III) titration. Two drops of phenosafranine were used as the indicator. The results of separate determinations of thallium(I) and thallium(III) are shown in Table 1.

For these determinations, a few ml of standard thallium(I) solution was placed in the titration vessel and saturated bromine water was added dropwise until the solution assumed a faint yellow colour. After 5 min, 3—4 drops of a 10 % solution of pure phenol in glacial acetic acid was added to the solution.

TABLE 2

Determination of copper(II)—iron(III) and thallium(I)—thallium(III) in mixtures

Metals	Taken (mg)	Found[a] (mg)	Deviation (mg)	s (mg)
Fe	0.577	0.579	0.002	0.004
Cu	0.642	0.643	0.001	0.001
Fe	1.154	1.153	0.001	0.003
Cu	0.321	0.323	0.002	0.003
Fe	0.292	0.289	0.003	0.001
Cu	1.284	1.291	0.007	0.002
Tl (I)	0.987	0.989	0.002	0.007
Tl(III)	0.932	0.925	0.007	0.010
Tl(I)	0.494	0.495	0.001	0.009
Tl(III)	1.864	1.882	0.018	0.013
Tl(I)	1.974	1.978	0.004	0.013
Tl(III)	0.466	0.463	0.003	0.008

[a]Mean of 3—4 determinations.

The solution was then diluted to 20 ml with 1 M sulphuric acid, stirred well and freed from air with carbon dioxide. The titration was then completed to the colourless-end-point of the indicator. The procedure was identical for thallium(III) except for the addition of bromine water and phenol.

Thallium(I) and thallium(III) in mixtures were determined by titrating the total thallium and the thallium(III) individually. The procedure was the same as that used for the separate determinations. The results are shown in Table 2.

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THE DETERMINATION OF NITRITE AND NITRATE BY THE RING-OVEN TECHNIQUE

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SUMMARY

Determinations of nanogram amounts of nitrite and nitrate individually and together, based on a variation of the ring-oven technique, are described. In the "segment technique" used, a stable standard scale is not necessary. Interferences have been studied. Nitrite in sausages can be determined.

The increasing importance of nitrites and nitrates in foods, agriculture, natural waters, industrial products, air pollution, etc., requires simple, quick and sensitive methods for their determination. The ring-oven technique [1], which is widely used for microanalyses of various substances, offers attractive possibilities for their detection via the Griess test [2] (with nitrate after reduction), which is based on production of a red azo dye on diazotization of sulphanilic acid with nitrous acid and subsequent coupling of the diazonium compound with α-naphthylamine. However, the colour of the red azo dye is not sufficiently stable for the establishment of a practicable standard scale in quantitative analyses for nitrite and nitrate by this technique. A new standard scale would have to be prepared every 4—5 h, which would place severe limitations on this method.

Recently [3, 4], a new method — the Segment Technique — has been worked out, to eliminate the need for the preparation of a stable standard scale. This new technique has been successfully applied for catalysed reactions in conjunction with the ring oven, when the amount of the reaction products is time-dependent. The technique can likewise be applied in cases where unstable reaction products appear in non-catalyzed reactions [5]. It was, therefore, considered worthwhile to examine this method for the determination of nitrite and nitrate.

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EXPERIMENTAL

Reagents

Sulphanilic acid solution

Dissolve 1 g of sulphanilic acid (Riedel) by warming in 100 ml of 30 % acetic acid.

α-Naphthylamine solution

Boil 0.03 g of α-naphthylamine (Riedel) in 70 ml of water; decant the colourless solution and mix with 30 ml of glacial acetic acid.

Store these Griess—Ilosvay reagents in amber coloured bottles and prepare freshly every two days. Mix equal volumes of the two solutions just before use.

Sodium nitrite solution

Prepare a 0.1 mg NO_2^- ml^{-1} solution from sodium nitrite (standardized with $KMnO_4$), and dilute this stock solution to obtain standard solutions containing 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 mg NO_2^- ml^{-1}. Label these solutions I, II, IV, VI, VIII and X, respectively.

Sodium nitrate solution

Prepare a 1.0 mg NO_3^- ml^{-1} solution and standardize by a modified Devarda Method. Prepare standard solutions, containing 0.005—0.05 mg NO_3^- ml^{-1}, in the same sequence as for nitrite, by dilution of this solution. Label these solutions in the same way as for nitrite solutions.

Apparatus

A ring oven (ROFA, Wien) with a working temperature of 110 °C was used.

Procedures

General procedure

Spot drops (1 μl) of the sample solution and of two different standard solutions at three points around the centre of the filter paper (MN 226 ORO; 5.5 cm diam., Macherey—Nagel) so as to form an equilateral triangle. Place the filter on the ring oven, and wash these three drops in the usual way from the centre to the ring zone to give three sharply outlined circular segments each about 10—20 mm long. Then spray the filter directly with the colour-producing reagent. Alternatively, produce the colour by applying the reagent to the three drops on the paper, and then wash the reaction product to the ring as usual. Compare the colours of these segments, to decide whether the concentration in the sample is higher or lower than the two standard concentrations, or if it is in between.

In further steps, apply the sample drop and one drop each of two suitably

chosen standard solutions to the three different points on a new filter paper and treat as described above. In most practical cases one can see to which standard concentration the unknown concentration corresponds most closely after the third comparison step.

To achieve a higher accuracy, it is necessary to carry out one or two more determinations with different numbers of drops of the unknown solution.

Whenever more than one drop of any of the solutions is applied to the same point on the filter paper, each drop must be dried with cold air before the next is added.

Determination of nitrite

Place 1 μl each of the unknown solution and of two different standard solutions of nitrite (preferably solutions IV and X to start with) on the three points of the filter paper. To these points apply 2 μl of the Griess—Ilosvay reagent and allow to react for 2 min. Wash the red azo dye into the ring zone on the ring oven with 10 % acetic acid (8—10 washings are sufficient). Compare the three segments obtained as explained above and repeat the procedure with various numbers of drops of the unknown nitrite solution and suitable standard nitrite solutions, to determine the exact amount of nitrite in the test solution. The following example will illustrate the procedure.

Number of drops of unknown	Standard solutions used	Colour of the unknown segment
1	IV—X	Between IV and X
1	IV—VI	More than VI
1	VI—VIII	More than VIII
1	VIII—X	Between, $\therefore$ = V
1/2	IV—VI	Between, $\therefore$ = V
1/4	II—IV	Between, $\therefore$ = III

Totals: 7/4 drops. Σ = 17

The unknown solution contains $17 \times 4/7 \times 0.005 = 0.0485$ mg NO_2^- ml^{-1} (0.005 = concentration of the lowest solution of the standard scale for nitrite.)

Some results of these studies are given in Table 1.

Determination of nitrate

The above procedure for nitrite is used for nitrate also, with either a nitrate or nitrite standard solution. In either case, apply the unknown and standard solutions to the three points on the filter paper, and apply 2 μl of freshly prepared Griess—Ilosvay reagent to each of these. Press the paper upside down on the surface of a zinc-coated iron plate with a smooth glass plate.

TABLE 1

Determination of nitrite

Taken (ng)	Found (ng)	Taken (ng)	Found (ng)
5.0	5.0	20.0	17.9
7.8	7.1	25.5	25.0, 25.8
10.0	10.0, 10.0	30.0	26.7
12,5	12.8	32.5	28.3
15.0	13.6, 15.0	35.0	33.3

After 1 min, repeat this procedure with the other side of the paper in contact with the zinc-coated plate; the nitrite obtained by the reduction of nitrate in this step reacts at once with the reagent applied previously. Wash the red azo dye obtained into the ring zone with 10 % acetic acid, and proceed as described for nitrite. If the nitrite standard solution has been used, multiply the results for nitrite by the factor NO_3^-/NO_2^- = 1.3478 to calculate as nitrate.

It proved better to use nitrite standard solutions for the determination of nitrite and nitrate. Some results are reported in Table 2.

Determination of nitrite and nitrate in same solution

First determine the nitrite content by the above method, and then analyze the same solution for the sum of nitrite and nitrate by the reduction method. Subtract the amount of nitrite obtained in the first step from the total nitrite found in the second step and multiply by the factor 1.3478 to find the amount of nitrate. Nanogram amounts of nitrite, in the presence of 100-fold amounts of nitrate can be determined with a maximum error of about 14 %.

Typical results are shown in Table 3.

TABLE 2

Determination of nitrate

(a) With nitrate standard solutions		(b) With nitrite standard solutions	
Taken (ng)	Found (ng)	Taken (ng)	Found (ng)
8.7	7.9	7.0	6.7
9.3	10.0	10.0	10.6
15.0	16.4	15.0	16.3
21.5	23.3	20.0	21.3
24.8	21.4	22.5	22.1
27.0	24.3	30.0	26.9
34.0	32.9	37.5	33.7
37.8	35.0	40.0	40.4

TABLE 3

Determination of nitrite and nitrate in the same solution

No.	Nitrite		Nitrate	
	Taken (ng)	Found (ng)	Taken (ng)	Found (ng)
1	4.5	4.2	82.5	89.8
2	5.0	4.5	25.0	26.9
3	5.0	4.6	250.0	288.7
4	7.5	7.9	25.0	27.7
5	7.5	7.1	100.0	91.5
6	15.0	15.7	25.0	24.2
7	15.0	12.9	250.0	316.5
8	15.0	14.2	150.0	149.3
9	25.0	26.6	25.0	24.0
10	25.0	21.4	250.0	209.7
11	25.0	24.3	75.0	68.3
12	40.0	37.1	25.0	22.4
13	40.0	37.1	82.5	96.3
14	40.0	34.3	250.0	262.5

Interferences

Interferences were studied by applying 1 μl of the solution of the diverse substance at one of the three points on the filter paper followed by 2 μl of Griess—Ilosvay reagent; at the second point (blank) only 2 μl of the Griess—Ilosvay reagent were placed, and the third point was not used. After 2 min, the spots were washed out with 10 % acetic acid, on the ring oven. These segments were marked I and III, respectively. At another point (II) on another filter paper, was applied 1 μl of nitrite or nitrate solution, and a drop of the diverse substance, while 1 μl of the pure standard nitrite or nitrate solution was applied at the second point (called IV) and the third point (called III) was kept blank. Each of the three points was treated with 2 μl of the reagent, and after 2 min the red azo dye produced was washed out into the ring zone as before. For nitrate, reduction was done, as described above, before the washing. The substance was considered not to interfere when segment I was identical to III and segment II was identical to IV.

The following substances in 10-fold amounts did not interfere with the determination of nanogram amounts of nitrite: acetate, chloride, sulphate, tin, arsenic, lead, glucose and ascorbic acid. The interference by phosphate could be removed by adding a drop of zirconium solution (0.1 mg Zr ml^{-1}) directly to the sample spot, before the addition of the reagent.

Tin, arsenic and lead in 10-fold amounts did not interfere with the determination of nitrate.

Determination of nitrite in sausages

This ring-oven determination of nitrite was tested on aqueous extracts (10g in 250 ml) of various sausages, which were also prepared and analyzed by the recommended AOAC procedure [6], at the Chem. Landesuntersuchungs-anstal Freiburg i.Br. (for which we express special thanks). The results of these studie are reported in Table 4.

TABLE 4

Determination of nitrite in sausages

(Results are given as ng μl^{-1})

Sample	1	2	3	4	5
AOAC method [6]	2.8	1.4	1.8	1.6	1.2
Present method	3.1	1.6	2.0	1.8	1.3

We are grateful to the Alexander von Humboldt-Stiftung which enabled this work to be completed by granting a Post-Doctoral Senior Fellowhip to one of us (M. H.)

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FLOTATION OF TRACES OF HEAVY METALS COPRECIPITATED WITH ALUMINUM HYDROXIDE FROM WATER AND SEA WATER

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SUMMARY

Microgram quantities of heavy metals in 1-l samples of water and sea water are quantitatively coprecipitated with aluminum hydroxide at pH 9.5. The precipitate is floated with the aid of sodium oleate and small nitrogen bubbles, separated and dissolved in 2 M nitric acid, and the heavy metals are determined by atomic-absorption spectrometry. The method is rapid and applicable to 9 heavy metals at the low p.p.b. level.

Preconcentration techniques for the atomic-absorption spectrometric determination of trace elements in water and sea water commonly include liquid—liquid extraction, ion-exchange, and coprecipitation [1]. In the present work, microgram quantities of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), and lead(II) in 1 l of water and artificial sea water, and cadmium(II) in 1 l of water are quantitatively coprecipitated with aluminum hydroxide. This bulky amorphous precipitate is difficult to filter, and centrifugation is cumbersome for large volumes. Therefore, a flotation technique [2], in which the precipitate is floated with the aid of sodium oleate and small nitrogen bubbles (0.1—0.5 mm diam.), has been applied. The precipitate is readily separated from the mother liquor and then dissolved in nitric acid for atomic-absorption spectrometry. The proposed method is simple and rapid, and applicable to the determination of heavy metals at the low p.p.b. level in water and sea water.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash model AA-1 Mark II atomic-absorption spectrophotometer with an SA-61 slit burner and a Hitachi model QPD53 recorder, and a Fujitsu well-type NaI(Tl) scintillation counter were employed. The flotation cell is illustrated in Fig. 1.

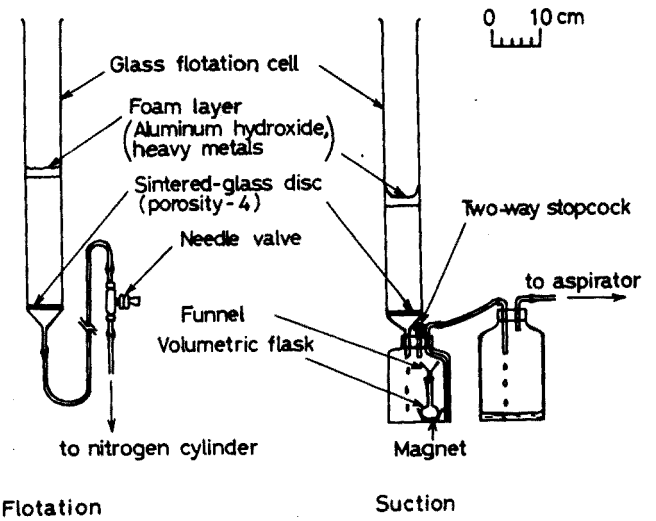

Fig. 1. Flotation and separation apparatus.

Reagents

An aluminum solution (10 mg Al ml^{-1}, in 0.5 M hydrochloric acid) was prepared from an aluminum chloride solution purified by anion-exchange (BioRad AG1-X8, 100—200 mesh, at 2 M chloride), and standardized by the gravimetric oxine method. Standard solutions (1 mg metal ml^{-1}, in 1 M hydrochloric or nitric acid) were prepared from chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, and lead metals. A sodium oleate solution (1 mg ml^{-1}) was prepared by dissolving sodium oleate (powder, Extra Pure Reagent, Nakarai Chemicals) in 99.5 % v/v ethanol with magnetic stirring. Artificial sea water was prepared by the formula of Lyman and Fleming [3]. Water was purified by distillation and ion-exchange. All reagents (reagent grade except for sodium oleate) were employed without further purification. ^{51}Cr, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{64}Cu, ^{65}Zn, and ^{115m}Cd were used as tracers.

Recommended procedure

Place 1 l of water sample in a 1-l beaker, and add 5 ml of aluminum solution and 2 ml of sodium oleate solution. Adjust the pH to 9.5 with 0.1 M aqueous ammonia to precipitate aluminum hydroxide, while stirring magnetically, and stir the solution for 15 min. Transfer the contents of the beaker (excluding the stirring bar) to a flotation cell, and wash the beaker with 50 ml of aqueous 0.1 M ammonia. Pass nitrogen at a flow-rate of 45 ml min^{-1} from the lower end of the cell for 2 min, to obtain complete mixing and flotation of the precipitate. Suck off the mother liquor through the sintered-glass disc,

and add 20 ml of 99.5 % (v/v) ethanol to break down the foam. Wash the precipitate with 50 ml of aqueous 0.1 M ammonia. Add 4 ml of 2 M nitric acid to the cell to dissolve the precipitate, collect the filtrate by suction in a 10-ml volumetric flask, wash the sintered-glass disc with 2 M nitric acid, and dilute to the mark with 2 M nitric acid. Determine heavy metals in the solution by atomic-absorption spectrometry. If the concentration of the required element exceeds 5 $\mu g\ ml^{-1}$, dilute the solution further, adjusting the nitric acid and aluminum concentrations.

For sea water, modify the above procedure as follows. Add 2 ml of sodium oleate solution 1 min before completion of the 15-min stirring, and proceed as described above. Add 2 ml of 10 M nitric acid to dissolve the precipitate, collect the filtrate in a 20-ml volumetric flask, wash the sintered-glass disc with 10 ml of 2 M nitric acid, and dilute to the mark with water.

Construct calibration curves with 10 ml (for water) or 20 ml (for sea water) of 2 M nitric acid solutions containing 50 mg of aluminum and 0—50.0 μg (for water) or 0—100 μg (for sea water) each of heavy metals.

The atomic-absorption equipment was operated under the following conditions: wavelengths (in nm) Cr 357.9, Mn 279.5, Fe 248.3, Co 240.7, Ni 232.0, Cu 324.7, Zn 213.9, Cd 228.8, and Pb 217.0; air 8.0 l. min^{-1}, acetylene 2.5 l min^{-1}; slit-widths 0.10 (entrance) and 0.15 mm (exit). For the determination of zinc and cadmium, the burner was shifted 15° from the optical path to decrease the sensitivity.

RESULTS AND DISCUSSION

The optimal pH for collecting traces of heavy metals

Aluminum hydroxide was precipitated at different pH values from 50 ml of solution containing 1 μg of a labeled heavy metal and 1 ml of aluminum solution. After the 30-min period of stirring, the precipitate was separated by centrifugation, and dissolved in 2 M nitric acid for γ-activity measurement. Chromium(III), manganese(II), iron(III), cobalt, copper(II), zinc, and cadmium were collected in greater than 95 % yields over the pH range 9—10.

Flotation and determination of traces of heavy metals

When 1 l of water was used, it was necessary to form a foam layer (2—3 cm thick) to support the precipitate on the surface of the solution and prevent its redispersion. Thus 2 ml of sodium oleate solution was required for satisfactory flotation and rapid suction. Table 1 shows that down to 1 p.p.b. of heavy metals were separated in greater than 95 % yields by the recommended procedure.

Since the absorbances of chromium, manganese, cobalt, and nickel in 2 M nitric acid solutions containing aluminum varied from those in aluminum- and nitric acid-free solutions, calibration curves were constructed as

TABLE 1

Flotation of heavy metals in 1 l of water or artificial sea water (Tracer experiments)

Element	Water		Artificial sea water	
	Added (μg)	Recovery (%)	Added (μg)	Recovery (%)
Cr(III)	1	96, 96	1	98
	10	96	50	100
	20	98		
Mn(II)	1	95, 100	1	100
	10	96	50	103
	20	95		
Fe(III)	1	95, 101	1	98
	10	100	50	99
	20	95	1000	96
	1000	101		
Co	1	95, 97	1	95
	10	96, 99		
Zn	1	95, 96	1	97
	10	99	50	100
	20	95		
Cd	1	96, 98	1	21, 37, 48
	10	97	50	24
	20	98		

described above. All calibration curves were linear up to at least 5 μg ml^{-1}, with maximum deviations of 0.1 μg ml^{-1}. No mutual interference among the heavy metals was observed in the determination. Table 2 shows the results obtained for nine heavy metals in water by the recommended procedure.

The blank values through the whole procedure were zero for chromium(III) cobalt, nickel, copper(II), cadmium, and lead, 0—1 μg for manganese(II), 1 μg for iron(III), and 0—2 μg for zinc.

When 1-l samples of artificial sea water were used, the sodium oleate solution was added immediately before the flotation, otherwise the essential foam layer was not formed. Because large amounts of magnesium coprecipitated with aluminum hydroxide, the precipitate was dissolved in 10 M nitric acid and the final volume was made up to 20 ml. Table 1 shows that down to 1 p.p.b. of chromium(III), manganese(II), iron(III), cobalt, and zinc can be separated in greater than 95% yields from artificial sea water. The low recovery of cadmium is due to its unsatisfactory coprecipitation with aluminum hydroxide. Sodium, magnesium, calcium, potassium, and strontium coprecipitated with aluminum hydroxide were determined by flame photometry with an air—acetylene flame or by EDTA titration, in order to obtain the separation factors* for the alkaline and

*Separation factor = $(Q_B/Q_A)/(Q_B^\circ/Q_A^\circ)$, where Q_A° is the quantity of the required element in the sample, Q_B° the quantity of the element to be separated in the sample, and Q_A and Q_B are the corresponding quantities after the separation

TABLE 2

Simultaneous determination of traces of heavy metals[a]

Elements[a] added (μg each)	Found (μg)								
	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd
Water samples									
5	5	5	4	4	4	5	5	4	5
20	19	18	19	19	19	19	20	21	20
50[b]	53	53	96	—[c]	48	53	50	54	52
500	500	500	490	460	500	460	460	490	470
Artificial sea-water samples									
10	10	10	9	10	10	10	11	12	—
20	21	22	18	21	18	18	20	18	—
40	39	36	40	38	37	37	37	37	—
250	230	230	230	250	240	250	250	240	—
500	500	430	490	460	450	480	460	470	—
	500	420	460	450	460	480	460	470	—

[a]Cr(III), Mn(II), Fe(III), Co, Ni, Cu(II), Zn, Cd, Pb.
[b]Except that 100 μg Fe and no Co were added.
[c]Not determined.

alkaline earth metals with respect to the required elements, except for cadmium. The separation factors were 10^{-4}—10^{-3} for sodium, calcium, potassium, or strontium, and 10^{-2} for magnesium. Washing the precipitate with 50 ml of aqueous 0.1 M ammonia was effective in reducing the separation factor for sodium, calcium, or potassium by a factor of 2—3, but was ineffective for magnesium. Magnesium (50 mg), sodium (15 mg), calcium (1 mg), potassium (1 mg) and strontium (0.1 mg) did not interfere with the determinations. Table 2 shows the results of the determination of 8 heavy metals by the recommended procedure. Corrections for the following quantities of impurities in 1-l samples of original artificial sea water were made: 1 μg each for cobalt, nickel, and copper(II), 1—2 μg for manganese(II), 1—3 μg for lead, and 2—3 μg each for chromium(III), iron(III), and zinc. The heavy metals at the p.p.b. level in artificial sea water could be determined with satisfactory results, but in the presence of 500 μg each of 9 elements, lower values were obtained for manganese(II).

The time required for the preconcentration was about 50 min.

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Short communication

MICRODESIGN FOR A CALCIUM-SENSITIVE ELECTRODE

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Intracellular calcium(II) activity is an important regulating factor in a number of cellular processes, and cell physiologists require reliable and easily accessible tools with which to measure this activity. A major step in this direction was taken with the utilization of aequorin, a protein isolated from a jellyfish [1]. Aequorin, however, though highly useful in some preparations has a number of disadvantages: it requires large cells, is not easy to calibrate and is difficult to obtain. Microelectrodes that will allow the measurement of intracellular calcium(II) activity in the same way as intracellular activities of Na^+, K^+ and Cl^- can be measured, would therefore be very useful. This communication describes a calcium-sensitive electrode that represents a major step towards meeting the requirements for sensitivity, selectivity and size posed by biological cells.

EXPERIMENTAL

The ion exchanger

The calcium chelate of di-(n-octylphenyl)phosphoric acid was allowed to dissolve for 24 h in dioctylphenylphosphonate in the weight ratio of 10:1; 0.2 g of this ion exchanger was combined with 0.08 g of polyvinylchloride dissolved in 5 ml of tetrahydrofuran [2].

The electrode

A glass microelectrode is drawn from Pyrex tubing (o.d. 1.8 mm) and the tip is broken to a diameter of 10—20 μm. The glass is siliconized in a saturated atmosphere of dimethyldichlorosilane [3]. The electrode is placed overnight with the tip down in a droplet of the ion-exchanger solution. This process draws a column of about 200 μm of the ion-exchanger solution into

the tip of the electrode, and then allows the tetrahydrofuran to evaporate. The procedure leaves a coat of polyvinylchloride-embedded ion-exchanger on the inner and outer surfaces of the glass and a clot of the electroactive material in the very tip of the electrode. (It is important to note that if the tetrahydrofuran is not fresh (free of peroxides), the ion exchanger will immediately become white, and there will be no sensitivity for calcium ions.) The rest of the glass capillary is filled with 10 mM $CaCl_2$ solution through a thin glass pipette.

The measuring cell

A Ag/AgCl electrode is inserted into the microelectrode and the potential difference between this and a calomel electrode is measured with a high impedance Keithley electrometer. The electrode assembly:

$$Hg \mid Hg_2Cl_2, KCl\ (s) \mid \text{test solution} \mid \text{membrane} \mid 0.01\ M\ CaCl_2 \mid AgCl \mid Ag \quad (1)$$

was held in a Faraday cage and tested in a series of calcium(II) solutions at room temperature.

Test solutions

All solutions were held at an ionic strength of 0.1 M. Six solutions were prepared as mixtures of $CaCl_2$ and NaCl with calcium concentrations ranging from 0.1 mM to 33.3 mM. Seven calcium buffer solutions were made up identically to those used by Růžička et al. [3], with *p*Ca values ranging from 3.5 to 8.4.

RESULTS AND DISCUSSION

Nine electrodes were tested. Their resistances were about 10^{11} Ohms, depending on tip diameter and length of ionic exchanger. The response to four test solutions is shown in Fig. 1. The responses of 7-week old electrodes to new test solutions are fully developed within 1 min. However, the response time of the electrodes decreases with age, that of a 1-day old electrode being 5 min to 15 min. No electrodes were functional after 7 weeks. Their loss of sensitivity was marked by a change in color of the electroactive membrane from gray translucent to white opaque.

Figure 2 shows calibration plots for two of the electrodes; averaged plots including all electrodes are not given because the absolute e.m.f. level varies significantly from one electrode to the next, so that the statistical variation in each point of an averaged plot would obscure the shape of the separate calibration curves. The variation in E_0 value does not impede the use of the electrodes, because each measurement of unknown solutions must be preceded and followed by measurements of standards. For the NaCl—$CaCl_2$ mixtures, the electrode response is almost linear, the average slope being

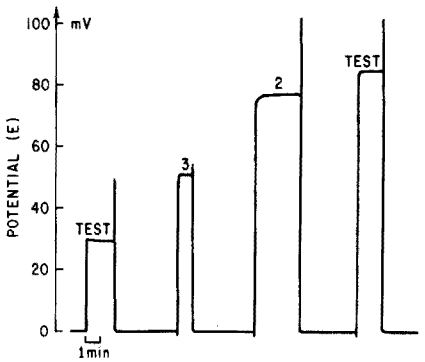

Fig. 1. Pen recording of the potential response of the microelectrode to two test solutions of unknown calcium(II) activity and two calibrating solutions, the *p*Ca values of which are shown above the response.

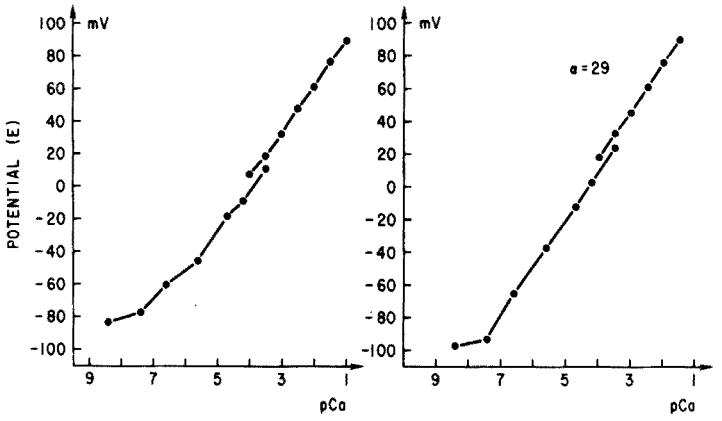

Fig. 2. Calibration curves for two calcium-sensitive microelectrodes.

29.0 ±2.7mV/*p*Ca (S = 2.7; N = 9). For the buffer solutions (Fig. 2), nearly straight lines are obtained down to ca. *p*Ca 6, below which the curve flattens out; no sharp detection limit can be seen. The curves in Fig. 2 are given as concentration plots; activity plots would be shifted to the left along the *p*Ca axis by 0.44 units [4]. The discontinuities in the curves correspond to the change from NaCl—$CaCl_2$ mixtures to buffer solutions; this shift is probably caused by the presence of maleic acid in the buffers. If the equilibrium constant [5] for the binding of calcium(II) to maleic acid (pK_{ass} = 2.43) were included in the calculation of the *p*Ca values of the buffer solutions, the lower part of the plots would be shifted by 0.25 *p*Ca units to the left, and the discontinuity would be eliminated.

Selectivity

The selectivity (K) of the electrode is described by the equation

$$E = E_0 + \frac{RT}{2F} \ln \left(a_{Ca} + \sum_i K_{Ca,i}\, a_i^{2/z_i}\right) \qquad (2)$$

where E is the potential in a mixed solution of calcium(II) and the ions $i = 1$ to $i = x$, E_0 is the standard potential, R, T and F have their usual meanings, and a_i is here the activity of either Na^+, K^+ or Mg^{2+}. Values of K were obtained by measuring E in pure solutions of 100 mM $CaCl_2$, NaCl, KCl and $MgCl_2$. The values obtained by the microelectrode for the employed ion exchanger agreed with those obtained with the macroelectrode [2].

Possibility for intracellular use

If an electrode is to measure the calcium(II) activity in living cells, it must be sensitive, selective and have a small tip. As for sensitivity, the electrode presented here is adequate. Intracellular calcium(II) activities are of the micromolar order [1], and previously designed microelectrodes made with liquid ion-exchangers by the authors (unpublished) all showed detection limits in the range of 10^{-4}—10^{-3} M calcium(II). This is the same limit as for the commercially available liquid ion exchangers for calcium and potassium. Only through an increase in the viscosity of the electroactive membrane by embedding the ion exchanger in polyvinyl chloride did it become possible to make an electrode that matched physiological levels [1]. The utilization here of the high-viscosity membrane in a microdesign seems to have improved sensitivity even further. If the calibration plots for the microelectrode (Fig. 2) are compared with the plots for the macroelectrode [2], it can be seen that the diffusely defined detection limit of the former is about one pCa unit higher than for the latter.

With regard to selectivity, sodium is the intracellular ion which can be assumed to interfere least. Potassium activities in living cells are about 5 orders of magnitude higher than calcium activities and are likely to contribute a significant response, but this interference can be compensated for fairly easily with the use of a potassium-sensitive microelectrode. Magnesium ion, however, presents a major problem; magnesium activities in living cells are not well described but can be expected to exceed the calcium levels by at least 3 orders of magnitude, which will limit the intracellular application of the electrode. Also, the 10-μm tip diameter is too large for intracellular work. However, the miniaturization of the polyvinyl chloride-based electrode has made it applicable in compartments down to nanoliter size, and we are at present working on a reduction of the tip diameter to 1 μm.

We would like to thank Dr. J. Růžička for his help in the early phase of the work, Dr. Ole Joern Jensen, Radiometer A/S, Copenhagen, for supplying the ion exchanger, and Kirsten Abel for valuable technical help.

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Short communication

THE DETERMINATION OF CHROMIUM(III) AND CHROMIUM(VI) BY TOTAL ANION EXCHANGE AND ATOMIC ABSORPTION SPECTROMETRY

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The determination of chromium by atomic absorption spectrometry (a.a.s.) does not discriminate between the various oxidation states of the element. Recently, a method was required for the rapid determination of the concentrations of each of the two main oxidation states of chromium in soil extracts, and this was achieved by combining total anion exchange with a.a.s.

Experimental

Apparatus

An EEL 240 atomic absorption spectrophotometer was used with air—acetylene and nitrous oxide—acetylene burners, and a chromium hollow-cathode lamp operated at 10 mA.

Reagents

Chromium(III) and (VI) solutions (1 000 μg ml^{-1}) were prepared from analytical reagent-grade chromium(III) chloride and potassium dichromate. Diluted (100×) aliquots of these stock solutions showed identical absorbances in the nitrous oxide—acetylene flame. Solutions of a wide range of cations (as chlorides or sulphates) and anions (as potassium salts) were prepared from analytical reagent-grade salts.

Procedure

Prepare a series of three calibration plots (plots 1—3), each covering the range 0—10 μg Cr ml^{-1}. For the first, analyse chromium(III) solutions for total chromium concentration in the conventional way with a nitrous oxide—acetylene flame. For the second plot, shake 10-ml aliquots of the series of standard chromium(III) solutions with 1 ± 0.05-g portions of Zerolit FF (ip, standard grade, Cl^--form) resin on a reciprocating shaker for 20 min and analyse the resulting solutions by the same a.a.s. procedure as before. For the third plot, treat and analyse aliquots of chromium(VI) solutions in exactly the same way.

For sample solutions, measure the absorbances before (B) and after (A) the treatment with the anion-exchange resin, under identical instrumental conditions. Estimate the approximate chromium(III) concentration from absorbance A using plot 2. Calculate the approximate chromium(VI) concentration by subtracting this chromium(III) concentration from the total chromium concentration found from absorbance B using plot 1, and estimate from plot 3 the absorbance contributed by this amount of chromium(VI), after the sample has been treated with the resin. Subtract this absorbance from absorbance A to give the corrected value for the chromium(III) absorbance, and use plot 2 to obtain the concentration. Subtract this chromium(III) value from the total chromium concentration (absorbance B, plot 1) to give the corrected chromium(IV) concentration.

Results and discussion

When 1 g of anion-exchange resin was shaken with 10-ml aliquots of chromate solution (10 μg ml^{-1}) for increasing periods of time, the chromium absorbances of the resulting solutions decreased gradually to a steady value over a period of 8 min. A shaking period of 20 min was adopted, but even after prolonged shaking the chromate ion is only 97 % absorbed, so that a correction for the chromate contribution to the total chromium absorbance after the anion exchange is necessary, unless a second absorption step is used.

Variations in the amount of resin (from 0.2 to 5.0 g) added to 10-ml aliquots of chromium(III) or (VI) solutions (10 μg ml^{-1}) did not affect the residual chromate absorbance, but increasing amounts of resin caused a small significant increase in the chromium(III) absorbance, hence 1-g portions of resin were weighed out for use.

In a brief preliminary assessment of the method, with air—acetylene flames, the chromium(III) absorbance was found to be enhanced by an impurity or breakdown product of the resin. This enhancement was also noted when deionized water was shaken with the resin and used to dilute the chromium(III) solutions, which confirmed that the effect results from interference in the a.a.s. determination and not from a concentration effect on shaking with resin. The interference was not observed in the nitrous oxide—acetylene flame, which was therefore chosen for subsequent work.

Instrumental conditions do not affect the accuracy of the method, but failure to optimize working conditions may affect precision adversely. A narrow monochromator slit width may be necessary to obtain linear calibration plots if an argon-filled hollow-cathode lamp is used. To obtain good precision, particularly when the Cr(VI):Cr(III) ratio is large or small (i.e. > 10 or < 0.1), the top standard and zero absorbance values must be checked (and adjusted if required) between every sample.

The effect of 100-fold amounts of a wide range of cations and anions on the determination of a mixture of 5 μg ml^{-1} of each of chromium(III) and

(VI) was investigated. Ammonium, Ca^{2+}, Cd^{2+}, Cs^{+}, Cu^{2+}, Fe^{3+}, Ga^{3+}, In^{3+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Rb^{+}, Sr^{2+}, Zn^{2+}, acetate, Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, PO_4^{3-} and SO_4^{2-} caused no detectable interference. Tl^{3+} and Pb^{2+} interfered in in the total chromium determination by precipitation of their insoluble chromates. Oxalate and citrate caused adsorption of chromium(III) onto the resin, probably as anionic complexes [1]. Lanthanum caused a slight enhancement in the determination of both chromium(III) and (VI) in the nitrous oxide—acetylene flame.

The method may be applied to the determination of chromium(III) and (VI) in 1 M HCl or up to 3 M acetic acid solutions without modification. For 3 M HCl, H_2SO_4 or H_3PO_4, an additional adsorption or approximation step is necessary, since the efficiency of the adsorption of chromate is reduced.

The results obtained for some simple mixtures of chromium(III) and (VI) are given in Table 1, which shows that the method provides a simple and rapid procedure for the sequential determination of chromium(III) and (IV) in solution.

TABLE 1

Analysis of some synthetic mixtures

Added (μg ml^{-1})		Found (μg ml^{-1})			
Cr(VI)	Cr(III)	Cr (total)	Cr(III)		Cr(VI)
			1st approx	2nd approx	
0.50	5.00	5.47	5.00	4.98	0.49
5.00	0.50	5.54	0.73	0.52	5.02
5.00	5.00	10.03	5.20	5.00	5.03
2.00	8.00	9.98	8.08	8.00	1.98
8.00	2.00	10.00	2.32	1.98	8.02

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Short communication

THE EFFECT OF ACIDS ON THE DETERMINATION OF THALLIUM BY ATOMIC ABSORPTION SPECTROMETRY WITH A GRAPHITE FURNACE

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With the increasing number of applications of electrothermal atomizers in atomic absorption spectrometry [1], the interference problems involved in their use are becoming more apparent. During the development of a method of determining thallium by this technique, serious interferences were encountered under certain acid conditions. Welcher et al. [2] have previously noted the interference of hydrochloric acid on the determination of thallium in a nickel-base alloy. In the work described here, the effects of nitric, perchloric, sulphuric and hydrochloric acids were studied, because, singly or in combination, these acids are widely used for dissolution of inorganic and organic samples. The interference by sodium chloride is also demonstrated.

Experimental

The Perkin Elmer Model 103 spectrophotometer used was equipped with an HGA 70 Graphite Furnace [3] and a Model 165 recorder. Nitrogen was used as the inert atmosphere. Sample aliquots (20 μl) were injected with Eppendorf micropipettes. The HGA 70 was operated on program 6 (ca. 750 °C) with an atomization voltage of 8V (ca. 2200 °C); 30-s drying (ca. 100 °C), 45-s ashing, and 10-s atomization times were employed throughout.

Absorption signals were measured at 276.8 nm, with a 0.2-nm band width; the thallium hollow-cathode lamp (Southern Spectral Sources Ltd.) was operated at 5 mA. A deuterium hollow-cathode lamp (Southern Spectral Sources Ltd) was used for background correction.

For the thallium standards thallium(III) nitrate was dissolved in distilled water, and the solution was diluted as necessary.

All thallium recoveries reported are calculated with respect to a thallium calibration graph obtained in the presence of 0.1 % (v/v) sulphuric acid.

Results and discussion

The effects of sulphuric, nitric, perchloric and hydrochloric acids, (0.001—1.0 % v/v) on the determination of a 0.5 μg Tl ml^{-1} solution were investigated. Over the ranges studied the effects of sulphuric and nitric acids are negligible, while those of hydrochloric and perchloric acids are severe, even at the lowest acidities (Fig. 1). Reduction of the ashing temperature in the cases of hydrochloric and perchloric acids did not improve the absorption signals. Most of these results are as expected, for thallium sulphate and nitrate should decompose to the more stable oxide during the ashing stage, whereas hydrochloric acid probably forms a volatile chloride, leading to loss of thallium before atomization. The severe signal suppression caused by perchloric acid is, however, surprising; the perchlorate would be expected to decompose to the oxide before atomization and therefore give results similar to the sulphate and nitrate, but the results indicate that the perchlorate decomposes through a volatile chloride compound.

It is well known that hydrochloric, nitric and perchloric acids are removed from sulphuric acid solutions on evaporation nearly to dryness. Sulphuric acid was therefore investigated as a means of removing the interferences of hydrochloric and perchloric acids; the results of adding 0.01 % (v/v) and 1.0 % (v/v) sulphuric acid, or 0.01 % (v/v) and 1.0 % (v/v) nitric acid, are shown in Figs. 2 and 3. It can be seen that sulphuric acid reduced the interferences more efficiently than nitric acid, that 1.0 % (v/v) sulphuric acid was more effective than the 0.01 % (v/v) addition, and that the interference of hydrochloric acid was more readily prevented than that of perchloric acid. These observations are in accordance with predictions based on the boiling points of the acids, the one anomaly being that 1.0 % (v/v) nitric acid is less

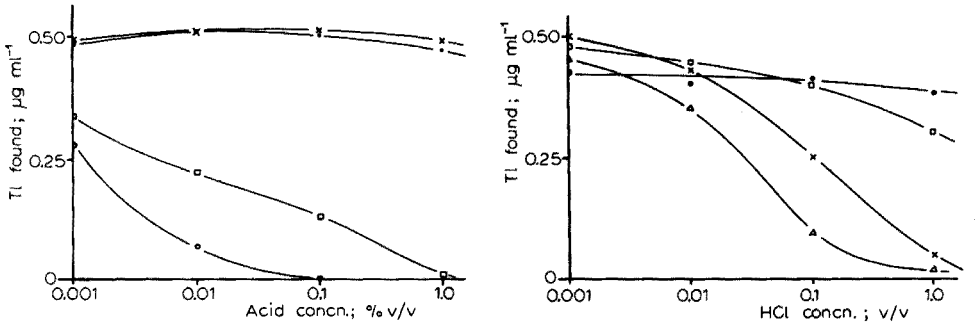

Fig. 1. Effect of acid concentration on the determination of 0.5 μg Tl ml^{-1}: (•) H_2SO_4; (×) HNO_3; (□) HCl; (○) $HClO_4$.

Fig. 2. Effect of added H_2SO_4 and HNO_3 on the determination of 0.5 μg Tl ml^{-1} in the presence of HCl: (•) 1.0 % v/v H_2SO_4; (□) 0.01 % v/v H_2SO_4; (△) 1.0 % v/v HNO_3; (×) 0.01 % v/v HNO_3.

efficient than 0.01 % (v/v) nitric acid in removing the hydrochloric acid interference.

When sodium chloride (10—1000 μg ml^{-1}) was added to the solutions, zero recoveries of thallium were obtained in all cases (Fig. 4). The addition of 0.01 % (v/v) sulphuric acid gave good recoveries of thallium in the presence of up to 100 μg NaCl ml^{-1}; addition of 1.0 % (v/v) sulphuric acid extended the range of tolerable sodium chloride concentrations to 1000 μg ml^{-1} (Fig. 4). Higher sodium chloride concentrations gave rise to background absorption effects which could not be satisfactorily compensated with the instrumentation used.

The addition of 1 % (v/v) sulphuric acid to the sample solution being injected into the graphite furnace enables the determination of thallium to be carried out in the presence of up to 1 % (v/v) hydrochloric acid, 0.1 % (v/v) perchloric acid and 1000 μg ml^{-1} sodium chloride, provided that close matching of standard solutions and samples, or a standard additions method is used.

The analytical application of these results can be illustrated by the determination of thallium in urine by a standard additions procedure after dilution of 1 ml of sample to 10 ml, which contains 1.0 % (v/v) sulphuric acid (Fig. 5). These plots clearly demonstrate the feasibility of determining thallium directly in urine, whereas previous methods have required either a nitric acid digestion of the sample [4] or the separation of thallium with sodium diethyldithiocarbamate [5].

The author acknowledges the technical assistance of B. Preston and C. Thom. This work is published by permission of the Directors of Tioxide International Limited.

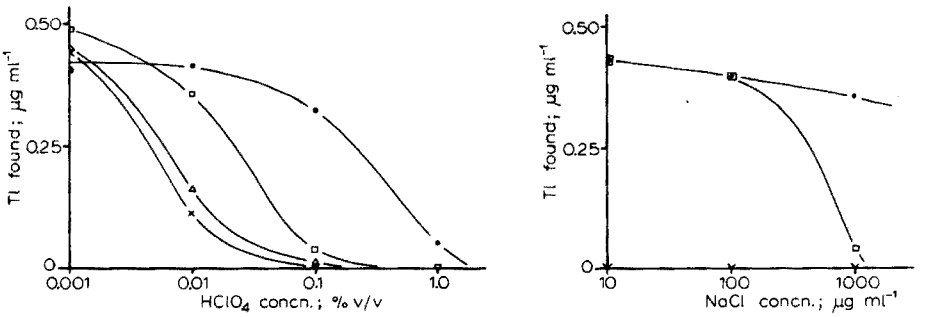

Fig. 3. Effect of added H_2SO_4 and HNO_3 on the determination of 0.5 μg Tl ml^{-1} in the presence of $HClO_4$. Symbols as for Fig. 2.

Fig. 4. Effect of added H_2SO_4 on the determination of 0.5 μg Tl ml^{-1} in the presence of NaCl: (×) no H_2SO_4 added; (□) 0.01 % v/v H_2SO_4; (•) 1.0 % v/v H_2SO_4.

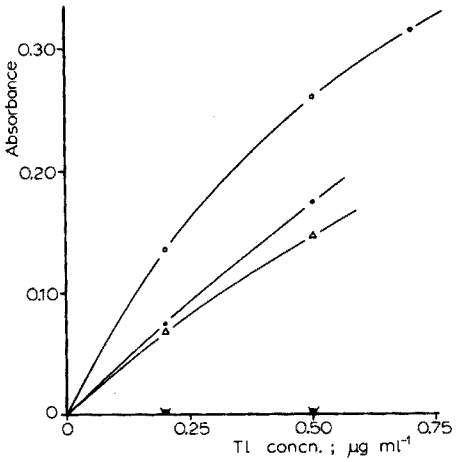

Fig. 5. Calibration graphs for the determination of thallium: (○) 1.0 % v/v H_2SO_4; (×) 10 % v/v urine; (□) 10 % v/v urine + 0.01 % v/v H_2SO_4; (●) 10 % v/v urine + 1.0 % v/v H_2SO_4; (△) 10 % v/v urine + 4.0 % v/v H_2SO_4.

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Short communication

DETECTION OF OZONIZED ORGANIC COMPOUNDS BY THE LUMINOL—PEROXIDE REACTION

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The chemiluminescence induced in the luminol—peroxide system by 1,2-diketones has been described previously [1]. The reaction presumably involves attack by nucleophilic peroxide on one of the carbonyl carbons to give a hydroperoxide that is capable of oxidizing the luminol. While the carbonyl carbon in 1,2-diketones has a relatively large partial positive charge because of the inductive effect of the neighboring carbonyl group, it is much less so for α,β-unsaturated ketones and 1,3-diketones, which do not give the chemiluminescent reaction.

Ozone is known to react with a variety of organic compounds to give keto and aldehydic products. Reactions are rapid and excess of reagent is readily removed from the system. It is feasible, therefore, that ozonization can produce compounds amenable to the luminol—peroxide system.

Experimental

Reagents

The luminol (Aldrich) was 0.0025 M in 0.20 M sodium hydroxide. The hydrogen peroxide (Mallinckrodt 30 %) was diluted (1 + 99) with 0.002 M tetrasodium ethylenediaminetetraacetate. The commercially available test compounds were prepared as 1.0 mg ml^{-1} solutions in water or methanol—water mixtures.

Equipment

The ozonizer (Welch Scientific Co.) consisted of two concentric glass tubes with tin foil coatings serving as electrodes. These were connected to a 1-in. induction coil and a d.c. power source. Air dried over silica gel was used as the source of oxygen.

The chemiluminescence was measured with the Aminco-Bowman spectrophotofluorimeter, with a 1-ml microcell and hypodermic injection as previously described [1].

Procedure

A 5-ml sample was ozonized for 10 min with an air flow rate of about 5 ml s^{-1} followed by a 3-min air purge of the system. Without delay (because of instability of certain of the products) a 0.2-ml aliquot was placed in the microcell and 0.2-ml volumes each of luminol and peroxide were introduced simultaneously. The chemiluminescence was measured at an emission wavelength of 410 nm, with the time—base mode of the instrument. The relative light intensities obtained, duplicate measurements corrected for molecular weight differences, are given in Table 1.

Results and discussions

The results for the ozonized compounds tested are given in Table 1. Ozonization of neat mesityl oxide is reported to give pyruvic aldehyde on hydrolysis [2]. However, the chemiluminescence yield for ozonization of aqueous mesityl oxide is closer in value to that for 1,2-diketones than that for pyruvic aldehyde [1]. The formation of a hydroperoxide via ozonization seems unlikely because only weak chemiluminescence is obtained with luminol in the absence of peroxide. The values for the alicyclic α,β-unsaturated ketones vary widely. Because 1,2-cyclohexanedione gave, as previously reported [1], a much lower yield than 2,3-hexanedione, it is suspected that a significant steric factor may be involved for compounds such as 2-cyclohexen-1-one. The relatively strong chemiluminescence for 1,3-diketones is possibly due to the oxidation of the activated methylene group to give a triketone. The weak chemiluminescence with ozonized 1,3-indanedione and 5,5-dimethyl-1,3-cyclohexanedione may be related to the steric effect for cyclic diones. Alkynes are reported to form 1,2-diketones on ozonation in aqueous solution, e.g. stearolic acid to 9,10-diketostearic acid [3].

TABLE 1

Chemiluminescence of various ozonized organic compounds

Compound	Relative intensity	Compound	Relative intensity
4-Methyl-3-penten-2-one	2800	1,3-Diphenyl-1,3-propanedione	6000
4-Phenyl-3-buten-2-one	3900	2,4-Pentanedione	1100
1-Penten-3-one	720	4,4,4-Trifluoro-1-(2-thienyl)-	
2-Cyclohexen-1-one	20	1,3-butanedione	2100
α-Ionone	830	ββ-Dimethylstyrene	50
β-Ionone	4400	1-Hexyne	100
d-Carvone	610	2,4-Hexadiyne	720
Pulegone	270	Ethynylbenzene	620
Isophorone	180	2-Butyn-1,4-diol	110
		3-Butyn-2-one	120

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Short communication

DUAL-WAVELENGTH SPECTROPHOTOMETRY PART VI. DETERMINATION OF PHENOL IN INDUSTRIAL WASTE AND THE DETERMINATION OF 2,4-DICHLOROPHENOL AND 2,4,6-TRICHLOROPHENOL IN MIXTURES BY FIRST DERIVATIVE SPECTRA

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The merit of recording the first-order differential coefficient of absorbance A or transmission T with respect to wavelength λ, i.e. $dA/d\lambda$ versus wavelength, has been pointed out [1—4] previously. First derivative spectra can be recorded easily by dual-wavelength measurements, if the wavelengths chosen are close to each other (usually 1—2 nm) and scanned simultaneously. Previous papers of this series have given a general discussion of this technique and its applications to various chemical problems; this communication describes its application to the rapid determination of phenol in industrial wastes, and to the determination of 2,4-dichlorophenol and 2,4,6-trichlorophenol in mixtures.

Experimental

Phenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol were purified by conventional methods.

Kaolin K 5 (Acid-washed American standard, Fischer Scientific Co.) was used for the preparation of turbid solutions.

A Hitachi 356 dual-wavelength spectrophotometer was used with 1-cm quartz cells. This apparatus can be used as a dual-wavelength and as a classical double-beam recording spectrophotometer. The baseline was recorded with reference to the pure solvent.

Determination of phenol in turbid solution

Figure 1 shows that the absorption spectrum of phenol in industrial waste is appreciably increased by the absorption of turbid materials, so that an accurate analysis of phenol in turbid solution is difficult by conventional spectrophotometry.

The first derivative spectra of phenol in turbid solutions containing different concentrations of kaolin are shown in Fig. 2, which shows that the distance between the maximum and minimum of the differential coefficient

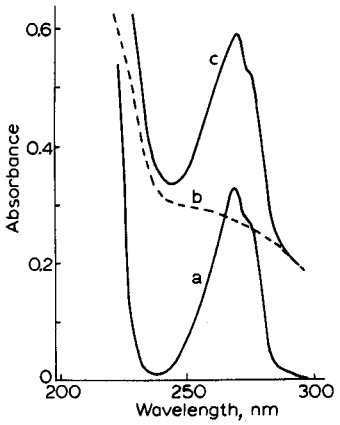

Fig. 1. Absorption spectra of phenol. (a) In aqueous solution. (b) Turbid industrial waste free from phenol. (c) Phenol in turbid industrial waste.

of the absorption band of phenol is constant, i.e. the background underlying the absorption band of interest has been eliminated. For the preparation of calibration curves, values between the baseline and a, between a and b, or between c and d can be taken (see Fig. 3).

The determination of 2,4-dichlorophenol and 2,4,6-trichlorophenol in mixtures

The absorption spectra of these compounds in aqueous solution are shown in Fig. 4. The derivative spectra of mixtures of 2,4-dichlorophenol with 10 p.p.m. and 20 p.p.m. of 2,4,6-trichlorophenol are shown in Fig. 5; the isosbestic point occurs at 312 nm, which corresponds to the maximum absorption wavelength of 2,4,6-trichlorophenol, i.e. $dA/d\lambda = 0$; at this wavelength any change of concentration of 2,4,6-trichlorophenol has no effect

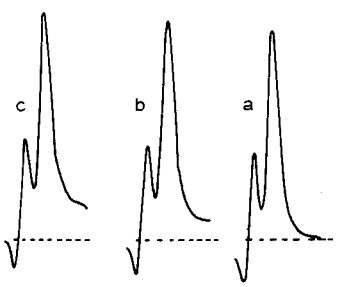

Fig. 2. Derivative spectra of phenol in different concentrations of turbid materials. Turbidity: a < b < c.

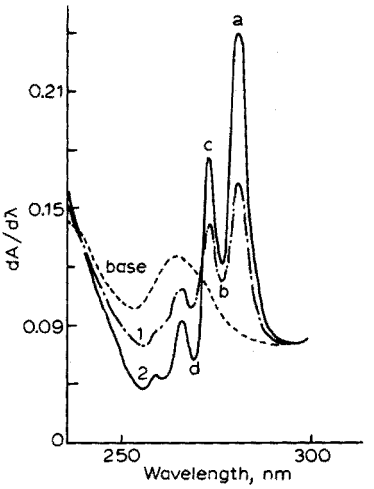

Fig. 3. Linearity of differential coefficient versus concentration; (1) 10 p.p.m. phenol, (2) 20 p.p.m. phenol.

on the determination of 2,4-dichlorophenol, for which a plot of $dA/d\lambda$ is linear over the range 0—15 p.p.m. The derivative spectra of mixtures of 2,4,6-trichlorophenol with various concentrations of 2,4-dichlorophenol are shown in Fig. 6; the differential coefficient $dA/d\lambda$ of 2,4-dichlorophenol is constant at 326 nm, i.e. the effect of concentration of 2,4-dichlorophenol on the value of $dA/d\lambda$ for 2,4,6-trichlorophenol is almost negligible. The apparent value of $dA/d\lambda$ for 2,4,6-trichlorophenol at 326 nm is $dA/d\lambda$ (2,4,6-trichlorophenol) plus k (constant). Thus, in the preparation of the calibration curve for 2,4,6-trichlorophenol, the addition of moderate amounts of 2,4-dichlorophenol is required. At 326 nm a plot of $dA/d\lambda$ for 2,4,6-trichlorophenol is linear over the range 0—20 p.p.m.

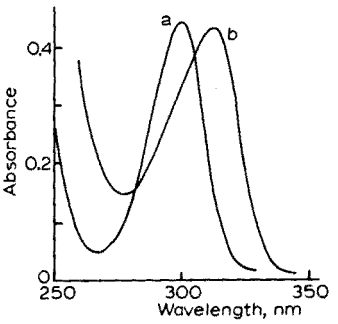

Fig. 4. Absorption spectra of 2,4-dichlorophenol [DCP, (a), 15 p.p.m.] and 2,4,6,-trichlorophenol [TCP, (b), 30 p.p.m.].

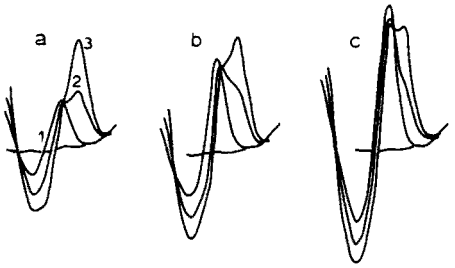

Fig. 5. Derivative spectra of mixture. (a) 1, 5 p.p.m. DCP; 2, plus 10 p.p.m. TCP; 3, plus 20 p.p.m. TCP. (b) 1, 10 p.p.m. DCP; 2, plus 10 p.p.m. TCP; 3, plus 20 p.p.m. TCP. (c) 1, 15 p.p.m. DCP, 2, plus 10 p.p.m. TCP; 3, plus 20 p.p.m. TCP. Slit 0.25 mm, $\Delta\lambda$ = 2 nm.

These theoretical discussions were confirmed by the results shown in Table 1 for various mixtures of DCP and TCP.

TABLE 1

Results for synthetic mixtures

Taken (p.p.m.)		Found (p.p.m.)	
TCP	DCP	TCP	DCP
20.0	0	20.0	0
17.5	2.5	17.2	2.4
15.0	5.0	15.3	5.1
10.0	10.0	10.3	10.2
5.0	15.0	5.3	14.8
2.5	17.5	2.8	17.3
0	20.0	0	20.0

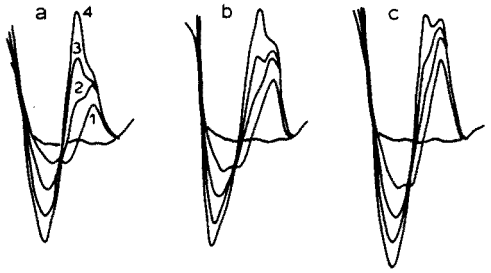

Fig. 6. Derivative spectra of mixture. (a) 1, 10 p.p.m. TCP; 2, plus 5 p.p.m. DCP; 3, plus 10 p.p.m. DCP; 4, plus 15 p.p.m. DCP. (b) 1, 15 p.p.m. TCP; 2, plus 5 p.p.m. DCP; 3, plus 10 p.p.m. DCP; 4 plus 15 p.p.m. DCP. (c) 1, 20 p.p.m. TCP; 2, plus 5 p.p.m. DCP; 3, plus 10 p.p.m. DCP; 4, plus 15 p.p.m. DCP. Slit 0.25 mm, $\Delta\lambda$ = 2 nm.

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Short communication

EFFECTIVE STORAGE OF DILUTE MERCURY SOLUTIONS IN POLYETHYLENE

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Investigators have expressed concern over the storage of natural waters which have mercury solutions of low concentration in polyethylene containers [1—3]. Under these circumstances, by some mechanism, substantial loss of the element occurs. Recently, Feldman [2] carefully examined this problem and established a condition which prevents such loss. Reliable storage in polyethylene was attained by the addition of $K_2Cr_2O_7$ and HNO_3 to the water at a final concentration of 0.05 and 5 %, respectively.

Analysis by neutron activation has shown the mercury content of several batches of high-purity nitric acid (Ultrex, J. T., Baker Chemical Company) to vary from 0.2 to 1 p.p.b. However, the mercury content of certain natural waters is of the order of parts per trillion [4, 5]. Thus acidification as prescribed would demand a substantial blank correction comparable with the mercury inherent in the sample.

Greenland ice has been analyzed for its mercury content [5] and, although the samples had been stored without additives in the liquid state in polyethylene for 6 years before assay, substantial quantities of the element were in solution. After such a lengthy interval, mercury would have been undetectable were the solutions unstable. These bottles received vigorous treatment with concentrated nitric acid before their use [6]. This circumstance together with observations regarding the behavior of mercury in polyethylene containers on neutron irradiation support the suggestion [7] that loss from solution may occur through a reductive process with ultimate diffusion of mercury vapor from the container.

In this study several conditions were examined in order to provide further information on the mechanism of mercury losses from solutions in polyethylene containers. Data are given which demonstrate that natural waters can be stabilized against such losses, by the introduction of a relatively small quantity of the sequestering amino acid, cysteine.

Experimental

Linear polyethylene bottles (1 l) were used as received from the supplier, or were filled with 16 M HNO_3 for 16 h at room temperature or with hot 16 M HNO_3 (89—90 °C) for 1 h, and then rinsed thoroughly with distilled water. Some bottles were filled with demineralized or distilled water and others with these waters adjusted to 0.16 or 1.6 M with HNO_3. Some additional bottles contained only the concentrated nitric acid and still others received melted snow recovered from the North Slope of Alaska (some acidified to 0.16 M with nitric acid), or from Greenland. Other natural waters studied were derived from Sweetwater River, Cuyamaca Lake and San Diego Bay, California. These waters were either examined as collected or pre-filtered through 0.45-μm membrane filters.

Some samples were treated with 1 ml of freshly prepared tin(II) chloride (about 10 ml of 12 M HCl in contact with several g of tin powder for 5 min); certain of the samples that received tin(II) chloride also contained 20 ml of 30 % hydrogen peroxide per liter of solution. In addition, some waters were made 0.3, 1.0, or 3.0 % with sodium chloride and others contained 1, 10, or 100 mg of cysteine per liter.

^{203}Hg activity (as $Hg(NO_3)_2$) was added to each, so that the final mercury concentration was 0.020—0.065 ng ml^{-1}. Immediately on preparation and at various other times, 30.0 g of the solution were decanted into a 50-ml plastic counting vial and the γ-ray activity was measured with a well-type sodium iodide detector coupled to a scaler. Counts corrected for radioactive decay were compared with the initial count to compute the fraction of mercury remaining in solution.

The tin(II)-treated samples were analyzed differently to permit assessment of the degree to which mercury was adsorbed to the container walls. The ^{203}Hg was isolated by the addition of copper nitrate (1 mg) to the sample and subsequent precipitation from solution with copper sulfide [8]. The sulfide was collected on a millipore membrane filter and then dissolved with aqua regia for counting. The walls of the container were also leached with aqua regia. The γ-ray activity of each fraction was compared with appropriate standards.

Results

The effect of bottle pre-treatment and acid concentration upon the storage of dilute mercury solutions in polyethylene containers is shown in Table 1. When demineralized water made 0.16 M with nitric acid was placed in non-acid-leached bottles, significant loss of mercury occurred, compared with the case of bottles soaked in 16 M HNO_3 for 16 h at room temperature. After 14 days, 33.3 and 85.9 % of the mercury remained in the aqueous phase for the respective bottles. Comparison of these data with those of similarly acid-treated bottles containing 0.16 M nitric acid in distilled water shows a

TABLE 1

Mercury remaining in solutions of varying acidity after different storage intervals

Liquid	Bottle treatment	HNO_3 Concn. (M)	Storage time (days)	^{203}Hg recovery (%)
De-mineralized water	Untreated	0.16	2	60.0
			5	49.3
			7	42.7
			12	36.7
			14	33.3
	Acid-leached room temp.	0.16	2	83.0
			7	81.5
			12	85.2
			14	85.9
Distilled water	Acid-leached room temp.	0.0	2	74.9
			9	58.0
		0.16	2	79.6
			4	74.2
			9	63.0
		1.6	5	88.9
			7	88.4
16 M HNO_3	Acid-leached room temp.	16	2	100.0
			21	100.5
			43	99.4
Melted snow (Barrow)	Acid-leached room temp.	0.0	2	85.4
			4	74.9
			7	58.4
			11	45.6
			21	22.5
		0.16	2	90.7
			4	80.3
			7	76.1
			11	64.4
			21	51.0
Distilled water	Acid-leached hot	0.0	3	101.1
			10	98.5
			21	99.7
Melted ice (Greenland)	Acid-leached hot	0.0	2	98.0
			7	97.0
			21	100.0
Lake—filtered	Acid-leached hot	0.0	2	97.6
			9	94.2
			58	80.4
Lake—unfiltered	Acid-leached hot	0.0	2	99.0
			58	94.5

TABLE 1 (continued)

Liquid	Bottle treatment	HNO_3 Concn. (M)	Storage time (days)	^{203}Hg recovery (%)
River—filtered	Acid-leached hot	0.0	2	86.3
			9	84.7
			58	82.3
River—unfiltered	Acid-leached hot	0.0	2	84.6
			9	79.5
			58	51.6
Sea water—filtered	Acid-leached hot	0.0	2	98.8
			9	100.3
			58	103.5
Sea water—unfiltered	Acid-leached hot	0.0	2	97.7
			9	98.9
			58	100.8

difference. Independently of the storage time, the loss of mercury from demineralized water is about 10—15 %; with distilled water the loss is greater and continuous with time. Further, as the acid concentration of distilled water is increased to 1.6 M, the losses diminish. The fraction of mercury retained by acidified melted snow as a function of storage time parallels that of solutions of distilled water of comparable acidity. Again, losses are greater if the snow is not acidified.

If the storage is in concentrated (16 M) nitric acid, preservation is complete for the full observation period of 43 days.

When the containers are leached with hot nitric acid the mercury in both distilled water and melted snow remains quantitatively in solution over the duration of time studied. However, except for sea water, when natural waters that contained mercury were placed in such bottles, loss of mercury was apparent especially in unfiltered river water. When these waters were treated with sodium chloride at a concentration equivalent to that of sea water (3 %), the mercury remained in solution for the 47 days under observation (Table 2).

If tin(II) is added to distilled water contained in hot acid-leached bottles, a rapid dissipation of mercury from solution occurs and only a small fraction of the loss is associated with mercury leachable from the container walls (Table 2). After 3—7 days only about 20 % of the mercury remains in the aqueous phase and about 10 % is associated with the walls. If hydrogen peroxide is added to the distilled water before the introduction of tin(II), the solution is preserved for at least 9 days, but some loss then occurs so that after 47 days only 3.6 % remains in solution and an additional 1.7 % is leachable from the walls.

The influence of cysteine on the storage of mercury in natural waters appears in Table 2. The addition of the 1 mg l^{-1} of this amino acid appears to be insufficient, while 10 mg l^{-1} effects a stable condition.

TABLE 2

Mercury remaining in variously treated solutions contained in either untreated or hot-acid leached bottles

Liquid	Bottle treatment	Solution treatment	Storage time (days)	^{203}Hg recovered (%)	
				From solution	From container walls
Distilled water	Hot-acid leach	$SnCl_2$	0	97.0	—
			3	15.4	15.0
			7	22.1	8.8
		H_2O_2 + $SnCl_2$	7	105.0	—
			9	101.2	—
			47	3.6	1.7
		NaCl (%)			
Lake—filtered	Hot-acid leach	0.3	47	93.3	
		1.0	47	101.1	
		3.0	47	100.5	
Lake—unfiltered	Hot-acid leach	0.3	47	71.6	
		1.0	47	101.2	
		3.0	47	103.3	
River—filtered	Hot-acid leach	0.3	47	83.5	
		1.0	47	94.6	
		3.0	47	99.9	
River—unfiltered	Hot-acid leach	0.3	47	88.2	
		1.0	47	94.0	
		3.0	47	102.9	
		Cysteine (mg/l)			
Lake—filtered	Untreated	10	5	97.6	
			28	100.9	
		100	5	99.0	
			28	100.0	
Lake—unfiltered	Untreated	1	5	101.7	
			28	90.6	
		10	5	101.0	
			28	99.0	
River—filtered	Untreated	1	5	94 5	
			30	95.2	
		10	5	102.6	
			30	98.4	
		100	5	99.0	
			30	99.0	
River—unfiltered	Untreated	1	5	98.4	
			30	96.0	
		10	5	100.3	
			30	102.6	
		100	5	99.0	
			30	99.0	

Discussion

From these results certain inferences can be drawn regarding the mechanism by which mercury is lost from solutions that are stored in polyethylene containers. The protection in storage afforded by nitric acid treatment of the containers and by hydrogen peroxide against the action of tin(II) chloride support the mechanism of loss by a reductive process. Acid treatment of containers, especially with hot nitric acid, apparently eliminates the active interfering sites. The hydrogen peroxide inhibits reduction by tin(II) while a sufficient concentration of peroxide remains in solution. As the peroxide spontaneously decomposes, the influence of the tin(II) is exerted and substantial losses become manifest.

The degree of protection provided to solutions by their treatment with nitric acid is related to the final acid molarity; with the concentrated acid the protection is complete. This action is probably effected through diminution and even complete vitiation of reducing or perhaps adsorbing substances.

The differing losses between demineralized and distilled water in similarly treated bottles may be attributable to the introduction of small amounts of resin material in the demineralization process. This material may exert a stabilizing influence toward the dissolved mercury, also through adsorption.

Even when interfering sites associated with the container are completely eliminated by hot acid treatment certain waters, such as the river and lake waters examined, still suffer losses. Apparently these waters contain reducing agents which transform the ionic form to the free metal with ultimate deposition and diffusion through the walls. When the ionic strength of these natural waters is increased by the addition of sodium chloride to a concentration equivalent to sea water, the loss is prevented, probably because of chloride complexation, so that the change in oxidation potential obviates the effect of the inherent reducing agents.

The stability of the cysteine—mercury complex [9] undoubtedly accounts for the results observed when only a relatively small amount of this amino acid is introduced into natural waters. In the presence of cysteine, the integrity of these waters was maintained even when stored in untreated containers. Thus the stability of this complex is such that it is unaffected by interfering agents in the solution or on the container.

The small quantity of cysteine required to establish a stable solution coupled with the fact that this reagent is available free from mercury provide the prerequisites for suitable treatment. Moreover, under the conditions previously described [8], in solutions containing 10 mg of cysteine per liter, mercury is recovered quantitatively (99.6 ± 0.9 %) by coprecipitation with copper sulfide. Thus cysteine does not interfere with a concentration step in an already developed analytical scheme.

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Book reviews

G. Svehla (Ed.), *Wilson and Wilson's Comprehensive Analytical Chemistry, Vol III*, Elsevier Scientific Publishing Company, Amsterdam, 1975, pp. ix + 399, price $51.95.

Volume III of this now well known series deals with five main topics.

G. Tölg writes on the elemental analysis of very small samples. This is a comprehensive account as befits the general title of the series. It is basically microchemical at the start, giving a fine account of the apparatus and methodology of handling small samples and their analysis for macro-components by conventional chemical techniques. However, the treatment does not stop there, but goes on to deal with trace analysis of very small samples. The gamut of separation and pre-concentration techniques is examined from the minute-sample angle: precipitation, distillation, solvent extraction, ion-exchange, chromatography, and electrophoresis. The applications of gravimetry, titrimetry, absorption and fluorescence spectrophotometry, atomic absorption and fluorescence spectrometry, voltammetry, x-ray — electron beam — and mass-spectrometry as well as radiochemical procedures, are described.

R. A. Chalmers discusses the rôle of standards and standardization in chemical analysis. The treatment is restricted, where it is factual, to a pure chemical basis. The problem of finding standard reference materials for all aspects of analytical chemistry is gigantic and may never be satisfactorily solved. The author directs attention to some of the collaborative work that has been done recently and highlights the problems that have arisen. This essay makes some pungent and relevant comments on the present situation. Much of this chapter merits the role of required reading for all chemistry graduates — not just those specializing in analytical chemistry.

M. Kozlowski and O. Songina write on the use of liquid amalgams in separation chemistry. This is a subject that has not often been reviewed, and this fascinating account should repay close study by most workers who are concerned with preconcentration and separation techniques. The exponents of anodic stripping voltammetry should also find some interesting ancillary information. The relevant areas of application of liquid amalgams in analytical chemistry — apart from their use as valence changers — is in the determination of impurities in high-purity metals, the analysis of alloys, insoluble or weakly dissociated compounds and as a general means of extraction and preconcentration of selected metals.

W. T. Elwell and D. F. Wood discuss comprehensively the determination of gases in metals by vacuum fusion and inert gas fusion. The methodology is described clearly and informatively, and the problems of analysing a wide range of metals are precisely set out. Whilst this chapter may be of more

restricted appeal than some of the others, it unquestionably deserves close scrutiny on the basis of its importance to modern technology.

K. W. Fung and G. Mamantov present a short account of electroanalytical chemistry in molten salt media, which highlights the problems encountered and the advantages gained by being able to study electrochemical phenomena directly in a fused melt. Particular attention is, of course, paid to electrode and cell design, and to the features of the various electroanalytical techniques operated in fused salt media. A series of useful tabular summaries at the end detail techniques, media, analytes, etc., with appropriate literature references.

This volume is somewhat heterogeneous in its subject content, but the articles are excellent and few people would not profit by studying its contents.

T. S. West

G. Svehla (Ed.), *Wilson and Wilson's Comprehensive Analytical Chemistry, Vol IV*, Elsevier Scientific Publishing Company, Amsterdam, 1975, pp. xvii + 374.

In contrast to Volume III, reviewed above, this one has the unifying theme of modern spectroscopic techniques. The text consists of three sections.

I. L. Marr writes a fairly extensive account of instrumentation for analytical spectroscopy, particularly that related to the basic components of source, dispersion and detection. The survey dovetails quite accurately into the work reviewed in the subsequent chapters. This section should prove invaluable to the general reader who must often be perplexed by some of the more specialized items of equipment used in spectroscopy.

G. F. Kirkbright and M. Sargent present a thorough account of flame-based atomic absorption and fluorescence spectroscopy. The historical evolution and background to the two techniques are discussed, and then the essential spectroscopic theory and instrumentation are surveyed. The discussion of flames, experimental techniques and interferences is unusually good and should be of considerable benefit to all who use these methods.

Frei, Frodyma and Lieu survey the much neglected field of diffuse reflectance spectroscopy. The contrast with the immensely successful technique of atomic absorption spectroscopy surveyed in the previous chapter is, of course, quite marked. These authors have the task of describing a technique that is not yet generally accepted but considerable potential for the study of surfaces and materials that are either too opaque to be measured by transmission or are colloidal and, therefore, give rise to scatter problems, etc. The theory of diffuse reflectance spectrometry, variations such as differential reflectance spectrophotometry, and the handling of multicomponent systems are discussed very lucidly, and the

section on instrumentation is thorough. The section on applications shows how wide-ranging a potential the technique has: reflectance measurements have been successful in analyses of pigments, biological materials, building materials, foodstuffs, geological specimens, paper pulp, pharmaceuticals, etc.

The editor's selection of the topics is excellent. The first review provides background information on spectroscopic hardware that is often hard to come by for the non-specialist. The second review provides a particularly fine account of an immensely successful modern technique, whilst the third review deals with a technique which appears to have real significance for the future.

T. S. West

S. Y. Pshezhetskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii and V. I. Tupikov, *E.p.r. of Free Radicals in Radiation Chemistry*, (Translated by P. Shelnitz), Halstead Press—John Wiley and Sons, New York, 1974, viii + 446 pp., price £18.70.

This book presents an account of the identification and study by e.p.r. spectroscopy of organic free radicals formed in radiochemical processes. Inorganic species have been deliberately excluded, the reader being referred to existing texts.

The introductory chapters deal with the absorption of ionizing radiation in the condensed phase and the fundamental principles of e.p.r., with particular emphasis on those features relevant to the trapping of radicals in solid crystalline matrices. The middle portion of the book covers experimental data and mechanism of formation of the radicals produced on irradiation of a variety of organic molecules, starting with hydrocarbons and working through monofunctional organic compounds to binary mixtures and polymers. After a section on the kinetics and mechanism of the destruction of trapped radicals at elevated temperatures, the final part deals with adsorption on solid surfaces and the photochemical reactions of free radicals. For this latter topic the authors have drawn heavily on their own work.

In an attempt to provide a comprehensive literature coverage, all available references have been included. However, the utility of the book in this respect is restricted by the two-year delay between the original Russian publication (1972) and the present edition, with the result that little of the material is less than four years old. Nevertheless, it contains a wealth of information and, though rather expensive, may thus find its way onto research library shelves.

R. M. Paton

Techniques of Electroorganic Synthesis, Part II, Edited by N. L. Weinberg (Techniques of Chemistry, Vol. V), John Wiley, New York, 1975, xiv + 1070 pp., price £22.00.

The emphasis on oxidative processes shown in Part I is continued in this Part in the chapter by N. L. Weinberg on electrochemical halogenation involving oxidation either of a halide or of a substrate. Reductions of many types of organic compound are treated by M. R. Riff in a manner too brief to allow for more than the simplest basic facts. Much more informative is the chapter by R. F. Nelson on N-heterocyclic compounds, which systematizes well the wealth of existing data. The discussion of the synthesis and reactions of organometallic compounds by W. J. Settineri and L. D. McKeever is also innovative. The closing chapter of the text, on polymers by B. L. Funt and J. Tanner seems to offer more practical information than the corresponding chapter in the compendium edited by M. Baizer.

An appendix of 390 pages lists values of half-wave potentials collected by H. Siegerman; solvent system, working electrode and reference electrode are listed but there is no information on techniques, current value or wave-shapes. However, this appendix will prove a useful source of preliminary information and a guide to original publications. The compounds are arranged according to their molecular skeleton and functional groups; this means that structurally related compounds can be compared, but leads to some confusion with polyfunctional compounds.

As in Part I, the tabulated summaries of compounds studied in the different chapters will prove very useful. The absence of an author index, which often can be used as a subject index, is regrettable, but worse is the absence of a detailed name index. The system used makes the location of information on a particular compound rather time-consuming.

This volume, even more than Part I, provides electroanalytical chemists with information on compounds that have been studied and that could be studied by polarography and related techniques. It can be strongly recommended.

P. Zuman

Galen W. Ewing and Harry A Ashworth, *The Laboratory Recorder,* (Laboratory Instrumentation and Techniques, Vol. 1) Plenum Press, New York, 1974, vii + 129 pp., price $21.70.

Few laboratory workers give much thought to their pen recorders, except when the pen jams or the ink ceases to flow. Readers of this useful little book should, however, improve the reliability of their experiments by giving the recorders the attention they deserve. The chapters are devoted to deflection recorders, servo recorders, X—Y recorders, oscillographs, paper feed and writing mechanisms, shielding and grounding, recorder specifications,

troubleshooting, and accessories. Integrators are not discussed in any detail. Commercial sources of recorders are listed in an appendix. The chapter on troubleshooting is perhaps the least satisfactory, but there really is no substitute for reading the appropriate manual.

The instruments are described in simple terms mechanically and electronically, so that this text can be recommended for students and for advanced workers who should have a better appreciation of what goes on behind the chart paper. It is unfortunate that the cost of the book will limit its widespread availability.

A. M. G. Macdonald

International Conference on Modern Trends in Activation Analysis, Edited by T. Braun and E. Bujdosó, Elsevier Scientific Publishing Co., Amsterdam, 1972, 929 pp., price $86.50.

This book is a collection of conference papers in three parts: Generalities and Computer Techniques; Thermal Neutron Activation and Radiochemistry (including biological sciences) and Photon Activation; and Charged Particle Activation and Analysis by Direct Observation of Nuclear Reactions.

There must be little point in producing this book at $86.50 when all the papers have already been published in the *Journal of Radioanalytical Chemistry*, Vols. 15 and 16 (1973). Also the subject matter is so diverse that very few people will want to refer to more than a few specialized papers.

L. G. Earwaker

K. Beyermann (translated by M. M. Abileah), *Chemistry*, Georg Thieme Publishers, Stuttgart, 1975, viii + 374 pp., price D.M. 19.80.

This is the English translation of Beyermann's "*Chemie fur Mediziner*", first published in 1971. The text is a good, unashamedly simple, general introduction to modern chemistry for medical students; useful features for the student are the inclusion of 902 questions which can be answered after careful reading of the text, and pages of formulae, with the compound's name printed on the reverse side of the paper, that can be cut out for revision purposes. The final section is devoted to analytical chemistry. The author has served his readers well by giving a concise account of errors, sampling, separation methods, modern qualitative tests, enzymatic and biological assays, and simple instrumental methods leading up to an elementary account of automation in clinical chemistry and its scope for future development.

This flexicover book is printed on rather inferior paper. The translator has forgotten occasionally to change German symbols and spelling; there is the

normal complement of minor printer's errors. The list of suggestions for further reading is given untranslated from the German version, which largely refers to German texts, and so is not helpful for English-speaking students.

D. M. W. Anderson

Actualites de Chimie Analytique, 23e Serie, Publieés sous la direction de J.-A. Gautier, P. Malangeau et F. Pellerin, Masson et Cie, Paris, 1975, 211 pp., prix 150 F.

This paperback is so flimsily bound that the cover fell off whilst it was being unwrapped and further physical disintegration occurred during the first reading of the text. The book is therefore structurally unsuitable for library use. The extortionate price asked will deter private purchasers, particularly when they are unlikely to be interested in more than one of the reviews that the book contains.

These reviews deal with: (1) Polarographic studies of the reactions of some haloquinones (J. Bonastre and S. Tellier); (2) ion-selective electrodes (J. Mertens et al.); (3) recent progress in organic peroxides in relation to lipids and solvents (V. Karnojitzky); (4) the use of gas chromatography in toxicology and for the analysis of drugs (J. Lebbe); and (5) recent developments in the liquid chromatography of amino acids and peptides (R. L. Munier). The treatment of the various topics is conventional but rather out-of-date. The two most up-to-date chapters contain a few references to work published in 1973, whereas one chapter does not seem to proceed beyond 1969, apart from references to French theses. There are various typographical errors, e.g. Hulanicki has become Hubamichi (p. 51).

This is a prime example of the type of book wherein unrelated miscellaneous reviews are lumped together, presumably in the hope that specialists will buy an extra 180 pages or so to get the few pages they might need. In actuality, only French-speaking readers who do not have reasonable access to the world literature might find this book useful.

A. M. Anderson

Techniques of Electro-Organic Synthesis, Part I, edited by Norman L. Weinberg, (Techniques of Chemistry, Vol. V), Wiley, New York, 1974, x + 917 pp., price £20.00.

The increasing interest in preparative electro-organic chemistry has recently been reflected by an increasing number of monographs covering this field. The book by A. Fry and M. R. Rifi serves as an introduction to the general

topic, whereas the present volume, like that edited by M. Baizer, has a wider approach. Both the latter books aim to cover the topic exhaustively, but, fortunately, this aim has not been accomplished; the pleasant consequence is that the two volumes are complementary rather than competitive, because of the different interests of the individual contributors.

The main emphasis of the present volume is on oxidation processes; 671 pages are devoted to oxidations. N. L. Weinberg discusses oxidation of aromatic compounds, olefinic and acetylenic compounds, phenols and a variety of other systems; R. F. Nelson describes pathways of oxidations of nitrogen compounds, and J. H. P. Utley oxidations of carboxylates. The first part of the text consists of a short introductory chapter by the editor, followed by chapters on experimental methods and equipment (F. Goodridge and C. J. H. King), and on approaches to the study of mechanisms of organic electrode reactions (B. E. Conway and E. J. Rudd). It seems doubtful that the choice of topics for discussion in the latter chapter is the most relevant to the general theme of the book, but such selection always reflects personal interests.

Each of the descriptive chapters is accompanied by extremely useful tabulated summaries of the compounds studied, the conditions used, and the yields obtained. The production is excellent, but an author index would have been useful, as would footnotes indicating where references are to be found.

For electroanalytical chemists with interests in organic analysis, this volume will prove an excellent source of information on the types of compound that can be studied. It can be strongly recommended, so that it is a pity it will be found only in larger libraries because of its cost.

P. Zuman

V. A. Nazarenko, *Analytical Chemistry of Germanium*, Halsted Press — Wiley, New York, 1975, xii + 306 pp., price £12.25.

The IPST editions of this series of original Russian monographs on the analytical chemistry of the elements, begun some years ago, are now appearing fairly regularly as "Halsted Press Books". This volume on germanium is a translation of the Russian edition which was published in Moscow in 1973. The text follows the established pattern of this series and deals in turn with the chemico-analytical characteristics of germanium and its compounds, qualitative reactions of germanium, gravimetric, titrimetric and photometric methods of determination, polarographic, amperometric, spectral and other methods, the determination of germanium in natural and industrial materials, and finally the determination of impurities in germanium and its compounds.

The considerable technical importance of this element, particularly in its

application in electronics, and its recovery from industrial wastes in which it may occur in small quantities, present particular chemical problems which demand accurate analytical data. The present volume describes in sufficient detail the most important methods to be used in particular circumstances, and the analyst is offered a wide range from which to select an appropriate method. In common with other titles in this series, the book contains a comprehensive bibliography (1450 references) with a supplementary list which brings the text up to 1971.

This is a worthy addition to an admirable series of volumes and will prove indispensable to anyone directly concerned with the chemistry and technology of germanium. It will also establish itself as a standard reference source book on the analytical chemistry of this interesting element.

W. I. Stephen

L. Meites and P. Zuman, *Electrochemical Data. Part I. Organic, Organometallic, and Biochemical Substances, Vol. A*, Wiley, New York, 1975, xi + 727 pp., price £17.00.

The literature on polarography and related techniques now contains roughly 35000 references, and assimilation of the vast amount of data contained therein is a problem which has not been solved by international collaboration of the selfless kind which led to the invaluable "Stability Constants" of Sillen and Martell. Professors Meites and Zuman, leading an accomplished team of six collaborators, and supported by the U.S. National Institutes of Health, have now started to ameliorate this situation. The critical compilation of data in this first volume is limited to organic compounds with eleven or fewer carbon atoms and to data published in the period 1960—1971.

The bulk of the book consists of a 480-page Table, in which are given the empirical formula, name and structural formula of the compounds, the solvent, medium pH, ionic strength and temperature for measurements, the electrodes and apparatus used, the characteristic potential, n-value, electrokinetic data, products, reference and appropriate remarks. Table II lists the structural formulae of all the compounds mentioned, Table III (114 pp.) the mechanisms of the half-reactions, and Table IV the names of the compounds in alphabetical order. Table V—VIII are indexes for the functional groups, solvents, techniques and indicator electrodes involved in Table I. Table IX provides a key to literature citations and Table X is an author index.

The authors have set themselves a massive task, which should be of immense value to all interested in electrochemistry. Undoubtedly, this series must be purchased by every large library. Unfortunately, the authors have been ill-served by their publishers. The normally admirable Wiley book

production system has lapsed badly with this volume; the Introduction, which is essential reading if the Tables are to be used properly, and Table I itself (all 480 pages of it) are barely legible because of excessive reduction of the typescript. A magnifying glass is essential equipment for all intending readers unless they have remarkably good eyesight.

The publishers must consider a larger format for subsequent volumes, for this series will be much thumbed in many libraries.

A. M. G. Macdonald

S. S. Nargolwalla and E. P. Przbylowicz, *Activation Analysis with Neutron Generators*, Wiley—Interscience, New York, 1973, 662 pp., price £19.65.

The subject of neutron activation analysis has been tackled by several authors and is usually centred around the nuclear reactor as a neutron source. In this book the authors set out to provide all the information required to set up and operate an accelerator-based neutron activation analysis facility which would fall well within the resources and capability of most industrial or research establishments. In this aim they have succeeded admirably and have produced a well written book crammed full of useful diagrams, graphs and Tables.

The neutron activation analysis technique is described in Chapter 1 along with the advantages, disadvantages, costs and applications. In Chapter 2 the production and interaction of fast neutrons is explored. While being written in terms easily understood by the non-nuclear physicist, much information such as tables of cross-sections and thick and thin target yields which are of use to the expert, is also included. Chapter 3 gives a breakdown on the various types of neutron generator available with details of their neutron-producing targets. Radiation hazards and shielding are treated extensively in Chapter 4 and diagrams of the physical layout of several existing facilities are included as a guide. Chapters 5 and 6 deal with the preparation and transport of samples and the sources and reduction of systematic error respectively.

Probably the most important chapter is the last, which occupies almost half the book. Here each element which can be measured with reasonable sensitivity is tabulated, together with all the data necessary to optimize conditions for its analysis. Equally useful is the list of likely interfering reactions.

Finally, in the appendices the sensitivity of all elements to analysis by thermal, 3-MeV and 14-MeV neutrons is tabulated.

This book is a must for any group contemplating entering the field of neutron activation analysis with accelerators, and would also be of great assistance to established laboratories.

L. G. Earwaker

Analytica Chimica Acta, 81 (1976) 227—228

Announcements

XVIIth INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY, 1976

The XVIIth International Conference on Coordination Chemistry will be held on 6—10 September, 1976, in Hamburg (Federal Republic of Germany). The Conference will be concerned with recent developments of coordination chemistry in the following fields:

1: Structure and bonding.
2: Novel synthetic routes.
3: Kinetics and reaction mechanisms.
4: Catalytic and technological aspects.
5: New types and concepts in coordination compounds.
6: Bio-coordination chemistry.

Further details and registration forms may be obtained from Dr. W. Fritsche, c/o Gesellschaft Deutscher Chemiker, P.O. Box 90 04 40, D-6000 Frankfurt/Main 90 (Federal Republic of Germany).

SIXTH ANNUAL SYMPOSIUM ON RECENT ADVANCES IN THE ANALYTICAL CHEMISTRY OF POLLUTANTS, 1976

The 1976 Symposium on the latest advances in the analytical chemistry of pollutants will be held in Vienna on April 21—23, 1976. This annual symposium has previously been held in Halifax (Canada), Athens (Georgia), Basle and Jekyll Island (Georgia). Once again, scientists from 10 countries have been invited; 3 main lectures on the relations between environmental protection and society, industry and the universities, and 25 specialist lectures on the fields of inorganic and organic trace analysis are planned. Discussions will be organized on the problems of air and water sampling; transport, distribution, and conversion procedures; data compilation.

The Presidents of the meeting, Prof. Dr. H. Malissa, Technische Hochschule Wien, Getreidemarkt 9, A-1060 Wien, and Prof. Dr. R. W. Frei, Postfach 182, CH-4013 Basle, will be pleased to supply further information.

Pittsburgh Applied Analytical Chemistry Award

The Society for Analytical Chemists of Pittsburgh, one of the sponsors of The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, announces the establishment of the "Pittsburgh Applied Analytical Chemistry Award". The Pittsburgh Applied Analytical Chemistry Award will acknowledge important contributions to the literature in the area of applied analysis. Papers published between January 1, 1969 and December 31, 1974 which demonstrate usefulness in solving real problems in analytical chemistry will be considered for the first award in 1976. The annual award will consist of a $1,000 prize and a suitable acknowledgement to the author(s). Papers may be nominated by the author(s) or by any other individual.

The award has been established in order to promote and acknowledge significant contributions to the literature that have a direct application for the practicing analytical chemist. The award will be given annually for a paper published in the previous five years. Once a paper has been nominated, it will be considered each year that the paper meets the publication date criteria.

Further information can be obtained from: Dr. Gerald Walsh
Pittsburgh and Allegheny County
Crime Laboratory
311 Ross Street
Pittsburgh, PA 15219

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Erratum

Elo Harald Hansen and Niels Rhod Larsen, A graphical method for evaluating the dynamic measuring range of potentiometric gas-sensing electrodes, Anal. Chim. Acta, 78 (1975) 459

On p. 459, line 9 of the text should read :

"extremely high selectivity of these sensors. In previous publications on potentiometric . . ."

On p. 460, line 30 should read :

"$p' < p$, e.g. at $pH_s = pK_a - 1$, $p' = 0.1$ where $\mu_s \approx \mu_e$.

On p. 461, the sentence starting on line 5 of the *Discussion* should read :

The theoretical lower sensitivity limit, determined by the ammonia concentration in the electrolyte solution itself, is therefore, for the above two electrolyte concentrations (10^{-1} M and 10^{-3} M), $[NH_3]_s = 6 \cdot 10^{-6}$ M (point 1) and $6 \cdot 10^{-7}$ M (point 2), respectively.

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