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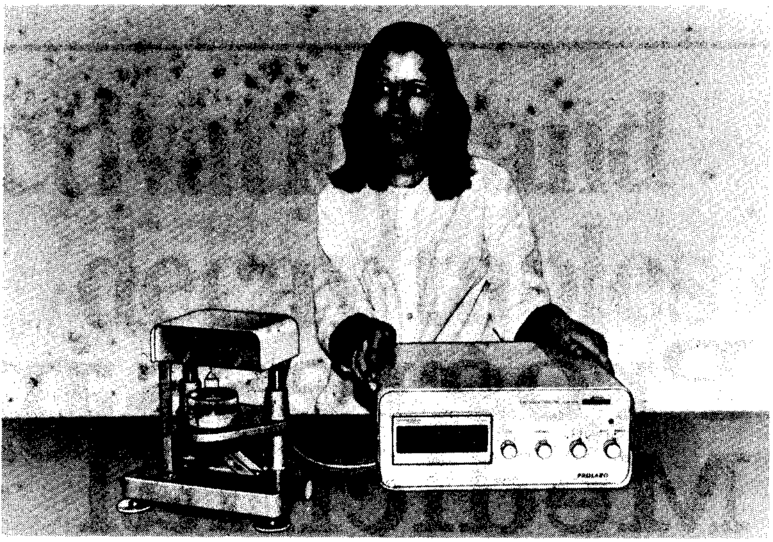

Tensiomètre PROLABO à équilibrage automatique et lecture numérique directe en dyne/cm

›uveau tensiomètre automatique est destiné ie le tensiomètre Dognon-Abribat à la mesure précise des tensions superficielles et inter-es. C'est un instrument élaboré aux possi-ı très étendues:

ıilibrage automatique par le jeu de servo-:anismes.

:ture numérique sans facteur personnel.

:ture directe de la tension en dynes par cm, s aucun calcul.

ıgistrement de la tension superficielle sur un :mètre enregistreur banal, donnant aussi une :ure directe en dyne/cm.

éthode de mesure des tensions mise en e est celle de la lame mouillée ou de l'étrier NF T 73.060, immergé à l'interface liquide-air ou liquide-liquide.

Les mesures peuvent s'effectuer aussi bien en équilibre **statique** (méthode de Wilhelmy) que par arrachement **dynamique.**

Les résultats sont remarquablement **reproductibles;** la sensibilité de l'instrument est de **0,1 dyne/cm.**

Les mesures sont extrêmement **rapides:** à peine la lame ou l'étrier est-il immergé que l'appareil s'équilibre automatiquement, et la tension se trouve affichée sur le cadran en dyne/cm.

Les indications du tensiomètre étant **instantanées,** on peut suivre l'évolution de la tension au cours du temps, et **enregistrer** graphiquement ses variations.

ıls • Les tensions superficielles des liquides, et les tensions interfaciales des liquides entre eux iennent dans tous les phénomènes de surfaces, dans les problèmes de mouillage, de dispersion poudre solide dans un liquide, de dispersion d'un liquide dans un autre liquide peu miscible,

omprend donc l'intérêt du tensiomètre pour l'étude des solutions détergentes, des liquides de ıent de minerais, des bains d'électrolyse, des colles, des peintures et vernis, des catalyseurs, uspensions, des solutions colloïdales, etc... Sant compter l'étude des liquides biologiques.
ısion superficielle des liquides est une constante physique dont la mesure systématique se révèle ıeuse. Elle est à la fois un indice de pureté et de propreté superficielle.
tensiomètre manuel de Dognon-Abribat est un excellent instrument lorsqu'il s'agit de faire diquement quelques mesures ou d'organiser des travaux pratiques d'élèves, on préfèrera le ıau tensiomètre automatique dans les laboratoires de recherches, les laboratoires de mesures ques et les laboratoires de contrôle industriel devant exécuter de nombreuses mesures.
ême tensiomètre convient pour faire rapidement et avec précision des mesures isolées ou en ou pour suivre et enregistrer en continu des tensions variables. Dans beaucoup de problèmes ıues, l'étude des variations de la tension sous l'effet de divers paramètres est du plus haut ıt. Ses qualités offrent des possibilités nouvelles pour l'étude scientifique des tensions super-es et interfaciales et pour son exploitation pratique en milieu industriel.

PROLABO

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Activation and decay tables of radioisotopes

by E. BUJDOSÓ, *Research Institute for Non-ferrous Metals, Budapest, Hungary,* I. FEHÉR, *Central Research Institute for Physics, Budapest, Hungary and* G. KARDOS, *UNIVAC, Division of Sperry Rand France, Paris, France.*

1973. 576 pages. Dfl. 100.00 (about US$38.50) ISBN 0-444-99937-X

With the widening use of radioisotopes in science and industry, the calculation of the activity of a sample irradiated by thermal neutrons and the rate of decay has become a routine task in many laboratories. The book greatly facilitates such calculations by means of tables compiled with the aid of a computer.
Activation and decay data are presented including half-lives, gamma-ray energies and intensities of 249 radioisotopes formed by (n,γ) reactions on 173 stable isotopes of 80 elements.
These clear tables will be of great help in activation analysis and in other investigations connected with the production and use of radioisotopes.

Contents:
Introduction. **Explanation of the Tables.** Nuclear data. Activity calculation. Decay calculation. Data of the table on activation by (n,γ) reactions and on the decay of activity. Calculation of the activation by (n,γ) reactions by use of the tables. Calculation of the daughter activity. Data of the table on daughter element formation. Calculation of the daughter activity by the use of the table. Calculation of the expected counting rates. Key to the numerical values. **Examples of how to use the Tables.** Calculation of the disintegration and counting rates of ^{24}Na produced by the irradiation of sodium. Calculation of the activity of ^{131}I produced by the irradiation of tellurium. **References. Activation and Decay Tables. Index to the Target Nuclides. Index to the Radionuclides.**

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PHYSICAL INORGANIC CHEMISTRY MONOGRAPH

Series editor: M. F. LAPPERT

MASS SPECTROMETRY OF INORGANIC AND ORGANOMETALLIC COMPOUNDS

by M. R. LITZOW, *Union Carbide Corporation, Cincinnati, Ohio, U.S.A.*
and T. R. SPALDING, *Chemistry Department, The City University, London, Engla*

1973. 636 pages. Dfl. 150.00 (about US$52.60) ISBN 0-444-41047-3

Over the past 10 years mass spectroscopic methods have developed rapidly an their significance for chemists interested in inorganic and organometallic con pounds is fully realized. Compounds of almost all the Main Group and Transitio Metal elements have now been studied and some correlations between the effec of structure, electronic configuration and mass spectra are emerging. Therm chemical data is also being obtained on a wide variety of compounds by mas spectrometric techniques.

The present book is the first to cover this expanding field in detail. It is written i two parts, the first dealing in a general way with the basic instrumentation, techn ques and the information obtainable from mass spectrometry. This section will b particularly helpful for readers who are not entirely familiar with the possibiliti of mass spectrometry.

The second part deals with each Main Group and the compounds of Transitio Metals and some Noble gas compounds. The spectra and fragmentation of a larg number of different types of compounds are discussed in full. The general level this second part is for the chemist who uses mass spectrometry as a diagnost tool and is interested in the fragmentation behaviour of the compounds he studie No other book has covered the ground in such detail.

CONTENTS:

PART I. Introduction. Basic instrumentation (M. R. Litzow). Mass spectra and type of ions observed (M. R. Litzow). Information obtainable using mass spectromet (M. R. Litzow).
PART II: Introduction (T. R. Spalding). The Group I elements (M. R. Litzow). Th Group II elements (M. R. Litzow). The main Group III elements (M. R. Litzow). Th main Group IV elements (T. R. Spalding). The main Group V elements (T. R Spalding). The main Group VI elements (M. R. Litzow). The main Group VII element (M. R. Litzow). Compounds of the transition metals (M. R. Litzow). The rare gase (M. R. Litzow). Index.

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LIBRATION TECHNIQUES USED IN THE DIRECT DETERMINATION ATMOSPHERIC METALLIC POLLUTANT LEVELS (10^{-10}–10^{-12} g)

V. ROBINSON* and D. K. WOLCOTT
artment of Chemistry, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)

ceived 15th February 1973)

In the development of a system for direct measurement of metallic air and uid samples by atomic absorption spectroscopy[1–5], it quickly became apparent t calibration of the instrument would be a crucial problem. The average bient air concentrations of most metallic pollutants is 0.1 μg m^{-3} or less, and ce the quantity of air which is sampled by the instrument is *ca.* 50 cm^3, the trument is detecting metals in a range around 10^{-11} g. Calibration techniques st thus be able to introduce these minute quantities into the instrument with od accuracy and precision.

It should also be noted that there are numerous accounts of high sensitivities ng obtained with new atomizing systems. In order for these spectroscopic advances be translated into advances in analytical methods, reliable calibration data st be obtained readily.

To be of maximum versatility, any chosen calibration system should be dely applicable, and it should be rapid, easy to operate, and inexpensive.

An instrument has been developed and previously described which can detect merous metals in the air by atomic absorption spectroscopy. The problem of ating the absorption signal to the concentration of the metal in the air presented ny problems. At this time, it appears that most of these problems have been ercome. It is the purpose of this paper to present the different calibration hniques used in this laboratory.

MOVAL OF IMPURITIES BY SCRUBBING

One of the early methods used for calibration was to scrub air from a npressed air tank and to determine the quantity of metal compounds present. rious scrubbing agents were used[6–8] (depending upon the element of interest) l the scrubbed material was analyzed by standard methods after sufficient terial had been collected to be detected.

The tank air was then analyzed on the instrument used here. The absorption nal obtained was equivalent to the concentration found by analysis of the tank air.

The technique was subject to many difficulties. Depending on the contration levels involved, the period of time required to collect an analyzable sample s always many hours and for some elements was days and even weeks long. The

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[*] To whom correspondence should be directed.

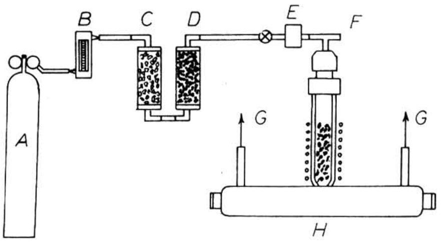
concentration of metal in the air varied from tank to tank and calibration data were not transferable between tanks. Moreover, in some cases, the entire contents of a tank had to be sampled to get a single reading. Many different scrubbing agents were necessary. Finally, after the procedure had been completed, only one point of the relationship between concentration and absorption signal had been obtained. A "calibration curve" was constructed by drawing a second point through the origin and assuming a linear relationship—a hazardous process.

The method was used for the calibration of lead and copper, but was abandoned because of its unwieldiness.

Source of clean air

An essential part of direct analysis for atmospheric pollution levels is a source of clean air to provide a "zero" absorption signal. The system used is shown in Fig. 1. All of the work thus far done has shown that activated charcoal is highly effective for removing contaminants from air streams. A calcium chloride drying column was placed before the charcoal column to remove water vapor; which, if not removed, rapidly reduced the adsorptive capacity of the charcoal. A Millipore filter was placed after the charcoal to trap any particulates or charcoal powder. Indications were that the scrubbing system was highly efficient for removing metallic contaminants from the reference air stream.

Ambient air signals were measured as the difference between the "clean" air stream and the ambient air signal. Data were taken by the addition of known amounts of standard material to clean air.



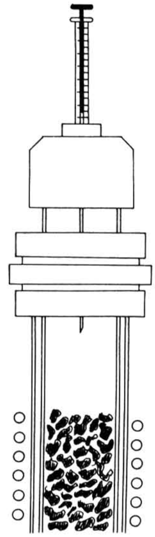


Fig. 1. Schematic diagram of purification train to produce clean air. (A) Compressed air tank; (B) flowmeter; (C) calcium chloride drying column; (D) activated charcoal column; (E) Millipore filter; (F) constant pressure head; (G) exhaust; (H) absorption tube.

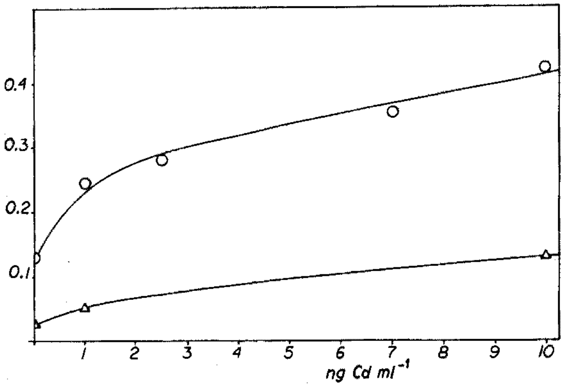
Fig. 2. Liquid injector. A known volume of liquid sample is injected onto the hot carbon bed where atomization takes place.

IRECT DROP LIQUID INJECTOR

A known volume of solution containing a known concentration of the element interest was dropped onto the bed of hot carbon, used for atomization. A icroliter syringe was used for sample introduction (Fig. 2). When the solution ruck the hot carbon, volatilization and atomization occurred, and a "plug" of ee atoms entered the light path. The resulting atomic absorption signal was easured by peak height.

Since atomic absorption depends only on the number of free atoms in the ght path, then, if it is assumed that all atoms in the "plug" enter the light path efore any are swept out, the peak absorbance signal can be related to an ambient r concentration. It can be considered that the number of atoms generated are ntained in the volume of air in the absorption tube. After correcting for mperature, the concentration per unit volume can be calculated. By preparing veral solutions with different concentrations, a calibration curve relating concenation and volume can be prepared.

In practice, it was necessary to introduce quantities of 10^{-11} g or less in ngle drops. Solutions containing 10^{-6}–10^{-9} g ml^{-1} were prepared. It was ecessary to prepare such solutions from more concentrated solutions (1000 p.p.m.) nmediately before use to avoid the problems of sample loss by plating on the ntainer.



ig. 3. Plot of data for aqueous solutions of cadmium. (○) Direct drop; (△) platinum loop.

For cadmium, the 228.8-nm resonance line was used. The sample consisted f 4 μl of cadmium chloride solution containing $4 \cdot 10^{-12}$–$4 \cdot 10^{-11}$ g Cd in eionized water; the gas flow-rate was 200 cm^3 min^{-1}. The results obtained are lotted in Fig. 3. By standard addition the deionized water was found to contain $5 \cdot 10^{-3}$ μg Cd ml^{-1}. By considering the cell volume as $3 \cdot 10^{-5}$ m^3, a calibration urve could be calculated for air samples, as shown in Fig. 4.

Molecular absorption was determined by replacing the atomic line source ith a deuterium lamp and measuring broad-band absorption across the spectral itwidth of the 228.8-nm Cd line. Molecular absorption by the solvent as a nction of flow rate was measured, with a deuterium broad-band source (Fig. 5).

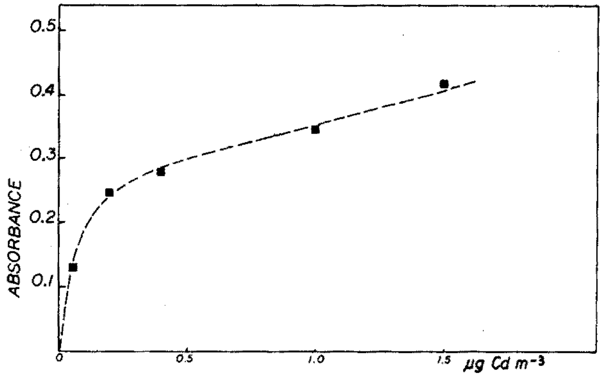


Fig. 4. Calculated calibration curve for cadmium in air samples.

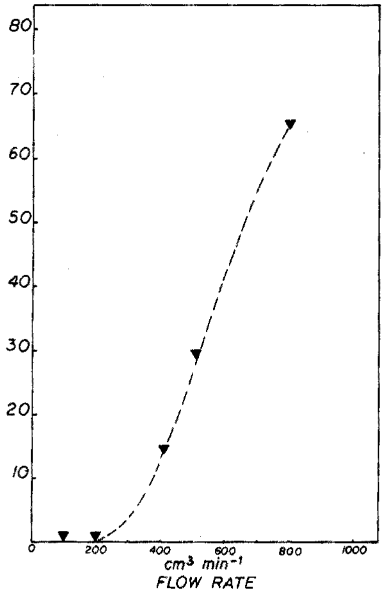


Fig. 5. Molecular absorption as a function of flow rate.

At these concentration levels, impurities normally not noted in water an other solvents become very apparent and can create serious blank problem Preparing sufficiently pure solvents is difficult and at these levels, very ma problems arise. However, it should also be noted that these problems indicate th the method is capable of analyzing "pure" liquids with comparative ease.

The direct drop technique has many advantages. Any soluble compound wi reasonable purity can be used. Since all the drop is used in the measureme any impurities only affect the result to the extent of one degree of impurity. Th is in contrast to evaporation techniques in which they may be preferentially vaporize The method is very rapid, and the cost is minimal.

Precision was about 10% r.s.d., but work is under way to improve t precision, by modification of the microliter syringe. The major source of error w e difficulty of introducing a reproducible volume of liquid. Often a portion would ng up on the syringe tip and not fall on the bed. Molecular absorption by e solvent was observed at air flow rates above 250 cm^3 min^{-1}, but at lower ow rates, combustion of solvent to non-absorbing species was complete, and this roblem was eliminated.

ATINUM LOOP INJECTOR

In another attempt to use liquid solutions for calibration, a platinum loop jector was constructed. In this technique, a microliter sized liquid sample was ringed onto the platinum loop which was placed just below where the syringe p lies in Fig. 2. The loop was then heated to about 1600° by a high-amperage rrent, so that the standard solution was volatilized, the vapor flowing through e atomizer into the light path, and giving rise to an absorbance peak. The peak ight was related to an air concentration, with the same assumptions as described r the mercury vapor "plug" inject and the direct drop technique.

The technique was tested for cadmium under conditions similar to those used ith the direct drop injector. The results obtained are plotted in Fig. 3. As in the rect drop experiment, molecular absorption was monitored with a deuterium road-band source, and was found to be negligible.

The platinum loop injector, like the direct drop, used solutions, was rapid d economical, and easy to use. However, the precision was noticeably poorer an that of the direct drop technique. Also, as the peaks were broader, and peak ight was less than for the same amount of metal by direct drop, it would seem at this method does not fulfill the assumptions necessary to relate peak height air sample concentrations. However, the platinum loop should still be usable for quid samples.

RECT INTRODUCTION ON CARBON CHIPS

In the carbon chip technique, a microliter sample of liquid solution was ringed directly onto a carbon disc Ultracarbon U-7;(1/32 in. thick × 1/4 in. ameter). The carbon chip was then dropped directly onto the carbon bed, where coupled with the r.f. heating field, volatilizing and atomizing the sample. The ee atoms produced an absorbance peak which was related to an air concentration previously described.

The method has wide applicability, and is simple and inexpensive. However, recision was very poor. It was noted that if the solution soaked into the disc ther than remaining on the surface, peak height was much reduced.

The technique was tested for cadmium chloride (2-μl samples) at the 228.8-m cadmium line, with a lamp current of 25 mA and an air flow rate of 200 n^3 min^{-1}. The absorbance arising from blank chips varied from 0.042 to 0.055, hereas that from 2.10^{-10} g Cd varied from 0.771 to 0.958; unfortunately, when e chips were visibly porous (*i.e.* hairline cracks were evident), the measured bsorbance decreased by 30–50%. The discs used were treated by heating for 24 h t 1000° under flowing nitrogen. With this pre-treatment, no molecular absorption ould be expected, and none was observed when the hydrogen lamp was used.

THE USE OF A VAPOR DIFFUSION CELL

The vapor diffusion cell described by Altshuller and Cohen[9], was used calibration of the system for lead, with lead tetraethyl.

The device used is shown in Fig. 6. In operation, lead tetraethyl permea up the long capillary tube into the diluent chamber, where it is dispersed into pure air stream. The rate of diffusion is described by:

$$r = \frac{2.303\, DMPA}{RTL} \log \frac{P}{P-p}$$

where r = diffusion rate, D = molecular diffusion coefficient of vapor, M = molecu weight of vapor, P = total pressure in diffusion cell, A = cross-sectional area of diffusion tube, p = partial pressure of vapor at T, T = temperature, R = gas consta and L = length of diffusion cell.

The diffusion coefficient of tetraethyllead was not available in the literatu

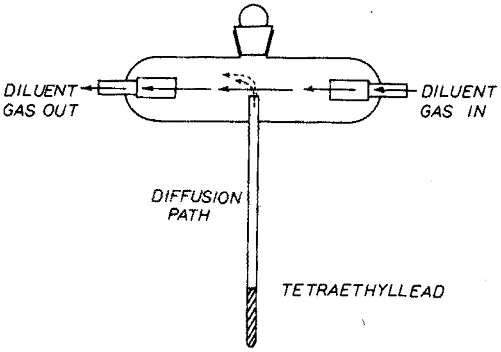


Fig. 6. Evaporation calibration technique developed by Altshuller and Cohen[9]. Tetraethyllea evaporated at a slow, controlled rate into the diluent gas stream. The rate of evaporation is meas by weight loss.

so the rate of diffusion could not be calculated directly. The system was theref calibrated by weight loss. By holding all variables constant except A, it was possi to calibrate several tubes by weight loss and calculate the diffusion rates of smaller tubes. By using several tubes of varying cross-sectional areas (*i.e.*, 1–10 diameter), it was thus possible to obtain a calibration curve.

The diffusion technique is quite useful for calibrating systems for l analysis. However, attempts to extend this technique to other elements were fruitful, owing to the small number of metal compounds with the requisite pur volatility, and stability in air. Moreover, the initial calibration of the diffusion tu was found to be extremely time-consuming, several weeks were necessary to obt a discernible weight loss, and strict temperature control (*i.e.*, ±0.1°) over s extended time periods was difficult. Another serious disadvantage is the prese of impurities, such as hydrocarbons, in the tetraethyllead. They evaporate with metal compound and cause direct error in the measurement of the actual weight tetraethyllead lost during evaporation.

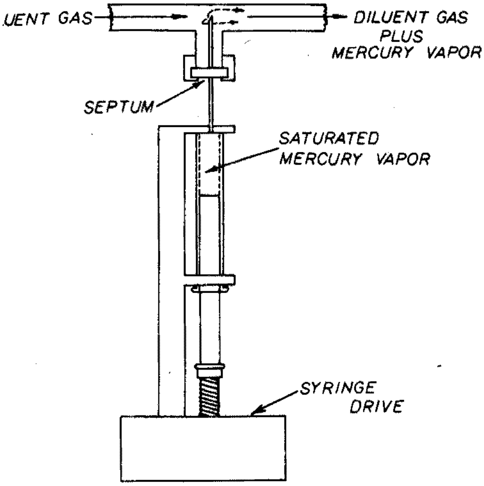
RINGE INJECTION OF VAPORIZED METAL COMPOUNDS

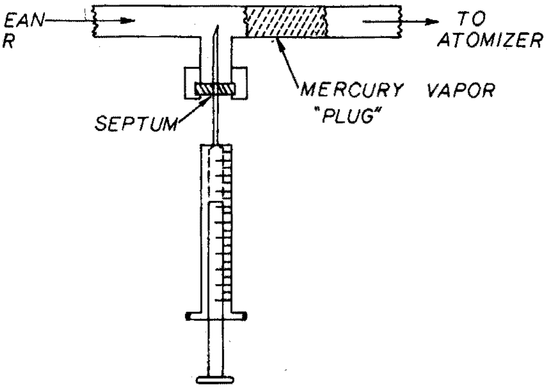
The injection of saturated vapors, both by a motor-driven syringe or by plug jection, was used for calibration of the system for mercury.

In the first technique (Fig. 7), a constant volume of saturated mercury vapor s injected into an airstream flowing at 1.0 l min^{-1} by motor-driven syringe. By rying the speed of the syringe, different concentrations were obtained.

In the second technique, different volumes of saturated mercury vapor were jected directly into the flowing air stream as a plug. Since atomic absorption is lated to the number of absorbing atoms, the peak heights resulting could be lated back to an ambient air concentration by considering the cell volume (Fig. 8).

Both vapor injection techniques are simple to use, and rapid and inexpensive, t they are of an extremely limited nature, applying only to air-stable compounds th high (and accurately known) vapor pressures at room temperature.





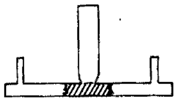
g. 7. Injection of metal vapor (continuous injection). The metal in the form of a vapor is swept at a ntrolled rate into the atomizer.

g. 8. Schematic diagram of the metal vapor injector (plug injection).

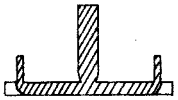
RELATING PEAK HEIGHT TO AMBIENT AIR CONCENTRATION

If the species used for calibration were injected into the atomizat system in such a manner (*i.e.*, "plug" injection) as to give rise to a peak, the p absorbance value (*i.e.*, peak height) can be related to an ambient air concentrat by making the following assumptions: (*a*) atomizer efficiency is equal for "pl injection and steady-state flowing injection; (*b*) all atoms contained in the "pl enter the light path and contribute to the absorbance peak before being swept ou the cell.

If these conditions hold, and since the phenomenon of atomic absorptio related only to the number of free atoms in the light path capable of absorbi the situation is analogous to that shown in Fig. 9. Both plug inject and ambi air signal will be the same.



A. PLUG INJECT—LIGHT PATH
CONTAINS N ATOMS



B. CONTINUOUS INJECT—LIGHT PATH
CONTAINS N ATOMS

Fig. 9. "Plug" injection principle. If the absorbance is the same in cases A and B, the numbe atoms N in the light path is equal in each case. Assuming that N is related to the concentra of metal injected in each case, the concentration of metals in the air can be calculated.

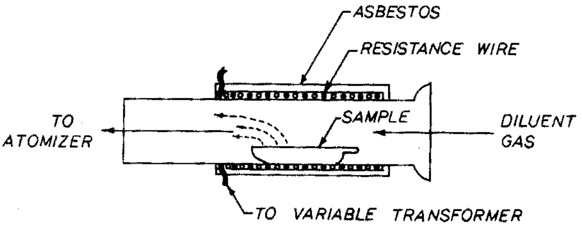


Fig. 10. High-temperature volatilization cell for metals and metal salts.

It is reasonable to assume that condition (*b*) is fulfilled, since the p absorbance is recorded in 1 s or less after injection, and with a cell volume $30\ cm^3$ and a flow rate of $150\ cm^3\ min^{-1}$ the residence time of plug in the should be *ca.* 12 s.

H-TEMPERATURE VOLATILIZATION OF METALS AND SALTS

In this technique, a weighed quantity of pure metal or metal salt was placed porcelain boat inside a small furnace (Fig. 10). The furnace was heated, an stream was passed over the boat to sweep the volatilized metal into the nizer, and the atomic absorption signal was measured. The furnace was then oved and placed in a hood, and the heating conditions were duplicated. The air am was routed through a nitric acid scrubber for two weeks. At the end of that the quantity of metal trapped by the scrubbing solution was analyzed by ventional atomic absorption. By using several furnace temperatures, various ction rates were obtained and the relationship between absorption signal and al concentration was obtained.

The principal advantage of this calibration technique was in its wide range pplicability. Much higher temperature can be used and many more compounds be volatilized.

In practice, however, it was found that the procedure suffered from several dvantages. The most important was the lack of purity of the materials used. ces of slightly more volatile materials were preferentially vaporized. At the very concentration levels encountered in these techniques, these traces were major rces of error because they were present in significant quantities in the vaporized erial. In addition, at the elevated temperatures used, slow chemical reactions veen the standard compound and trace impurities in the atmosphere used to ep the vapor into the atomizer caused secondary reactions and other sources rror.

Another major disadvantage of the method was the long time necessary for procedure. However, successful volatilization was achieved with cadmium ride, cadmium sulfide, cadmium sulfate, lead chloride, lead phosphate, lead onate, mercury(II) chloride, mercury(II) sulfate and mercury(II) nitrate. Diffiies were found with arsenic metal and arsenic trioxide owing to insufficient perature control; and with copper metal (which reacted with traces of oxygen to copper oxide), copper oxide (which did not volatilize), copper(II) chloride iodide (which decomposed to copper oxide), and copper(I) chloride (from ch impurities volatilized preferentially).

CLUSION

Several techniques have been examined for calibration of atomic absorption ems operating at very low concentration levels. The most reliable technique lved dropping microliter quantities of metal solutions onto the atomizer. The tions were made up at various concentrations in the ng ml^{-1} range. The low centrations involved making up fresh solutions immediately before use to inate loss on the sides of the vessel.

This investigation was supported by Research Grant R-800771, Air Pollution trol Office, Environmental Protection Agency.

MARY

Techniques for calibrating atomic absorption systems at low concentration

levels down to 10^{-13} g have been examined. The most reliable method of t examined was the direct injection of a liquid drop (microliter quantities) contai the metal of interest at the ng ml^{-1} level. The dilute solutions were mad immediately before use to avoid problems involved in plating out of the metal o surface of the container. The technique can be used to calibrate the signals obt from ambient air samples.

RÉSUMÉ

Des techniques sont examinées pour permettre le calibrage de syst d'absorption atomique, à des concentrations très faibles de l'ordre de 10^{-13} méthode qui convient le mieux consiste en une injection directe d'un liquid quantité de l'ordre du microlitre, contenant le métal à analyser (ng ml^{-1}). solutions diluées sont traitées immédiatement, pour éviter que le métal ne se dé sur les parois du récipient. Cette technique peut être utilisées pour calibre signaux obtenus avec des échantillons d'air ambiant.

ZUSAMMENFASSUNG

Es wurden Verfahren für die Eichung von Atomabsorptionssysteme niedrigen Konzentrationen bis zu 10^{-13} g herab geprüft. Die zuverlässigst untersuchten Methoden war die direkte Injektion eines flüssigen Tropfens i Grössenordnung von Mikrolitern, der das betreffende Metall im Konzentrat bereich ng ml^{-1} enthielt. Die verdünnten Lösungen wurden unmittelbar vo Verwendung bereitet, damit Schwierigkeiten durch die Abscheidung des M an der Gefässoberfläche vermieden wurden. Das Verfahren kann auf die Eichun Signalen angewendet werden, die bei Proben der Umgebungsluft erhalten we

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TERMINATION OF TERBIUM AND DYSPROSIUM BY ATOMIC SORPTION SPECTROMETRY

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With increasing demand for rare-earth elements for industrial purposes, id and accurate analytical methods for individual rare-earth elements in the sence of other rare-earth elements are of growing importance. Terbium and sprosium have been determined by spectrophotometry, emission spectrography, me emission spectrometry, atomic absorption spectrometry, X-ray fluorescence ctrometry, X-ray or electron excited luminescence spectrometry, neutron activa- n, mass spectrometry, etc. Among these analytical methods, atomic absorption ctrometry has several advantages, such as easy pretreatment of a sample, easy eration of the instrument, and freedom from spectral interferences.

Several investigators[1–8] have studied the atomic absorption behavior of bium, dysprosium and other rare-earth elements. A few studies of matrix cts on such determinations and of practical determinations of individual rare- th elements in rare-earth mixtures by atomic absorption spectrometry have been orted[6,7], but no details have been published for terbium and dysprosium.

In this work, the effects of several inorganic acids, common metal ions, e-earth elements and organic solvents on the atomic absorption of terbium d dysprosium were studied, and terbium and dysprosium were determined in thetic and practical samples.

PERIMENTAL

paratus

A Nippon Jarrell-Ash model AA-1E atomic absorption–flame emission ctrometer with a nitrous oxide–acetylene flame slit burner was used. Varian- chtron hollow-cathode lamps for terbium and dysprosium were used as radiation rces. A John Fluke 415B high-voltage power supply was used to power a V R-106 photomultiplier. A preamplifier, based on Philbrick-Nexas operational plifiers and a Yokogawa-Hewlett Packard 4403 tuned null detector, was used amplify the output of photomultiplier. A National VP-654A pen recorder s also used.

agents

Stock solutions containing 20 mg ml^{-1} of terbium or dysprosium were pared by dissolving these oxides (Shin-Etsu Chemical Co., 99.99% purity) in *M* hydrochloric acid. Other rare-earth stock solutions were prepared by dissolving the rare-earth oxides (Shin-Etsu Chemical Co., 99.9 or 99.99% pu in hydrochloric acid. All other chemicals were prepared from analytical-g reagents (Wako Pure Chemicals).

Procedure

The optimal experimental conditions were established by atomizing solut containing 300 p.p.m. terbium and 100 p.p.m. dysprosium, respectively (Tabl

TABLE I

EXPERIMENTAL CONDITIONS

	Terbium	*Dysprosium*
Wavelength (nm)	432.6	404.6
Slitwidth (μm)	100	100
Spectral bandwidth (nm)	0.16	0.16
Combustion gas flow rate (l min^{-1})		
N_2O	6.7	6.7
C_2H_2	4.6	4.6
Hollow-cathode lamp current (mA)	16	16
Observation height above the burner head (mm)	7	7

RESULTS AND DISCUSSION

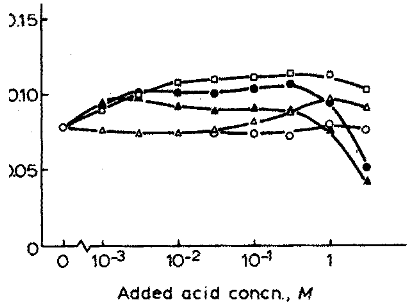
Effects of inorganic acids

In the determination of terbium and dysprosium in various samples, samples must be dissolved in inorganic acids, the kind and concentratior which must therefore be considered. The effects of several inorganic acid concentrations of 10^{-3}–3 *M* on the absorption of terbium (300 p.p.m.) dysprosium (100 p.p.m.) were investigated. The acids used were hydrochl acid, nitric acid, perchloric acid, sulfuric acid and phosphoric acid. The res are shown in Figs. 1 and 2.

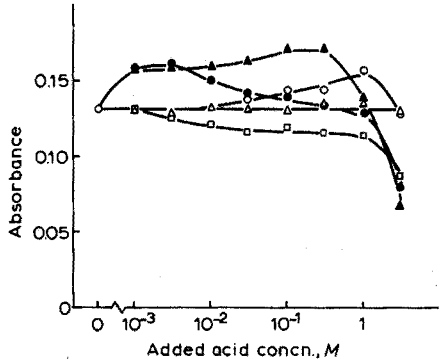
Hydrochloric acid up to 3 *M* and nitric acid up to 0.1 *M* had little e on the absorption of terbium. Nitric acid at 0.3–3 *M* increased the absorp by 15–25%, perchloric acid at $3 \cdot 10^{-3}$–3 *M* by 30–45%, sulfuric acid at 10^{-3} *M* by 20–35%, and phosphoric acid at 10^{-3}–0.3 *M* by 15–25%. Sulfuric acid at decreased the absorption by 35%, and phosphoric acid at 3 *M* by 45%.

Nitric acid up to 3 *M* did not affect the absorption of dyspros Hydrochloric acid at 0.1–1 *M* increased the absorption by 10–20%, sulfuric at 10^{-3}–0.1 *M* by 10–20%, and phosphoric acid at 10^{-3}–0.3 *M* by 20– The absorption decreased gradually with increasing concentrations of perchl acid, a 35% decrease being observed at 3 *M* perchloric acid. Sulfuric aci 3 *M* decreased the absorption by 40%, and phosphoric acid at 3 *M* by 50%.

It can be seen that hydrochloric, nitric and perchloric acids each different effects on the absorption of terbium and dysprosium.



. 1. Effects of inorganic acids on the absorption of terbium. Tb concn. 300 p.p.m. (○) HCl,) HNO_3, (□) $HClO_4$, (●) H_2SO_4, (▲) H_3PO_4.



. 2. Effects of inorganic acids on the absorption of dysprosium. Dy concn. 100 p.p.m. (○) 1, (△) HNO_3, (□) $HClO_4$, (●) H_2SO_4, (▲) H_3PO_4.

fects of metal ions

Some common metals, as well as other rare-earth metals, were selected study interfering effects on the absorption of terbium and dysprosium; the ıcentrations studied ranged from 10 to 10000 p.p.m. with 300 p.p.m. terbium 100 p.p.m. dysprosium. The common metal ions used were Li, Na, K, Mg, , Sr, Ba, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Al. The results are shown in ;s. 3 and 4.

The absorption of terbium decreased in the presence of 30–300 p.p.m. of following metal ions, but increased by 25–90% in the presence of 3000–10000 .m.: Li, Na, K, Mg, Ca, Cr, Mn, Fe, Ni and Pb. Zinc (30–3000 p.p.m.) reased the absorption. The absorption almost doubled in the presence of 1000–)00 p.p.m. strontium. The absorption increased with increasing concentrations barium; 10000 p.p.m. increased the absorption by 90%. Copper up to 300 .m. had little effect but 1000–10000 p.p.m. increased the absorbance by 40–50%. absorption increase of 35% was caused by 300 p.p.m. aluminum but a rease of 70% was caused by 10000 p.p.m.

The absorption of dysprosium decreased by 25–75% in the presence of)0–10000 p.p.m. of Li, Na, K, Mg, Ca, Sr, Ba and Cr. The presence of)0–10000 p.p.m. manganese or lead increased the absorption by 20–40%. Iron, kel, copper and zinc up to 10000 p.p.m. had little effect. The absorption in- ased by 25–40% in the presence of 100–300 p.p.m. of aluminum, but decreased 65% in the presence of 10000 p.p.m.

The absorption of terbium and dysprosium increased with increasing con- ıtrations of other rare-earth elements. The presence of 3000 p.p.m. of these reased the absorption of terbium by 70–100% and that of dysprosium by -80%. As shown in Fig. 4, the effects of the other rare earths on the sorption of terbium and dysprosium were mainly classified within three groups.

fects of organic solvents

The effects of alcohols on the absorption of terbium (300 p.p.m.) and

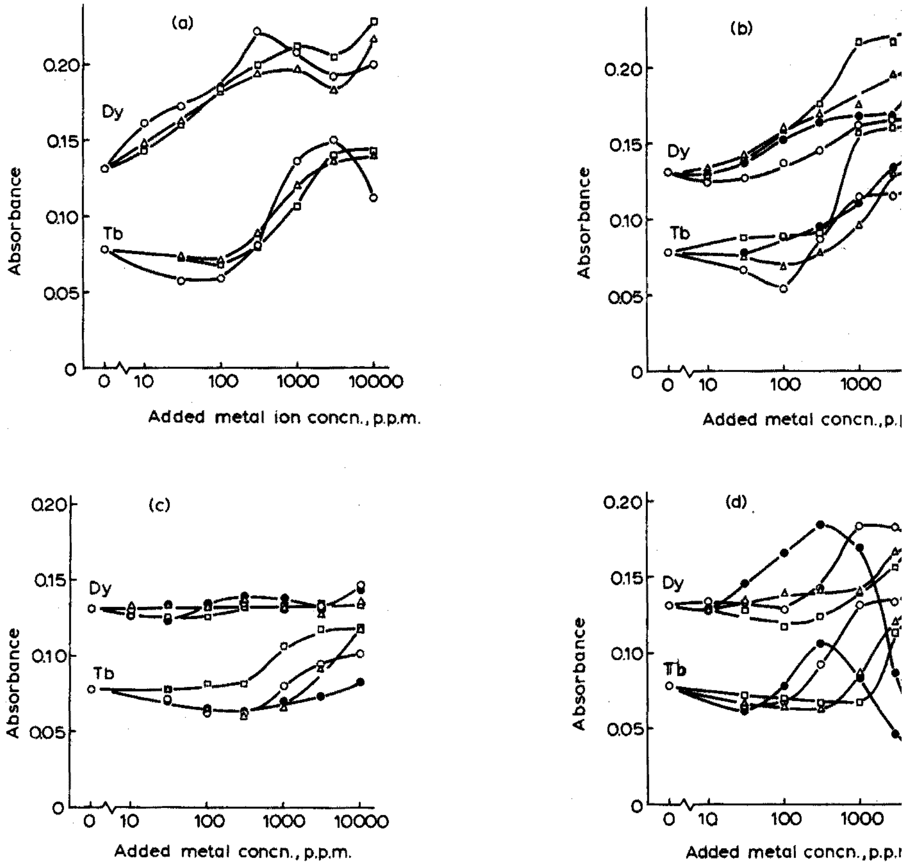


Fig. 3. Effects of common metal ions on the absorption of terbium and dysprosium. Tb 300 p.p.m.; Dy concn. 100 p.p.m. a: (○) Li, (△) Na, (□) K. b: (○) Mg, (△) Ca, (□) Sr, (c: (○) Fe, (△) Ni, (□) Cu, (●) Zn. d: (○) Cr, (△) Mn, (□) Pb, (●) Al.

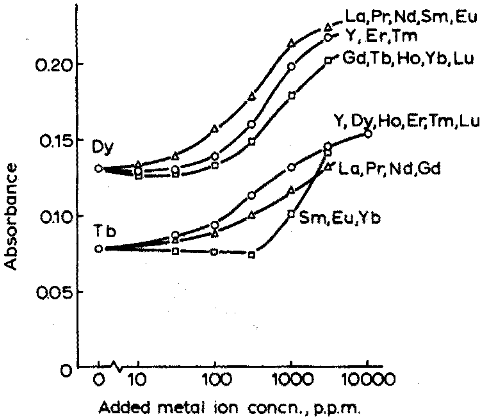


Fig. 4. Effects of rare-earth elements on the absorption of terbium and dysprosium. Tb conc p.p.m.; Dy concn. 100 p.p.m.

ABLE II

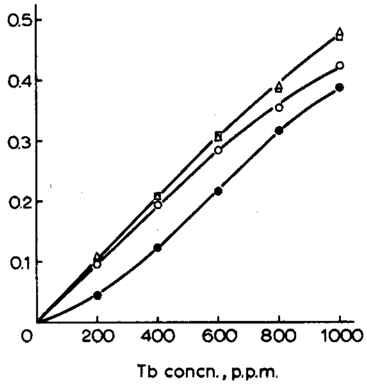
FFECTS OF ALCOHOLS ON THE ABSORPTION OF TERBIUM AND DYSPROSIUM

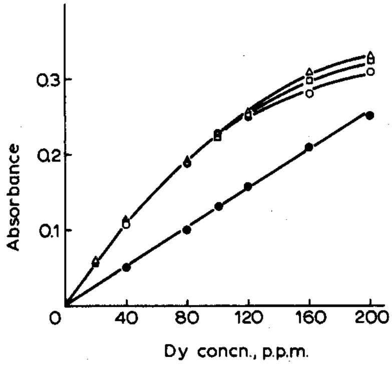
olvent (v/v %)		*Absorption ratio*	
		Terbium	*Dysprosium*
queous		1.00	1.00
lethanol	40	1.03	0.80
	80	1.82	1.77
	95	1.95	2.58
thanol	40	0.92	0.69
	80	1.52	1.42
	95	2.01	2.19
ropanol	40	1.15	0.91
	80	1.29	1.05
	95	1.55	1.39

ysprosium (100 p.p.m.) were investigated. Methanol, ethanol and propanol were sed in amounts of 40, 80 and 95% in volume. Table II shows that the resence of 40% alcohol tended to decrease the absorption, particularly for ysprosium, whereas 80%–95% alcoholic solutions caused marked increases for both ietals.

'alibration curves

Calibration curves for terbium in the range 0–1000 p.p.m. and dysprosium 1 the range 0–200 p.p.m. are shown in Figs. 5 and 6. Curves were prepared or terbium or dysprosium alone, and for terbium or dysprosium with addition f 1% potassium, 1% yttrium, or 1% lanthanum. The calibration curve for rbium alone (Fig. 5) was concave in the range 0–400 p.p.m. and convex in





ig. 5. Calibration curves for terbium. (●) Tb alone, (○) Tb+1% K, (△) Tb+1% Y, (□) Tb+1% a.

ig. 6. Calibration curves for dysprosium. (●) Dy alone, (○) Dy+1% K, (△) Dy+1% Y, (□) y+1% La.

the range 800–1000 p.p.m.; the sensitivity was increased by addition of potassi yttrium or lanthanum, the curves becoming linear in the range 0–600 p.p.m., still bending slightly in the range 600–1000 p.p.m..

The calibration curve for dysprosium alone (Fig. 6) was linear in range 0–200 p.p.m.; the additives increased the sensitivity but greatly decrea the linear range.

Analysis of synthetic samples

Samples containing various amounts of terbium and dysprosium oxi were made up with yttria as shown in Table III. The total concentration Tb_4O_7, Dy_2O_3 and Y_2O_3 in each sample solution was 1 g/100 ml. Sample soluti containing high concentrations of terbium or dysprosium were diluted to appropriate concentration for the atomic absorption measurements, and 1% potassium ion was added to this solution for both terbium and dysprosi The results obtained are shown in Table III. The values found for terbium

TABLE III

RESULTS FOR TERBIUM AND DYSPROSIUM IN SYNTHETIC SAMPLES[a]

Sample no.	*Tb_4O_7 concn.*			*Dy_2O_3 concn.*		
	Theoretical (%)	*Found (%)*	*Relative error (%)*	*Theoretical (%)*	*Found (%)*	*Relative error (%)*
1	30.0	29.2	+2.7	0.1	0.10	0
2	10.0	10.5	+5.0	0.3	0.31	+3.3
3	3.0	3.10	+3.3	1.0	0.97	−3.0
4	1.0	0.96	−4.0	3.0	2.85	+5.0
5	0.3	0.31	−3.3	10.0	10.3	+3.0
6	0.1	—	—	30.0	30.3	+1.0

[a] Sample composition: the amounts of Tb_4O_7 and Dy_2O_3 taken are given in columns 2 and the Table; in all cases, the composition was made up to 100% with Y_2O_3.

TABLE IV

RESULTS FOR TERBIUM AND DYSPROSIUM IN SAMPLES OF RARE-EARTH OXIDES[a]

Sample no.	*Tb_4O_7 concn.*			*Dy_2O_3 concn.*		
	Concn. (%)	*s_r (%)*	*by FE[b] (%)*	*Concn. (%)*	*s_r (%)*	*by FE[b] (%)*
1	1.27	6.0	1.38	3.98	2.7	4.08
2	0.76	6.0	0.94	2.36	1.2	2.45
3	—	—	—	0.71	2.3	0.74
4	—	—	—	0.04	6.6	0.04
5	0.41	4.9	0.33	0.58	4.1	0.61

[a] Each value is the mean of 5 determinations.
[b] Values measured by a flame emission method.

he range 0.3–30.0% Tb_4O_7 had a relative error of +5.0 to −4.0% compared o the theoretical values; 0.1% Tb_4O_7 could not be determined accurately. The alues found for dysprosium in the range 0.1–30.0% Dy_2O_3 had a relative error f +5.0 to −3.0% compared to the theoretical values.

nalysis of rare-earth oxides

Terbium and dysprosium were determined in practical samples of rare-arth oxides (a crude grade material used in an ion-exchange separation process). he rare earth oxides (1 g) were dissolved in hydrochloric acid, and diluted o a volume of 100 ml. The results (Table IV) are considered to be satis-actory, and are in good agreement with results obtained by a flame-emission ethod.

UMMARY

For the determination of terbium and dysprosium by atomic absorption pectrometry, the effects of several inorganic acids, metal ions and alcohols were tudied. The two metals were determined in the presence of yttria and in rare-arth oxides with satisfactory results.

ÉSUMÉ

Une étude est effectuée sur la spectrométrie par absorption atomique du rbium et du dysprosium. On examine l'influence de divers acides inorganiques, e divers ions métalliques et des alcools. Les dosages de ces deux métaux ont onné des résultats satisfaisants, en présence d'oxyde d'yttrium et d'oxydes de rres rares.

USAMMENFASSUNG

Der Einfluss von verschiedenen anorganischen Säuren, Metallionen und lkoholen auf die Bestimmung von Terbium und Dysprosium durch Atom-bsorptionsspektrometrie wurde untersucht. Die beiden Metalle konnten in Gegen-art von Yttriumoxid und in Seltenerd-Oxiden mit zufriedenstellenden Ergebnissen estimmt werden.

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PRECISE SPECTROPHOTOMETRIC DETERMINATION OF A MAJOR ONSTITUENT IN PURE MATERIALS

PPLICATION TO PURE MAGNESIUM METAL

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Gravimetric methods of analysis are more precise than other techniques, but e tedious in operation and are not always accurate because of coprecipitation. olorimetric methods are superior to titrimetry in rapidity but inferior in precision, so at colorimetry is not suitable for the determination of major constituents. trimetric procedures also often lack sufficient precision for the determination of the ajor constituent in highly pure materials, because of difficulties in end-point tection.

The aim of the work described here was to achieve a precision in colorimetry ith an ordinary spectrophotometer the same as, or better than, the precision tainable in titrimetry; and then to extend this method to a direct colorimetric say of a pure substance, the purity of which had been indirectly determined reviously by subtracting the whole content of impurities from 100%. If this new olorimetric technique can be applied for assay purposes in manufacturing processes, he method would provide a convenient means of quality control for pure products.

eneral outline of the proposed method

A sample is dissolved to give a solution containing a suitably large amount of he principal metal constituent. After the pH of this solution has been adjusted, most all of the metal is masked by the accurate addition of an amount of a helating agent. The small excess of metal ion remaining is then determined pectrophotometrically with an appropriate colour-developing agent.

If 99.9% of the metal has been reacted with the chelating agent, and the esidual 0.1% of the metal is spectrophotometrically determined with a relative recision of better than 1%, the final relative error of the proposed method should be ss than 0.001%. Of course, the chelating agent cannot be added without the ntroduction of some error, but the total error in the proposed method is smaller han that attainable in titrimetric analysis, even if the volumetric errors in this method are almost the same as those in titrimetry, since judgement of the quivalence point affects directly the results in titrimetry.

heory

The optimal conditions, *i.e.*, the pH and the concentrations of the metal to be determined, the chelating agent and the colour-developing agent, can predicted from a theoretical spectrophotometric titration curve of the metal which the chelating agent corresponds to a titrant and the colour-develop agent to a metallochromic indicator.

The following symbols are used here.

M	Free ion of a metal to be determined.
L	Free ligand or chelating agent for the metal.
I	Free metallochromic reagent.
ML and MI	Metal–ligand chelate and metal–metallochromic reagent comp respectively.
K_L and K_I	Apparent stability constant of ML and MI, respectively.
C_M, C_L and C_I	Total concentrations of the metal, the chelating agent and metallochromic reagent, respectively.
A	The absorbance at a certain wavelength.
ε_{MI}	Apparent molar absorptivity of the MI complex at this wavelen
ε_I	Apparent molar absorptivity of the metallochromic reagent itsel this wavelength.
Y	Ratio of [MI] to [I].

The following equations can be obtained:

$$K_LY^3+(K_L+C_IK_IK_L+K_I-C_MK_IK_L+C_LK_IK_L)Y^2$$
$$+K_I(C_IK_I-C_MK_I+1-C_MK_L+C_LK_L)Y-C_MK_IK_L=0$$

$$A=\varepsilon_{MI}[MI]+\varepsilon_I[I]=C_I/(1+Y)$$

If definite values for K_L, K_I, C_L, C_I and C_M are introduced into eqn. (1), Y value can be obtained from the computer programme described in a previc paper[1], in which $\alpha=[MI]/C_I=Y/(1+Y)$. The absorbance at a certain waveleng A is then calculated from eqn. (2).

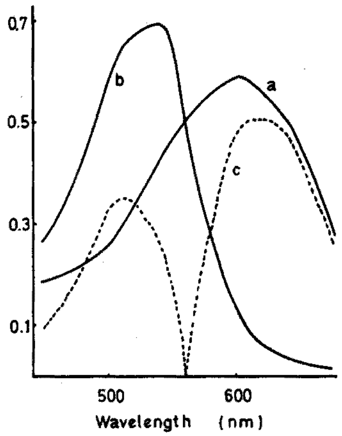
Optimal conditions for the determination of purity of magnesium

To a solution containing magnesium at *ca.* pH 10 are added ethylenediamii tetraacetic acid (EDTA) as the chelating agent and 1-(1-hydroxy-4-methyl phenylazo)-2-naphthol-4-sulfonic acid (calmagite) as the colour-developing reage The final concentration of each can be denoted by C_M, C_L and C_I, respective

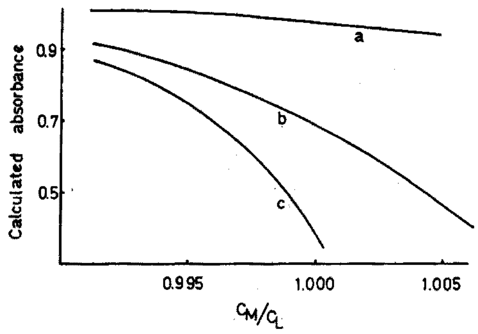
The absorption spectra of calmagite and the magnesium–calmagite compl are shown in Fig. 1. The difference of absorbance between the magnesium compl and the reagent blank shows maxima at 510 nm and 620 nm, the latter bei larger than the former. In this work, the absorbance at 620 nm was measure this corresponds to the concentration of the free calmagite [I]. The mo absorptivities of calmagite (ε_I) and the magnesium–calmagite complex (ε_{MI}) w experimentally found to be $1.12\cdot10^4$ and $1.10\cdot10^3$ at 620 nm.

For the given conditions, the absorbance at 620 nm (A) can be calcula from eqns. (1) and (2), and an absorbance curve can be drawn against the value C_M/C_L; this plot corresponds to a kind of titration curve.

Concentration of the metal to be determined. The change of the absorbance shown against a small change in the C_M/C_L ratio in Fig. 2; in each case, pH 10 and $C_I=10^{-4}$ M, whereas C_M is 10^{-1}, 10^{-2} and 10^{-3} M. The worki



g. 1. Absorption spectra. (a) Calmagite, $5 \cdot 10^{-5}$ *M* against water; (b) magnesium–calmagite complex, 10^{-5} *M* against water; (c) difference of absorbances between (a) and (b).

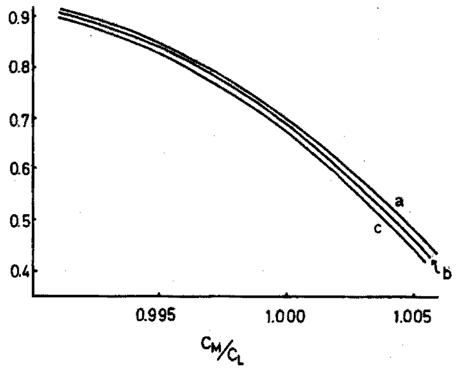


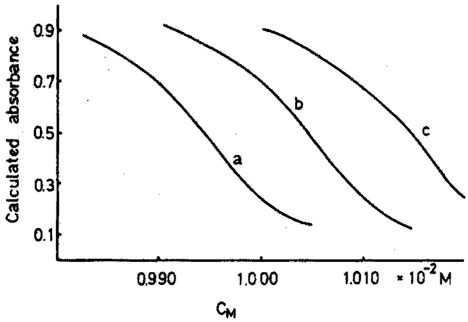
g. 2. Effect of C_M on working curve for $K_L = 10^{8.2}$, $K_I = 10^{5.7}$, $C_I = 10^{-4}$ *M* and $C_L \approx C_M$. C_M:) 10^{-3} *M*; (b) 10^{-2} *M*; (c) 10^{-1} *M*.

rve is flat when C_M is 10^{-3} *M*, but is too sensitive when C_M is 10^{-1} *M*. A mbination of $C_M = 10^{-2}$ *M* and $C_L = 10^{-2}$ *M* seems to be optimal, because the rve is almost linear and covers the expected range of the variation of the etal concentration.

Concentration of the chromogenic reagent. The effect of C_I on the working rve was investigated for pH 10 and $C_L \approx C_M \approx 10^{-2}$ *M*. As shown in Fig. 3, variation C_I of *n*% results in a relative error of 0.005·*n*% for the magnesium conntration of the sample.

Effect of pH. For $C_L \approx C_M \approx 10^{-2}$ *M* and $C_I = 10^{-4}$ *M*, plots similar to ose shown in Fig. 3 (with corrected K_L and K_I values for change in pH)





g. 3. Effect of C_I on working curve for $K_L = 10^{8.2}$, $K_I = 10^{5.7}$ and $C_L \approx C_M \approx 10^{-2}$ *M*. C_I: (a) 1·10^{-4} *M*; (b) 1.00·10^{-4} *M*; (c) 0.99·10^{-4} *M*.

g. 4. Effect of C_L on working curve for $K_L = 10^{8.2}$, $K_I = 10^{5.7}$, and $C_I = 10^{-4}$ *M*. C_L: (a) 0.99·10^{-2} *M*;) 1.00·10^{-2} *M*; (c) 1.01·10^{-2} *M*.

indicated that a variation of 0.1 in the pH gives an error of 0.005% for t concentration of magnesium.

Concentration of the chelating agent. As seen in Fig. 4, a variation in C_L n% gives a relative error of n% in the magnesium concentration of the samp The precision of the proposed method depends mainly on the constancy of t concentration of the chelating agent.

Although the chelating agent is measured with a pipette and diluted in volumetric flask, it is not very difficult to control the precision of measureme with a 10-ml pipette and a 50-ml flask within a relative standard deviation ±0.02%, provided that the same measuring utensils are used during a series experiments, or each utensil is properly calibrated. Weight burettes could be us instead of volume measurements, but this was not considered necessary with care work.

DETERMINATION OF PURITY OF MAGNESIUM METAL

Apparatus

Absorbances were measured with a Hitachi Perkin-Elmer Type 139 spect photometer, equipped with 1-cm cells.

Special solutions

Water, redistilled in a glass still after distillation and ion exchange, was use

Standard magnesium solution, $5.000 \cdot 10^{-2}$ M. Dissolve an appropriate amou of magnesium metal of known purity in a small amount of 1 M hydrochloric ac and dilute to 1 l with water.

Buffer, pH 10.05. Dissolve 70 g of ammonium chloride in a mixture of 570 of ammonia and 430 ml of water.

EDTA solution, $5.00 \cdot 10^{-2}$ M. Dissolve 9.31 g of the disodium salt (dihydrat in 500 ml of water.

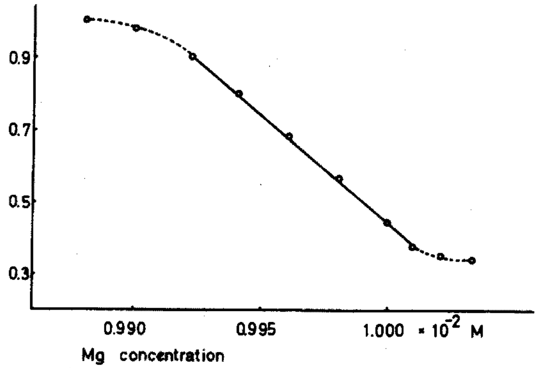
Calmagite solution, $1.00 \cdot 10^{-3}$ M. Dissolve 0.358 g of calmagite in 250 ml water.

Procedure

Weigh 1.216 g of a magnesium metal sample to use a working cur such as that shown in Fig. 5, which can cover the magnesium purity ran 99.2–100.0%. If sample weights outside a narrow range from this weight a taken, working curves must be prepared appropriately. Dissolve it in a sma amount of hydrochloric acid and dilute to 1 l with water. Measure accurate 10.0 ml of the magnesium sample solution into a 50-ml volumetric flask and a 5 ml of buffer solution, 1 ml of 12% (w/v) potassium cyanide solution and 2 ml aqueous (1 + 1) triethanolamine solution. Add accurately 10.0 ml of EDTA soluti and 5.00 ml of calmagite solution, and dilute to the mark with water. Measure t absorbance at 620 nm against water.

Obtain the magnesium content in the 50-ml flask from the working cur and then calculate the magnesium purity of the sample.

Prepare a working curve by the procedure given above, using the magnesiu standard solution (Fig. 5). It is necessary to use the same measuring utensils for t working curve as those used for the samples, or to calibrate the utensils separatel



ig. 5. Working curve for magnesium under the optimal condition. Wavelength 620 nm, pH 10.05, $_{\text{L}}$(EDTA) = 10^{-2} *M*, and C_{I} (calmagite) = 10^{-4} *M*.

ABLE I

FFECT OF IMPURITIES ON MAGNESIUM DETERMINATION

	Impurity added (%)	*Absorbance*[a]	*Combined impurity added (%)*	*Absorbance*[b]
l	0.8	0.901	0.03	0.571
u	0.8	0.900	0.03	
e	0.8	0.901	0.03	
n	0.8	0.900	0.03	
i	0.8	0.901	0.03	
n	0.8	0.901	0.03	

The absorbance for the original magnesium metal was 0.900.
The absorbance for the original magnesium metal was 0.570.

ffect of impurities

Magnesium metal usually contains traces of aluminium, copper, iron, anganese, nickel and zinc as impurities. These metals can be masked with potassium 'anide and triethanolamine as shown in Table I.

recision and analyses of samples

The accuracy and precision of this method for a magnesium metal of known ırity are shown in Table II. The relative error of the average was 0.00%, and e relative standard deviation was 0.014%.

In a final test, three magnesium metal samples were assayed (Table III). he authorized purity was given conventionally by subtracting the total amount ' the impurities from 100%. In the proposed method, however, the purity was rectly determined by spectrophotometry. The values determined by this method ere in good agreement with the authorized purities. The direct method of assay ould be readily adapted for continuous analysis in a quality-control system.

The authors wish to express their thanks to the Furukawa Magnesium Co., td. and the Japan Magnesium Committee for providing magnesium samples.

TABLE II

ACCURACY AND PRECISION OF THIS METHOD

Mg taken[a] *(g)*	*Mg found* *(g)*	*Recovery* *(%)*
1.2144$_8$	1.2145	100.00
	1.2143	99.99
	1.2143	99.99
	1.2143	99.99
1.2131$_8$	1.2133	100.01
	1.2133	100.01
	1.2132	100.00
	1.2135	100.03
1.2087$_8$	1.2087	99.99
	1.2085	99.98
	1.2086	99.99
	1.2089	100.00
1.2066$_8$	1.2067	100.00
	1.2066	99.99
	1.2069	100.02
	1.2066	99.99
	Average	100.00
	s_r	0.014

[a] Calculated from the amount of a magnesium metal sample and its authorized purity.

TABLE III

ASSAY OF MAGNESIUM METAL

Sample	*Authorized assay* *(%)*	*Assay by proposed method (%)*	*Mean*
A	99.98$_7$[a]	100.02	99.99
		99.97	
		99.99	
B	99.957$_7$[b]	99.96	99.96
		99.96	
		99.95	
C	99.92$_6$[a]	99.92	99.93
		99.92	
		99.95	

[a] The Furukawa Magnesium Co., Ltd.
[b] The Japan Magnesium Committee.

SUMMARY

A spectrophotometric method is proposed for the direct assay of pu materials. The bulk of the metal to be determined is reacted with an accurat measured amount of a chelating agent, and the small excess of metal ion is determin spectrophotometrically with a chromogenic reagent. The optimal conditions can

predicted by drawing the theoretical spectrophotometric titration curves near the equivalent point of a supposed titration with the chelating agent as titrant and the chromogenic reagent as indicator. The method was applied to pure magnesium metal with EDTA as the chelating agent and calmagite as the chromogenic reagent, and the relative standard deviation was found to be 0.014%. The accuracy and precision appear to be much better than those attainable by titrimetry or differential spectrophotometry.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le contrôle direct de substances pures. La masse du métal est traitée par une certaine quantité de chélatant, mesurée avec précision. Le métal en léger excès est dosé spectrophotométriquement au moyen d'un réactif chromogénique. Les conditions optimales peuvent être prévues à l'aide des courbes de titrage spectrophotométrique théoriques. Cette méthode a été appliquée à l'analyse du magnésium métallique pur, en utilisant l'EDTA comme chélatant et la calmagite comme réactif chromogénique. La déviation standard relative est de 0.014%. L'exactitude et la précision semblent beaucoup meilleures que celles obtenues par titrimétrie ou par spectrophotométrie différentielle.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode für die direkte Bestimmung von reinen Materialien vorgeschlagen. Der Hauptanteil des zu bestimmenden Metalls wird mit einer genau gemessenen Menge eines Chelatbildners umgesetzt, und der kleine Überschuss des Metallions wird spektrophotometrisch mit einem chromogenen Reagenz bestimmt. Die optimalen Bedingungen können vorhergesagt werden, indem die theoretischen spektrophotometrischen Titrationskurven in der Nähe des Äquivalenzpunktes einer angenommenen Titration gezeichnet werden, bei der der Chelatbildner als Titrant und das chromogene Reagenz als Indikator verwendet werden. Die Methode wurde auf reines Magnesiummetall mit EDTA als Chelatbildner und Calmagit als chromogenem Reagenz angewendet, wobei die relative Standardabweichung zu 0.014% ermittelt wurde. Genauigkeit und Reproduzierbarkeit scheinen viel besser als jene zu sein, die durch Titrimetrie oder Differential-Spektrophotometrie erzielt werden können.

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PECTROPHOTOMETRIC STUDY AND EXTRACTION OF NIOBIUM(V) OMPLEXES WITH CATECHOL AND ITS DERIVATIVES AS ION-PAIRS ITH QUATERNARY AMMONIUM IONS

PPLICATION TO THE SEPARATION OF NIOBIUM FROM OTHER EFRACTORY METAL IONS

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eceived 1st January 1973)

The niobium(V)–catechol system and its reaction products in aqueous solu-on have been described in earlier papers, which dealt with the direct photometric etermination of the metal ion[1] and later, its extraction[2]. The reaction between techol and titanium(IV) has been spectrophotometrically studied between pH 0 and 8.0; and the species formed in solution and the extraction behaviour have een established[3,4]. The complexes formed between vanadium and catechol (or s derivatives) have been more extensively studied: the composition of the roducts[5–7], the effect of the oxidation state of vanadium[8,9], the equilibrium onstants[10–12] and the spectrophotometric determination of vanadium[13] have been escribed by various workers.

Several authors, particularly Havelkova and Bartusek[14], who compiled revious work on the subject, have dealt with molybdenum–catechol complexes. atechol derivatives have been used by Halmekoski in connection with both molyb-enum[15] and tungsten[16]. Basic studies on tungsten–catechol complexes have been ade by Brown[17] and Chernaya *et al.*[18]

Numerous papers, mainly within the Russian literature, have been written n the extraction of complexes of the above-mentioned metals, both directly or rough the formation of ion-pairs with protonized bases or organic cations (tetra-henylarsonium, trialkylphosphonium, quaternary ammonium, etc.). Vrchlabsky and ommer[2,19] have reviewed this literature up to 1968.

The present paper is concerned first with a study of the niobium(V) com-lexes formed with catechol (or its derivatives) in aqueous solution, and then with e liquid–liquid extraction of the ion-pairs formed between these complexes and a uaternary ammonium salt. Analogous studies, restricted to the optimal conditions und for niobium(V), were conducted on four other refractory metals, titanium(IV), nadium(V), molybdenum(VI) and tungsten(VI). The information thus gathered as applied to the separation and determination of niobium(V) in binary mixtures ith these other refractory metal ions, by means of liquid–liquid extraction and ectrophotometric measurement in the organic phase.

EXPERIMENTAL

Reagents

Solutions of metal ions. $5\cdot10^{-3}$ *M* Nb(V), Ti(IV) and Mo(VI) solutions w prepared in 15% tartaric acid and 4% (v/v) sulphuric acid; $5\cdot10^{-3}$ *M* vanadium(solution was prepared in 4% (v/v) sulphuric acid and $5\cdot10^{-3}$ *M* tungsten (VI) in wa alone.

Diphenols. The diphenols used were catechol, 3-methylcatechol, 4-meth catechol, 3-methoxycatechol, 4-chlorocatechol, 3-isopropylcatechol, 3,6-diisoprop catechol, 4-tert-butylcatechol, and 3-tert-butyl-5-methylcatechol. Except for catech all the other diphenols (Aldrich Chemicals) were purified by sublimation.

Quaternary ammonium salts. Tetramethylammonium bromide (Eastm Kodak), tetraethylammonium bromide, phenyltrimethylammonium iodide, lauryl methylammonium bromide (Eastman-Kodak), methyltributylammonium iodi n-butyl-tri-n-propylammonium iodide (Eastman-Kodak), tetrapentylammoni chloride (Eastman-Kodak), dibenzyldimethylammonium bromide, trioctylprop ammonium bromide, hexadecyltrimethylammonium chloride (Eastman-Koda hexadecylbenzyldimethylammonium chloride, acetohydrazidetrimethylammoni chloride, laurylnaphthyldimethylammonium chloride, and hexamethylenetetrami methylammonium iodide were examined. Except where indicated, these bases w obtained from K&K. Whenever possible, aqueous solutions of convenient conc tration were prepared; when concentrations higher than the solubilities were quired, a weighed amount of solid was added in each test. For water-insoluble sa organic solvents were used.

Solvents. Ethyl, butyl, amyl and 4-methyl-2-pentyl acetates, ethyl propiona 2-ethylhexanol, iso-octane, 2-ethylchlorohexane, cyclohexane, benzene, tolue methyl isobutyl ketone (MIBK), diisobutylketone, carbon tetrachloride, chlo form, 1,2-dichloroethane, trichloroethylene and 1,1,2,2-tetrachloroethane were analytical-reagent grade or were purified before use.

Instrumentation and equipment

Absorbances were read in a Beckman DU spectrophotometer in 1-cm qua cells. pH was measured with a Beckman H-3 pH meter. Extractions were co ducted in 110 × 18 mm Pyrex test tubes provided with polyethylene stoppers; ficient contact between phases was ensured by means of a modified reciprocati shaker.

Procedures

Colour development. A solution of suitable concentration in sodium sulph was prepared, to which successive additions were made of: (*a*) the diphenol; acid or base, as required, to attain the pH value sought (when acid was added, t sulphite concentration decreased proportionally, and sodium sulphate was add to keep the ionic strength at 0.6, the same value given by the maximum concentrati of sodium sulphite at pH 7.30); (*c*) an aliquot of the metal ion to be tested; (*d*) wa up to *ca.* 0.5 ml less than the final volume. At this point, the solution was hea in a water bath at the required temperature for a definite time, and, after cooli the volume was completed with water.

Dilutions of any metal ion solutions which did not contain tartaric lphuric acids, were supplemented with these reagents in appropriate amounts give 15% (w/v) and 4% (v/v), respectively, referred to the metal aliquot.

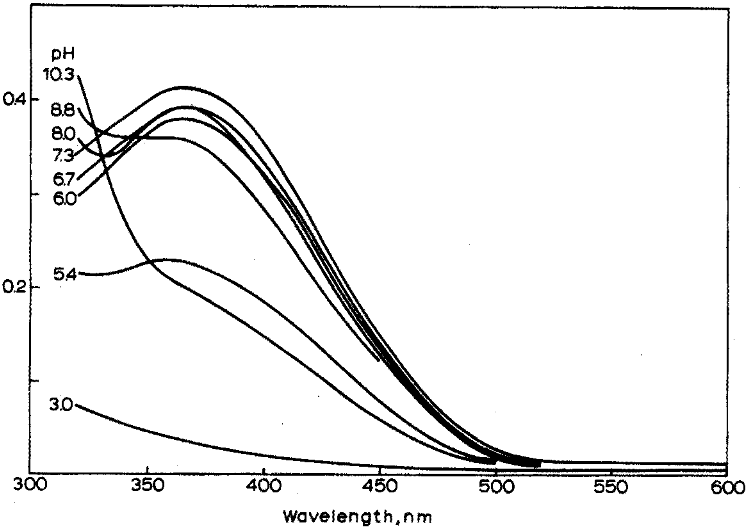
Extraction. To a 3.00-ml aliquot of the aqueous solution prepared as above, ere added 0.030 ml of an aqueous solution or a weighed amount of the quaternary mmonium salt to attain the desired final concentration, and then the same volume f organic solvent as that of aqueous phase. The mixture was equilibrated by haking the tubes horizontally in a reciprocating shaker; this required 1 min at a te of 200 cycles per minute. After the two phases had separated, anhydrous dium sulphate was added to the organic extract, both to dehydrate it and help reak up any emulsion. In some cases it was still necessary to warm the extract 35–45° to obtain clear solutions suitable for spectrophotometric measurement.

PECTROPHOTOMETRIC STUDIES IN AQUEOUS MEDIA

iobium(V)–catechol system

On the basis of earlier studies[1,2], a tentative metal : diphenol ratio of 1 : 3,300 as used for $6 \cdot 10^{-5}$ *M* niobium(V). The optimal pH value for the formation of e niobium(V)–catechol complex was found by simply mixing reagents at 15–20° nd spectrophotometrically scanning between 320 and 420 nm after 30–60 min of olour development. Figure 1 shows the spectra for pH values between 3.00 and 0.30. At 15–20°, the absorbance of the system at pH 7.30 increased with time; ere was an increase of 15% at the wavelength of maximal absorbance during the eriod 1–24 h after mixing. This can be attributed to an inhibiting effect of tartaric cid on the complex formation in acidic solutions, as suggested by Patrovsky[1] though the ageing effect mentioned by Fairbrother *et al.*[20] cannot be excluded.

A pH range of 6.7–8.0 (see Fig. 1) was selected for a study of the effect of eating on colour development. Initially, a temperature of 70° was chosen, and it



ig. 1. Spectra of the niobium(V)–catechol system at different pH values. Nb(V), $6 \cdot 10^{-5}$ *M*; catechol, 2 *M*; temperature, 15–20°; time of colour development, 30–60 min.

was found that absorbance values were unaffected by the time of heating in t range 6–9 min. However, when the temperature of heating was varied, 70° w shown to be inadequate, a temperature of 85–90° being necessary (Table I).

The influence of the catechol concentration within a restricted range betwe 0.15 and 0.30 *M*, was then studied at pH 7.30. The results (Table II) indicated steady increase in absorbance, in contrast to Vrchlabsky and Sommer's findin for the same metal : catechol ratio at a lower pH. The difference might be attribut to a competitive effect of tartaric acid within the pH range tested.

TABLE I

ABSORBANCE AS A FUNCTION OF TEMPERATURE OF HEATING

($5 \cdot 10^{-5}$ *M* Nb(V), 0.2 *M* catechol, pH 7.0 or 7.3, 6-min heating time, 360 nm)

Temperature (°)	50	70	85	90
Abs. at pH 7.00	0.392	0.475	—	0.488
Abs. at pH 7.30	0.410	0.500	0.510	0.513

TABLE II

ABSORBANCE AS A FUNCTION OF CATECHOL CONCENTRATION

($5 \cdot 10^{-5}$ *M* Nb(V), pH 7.3, 6-min heating time, 360 nm)

Catechol concentration (*M*)	0.15	0.2	0.25	0.3
Abs. after heating at 85°	—	0.511	0.531	0.548
Abs. after heating at 70°	0.460	0.498	0.517	0.533

The stability of the absorbance was then checked as a function of time elaps after colour development for 6 min at 70° in solutions of pH values between and 8.80. The variations in the absorbances read between 0.5 and 24 h were less th 2% in every case; the highest absorbance was again found at pH 7.3.

To summarize, the optimal conditions for the niobium(V)–catechol reacti are: heating temperature, 85°; time of heating, 6 min; pH range, 6.70–8.00. F these conditions, an increase in the catechol : metal ratio from 4,000 : 1 to 6,000 for $5 \cdot 10^{-1}$ *M* niobium(V), causes a 7% difference in the absorbance value, whi suggests a need for higher ratios. However, these were not examined because t absorptivity, reproducibility and stability for a 4,000 : 1 ratio were considered sat factory, and because the catechol derivatives for comparative studies were availab only in limited quantities.

The reaction of niobium(V) with catechol derivatives

The study of the various catechol derivatives was restricted to the followi conditions: (*a*) pH values, 7.30, 6.60, 5.80 and 4.00; (*b*) heating time, 3 or 6 m (*c*) temperature, 15–20°, 50°, 60°, 70°, 80° and 90°. The principal catechol derivati tested are listed in Table III. The solubility of 3-methoxycatechol at room tempe

ABLE III

ONDITIONS FOR DEVELOPMENT OF MAXIMUM COLOUR INTENSITY AND OPTICAL ROPERTIES OF NIOBIUM(V)–DIPHENOL SYSTEMS

$\cdot 10^{-5}$ *M* Nb(V); 0.2 *M* diphenol unless otherwise specified; heating time, 6 min)

iphenol	*pH range*	*Minimum temp. of heating (°)*	*Absorbance increase in 24 h (%)*	*λ_{max} (nm)*	*Molar absorptivity (l mole^{-1} cm^{-1})*
atechol	6.7–8.0	85	2	365	$1.02 \cdot 10^4$
-Methylcatechol	6.6–7.3	70	2	365	$9.4 \cdot 10^3$
-Methylcatechol	6.6–7.3	80	0.2	365	$9.4 \cdot 10^3$
-Chlorocatechol	5.8–6.6	70	1	380	$1.36 \cdot 10^4$
-Methoxycatechol	6.6–7.3	70	5	360	$9.0 \cdot 10^3$
-Isopropylcatechol[a]	7.3	70	2.5	355–360	$9.2 \cdot 10^3$

0.1 *M* solution used, and the time of heating at 70° was only 3 min.

re did not allow a final 0.2 *M* solution, so that it was necessary to centrifuge the ixture just before the spectrophotometric measurement to remove the reagent hich crystallized on cooling. 3-Isopropylcatechol was still less soluble, and a 0.1 *M* olution was used. 4-Tert-butylcatechol was so insoluble that it was used for the ake of comparison only in extraction experiments, under the same conditions as -isopropylcatechol. 3,6-Diisopropylcatechol and 3-tert-butyl-5-methylcatechol ormed yellow solutions on heating, even in the absence of niobium(V), because of xidation or polymerization, and so were not considered further.

Table III summarizes the conditions of maximal colour development and he optical properties of the reaction products formed between niobium(V) and he different catechol derivatives considered.

iscussion

The optimal pH ranges are close to conditions of neutrality, decreasing from 7–8.0 for catechol to 5.8–6.6 for 4-chlorocatechol in the following sequence: atechol ≧ 3-methylcatechol = 4-methylcatechol = 3-methoxycatechol > 4-chloroatechol. Catechol derivatives react in slightly more acidic media than catechol itself.

The temperature required to attain maximal development of the coloured pecies also decreased from catechol to its derivatives, the sequence being catechol > -methyl > 4-chloro = 3-methyl = 3-methoxy = 3-isopropyl. Among those derivatives hich react within the same pH range, 4-methylcatechol needs a higher temperature.

The coloured complex formed with 4-methylcatechol was the most stable, hough the complexes produced by catechol and the 3-methyl and 4-chloro erivatives did not change more than 2% during 24 h. The complexes formed with he 3-methoxy and 3-isopropyl derivatives were less stable.

The wavelength of maximal absorption was usually close to 365 nm but for he chlorinated derivative, it shifted to 380 nm. A bathochromic shift of 5–10 nm as obtained with the 4-methoxy and 3-isopropyl derivatives.

TABLE IV

ABSORBANCE OF ORGANIC EXTRACTS WITH DIFFERENT QUATERNARY AMMONIUM SALTS IN VARIOUS SOLVENTS

($5 \cdot 10^{-5}$ *M* Nb(V), 0.2 *M* catechol, pH 7.3; heating at 85° for 6 min; volume ratio of aqueous phase to solvent 1:1)

QA salt	*Solvent concn. (M)*	*Ethyl acetate*	*Butyl acetate*	*Amyl acetate*	*4-Methyl-pentyl acetate-2*	*Ethyl propionate*	*2-Ethyl-hexanol*	*Cyclo-hexane*	*MIBK*	*DIBK*
Phenyltrimethyl-	$2.5 \cdot 10^{-2}$	0.200	0.125	0.120	0.040	0.120	0.125			
ammonium	$5 \cdot 10^{-3}$	0.139	0.060	0.040	0.020	0.050	0.040			
Lauryltrimethyl-	$2.5 \cdot 10^{-2}$	0.539	0.429	0.440	0.280	0.450	0.539		0.720	0.770
ammonium	$5 \cdot 10^{-3}$	0.587	0.608	0.551	0.562	0.637	0.505	[a]	0.880	
Methyltributyl-	$2.5 \cdot 10^{-2}$	0.680	0.705	0.580	0.630	0.720	0.460		0.905	0.870
ammonium	$5 \cdot 10^{-3}$	0.520	0.530	0.460	0.375	0.550	0.350		0.860	0.820
Tetrapentyl-	$2.5 \cdot 10^{-2}$	0.603	0.650	0.593	0.609	0.658	0.550	0.502	0.900	0.780
ammonium	$5 \cdot 10^{-3}$	0.644	0.670	0.587	0.630	0.680	0.548	0.444		0.820
Dibenzyldimethyl-	$2.5 \cdot 10^{-2}$	0.700	0.732	0.605	0.630	0.740	0.510		0.900	0.800
ammonium	$5 \cdot 10^{-3}$	0.635	0.705	0.572	0.500	0.710	0.475	[b]	0.930	0.800
Acetohydrazide-	$2.5 \cdot 10^{-2}$	0.070	0.010						0.420	
methylammonium	$5 \cdot 10^{-3}$	0.080	0.010	0.020				0.000	0.410	
Methylhexamethylene-	$2.5 \cdot 10^{-2}$									
tetramine	$5 \cdot 10^{-3}$	0.010	0.010	0.015						

	Benzene	Toluene	Chloro-form	1,2-Dichloro-ethane	Trichloro-ethylene	Chloro-ethane	Chloro-hexane	Tetra-chloride	Iso-octane	
Lauryltrimethyl-ammonium	2.5·10⁻²	0.695		0.700	0.761	0.650	0.770		[e]	[f]
	5·10⁻³	0.730[c]	0.710[d]	0.740	0.770	0.630	0.775			
Methyltributyl-ammonium	2.5·10⁻²	0.730	0.580	0.795	0.780	0.740	0.850			
	5·10⁻³	0.592	0.240	0.825	0.820	0.490	0.880	[g]		
Tetrapentyl-ammonium	2.5·10⁻²	0.630	0.566	0.820	0.845	0.721	0.840		0.645[j]	
	5·10⁻³	0.670[h]	0.470[i]	0.805	0.840	0.749	0.845			[k]
Dibenzyldimethyl-ammonium	2.5·10⁻²	0.700	0.650	0.735	0.740	0.631	0.744			
	5·10⁻³	0.715[i]	0.640[l]	0.735	0.735	0.523	0.730	[m]	[b]	[b]

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[a] Solid excess of QA salt and ion-pair at the interphase. [b] No extraction, with total discolouration of both phases. [c] An intermediate third phase is formed containing the ion-pair; addition of 3% 2-ethylhexanol leads to a single organic phase. [d] 3% and 10% 2-ethylhexanol are required to obviate the third phase, in the case of the lower and higher quaternary ammonium concentrations, respectively. [e] Ion-pair at interphase. [f] 15% 2-ethylhexanol addition allows extraction of excess quaternary ammonium and ion-pair for the lower quaternary ammonium concentration, not for the higher. [g] No extraction. [h] The third phase first formed is eliminated by the addition of 3% chloroform. [i] Lower and higher quaternary ammonium concentrations require 5% and 10% 2-ethylhexanol, respectively, to give a single organic phase. [j] 25% 2-Ethylhexanol dissolves the ion-pair first precipitated, into the organic phase. [k] Precipitate at interphase; no improvement by addition of up to 25% 2-ethylhexanol to the organic phase. [l] The third phase becomes miscible by adding 3% 2-ethylhexanol for both concentrations. [m] Yellow precipitate in aqueous phase; no extraction.

The molar absorptivities of the complexes formed with the derivatives, lower than that with catechol and were quite close to each other (9.0–9.4· except in the case of 4-chlorocatechol, for which the value was 35% higher than obtained with catechol.

LIQUID–LIQUID EXTRACTION STUDIES

Niobium(V)–quaternary ammonium salt ratios of 1:100 and 1:500 used in studying the degree of extraction into different solvents of the niobium catechol (or derivatives) complexes. It was known[21†22] that similar niobium pyrogallol complexes were quantitatively extracted in a single contact with acetate if this ratio was not more than 1:100.

Tests were begun with eighteen solvents, as mentioned under *Reag* and up to seven quaternary ammonium salts were used in some cases. All variables remained unchanged at: Nb(V), $5 \cdot 10^{-5}$ *M*; catechol, 0.2 *M*; pH, volume ratio of aqueous:organic phases, 1:1; ionic strength, 0.6. Experim results are given in Table IV. The behaviour of the different solvents tested ca

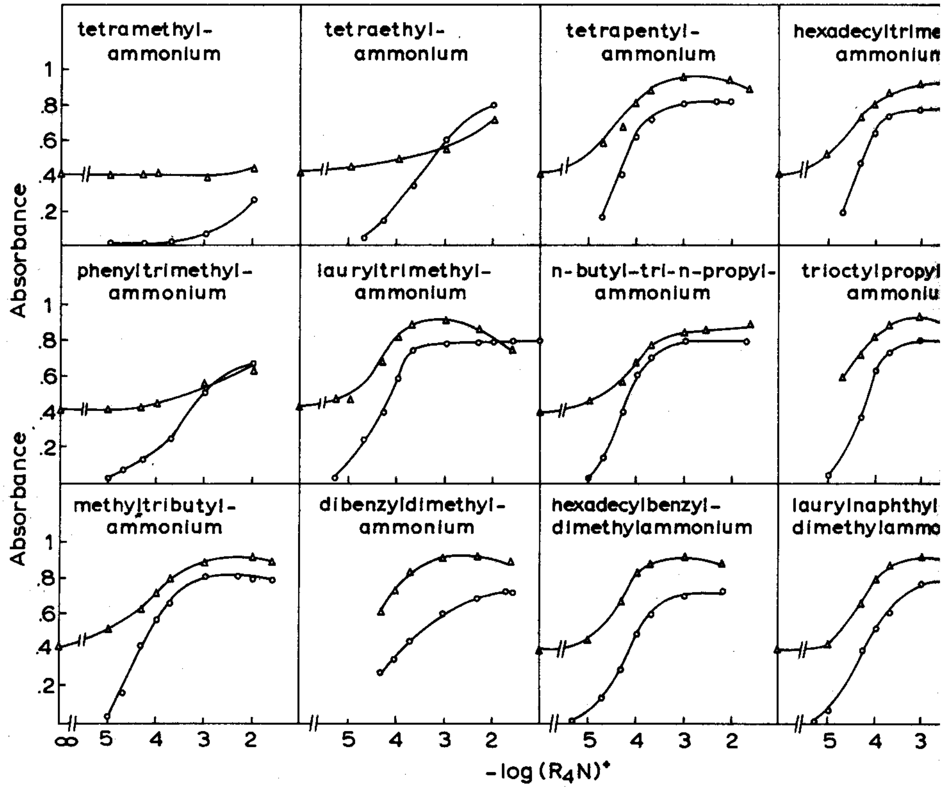
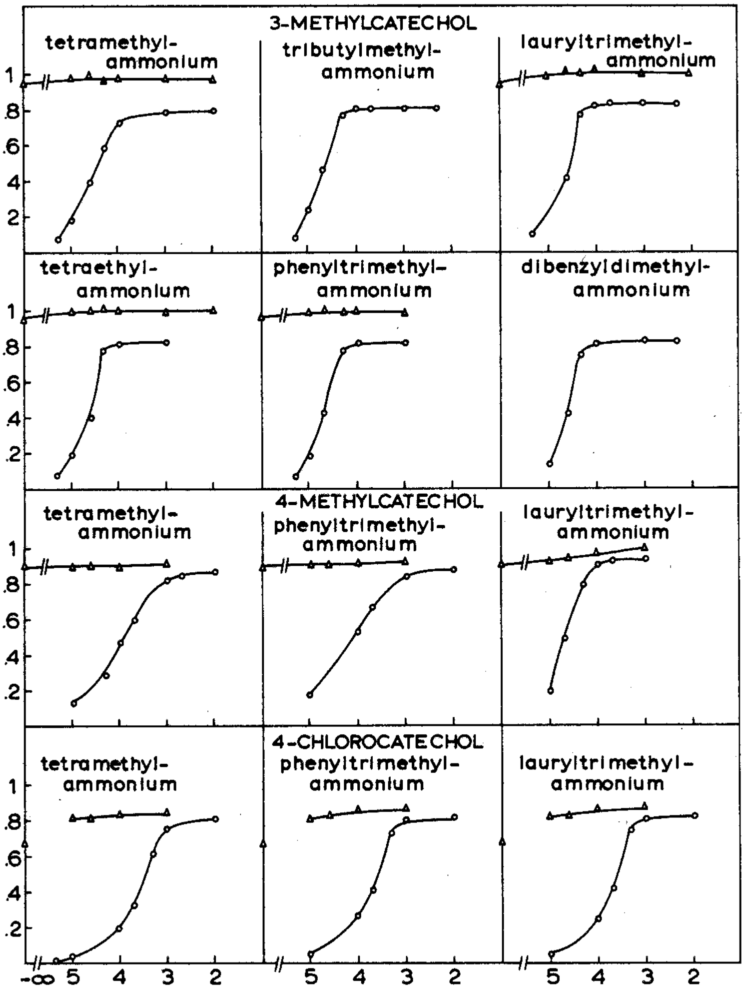


Fig. 2. Extraction of the niobium(V)–catechol system as ion-pairs with quaternary ammonium i different concentrations, as measured by the absorbance of the organic extracts in methyl iso ketone (△), and 1,2-dichloroethane (○). Nb(V), $5 \cdot 10^{-5}$ *M*; 0.2 *M* diphenol; pH of aqueous sol 7.3.

ummarized as follows. Chlorinated hydrocarbons and ketones allow a rapid eparation, and provide the highest absorbance values. Esters, in general, are about s efficient as chlorinated hydrocarbons and ketones, but they are prone to emulsify everely and separate only slowly. The ion-pairs formed are not extracted into ydrocarbons, broadly speaking, though extraction may occur if mixtures of hydro-arbons with polar solvents, *e.g.* higher alcohols, are used. Carbon tetrachloride s the exception among chlorinated hydrocarbons, but extraction does occur if it s mixed with 2-ethylhexanol.

In view of these results, MIBK and 1,2-dichloroethane, which were readily vailable, were chosen for further extraction experiments in which the type of di-henol and the nature and concentration of the quaternary ammonium salt were xamined. The results obtained are shown in Figs. 2–4.



ig. 3. Extraction of niobium(V)–catechol derivative complexes as ion-pairs with quaternary am-onium ions. Conditions and symbols as in Fig. 2.

Discussion

The extraction of niobium(V)–catechol (or derivative)–quaternary ar monium ion-pairs is nil or very poor in solvents of low dielectric constant (*e.* hydrocarbons). The efficiency of extraction, for a given quaternary ammonium sa increases as the polarity of the solvent increases, up to the point that MIBK extrac the coloured complexes formed even without the quaternary ammonium cation; tl efficiency of this latter type of extraction decreases in the order: 3-methylcatechol 4-methylcatechol > 4-chlorocatechol > catechol (Fig. 3).

All the substituted catechols tested were more efficient in favouring extractic than catechol itself. Their effectiveness increased with chain length, up to the poi that substituents with chains containing three or more carbon atoms made tl extraction feasible without the quaternary ammonium ion; either MIBK or 1,2-c chloroethane could be used as solvent (Fig. 4). Basically, however, there was r appreciable difference in this type of extraction which could be attributed to su stituents.

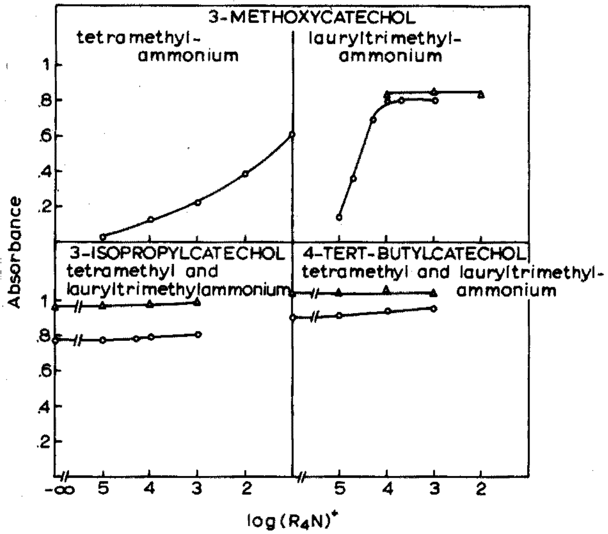


Fig. 4. Extraction of the niobium(V) complexes with 3-methoxycatechol, 3-isopropylcatechol and 4-tei butylcatechol as ion-pairs with quaternary ammonium ions. Conditions and symbols as in Fig. 2.

The effect of the substituents on the extraction of ion-pairs for the same coi centration of a given quaternary ammonium cation followed the sequence: 4-ter butyl > 3-isopropyl > 3-methyl > 4-methyl > 4-chloro > 4-methoxy. 3-Methylcat chol was more effective than 4-methylcatechol when small or light quaternary an monium ions were used; with heavier ions, there was no significant difference betwe the two positions.

The study of the extraction of the niobium(V)–catechol complex into 1,2-d chloroethane (Fig. 2) showed that the extraction was more efficient, the heavi the quaternary ammonium ion. However, there was no difference whether the san number of total carbon atoms formed aromatic rings or aliphatic chains; syn metry in the quaternary amonium cation seemed to have no effect.

THE BEHAVIOUR OF OTHER REFRACTORY METAL IONS

It was hoped to apply the results described above to the separation of niobium(V) from other refractory metal ions, *i.e.*, Ti(IV), V(V), Mo(VI) and W(VI). A study of the behaviour of these ions under the optimal conditions for niobium(V) was therefore undertaken. The influence of diphenol concentration was not considered for Ti(IV), Mo(VI) and W(VI) as that required by niobium(V) exceeds those recommended for titanium(IV)[3], molydenum(VI)[14] and tungsten(VI)[16,18].

Aqueous systems

Titanium(IV). The optimal pH range and temperature to develop a colour for a heating time of 6 min were examined in a system which was $5\cdot10^{-5}$ *M* in titanium(IV) and 0.2 *M* in diphenol. In contrast to niobium(V), titanium(IV)–catechol attains maximal colour intensity at room temperature. The spectrum of the reaction product is included in Figure 5. Other diphenols tested, *i.e.* the 3-methyl, 4-methyl, and 4-chloro derivatives, behaved similarly; the main features of these systems are shown in Table V. The absorbances obtained with catechol itself remained unchanged after 24 h, whereas those obtained with the derivatives increased by 1%.

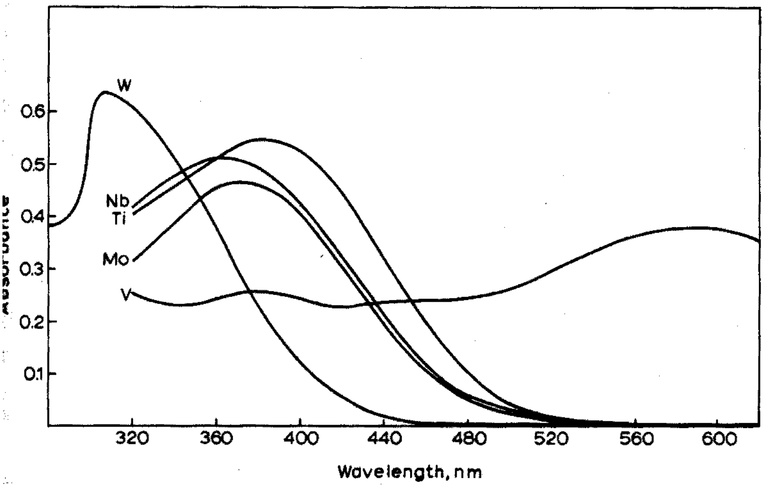


Fig. 5. Spectra of metal–catechol systems at pH 7.30. Catechol, 0.2 *M*; Nb(V), Ti(IV) and V(V), $5\cdot10^{-5}$ *M*; Mo(VI) and W(VI), $1\cdot10^{-4}$ *M*. Temperature, 15–20° (except for Nb(V), 85°). Time elapsed between mixing (or heating) and reading, 30–60 min.

Vanadium(V). The effect of the catechol concentration on the reaction with vanadium(V) to generate the blue complex (or complexes)[8,9,12] of vanadium(IV) with a maximal absorbance wavelength at 590 nm, was studied for $5\cdot10^{-5}$ *M* V(V) at pH 7.30.

The effect of temperature was investigated and the colour stability with time was followed. Table VI shows the results obtained. The spectrum obtained at room temperature is given in Fig. 5.

TABLE V

OPTICAL PROPERTIES OF DIPHENOL COMPLEXES WITH TITANIUM, VANADIUM, TUNGSTEN AND MOLYBDENUM

(0.2 *M* diphenol; $5 \cdot 10^{-5}$ *M* Ti(IV) or V(V); 10^{-4} *M* W(VI) or Mo(VI); pH 7.3)

Diphenol	*Titanium*		*Vanadium*		*Tungsten*		*Molybdenum*	
	λ_{max} *(nm)*	*E* $(l\ mole^{-1}\ cm^{-1})$	λ_{max} *(nm)*	*E* $(l\ mole^{-1}\ cm^{-1})$	λ_{max} *(nm)*	*E* $(l\ mole^{-1}\ cm^{-1})$	λ_{max} *(nm)*	*E* $(l\ mole^{-1}\ cm^{-1})$
Catechol	380	$1.09 \cdot 10^4$	590	$7.5 \cdot 10^3$	305	$6.4 \cdot 10^3$	405	$4.6 \cdot 10^3$
3-Methylcatechol	380	$1.10 \cdot 10^4$	590	$7.8 \cdot 10^3$	300	$6.1 \cdot 10^3$	405	$4.3 \cdot 10^3$
4-Methylcatechol	390	$1.15 \cdot 10^4$	605	$7.6 \cdot 10^3$	315	$6.7 \cdot 10^3$	410	$4.5 \cdot 10^3$
4-Chlorocatechol	390	$1.24 \cdot 10^4$	600	$8.6 \cdot 10^3$	320	$7.3 \cdot 10^3$	405	$4.7 \cdot 10^3$

ABLE VI

BSORBANCES AT 370 AND 590 nm OF THE VANADIUM(V)–CATECHOL SYSTEM AS A UNCTION OF DIPHENOL CONCENTRATION AND ELAPSED TIME

5·10^{-5} *M* vanadium(V); pH 7.3; heating time at 90°, 6 min; elapsed time is between colour developent and absorbance measurement)

ime lapsed h)	*Catechol concn. (M)*	*2·10^{-3}*		*2·10^{-2}*		*2·10^{-1}*		*1*
	Wavelength (nm) *Temp. (°)*	*590*	*370*	*590*	*370*	*590*	*370*	*590*
1	15–20	0.036	0.042	0.186	0.114	0.379	0.236	0.450
	90	0.030	0.041	0.184	0.115	0.370	0.236	—
8	15–20	0.037	0.043	0.184	0.115	0.375	0.240	0.450
	90	0.035	0.044	0.189	0.125	0.375	0.245	—
4	15–20	0.042	0.041	—	—	0.379	0.250	0.441
	90	0.052	0.059	0.201	0.136	0.377	0.253	—

Other diphenols were studied only at pH 7.30 for a diphenol concentration f 0.2 *M*; the main features of the resulting reaction products are listed in Table V. here was no change in the absorbance readings with any of the reagents after 24 h.

Tungsten(VI). Temperature, from room level up to 90°, had no effect on he colour development for a system which was 1·10^{-4} *M* in tungsten(VI) and 0.2 *M* in catechol at pH 7.30. The spectrum of the reaction product (Fig. 5) shows liscrepancies with previously mentioned positions of maximal absorbance[16–18] able V gives the spectral characteristics of the tungsten(VI)–diphenol systems tudied. The absorbances obtained with catechol decreased by 2% after 24 h; the bsorbances with 3-methylcatechol remained unchanged but those with 4-methylatechol and 4-chlorocatechol increased by 1–2%.

Molybdenum(VI). Studies of the molybdenum(VI)–catechol systems were nade with 1·10^{-4} *M* molybdenum(VI) and 0.2 *M* diphenol at pH 7.3. Temperature, p to 90°, did not affect the colour intensity attained after 6 min of heating. The nolybdenum(VI)–catechol spectrum is given in Fig. 5. The main optical properties f the four systems considered are recorded in Table V. The absorbances increased y no more than 1% after a standing time of 24 h.

Discussion. The above tests, made under similar conditions to those used or niobium(V), show that at the optimal pH value found for the niobium(V)–atechol reaction, the reaction with the other refractory metals is independent of emperature, and reaches maximal intensity within 6 min at 15–20°. The colours ormed are stable, any variation in absorbance being not more than 2% after 24 h.

The molybdenum(VI) and titanium(IV) complexes show wavelengths of naximal absorbance higher than those for niobium(V), *i.e.* 405–410 and 380–390 m, respectively, depending on the diphenol; for tungsten(VI) the maximal aborbances occur at shorter wavelengths, 300–320 nm, for different derivatives. In he case of vanadium(V), the dome with a wavelength of maximal absorbance round 590 nm, in addition to the complex with a maximum at 375–380 nm, suggests hat an oxidation–reduction reaction takes place.

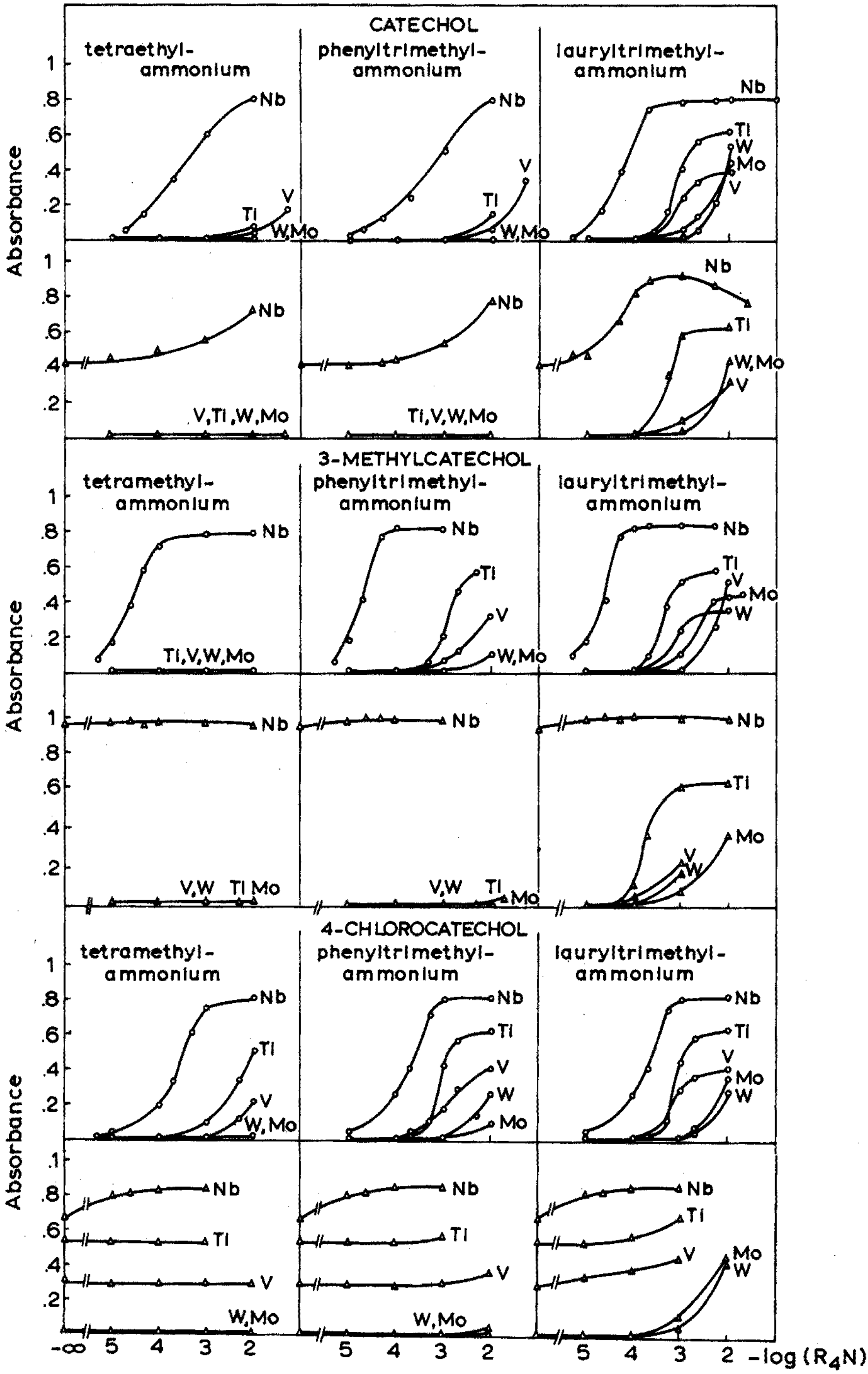


Fig. 6. Comparative extraction behaviour of the metal–catechol, metal–3-methylcatechol and meta 4-chlorocatechol systems with increasing concentrations of quaternary ammonium ions. pH 7.3 I=0.6. Solvents: methyl isobutyl ketone (△) and 1,2-dichloroethane (○). Nb(V), Ti(IV) and V(V $5 \cdot 10^{-5}$ M; Mo(VI) and W(VI), $1 \cdot 10^{-4}$ M; diphenol, 0.2 M.

The molar absorptivities decrease in the following order: V(V) > W(VI) > o(VI), lying in the ranges 7.5–8.6, 6.1–7.3, and 4.3–4.7, times 10^3 in every case. he molar absorptivities for the titanium complexes are much higher, lying in the nge 1.09–1.24·10^4 (Table V).

iquid–liquid extraction

Extraction tests were made with MIBK and 1,2-dichloroethane on the metal– techol systems with tetraethylammonium, phenyltrimethylammonium and lauryl- imethylammonium ions. The metal–catechol derivative systems with tetramethyl- nmonium, phenyltrimethylammonium and lauryltrimethylammonium ions were so examined. All these tests were made at pH 7.3 and ionic strength, 0.6; the con- ntrations of metal ions used were 10^{-4}–10^{-5} *M* (see Fig. 6). The absorbances of e organic extracts were read at 380 nm for Ti(IV), 590 nm for V(V), 405 nm for o(VI), and 350 and 330 nm for W(VI) in MIBK and 1,2-dichloroethane, respec- vely. The results obtained are shown in Fig. 6. The extraction behaviour of the methylcatechol complexes was very similar to that of the 3-methylcatechol mplexes, hence detailed plots are not shown for the former.

The titanium(IV) and vanadium(V) complexes with 4-chlorocatechol were tracted into MIBK without a quaternary ammonium salt (similarly to niobium-)), but this was not the case for the reaction products with catechol, 3-methyl- 4-methylcatechol (in contrast to niobium(V)).

The nature of the catechol substituents used did not create any vital dif- rences in extraction behaviour within the concentration of quaternary ammonium lts studied. However the complexes of the four elements did not show the same ends, their behaviour changing with solvent and even more with the quaternary nmonium ion used. Except for the above-mentioned cases of direct extraction, the ther four metal ions needed appreciably higher concentrations of quaternary am- onium salt than those required by the niobium(V) compounds for extraction, hich was still rarely complete.

inary mixtures

Binary mixtures of niobium(V) with one of the above refractory metal ions ere studied under conditions for which reasonably satisfactory separations could expected on the basis of the results shown in Fig. 6. Some 1:1 mixtures of ·10^{-5} *M* niobium(V) were accordingly prepared with one each of Ti(IV), V(V), o(VI) and W(VI). The results obtained are given in Table VII.

NCLUSIONS

Because of the similar wavelengths of maximal absorption and the proximity the molar absorptivities, simultaneous determinations of Nb(V), Ti(IV), V(V), o(VI) and W(VI) based on direct spectrophotometric measurement of the com- exes formed with catechol (or derivatives) would be possible only in aqueous utral solution for binary mixtures of vanadium(V) with any of the other four ements, or for tungsten(VI) with either molybdenum(VI) or titanium(IV). The tter possibility has already been discussed[13] for other conditions.

A definite improvement can be attained in the case of niobium(V) by liquid–

TABLE VII

RELATIVE ERROR IN THE RECOVERY OF NIOBIUM(V) BY EXTRACTION FROM BINARY MIXTURES

([Nb] ≡ [Ti, V, Mo or W] = 10^{-5} *M*)

System[a]	*Quaternary ammonium ion concentration (M)*	*Solvent*[b]	*Relative error (A %)*
Nb–Ti–catechol–LTMABr	$1 \cdot 10^{-4}$	DCE	2
Nb–Ti–3-methylcatechol–TMABr	$1 \cdot 10^{-4}$	MIBK	−3
Nb–Ti–catechol–TEABr	$1 \cdot 10^{-2}$	MIBK	−3
Nb–Ti–catechol–LTMABr	$1 \cdot 10^{-4}$	MIBK	−4
Nb–Ti–catechol–TEABr	$1 \cdot 10^{-2}$	DCE	6
Nb–Ti–3-methylcatechol	0	MIBK	−6
Nb–V–3-methylcatechol–LTMABr	$1 \cdot 10^{-4}$	DCE	0
Nb–V–catechol–LTMABr	$1 \cdot 10^{-4}$	MIBK	−3
Nb–V–catechol–TEABr	$1 \cdot 10^{-2}$	DCE	4
Nb–V–3-methylcatechol–TMABr	$1 \cdot 10^{-4}$	DCE	4.1
Nb–V–catechol–TEABr	$1 \cdot 10^{-2}$	MIBK	−4.5
Nb–V–3-methylcatechol	0	MIBK	−5
Nb–V–catechol–LTMABr	$1 \cdot 10^{-4}$	DCE	−5.5
Nb–Mo–catechol–TEABr	$1 \cdot 10^{-2}$	DCE	−1.5
Nb–Mo–3-methylcatechol–TMABr	$1 \cdot 10^{-4}$	DCE	1.5
Nb–Mo–3-methylcatechol–LTMABr	$1 \cdot 10^{-4}$	DCE	−4
Nb–W–catechol–TEABr	$1 \cdot 10^{-2}$	DCE	−1.2
Nb–W–3-methylcatechol–LTMABr	$1 \cdot 10^{-4}$	DCE	−3.5
Nb–W–3-methylcatechol–TMABr	$1 \cdot 10^{-4}$	DCE	−4.3

[a] LTMABr = lauryltrimethylammonium bromide; TEABr = tetraethylammonium bromide; TMABr = tetramethylammonium bromide. [b] Solvent: DCE = 1,2-dichloroethane; MIBK = methyl isobutyl ketone.

liquid extraction into MIBK or 1,2-dichloroethane, of some niobium(V) complexes formed with catechol (or its derivatives) complexes. In general, the formation of extractable ion-pairs between these niobium(V)–catechol complexes and a quaternary ammonium cation makes it possible to separate binary mixtures of niobium(V) with equimolar solutions of Ti(IV), V(V), Mo(VI) or W(VI), under selected experimental conditions.

Systems which were shown to be the most efficient for this extraction, with an error not larger than ±3% for $5 \cdot 10^{-5}$ *M* niobium(V), are:

(*a*) for Nb(V)–Ti(IV): catechol–lauryltrimethylammonium bromide–1,2-dichloroethane, or 3-methylcatechol–tetramethylammonium bromide–MIBK;

(*b*) for Nb(V)–V(V): catechol–lauryltrimethylammonium bromide–MIBK or 3-methylcatechol–lauryltrimethylammonium bromide–1,2-dichloroethane;

(*c*) for Nb(V)–Mo(VI): catechol–tetraethylammonium bromide–1,2-dichloroethane, or 3-methylcatechol–tetramethylammonium bromide–1,2-dichloroethane;

(*d*) for Nb(V)–W(VI): catechol–tetraethylammonium bromide–1,2-dichloroethane.

UMMARY

The reactions of niobium(V) with catechol and several substituted derivatives ere studied. Optimal conditions for colour development in the niobium(V)–atechol system are: pH 6.7–8.0, and heating at 85° for at least 6 min; the wavelength f maximal absorption is 365 nm, and the molar absorptivity is $1.02 \cdot 10^4$. Catechol erivatives require lower temperatures and develop colours with niobium(V) in eutral or slightly acidic solutions. The best of the derivatives studied were 3-methyl-atechol and 4-chlorocatechol. Extraction of the ion-pairs formed between niobium-V)–catechol and different quaternary ammonium ions, was studied with representa-ive solvents. Similar studies were made on other refractory metal ions, *i.e.*, Ti(IV), (V), Mo(VI) and W(VI), under the optimal conditions for the reaction with iobium(V). Separations of binary (1:1) mixtures of niobium(V) with Ti(IV), (V), Mo(VI) or W(VI) at the $5 \cdot 10^{-5}$ *M* level were shown to be possible under he predicted conditions.

ÉSUMÉ

Une étude est effectuée sur les réactions du niobium(V) avec le catéchol t avec plusieurs de ses dérivés. Les conditions optimales pour le développement e la coloration sont: pH de 6.7 à 8.0, chauffage à 85° pendant 6 min au moins. 'absorption maximum se trouve à 365 nm; le coefficient d'extinction molaire est de $.02 \cdot 10^4$. Les dérivés du catéchol ne nécessitent pas une température aussi élevée t réagissent en solutions neutres ou légèrement acides. Les meilleurs de ces com-osés sont: le méthyl-3-catéchol et le chloro-4-catéchol. Une étude similaire a été ffectuée avec d'autres ions de métaux réfractaires: Ti(IV), V(V), Mo(VI) et W(VI). es séparations de mélanges binaires (1:1) du niobium(V) d'avec Ti, V, Mo et W, n quantités de l'ordre de $5 \cdot 10^{-5}$ *M* sont possibles dans les conditions indiquées.

USAMMENFASSUNG

Es wurde die Reaktion von Niob(V) mit Brenzcatechin und einigen sub-tituierten Derivaten untersucht. Die optimalen Bedingungen für die Entwicklung er Färbung im Niob(V)–Brenzcatechin-System sind: pH zwischen 6.7 und 8.0 und rwärmen auf 85° während mindestens 6 min. Die Wellenlänge der maximalen bsorption ist 365 nm und der molare Extinktionskoeffizient $1.02 \cdot 10^4$. Die Derivate rfordern niedrigere Temperaturen und führen zur Farbentwicklung im neutralen der schwach sauren Medium. Die Extraktion der zwischen Niob–Brenzcatechin nd verschiedenen quaternären Ammoniumionen gebildeten Ionen-Paare wurde mit inigen repräsentative Lösungsmitteln untersucht. Ähnliche Untersuchungen wurden uch mit anderen Metallionen durchgeführt, z.B. mit Ti(IV), V(V), Mo(VI) und V(VI), wobei die optimalen Bedingungen für die Reaktion mit Niob(V) gewählt urden. Trennungen von binären Gemischen (1:1) von Nb(V) mit Ti(IV), V(V), o(VI) oder W(VI) im Bereich $5 \cdot 10^{-5}$ *M* sind unter den angegebenen Bedin-ungen möglich.

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PECTROPHOTOMETRIC STUDY OF A HAFNIUM–HEMATEIN HELATE

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Received 18th August, 1972)

The present paper is concerned chiefly with the formation of an analytically seful chelate of hematein with hafnium, and with a discussion of its nature and pectrophotometric properties. Attention is drawn to the control of pH and reagent oncentration for obtaining the maximal amount of the coloured compound in olution. The composition as well as the stability constant and free energy of ormation of the chelate are described.

There is a need for rapid and accurate micromethods for the determination of afnium, and several chromogenic reactions have been proposed in recent years[1,2]. n seeking a satisfactory method for hafnium, it was found that hematein, obtained y oxidation of hematoxylin, could be used as a reagent, simply by adjusting the H of the medium to an appropriate value.

Hematein has been used by Newcombe *et al.*[3] for the colorimetric etermination of germanium. Dick and Salim proposed it for the chromatographic dentification of cations of the periodic group III-A elements, and it has also been pplied in spectrophotometric determinations of zirconium, thorium and uranium[5].

Dubský and Chodáka[6] prepared several solid salts of hematein with different etals. Both hematoxylin ($C_{16}H_{14}O_6$) and its oxidized form hematein ($C_{16}H_{12}O_6$) re aromatic dyes used as pH indicators. They have two coordinating centers and an form fairly strong chelates with highly charged cations even at acidic pH alues.

XPERIMENTAL

pparatus

A Spekol (Zeiss, Jena) spectrophotometer, with 1-cm cells was used for most bsorption measurements. All spectra were obtained with a Specord (Zeiss, Jena) ecording spectrophotometer. pH was measured with a Metrohm pH meter model 50-B.

eagents

Standard hafnium solution ($1.0 \cdot 10^{-3}$ M). Pure hafnium metal was dissolved the minimal amount of hydrofluoric acid; the solution was fumed with sulfuric cid and then diluted with water, before treatment with ammonia solution in order give 50 ml of a solution with a pH around 2. This stock solution was further diluted with buffer pH 2.0 to the required concentration.

Hematein solution. A standard hematein solution was prepared by oxidatio hematoxylin with hydrogen peroxide. Hematoxylin (British Drug Houses) recrystallized twice from hot water, washed with ice water and ice-cold ethanol, dried to constant weight. The purified dye (1.50 g) was then dissolved in a mix of 250 ml of water and 100 ml of 95% ethanol; 10 ml of 6% hydrogen pero were added and the solution was kept in a boiling water bath for 20 min. resulting hematein solution was cooled and made up to 500 ml with water. solution was stable for at least two months at 20°. In the pH range 2–5, it sho only a slight color which did not interfere with the spectrophotometric investiga of the hafnium complex.

Buffer pH 2.0. This was prepared by mixing 26.5 ml of 0.2 *M* hydrochl acid and 125 ml of 0.2 *M* potassium chloride and diluting to 500 ml with w The pH was checked with a pH meter.

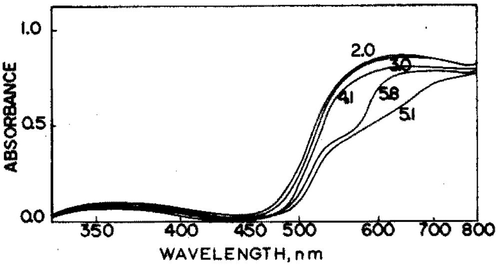
Procedure for calibration curve

Prepare from the stock hafnium solution, by dilution with buffer pH five other solutions containing 3–25 μg of hafnium per ml. Pipet 1.0 ml of into 10-ml volumetric flasks. Add 2 ml of the hematein stock solution, dilute to mark with buffer pH 2.0 and mix. Read the absorbance at 520 nm again reagent blank within 10–60 min.

RESULTS AND DISCUSSION

Formation and properties of the hafnium–hematein complex.

Hematein is an acid–base indicator, undergoing a color transition from yel to red to purple. In the pH range 2.0–5.0, its solution is light red and sh maximal absorption at *ca.* 640 nm. In acidic solution (optimal pH 2.0–4.0), hafn reacts with hematein to give a red-brown coloured complex. The compoun quite stable in the pH range 2.0–4.1, but outside this range it becomes increasi unstable. At pH 2.0, the complex is completely soluble, but at higher pH liable to precipitate on standing. This kind of behaviour seems to be q unusual, for the complexes formed by hematein with several other metal



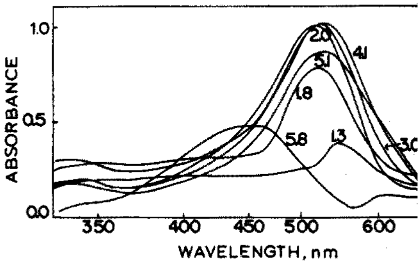


Fig. 1. Absorption spectra of hematein at different pH values (indicated on curves). Refer water.

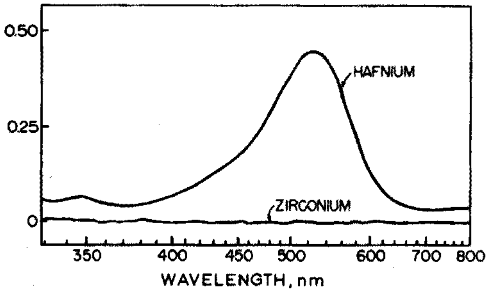
Fig. 2. Absorption spectra of the hafnium–hematein complex at different pH values (indicated on cu Reference: reagent blank.

ifferent pH values are quite insoluble in most of the known solvents[3].

The red-brown hafnium–hematein chelate shows maximal absorbance at 520 m at pH 2.0–5.0. The absorption spectra of the pure dye and of the chelate at ifferent pH values are shown in Figs. 1 and 2, respectively.

Zirconium also forms a chelate with hematein[5] but it differs from hafnium ı that the molar absorptivity of the complex (at 520 nm) is quite small in the ıost appropriate pH range for hafnium. When both metals are present in solution : the same molar concentration ($1 \cdot 10^{-5}$ M), zirconium does not interfere with ıe determination of hafnium (Fig. 3). However, if zirconium is four times more ɔncentrated than hafnium ($4 \cdot 10^{-5}$ M), it interferes significantly. In this way, hafnium ɔuld be determined directly in the presence of zirconium if the concentration of the tter is 10^{-5} M or less, at any pH between 2.0 and 4.0. The molar absorptivity of ıe zirconium–hematein chelate has been stated[5] as 4000 l mole^{-1} cm^{-1} at 500–520 m and pH 1.8.

Some properties of the hafnium–hematein complex are shown in Table I.



ig. 3. Absorption spectra of the hafnium and zirconium chelates with hematein at pH 2. [Hf]= r]=10^{-5} M.

ᴀBLE I

ɔME PROPERTIES OF THE HAFNIUM–HEMATEIN CHELATE AT 20°[a]

ax m)	*Colour*	*Optimal pH range*	*Molar absorptivity (l mole^{-1} cm^{-1})*	*Formation constant (1:2 comp.)*	*ΔG^0 of formation (approx.)*	*Sensitivity ($A=0.001$)*
0	Red-brown	2.0–4.0	58000 (pH 2.0)	$1.6 \cdot 10^6$ (pH 2.0) ($I=0.1$)	-8.32 kcal mol^{-1}	0.003 μg cm^{-2}

The acid dissociation constants of the dye are[12]: p$K_a=6.5$ and p$K_b=10.3$.

dherence to Beer's law

Beer's law is obeyed in the concentration range 3–25 μg of hafnium in) ml of final volume at 520 nm and pH 2.0.

ffects of pH and time

The effect of pH on the stability of the hafnium–hematein chelate was vestigated with Clark and Lubs buffers[7] in the range 1.3–3.75. The results are

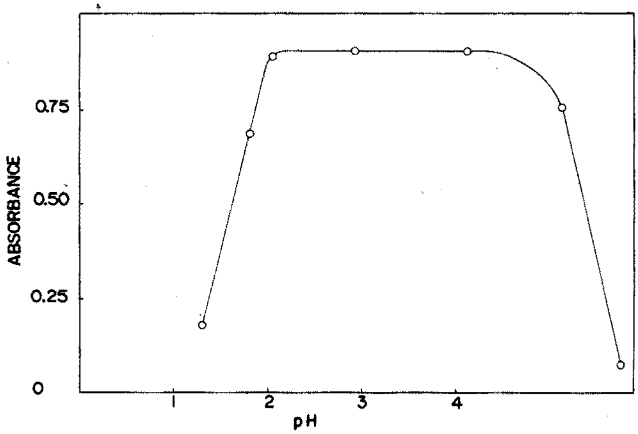


Fig. 4. Variation of absorbance with pH.

shown in Fig. 4. It can be seen that the hafnium chelate is stable over the range 2.0–4.0. However, towards the higher limit of this range, the hafni chelate is quite insoluble, hence the optimal working pH was selected as 2.0.

The hafnium chelate is stable for at least 1 h. The absorbance attains maximum after 10 min and stays constant during about 60 min, after which begins to fade very slowly. After 7 h, the colour has decreased by *ca.* 10%.

Sensitivity

Hematein is a sensitive reagent for hafnium. The molar absorptivity and Sandell sensitivity of the metal chelate, at pH 2.0 and 20°, are listed in Table I.

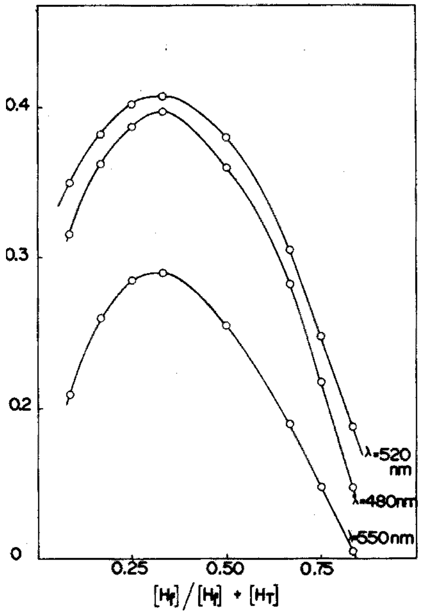
Stoichiometry of the coloured chelate

The stoichiometry of the reaction between hafnium and hematein investigated at pH 2.0 by the method of continuous variations[8,9]. The resu (Fig. 5) indicated the existence of a 1:2 metal–dye chelate for three differe wavelengths (480, 520, 550 nm).

The formation constant of the 1:2 hafnium–hematein chelate was determin spectrophotometrically by the method of Turner and Anderson[10], which applicable because Beer's law was obeyed. This constant was found to be 1.6·1 at ionic strength 0.1, pH 2.0 and 20°. From this value, the approximate f energy of formation was calculated as $\Delta G^0 = -8.32$ kcal mol^{-1}.

Effect of temperature

Sample solutions containing hafnium and blanks were treated identically wi the reagent and placed in water baths at different temperatures, ranging from 20° 90°. Absorbances were read at room temperature (20°), at intervals of 10 min, duri a period of 1 h. The results obtained were identical, showing that the time heating or the temperature have no effect on the final concentration of t chelate, if the absorbance is read at room temperature. However, if the absorbanc are read at higher temperatures, the results indicated that the higher the temperatu the more dissociated is the complex. For further work, all measurements were ma at 20° in a constant-temperature room.



g. 5. Composition of the hafnium–hematein chelate by the method of continuous variations at 1 2.0.

ffect of reagent concentration

In view of the relatively low value of the formation constant of the chelate, ɩtal complexation of hafnium was expected to require a large excess of hematein. /hen increasing amounts of hematein (as a 10^{-5} *M* solution) were added to a andard amount of hafnium ($8.1 \cdot 10^{-8}$ *M*) and the reaction was allowed to roceed, the results showed that maximal absorbance was achieved only when more ıan 4 ml of hematein solution was added. Thus the ratio of the dye to the metal ıould exceed 220. In practice, it was found advisible to use a ratio of hematein ı hafnium of 240.

:lectivity

Hematein reacts with several metal ions, especially highly charged ones, the ability of the chelate depending on the pH. A complete study of the interferences ı the reaction between hafnium and hematein will be presented at a later date.

Some anions must be absent, because they compete with hematein for ıfnium; such anions are fluoride, oxalate, citrate and EDTA. However, sulfate, :rchlorate, phosphate, silicate, chloride, bromide, iodide and nitrate show no interrence, under the conditions used.

onclusion

Hematein is a sensitive reagent for hafnium in acidic medium, forming a ıite stable chelate. Zirconium also gives a coloured complex with hematein, under ıe same conditions of pH, but the reaction is much less sensitive, so that ıfnium can be determined in the presence of zirconium when both are present at the same molar concentration ($1.0 \cdot 10^{-5}$ *M*).

The hafnium–hematein chelate is probably of the type $HfO[C_{16}H_{12}O_6]_2$. T absorption spectra of the chelate in the pH range 2.0–5.0 show only one defin absorption band. This may indicate only one electronic transition of the compl However, the structural configuration of this chelate is not easy to predict. Hafniu is known to have the coordination number eight in a series of complexes[11], b in view of the stoichiometry of the hematein chelate, it is not safe to assume th the eight coordinating groups are provided by the two reagent molecules. Ea hematein molecule has two coordinating centers, with a total of four donor grou two of them being *o*-hydroxyl groups and the other two being in the *o*-hydrox quinone group. Of these groups, only the last produces anions in solution. seems sterically difficult to engage all the four donor groups to the central me ion, and it is more probable that only the *o*-hydroxyquinone system is responsil for chelation.

The authors are indebted to Dr. E. F. R. Fraga for providing the pu hafnium metal, and to Miss Rosa 7. Figueras for valuable technical assistan One of the authors (N.V.) gratefully acknowledges a fellowship from the "Conselho Pesquisas UFRGS".

SUMMARY

A spectrophotometric study of an analytically useful hafnium chelate hematein is presented. The stoichiometry, the formation constant, the optimal p range and the free energy of formation of the chelate are described. Beer's law obtained in the range 3–25 μg of hafnium(IV).

The red-brown chelate, of probable formula HfO[hematein]$_2$, can be used f the colorimetric determination of hafnium in the presence of zirconium, if t molar concentrations of both metals are the same. The molar absorptivity of t hafnium chelate is $5.8 \cdot 10^4$ l mole^{-1} cm^{-1} at 520 nm and pH 2.0 at roo temperature.

RÉSUMÉ

Une étude spectrophotométrique du chélate hafnium–hématéïne est effectu en vue d'une application analytique. On examine stoechiométrie, constante formation, pH, énergie libre de formation. La loi de Beer s'applique de 3 à 25 de hafnium(IV). Le chélate formé, brun-rouge, de formule probable Hf [Hématéïne]$_2$ peut être utilisé pour le dosage colorimétrique du hafnium en présen de zirconium, à condition que les concentrations molaires des deux métaux soie pareilles (1.10^{-5} *M*). Le coefficient d'extinction molaire du chélate hafnium $5.8 \cdot 10^4$ l mole^{-1} cm^{-1} à 520 nm, à pH 2.0, à la température ordinaire.

ZUSAMMENFASSUNG

Es wurde ein analytisch anwendbares Hämateinchelat des Hafniums spektr photometrisch untersucht. Die Stöchiometrie, die Bildungskonstante, der optima

pH-Bereich und die freie Energie der Chelatbildung wurden bestimmt. Das Beersche Gesetz ist gültig im Bereich 3–25 μg Hafnium(IV). Das rotbraune Chelat mit der wahrscheinlichen Formel HfO[Hämatein]$_2$ kann für die kolorimetrische Mikrobestimmung des Hafniums in Gegenwart von Zirkonium verwendet werden, wenn beide Metalle in derselben molaren Konzentration vorliegen. Der molare Extinktionskoeffizient des Hafniumchelates ist $5.8 \cdot 10^4$ l mol^{-1} cm^{-1} bei 520 nm und pH 2.0 bei Raumtemperatur.

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YRIDYLAZO-DIAMINOBENZENES AS REAGENTS FOR COBALT

ECTROPHOTOMETRIC DETERMINATION OF COBALT IN LICATES AND METEORITES

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eceived 9th February 1973)

Among the many reagents employed for the spectrophotometric deter-ination of traces of cobalt in silicates, Nitroso R salt (sodium 1-nitroso-2-hydroxy-phthalene-3,6-disulphonate) is the best known and most widely used[1–3], because its superior selectivity and sensitivity. However, most workers prefer to use analytical wavelength of the red anionic complex other than that of maximal sorption because of the strong absorption of the reagent itself, and the relatively gh absorption of macro-amounts of iron normally present in silicates[3]. The nsitivity drops from 0.0019 µg Co cm^{-2} at 420 nm to 0.0059 µg Co cm^{-2} 540 nm.

As a possible alternative reagent, none has surpassed the sensitivity and lectivity of 4-(5-chloro-2-pyridylazo)-1,3-diaminobenzene (5-Cl-PADAB) recently nthesized and evaluated by Shibata *et al.*[4]. The molar absorptivity of its cobalt mplex is reported to be $1.13 \cdot 10^5$ l mole^{-1} cm^{-1} with a sensitivity of 0.00051 Co cm^{-2} at 570 nm. Under the optimal conditions established in their study, e determination of microgram amounts of cobalt is possible in the presence large amounts of other elements with only iron(III) and chromium(VI) terfering. Shibata *et al.*[5,6] have also mentioned the synthesis of 4-(2-pyridylazo)-3-diaminobenzene and 4-(5-bromo-2-pyridylazo)-1,3-diaminobenzene, and the balt reactions of these compounds. The molar absorptivities of the cobalt mplexes are $1.07 \cdot 10^5$ at 559 nm and $1.17 \cdot 10^5$ l mole^{-1} cm^{-1} at 573 nm, spectively[5,6], but no details of their applications have been published. The nsitivity of these reagents is remarkable compared to other structurally related es such as pyridylazonaphthols.

The potentialities of the reagents synthesized and studied by Shibata *et* .[4–6] led to the present investigation of these and other structurally related mpounds. The effect of various halogen substitutions on the pyridine ring in lation to the sensitivity and selectivity of their reactions with cobalt was studied. he six compounds prepared were: 4-(2-pyridylazo)-1,3-diaminobenzene (I; ADAB)[5,6]; 4-(5-chloro-2-pyridylazo)-1,3-diaminobenzene (5-Cl-PADAB)[4]; 4-(5-omo-2-pyridylazo)-1,3-diaminobenzene (5-Br-PADAB)[5,6]; 4-(5-iodo-2-pyridyl-

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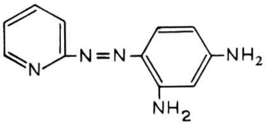
azo)-1,3-diaminobenzene (5-I-PADAB); 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene (3,5-Cl-PADAB) and 4-(3,5-dibromo-2-pyridylazo)-1,3-diaminobenzene (3,5-Br-PADAB).

Of these reagents, 5-Br-PADAB was the first to be prepared, and its application to the determination of cobalt in silicates and meteorites was investigated in detail.



I

EXPERIMENTAL

Synthesis of reagents

2-Pyridylazo-1,3-diaminobenzenes were prepared by coupling *m*-phenylenediamine with the 2-pyridyldiazotates in aqueous ethanol solution.

Starting materials. 2-Aminopyridine was purified[7] and used for subsequent preparation of halogen derivatives. *5-Chloro-2-aminopyridine* was obtained as white plates, m.p. 132° (lit. 130–2°), by direct chlorination of 2-aminopyridine in 20% sulphuric acid at room temperature[4]. *3,5-Dichloro-2-aminopyridine* was isolated after prolonged chlorination of the amine in 25% sulphuric acid. The exothermic reaction was allowed to proceed to a maximum of 75°, and the solution was re-warmed when the temperature fell to 40° and chlorinated for 30 min longer. The precipitate formed after neutralizing the cooled reaction mixture with potassium hydroxide was filtered, washed with water a few times and steam-distilled. The pure product was obtained as white crystals, m.p. 83–4° (lit. 84°) in about 70% yield. Chlorination in alcoholic medium[8] was less successful. *5-Bromo-2-aminopyridine* was prepared by bromination in cold ethanolic solution[9]. The purified product was obtained as off-white powder (m.p. 137–8°) after recrystallization from benzene. *3,5-Dibromo-2-aminopyridine* was obtained in high yield by treating a warm 20% sulphuric acid solution of the amine with an excess of bromine[10]. After several recrystallizations from acetone–water, the product was obtained as white needles, m.p. 104° (lit. 104–4.5°). *5-Iodo-2-aminopyridine* was prepared by the iodine/potassium hydroxide method[11]. The steam distillate was extracted with ether, including the solid which accumulated in the condenser. After the removal of ether and treatment with decolorizing charcoal, the product was crystallized from benzene–petroleum ether as shiny white plates, m.p. 128° (lit. 129°). The iodine/mercury(II) acetate method[12] failed to give the desired purity of the product; also the low yield obtainable for the preparation of *3,5-diiodo-2-aminopyridine* by the same route did not warrant further investigation.

m-Phenylenediamine dihydrochloride (BDH Laboratory Grade) was purified by boiling a concentrated aqueous solution with decolorizing charcoal, filtering under suction and precipitating by adding acetone to the cooled solution. The solid was washed with acetone and dried. *n-Butyl nitrite* was freshly prepared[13], distilled, and stored under refrigeration. *Sodium amide* (Fluka) and *sodium metal* were stored under anhydrous toluene.

Diazotization. Because of its simplicity, the Chichibabin and Ryazantsev ethod[14] was initially used for the preparation of all diazotates and the reaction oducts were used directly for the coupling reaction as described below. How- er, when some of the pyridylazo dyes thus obtained were examined under a larizing microscope, the crystals proved to be heterogeneous. One of these oducts, the 3,5-dibromopyridylazo derivative, was further investigated in an ort to identify its components, and, by repeated extraction with boiling petroleum her, a fraction was obtained which deposited white needles on further purifi- tion. Elemental analysis showed it to be unreacted 3,5-dibromo-2-aminopyridine, t the suspected dihalo-2-ethoxypyridine[15]. Thus, in order to obtain reasonably antitative diazotizations, different procedures were necessary according to the served reactivity. The diazotization method of Chichibabin and Ryazantsev[14] as successful only for 2-aminopyridine and its 5-bromo derivative. Sodium metal .4 g) was dissolved in 80 ml of absolute ethanol and 0.1 mole of the pure nine was added. After complete dissolution, 10 ml of n-butyl nitrite was added d the whole refluxed for 20 min. The diazotate then was allowed to cool.

For the diazotization of 5-chloro-, 3,5-dichloro- and 3,5-dibromo-2-amino- ridines, a high conversion rate was obtained by the method of Shibata *et al.*[4]. dium amide (2.5 g) was dissolved in 100 ml of absolute ethanol, 0.1 mole of e amine and 10 ml of n-butyl nitrite were added and the mixture was refluxed r 2–3 h. The 5-iodo derivative yielded only about 10% conversion to the azotate after 3 h of refluxing by this procedure. The difficulty was overcome isolating the sodium 5-iodo-2-pyridyldiazotate from the anhydrous ethereal action mixture by filtering and drying in vacuum as described by Gusev and churova[16].

Coupling reaction. m-Phenylenediamine dihydrochloride (18.1 g, 0.1 mole) was ssolved in 150 ml of water and added to the cooled diazotate solution rapidly th constant stirring. A weighed portion of the dry 5-iodo-2-pyridyldiazonium lt was suspended in ethanol and a calculated amount of *m*-phenylenediamine hydrochloride in aqueous solution was added.

In most cases the exothermic reaction commenced immediately and was ought to completion by warming to 50° for 30 min. With the 3,5-dihalo-2- ridyldiazotates it was necessary to accelerate coupling by introducing carbon oxide during heating. The warm reaction mixture was further diluted with water cause some turbidity and after several hours of standing a crystalline ecipitate formed; there was no advantage in allowing it to stand overnight or nger periods. After cooling in an ice bath, the crystals of the desired product ere filtered by suction; the dark supernatant liquid had no metal-chelating ac- ity. The crude product was washed with water until washings became colour- ss, then recrystallized from boiling ethanol by the addition of water and dried 100° overnight. Yields were 14–36% based on the halo-2-aminopyridines.

In attempts to synthesize the unsubstituted compound PADAB, no solid oduct could be isolated after the coupling reaction. Moreover, the product as unstable on standing, hence the separation of the chelating substance seemed sirable. Column chromatographic separation of the reaction mixture on activated umina produced two fractions, only one of which was active in terms of elating ability. The PADAB-enriched solution could not be effectively extracted in either polar or non-polar solvents under a variety of conditions. Never less, the fraction containing the chelating substance was successfully character by recording absorption curves of its cobalt complexes.

5-Cl-PADAB, red-brown crystals, m.p. 249–51°. Calc. for $C_{11}H_{10}N$ 53.8% C, 4.1% H, 28.3% N and 14.3% Cl; found: 53.4% C, 4.3% H, 28.4% and 14.5% Cl.

5-Br-PADAB, rusty brown crystals, m.p. 252–3°. Calc. for $C_{11}H_{10}N$ 45.2% C, 3.45% H, 24.0% N and 27.35% Br; found: 45.7% C, 3.4% H, 24.1% and 27.2% Br.

5-I-PADAB, dark red crystals, m.p. 248–50°. Calc. for $C_{11}H_{10}N_5I$: 39.0% 3.0% H, 20.65% N and 37.4% I; found: 38.6% C, 3.0% H, 19.2% N and 37.9

3,5-Cl-PADAB, red reflective crystals, m.p. 237–9°. Calc. for $C_{11}H_9N_5$ 46.8% C, 3.2% H, 24.8% N and 25.1% Cl; found: 46.8% C, 3.3% H, 24.6% and 25.8% Cl.

3,5-Br-PADAB, pink reflective crystals, m.p. 231–3°. Calc. for $C_{11}H_9N_5$ 35.6% C, 2.4% H, 18.9% N and 43.1% Br; found: 35.6% C, 2.3% H, 18.7% and 43.6% Br.

Reagents for spectrophotometric studies

Solutions ($1 \cdot 10^{-3}$ *M*) of the halogen-substituted pyridylazo-diaminobenz (5-Cl-PADAB, 5-Br-PADAB, 5-I-PADAB, 3,5-Cl-PADAB and 3,5-Br-PADAB) prepared by dissolving the requisite amount of pure reagent in 100 ml of abso ethanol. For analytical application, 0.01% 5-Br-PADAB dissolved in ethanol prepared. Stored in amber bottles, these solutions were stable for several mor A PADAB-containing solution in aqueous alcoholic medium was used immedi after column chromatographic separation of the coupling reaction mixture above).

Cobalt solution. A stock solution was prepared by dissolving 67.182 m "Specpure" tricobalt tetroxide in boiling concentrated sulphuric acid. After se hours of heating to complete dissolution, the solution was diluted to 1 working solution was prepared by diluting 50.00 ml of the stock solution to (3.36 μg Co ml^{-1}).

Buffer solution. Sodium acetate, 2 *M*.

Indicator solution. Quinaldine red (0.05 g) was dissolved in 100 ml of etha water (1 + 1).

All other reagents, chemicals and metal salts were of analytical grade.

Apparatus

Absorption spectra were recorded by Cary 14 and Unicam SP 1800 cording spectrophotometers with 10-mm silica cells. Fixed wavelength measurem for the calibration curve and cobalt analyses were obtained with a Pye-Uni SP 500 S-2 spectrophotometer equipped with automatic sample changer ar recorder. pH measurements were made with a Metrohm-Herisau Potentiog Type E 436.

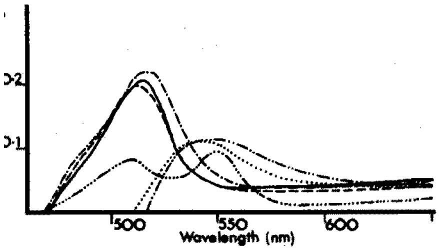
SPECTROPHOTOMETRIC STUDIES OF THE REAGENTS

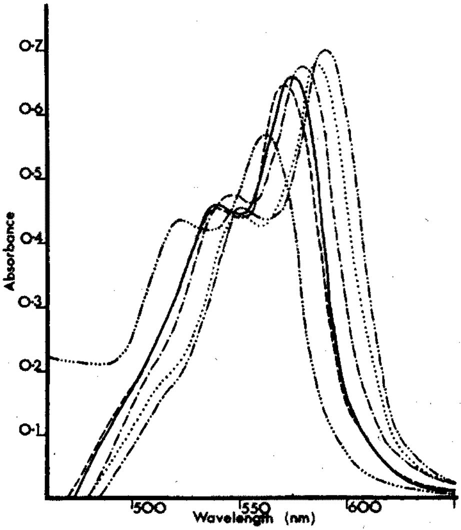
Colour reactions with metals

All the pyridylazo-diaminobenzenes examined reacted with cobalt(II obalt(III) in slightly acidic (pH 4–7) or alkaline (pH 8–10) medium to form a oloured chelate. Among common cations only Fe(II), Fe(III), Cu(I), Cu(II), Hg(II), i(II) and Zn(II) formed coloured chelates at pH 4–7. The following ions failed to give etectable coloration at either pH 4–7 or pH 8–10: Ca(II), Mg(II), Sr(II), Be(II), a(II), Pb(II), Sn(II), Sn(IV), Cr(III), Cr(VI), Mn(II), Al(III), Zr(IV), Ti(IV), (V), Ce(IV), Th(IV), La(III), Mo(VI) and U(VI). The presence of citrate, malonate, xalate, cyanide, dithiocarbamate and polyaminocarboxylic acids (*e.g.*, EDTA, CTA, etc.) inhibited the formation of the cobalt complexes. Large concentrations f fluoride, chloride, bromide, iodide, perchlorate, nitrate, sulphate, thiosulphate, hiocyanate, phosphate, sulphosalicylate, tartrate, hydrogen peroxide and hydroxyl-mine salts were without effect. The cobalt complexes could be formed by buffering ith either sodium acetate or hexamethylenetetramine. On addition of mineral acid .*g.*, HCl, HBr, H_2SO_4, etc.) the primary cobalt complexes changed into another ater-soluble species possessing significantly higher absorption characteristics. How-ver, no coloration was observed with any of the reagents in acidic solutions of obalt; this clearly indicates that the ligands are being protonated on the heterocyclic itrogen. Consequently, the quantitative formation of the primary cobalt com-lexes in a buffered medium is a pre-requisite for the measurement of absorption fter acidification.

bsorption spectra

The reagent solutions ($1 \cdot 10^{-4}$ *M*) absorb maximally in the vicinity of 460





ig. 1. Absorption curves of cobalt–pyridylazo-diaminobenzene complexes at pH 5. Measured against rresponding reagent blanks in 10-mm cells. Cobalt concentration: $5.7 \cdot 10^{-6}$ *M*, reagent concen-ation: $5 \cdot 10^{-5}$ *M*. (–·····–) PADAB; (–––) 5-Cl-PADAB; (——) 5-Br-PADAB; (–·–·–) 5-I-PADAB; ·····) 3,5-Cl-PADAB; (–··–) 3,5-Br-PADAB.

ig. 2. Absorption curves of cobalt–pyridylazo-diaminobenzene complexes after acidification to 2.4 *M* Cl against corresponding reagent blanks in 10-mm cells. Cobalt and reagent concentrations: $5.7 \cdot 10^{-6}$ and $5 \cdot 10^{-5}$ *M*, respectively. Curve markings as for Fig. 1.

nm measured against distilled water as reference. Absorption spectra of the co complexes formed in aqueous solution with the reagents at pH 5 (*i.e.* primary c plexes) are shown in Fig. 1. The curves show distinct peaks in the range 510- nm. The absorption spectra of the cobalt complexes in 2.4 *M* hydrochloric are shown in Fig. 2. These curves show two absorption maxima between 520- nm and 565–590 nm, respectively.

Molar absorptivities and reagent sensitivities

The molar absorptivity (ε) and sensitivity of cobalt complexes in 2.4 hydrochloric acid, calculated from the spectrophotometric data are showi Table I. The molar absorptivities found by Shibata[5] for some of the reag are also given for comparison.

TABLE I

MOLAR ABSORPTIVITY AND SENSITIVITY FOR THE COBALT COMPLEXES

Reagent	λ_{max}*(nm)*	ε*(l mole*$^{-1}$ *cm*$^{-1}$*)*	*μg Co cm*$^{-2}$	ε*(l mole*$^{-1}$ *cm*$^{-1}$*)* *(Shibata*[5]*)*
PADAB	565	$1.00 \cdot 10^5$	0.00059	$1.07 \cdot 10^5$
5-Cl-PADAB	570	$1.13 \cdot 10^5$	0.00052	$1.12 \cdot 10^5$
5-Br-PADAB	575	$1.16 \cdot 10^5$	0.00051	$1.17 \cdot 10^5$
5-I-PADAB	580	$1.18 \cdot 10^5$	0.00050	–
3,5-Cl-PADAB	585	$1.19 \cdot 10^5$	0.00050	–
3,5-Br-PADAB	590	$1.23 \cdot 10^5$	0.00048	–

Interferences

Of the five cations in various valency states which formed coloured c plexes at pH 4–7, only the chelates of iron were stable enough to w stand subsequent acidification. Although neither chromium(III) nor chromium formed coloured chelates, chromate interfered seriously by bleaching the co complex in mineral acid medium. The effects of interfering elements on absorption spectra of 5-Br-PADAB and its cobalt complex are shown in Fig. 3

It can be seen that the iron chelate of 5-Br-PADAB undergoes progres decomposition in 2.4 *M* hydrochloric acid and that chromium(III) does interfere significantly. After extended standing, cobalt (16.8 μg) was recov with a slight loss in the presence of iron (1 mg) as measured at the abs tion peak, whereas there was a significant enhancement at the secondary sorption peak (curve F, Fig. 3). Moreover, the iron chelate after acidifica could be decomposed rapidly at 50–60°. The interfering behaviour of chromi (VI) is easily overcome by reduction to the tervalent state.

Qualitative examination indicated that interferences with the other reag are similar to those found with 5-Br-PADAB.

Selectivity of cobalt reactions

Traces of cobalt can be detected selectively in the presence of many o elements. By masking iron(III) with fluoride and reducing chromium(VI) ydroxylamine the reaction of the pyridylazo-diaminobenzenes with cobalt becomes ecific. This approach thus offers a useful spot-test detection of cobalt.

eaction time and reagent concentration

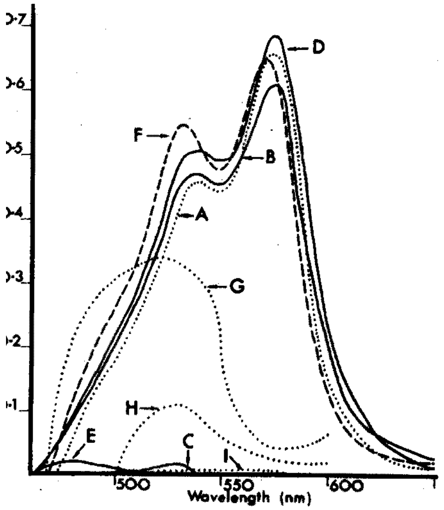
In pure solutions at pH 4–7, cobalt complexes of the reagents are formed ithin 1–2 min; in practice, however, 15-min standing is allowed in order to mpensate for the somewhat suppressive effects of macro-constituents normally esent in silicates. On acidification, the deeply coloured species are formed mediately. Within the range of 1.7–25.2 μg Co, 5 ml of ethanolic 0.01% dye lutions are sufficient; although larger reagent concentrations may be used.

olour stability

Cobalt complexes of 5-Br-PADAB, 3,5-Br-PADAB and 5-I-PADAB in 2.4 *M* ydrochloric acid showed no appreciable fading after 24 h in diffuse daylight.

ffect of various mineral acids and their concentration

As already pointed out, the primary cobalt chelates formed at pH 4–7 ith the six reagents can be changed into another species by adding some ineral acids. The effects of hydrochloric, hydrobromic, nitric, sulphuric, perchloric d phosphoric acids were qualitatively assessed. The choice and concentration mineral acids were quantitatively examined with 5-Br-PADAB and 3,5-Br-ADAB as chromogens for fixed amounts of cobalt, and hydrochloric, hydro-omic and sulphuric acids for acidification. The optimal concentration of ydrochloric acid was found to be within 2–5 *M*, which is similar to the range



3. The effect of Cr(VI), Cr(III) and Fe(III) on the absorption spectra of cobalt–5-Br-PADAB nplex in 2.4 *M* HCl. Measured against reagent blank in 10 mm cells. Final volume, 50 ml. ed concentration of cobalt (16.8 μg) where applicable. A = Co only, B = Co + 1 mg Cr(VI), C = + 10 mg Cr(VI), D = Co + 10 mg Cr(III), and E = 10 mg Cr(VI) only. (All measured within 2 h.) Co + 1 mg Fe(III), measured after 90 min. Decomposition curves of Fe(III)-complexes: G, H d I each containing 1 mg Fe(III) only and measured after 10, 90 and 120 min standing, pectively.

suggested by Shibata *et al.*[4]. The absorption curves of the cobalt chelates HCl (2.4 *M*), HBr (3.0 *M*) and H_2SO_4 (1.8 *M*) showed good agreement on for samples acidified by hydrochloric and sulphuric acids; the primary cob chelates of the monobromo and dibromo derivatives acidified with hydrobron acid (3.0 *M*) showed lower absorbances without change in the λ_{max} values. T molar absorptivities compare as follows: for 5-Pr-PADAB, $1.15 \cdot 10^5$ (2.4 *M* HC $1.03 \cdot 10^5$ (3.0 *M* HBr) and $1.15 \cdot 10^5$ (1.8 *M* H_2SO_4); for 3,5-Br-PADAB, 1.23·1 (2.4 *M* HCl), $9.81 \cdot 10^4$ (3.0 *M* HBr) and $1.21 \cdot 10^5$ (1.8 *M* H_2SO_4). There is obvious explanation for the anomalous behaviour of hydrobromic acid. Subs quently hydrochloric acid was chosen for all quantitative applications.

Calibration curve

Eleven concentration points were prepared within the range of 1.7–25.2 Co/50 ml with 5-Br-PADAB as reagent. Absorbances were measured at 580 n in 10-mm quartz cells against a reference blank solution. Beer's law was obey over this range, within 0.82% of the value.

APPLICATION TO ANALYSIS OF SILICATES

The interference studies of iron(III), chromium(III) and chromium(V shown in Fig. 3 imply certain limiting parameters within which cobalt may determined in complex silicates. Although curve F in Fig. 3 suggests a reasonab tolerance for iron, the macro-amount of this element commonly present silicates is undesirable and its removal by solvent extraction is recommended.

In most silicates, iron(II) is present in large excess over chromium, hen chromate is rarely encountered. Likewise, the Cr(III)/Co ratio of $10^4/17$ (cur D, Fig. 3), which gives a slight positive error, is unusual in natural silicates.

Recommended procedure for the determination of cobalt in silicates and meteorit

Sample dissolution and solvent extraction. Weigh *ca.* 500 mg of fine powdered silicate rock (−200 mesh) in a platinum evaporating dish, moist with a few drops of water and add 3 ml of 50% sulphuric acid and 15 ml concentrated hydrofluoric acid. Evaporate with occasional stirring on a wat bath to near dryness, add a further 5 ml of hydrofluoric acid and evapora again to incipient crystallization. Transfer the dishes to a hot plate set on lo heat, and gradually increase heating until copious fumes of sulphur trioxide a evolved. Dissolve the cooled salts in 10 ml of water by warming, and transf the contents to a 250-ml beaker by thorough rinsing with 7 *M* hydrochlo acid. Add 5 ml of saturated bromine water, and then evaporate to a sma volume. After cooling, transfer the contents to a 250-ml separatory funnel l washing the beaker several times with 7 *M* hydrochloric acid. Extract iron(II chloride by vigorously shaking with 50 ml of isobutyl methyl ketone (MIBI for 1 min. After the phases have separated, drain the acidic layer to t same beaker, shake the organic extract with four 5-ml portions of 7 *M* hydr chloric acid and drain each portion to the beaker. Bring the acidic soluti cautiously to the boil and add a few ml of saturated bromine water after abo half the solution has evaporated. Continue evaporation until most acid is remove ute with water and bring to the boil if necessary to dissolve salts. Dilute e cooled solution to 100 ml in a volumetric flask.

Certain basic and ultra-basic rocks may contain some mineral grains inel, ilmenite, magnetite, chromite, etc.) which resist hydrofluoric acid. In this se the insoluble minerals should be collected by filtration and the ashed idue fused in a platinum crucible with potassium pyrosulphate, leached with ter and then returned to the main fraction. Then iron should be extracted th MIBK from the combined solution as described. Hydrofluoric acid could used alone for the decomposition of silicate rocks containing appreciable ounts of resistant minerals by applying a bomb technique[17] at elevated nperatures.

Meteorites composed of silicates+sulphides and silicates+metal may be ought into solution by the hydrofluoric–sulphuric acid method and subsequent atment with hydrochloric acid. Iron meteorites lacking silicate inclusions may be solved in hydrochloric acid in the presence of a few drops of nitric acid. After mplete oxidation of iron to iron(III) with bromine in 7 *M* hydrochloric acid, n is removed by MIBK extraction as for silicates. The resulting sample solutions ntaining a minimum amount of acid are diluted to a convenient volume and quots are taken for subsequent measurements.

Colour development and measurement. Pipette suitable aliquots not exceeding ml and containing up to 25 μg of cobalt into 50-ml volumetric flasks. Add a v drops of 0.05% quinaldine red indicator and adjust the pH to 1–2 with ute ammonia solution. At the first appearance of a reddish colour, the solution ould be free of opalescence (*i.e.*, formation of hydroxides). Add 5.00 ml of anolic 0.01% 5-Br-PADAB solution, mix and add 5 ml of 2 *M* sodium acetate. low the solution to stand for 15 min after thorough mixing. Add 10 ml of ncentrated hydrochloric acid, mix, and cool to room temperature. After diluting volume, measure the absorbance at 580 nm against a reagent blank as reference ing 10-mm quartz cells. Calculate the concentration (p.p.m.) of cobalt from the libration data. The analysis should be carried out at least in duplicate (inpendent weights).

The calibration curve and the reagent blank were prepared by treating asured aliquots of cobalt solution (0–25.2 μg Co ml^{-1}) as described under olour development and measurement”.

sults and discussion

The results obtained on standard rocks and other materials are presented Table II.

Because of the extreme sensitivity of 5-Br-PADAB, only small sample sizes e required, and cobalt contents above 1000 p.p.m. in meteoritic specimens are tter determined by the less sensitive nitroso R salt method[3]. However, a scarcity available sample may warrant the use of this reagent at the expense of a ssible error due to non-homogeneity.

Attempts were made to avoid the preliminary removal of iron by a deiled examination of the following reactions: masking iron with fluoride or tartrate, d decomposing the iron(III)–5-Br-PADAB complex formed by heating. Fixed ounts of cobalt and iron solutions, as well as total silicate dissolutions, were treated separately with increasing amounts of 10% ammonium fluoride or 20 sodium tartrate, the pH was adjusted to 7, and the colour was developed recommended. In a further set of tests, a large excess of 5-Br-PADAB was us to complex all iron and cobalt present.

The main conclusions were as follows. Iron was effectively masked fluoride or tartrate ions only in the iron(III) state, as expected; but low r coveries for cobalt were obtained. The presence of macro-amounts of aluminiu calcium and magnesium caused difficulties when fluoride was used for maski because of the formation of sparingly soluble fluoride salts. Troublesome turbidi persisted after acidification, and the corrosive effect of fluoride on glass was marke When tartrate was used, iron(III) imparted a yellow colour with tartrate which inte fered with the reagent reference.

TABLE II

DETERMINATION OF COBALT IN SILICATES AND METEORITES

(Results in p.p.m.)

Sample	*Range*[a]	*Kaye*[b]	*Others*	*This work*
Granite G-1	1.9–<10	2.3	–	3.6 ± 0.1
Granite G-2	2–21	4.5	–	4.9 ± 0.2
Granodiorite GSP-1	<3–22	7.0	–	9.0 ± 0.5
Andesite AGV-1	10–30	15	–	15.7 ± 0.4
Basalt BCR-1	29–60	37	–	36.2 ± 1.3
Diabase W-1	33–53.7	48	–	48 ± 0.5
Peridotite PCC-1	80–300	115	–	112 ± 1.8
Dunite DTS-1	96–200	145	–	143 ± 2.8
Mild Steel, BCS 272	–	–	0.25% (Cert)	2455 ± 3.7
Lake Labyrinth (Olivine-hypersthene meteorite)	–	–	435[c]	475 ± 2
Boxhole (Iron meteorite)	–	–	0.48%[d]	4870 ± 10

[a] F. J. Flanagan, *Geochim. Cosmochim. Acta*, 33 (1969) 81.

[b] M. Kaye, Preferred values for Interlaboratory Rock Samples, Department of Geology, A.N.U., 19 (personal communication).

[c] L. Greenland and J. F. Lovering, *Geochim. Cosmochim. Acta*, 29 (1965) 821.

[d] C. F. Lewis and C. B. Moore, *Meteorit.*, 6 (1971) 195.

The unrealistically large excess of reagent necessary to chelate quantitative both iron and cobalt was also unsuccessful, because the absorbance measuremen against an intense reagent blank background required large slit adjustment; mor over, the substantial positive error in the cobalt recoveries made this approach usele

In summary, however attractive a procedure for the direct measurement traces of cobalt may be, no simpler or more reliable solution than the MIB extraction of iron was found. As indicated in this study, up to 50 times as mu iron as cobalt can be tolerated if the iron complex is decomposed by either standi or heating. In silicates, however, this ratio is far too unfavourable.

NCLUSIONS

This comparative study of six pyridylazo-diaminobenzenes including the agents of Shibata *et al.*[4–6] indicates that the nature and number of halogen bstitutions on the pyridine ring has a direct bearing on the sensitivities of their actions with cobalt. The increasing atomic radii of halogens (Cl→I) in the mono- logenated derivatives show an increase in molar absorptivity of their cobalt com- exes accompanied by a shift of λ_{max} towards longer wavelength. Likewise, the imber of halogens introduced in the pyridine ring enhances sensitivities even rther when compared to the corresponding monohalo derivatives. These com- unds offer a choice of reagent for the determination of microgram quantities of balt. Their extreme sensitivity and virtual freedom from interference should make em widely applicable as colorimetric reagents in geochemical, biological, pharma- logical and industrial fields.

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MMARY

Six pyridylazo-diaminobenzenes have been synthesized and assessed as chro- ogens for the spectrophotometric determination of traces of cobalt. Five of the agents having chloro-, bromo- and iodo-substitutions on the heterocyclic ring ow high colour stabilities and extreme sensitivities in their reactions in strongly idic medium. The effective molar absorptivities range between 1.00 and $1.23 \cdot 10^5$ l ole^{-1} cm^{-1}. Only iron and chromium(VI) interfere; the presence of fluoride and droxylamine makes the reactions specific. 4-(5-Bromo-2-pyridylazo)-1,3-diamino- nzene has been applied to the determination of cobalt in silicate rocks and eteorites with good precision and accuracy.

SUMÉ

Six pyridylazo-diaminobenzènes ont été synthétisés et essayés comme réactifs romogènes pour le dosage spectrophotométrique des traces de cobalt. Cinq d'entre x avec groupes chloro-, bromo- et iodo- fixés sur le noyau hétérocyclique présen- it une très grande stabilité de couleur et des extrèmes sensibilités, dans leurs actions en milieu très acide. Les coefficients d'extinction molaire sont compris entre 0 et $1.23 \cdot 10^5$ l mol^{-1} cm^{-1}. Seuls fer et chrome(VI) interfèrent. La présence de iorure et d'hydroxylamine rend les réactions spécifiques. Le 4-(5-bromo-2-pyri- lazo)-1,3-diaminobenzène est utilisé pour le dosage du cobalt dans les silicates les météorites, avec une bonne précision et une bonne exactitude.

SAMMENFASSUNG

Sechs Pyridylazo-diaminobenzole wurden synthetisiert und als chromogene

Reagenzien für die spektrophotometrische Bestimmung von Kobaltspuren unte sucht. Fünf der Reagenzien, die am heterocyclischen Ring durch Chlor, Brom u Jod substituiert sind, zeigen hohe Farbbeständigkeiten und extreme Empfindlic keiten bei ihren Reaktionen in stark saurem Medium. Die effektiven molaren E tinktionskoeffizienten liegen zwischen 1.00 und $1.23 \cdot 10^5$ l mol^{-1} cm^{-1}. Nur Eis und Chrom stören; durch die Gegenwart von Fluorid und Hydroxylamine werden d Reaktionen spezifisch. 4-(5-Brom-2-pyridylazo)-1,3-diaminobenzol wurde mit gut Reproduzierbarkeit und Genauigkeit auf die Bestimmung von Kobalt in Silica gesteinen und Meteoriten angewendet.

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YNTHESES AND SPECTROPHOTOMETRIC STUDIES OF AZO DYES ONTAINING *m*-DIMETHYLAMINOPHENOL AS ANALYTICAL EAGENTS

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eceived 1st February 1973)

During the past twenty years, the analytical application of 2-pyridylazo comounds has been studied extensively. Two representatives of this group, 1-(2-yridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)resorcinol (PAR), have proved o be very versatile reagents for metals[1]. Although neither reagent is selective as a hromogenic agent or an extractant, new selective 2-pyridylazo derivatives have een proposed by several workers. Much of the important work on these derivatives as been carried out in Russia, in particular by Talipov[2] and Gusev[3] and coorkers.

In a search for new sensitive and selective reagents, a thorough study of ome azo compounds containing 5-substituted pyridine has been made[4–7]. At the resent time, the main purpose of the work is to prepare sensitive organic reagents hich have molar absorptivities of the order of 10^5 for different metals. As is well nown, such organic reagents were very rare until a few years ago.

In previous papers[8,9] the authors have already reported that one of these ompounds, 4-[(5-chloro-2-pyridyl)azo]-1,3-diaminobenzene, possesses very high ensitivity for cobalt; the molar absorptivity of the cobalt complex being $1.13 \cdot 10^5$ l ol^{-1} cm^{-1}. Moreover, the 4-(2-pyridylazo)-1,3-diaminobenzene and 4-(5-bromo--pyridylazo)-1,3-diaminobenzene reagents also exhibit remarkably high sensitivity or cobalt, the molar absorptivities being $1.07 \cdot 10^5$ and $1.17 \cdot 10^5$ l mol^{-1} cm^{-1}, espectively[10,11]. In the case of these reagents the *p*-amino group opposite the azo roup may play a very important role in the high molar absorptivity and stability f the metal complex. Therefore, one would expect to obtain new highly sensitive eagents for metals by introducing the dimethylamino group, which is a strongly lectron-donating group, in the *para* position next to the azo group. In the present aper, the preparation of fifteen azo derivatives (formulae 1–15) of *m*-dimethylaminohenol, and the colour reaction of these reagents with some metal ions in aqueous olution are reported.

It was found, as expected from the composition, that these heterocyclic azo erivatives are very sensitive chromogenic reagents. Furthermore, pyridylazo comounds formed the most sensitive colour complexes. For example, the molar bsorptivities of the copper, zinc and nickel complexes of 2-[2-(5-bromopyridyl)-zo]-5-dimethylaminophenol were found to be 1.0, 1.33 and $1.28 \cdot 10^5$ l mol^{-1} m^{-1}, respectively.

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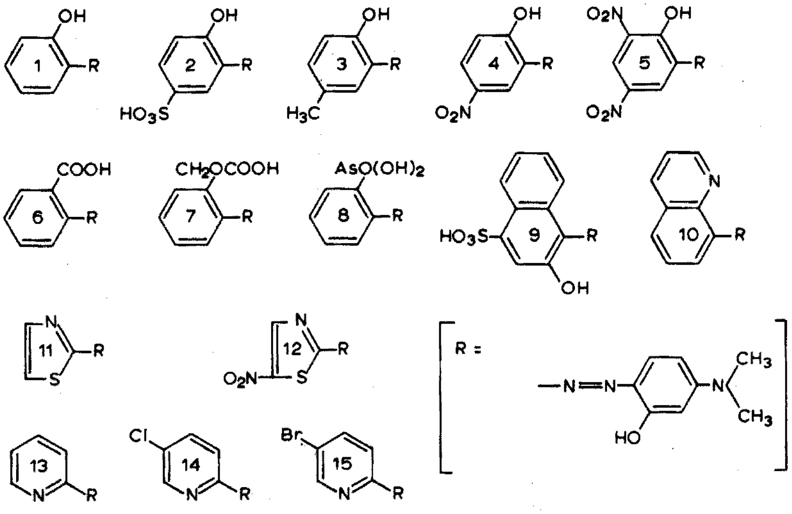


EXPERIMENTAL

Reagents

Standard metal solutions. A high-purity metal (99.999%) was dissolved in nit acid (1+1) or hydrochloric acid (1+1), and 10 ml of perchloric acid was add The mixture was evaporated until fumes of perchloric acid appeared. After cooli the solution was diluted to 1 l with distilled water and a 10^{-2} *M* solution w finally prepared.

Buffer solutions. 0.2 *M* Acetic acid–0.2 *M* sodium acetate, 0.2 *M* ammonia– *M* ammonium chloride, and diluted hydrochloric acid were used for pH adjustme

10^{-3} M Reagent solutions. An ethanolic or aqueous solution was prepar from the pure materials (see below). The solutions were stable for several mont if stored in an amber bottle.

Organic solvents were purified by the usual methods. All the other reage used were made from high-purity materials or purified reagents, and all solutio were prepared with redistilled water.

Apparatus

Elemental analyses were measured with a Model MT-2 Yanagimoto CH corder. Absorbance curves and infrared spectra were measured with a Model 3 Hitachi recording spectrophotometer with 1-cm cells and a Hitachi G3 infrar recording spectrophotometer. A Hitachi-Horiba M5-type glass electrode pH me was used.

Preparation of reagents

The reagents were prepared by coupling *m*-dimethylaminophenol with t appropriate diazotate in aqueous or alcoholic solution.

2-[1-(2-Hydroxyphenyl)azo]-5-dimethylaminophenol (1). *o*-Aminophen (0.54 g) was dissolved in 25 ml of 0.5 *M* hydrochloric acid, and diazotized 0–5° with sodium nitrite solution by the usual method. *m*-Dimethylaminophen

g) was dissolved in 25 ml of 1 *M* sodium hydroxide solution, and the diazo ution was added dropwise to this solution at 0–5°, after which the mixture was ken for about 2 h. The mixture was left overnight and then neutralized, and precipitated crude materials were filtered. The precipitate was dissolved in small tions of dilute sodium hydroxide solution and reprecipitated from neutral aqueous anolic solution (1+3). The dark red needles obtained sublimed at about 175°. *alysis.* $C_{14}H_{15}N_3O_2$ requires: 65.05% C, 5.9% H, 16.3% N; found: 65.1% C, % H, 16.6% N.

2-[1-(2-Hydroxy-5-sulfophenyl)azo]-5-dimethylaminophenol (2). This was pared by treating the 2-aminophenol-4-sulfonic acid (0.94 g) with *m*-dimethylinophenol (0.7 g) in the above manner. Red-purple needles were obtained. *alysis.* $C_{14}H_{15}N_3O_5S$ requires: 49.8% C, 4.5% H, 12.45% N; found: 45.2% C, % H, 10.8% N.

2-[1-(2-Hydroxy-5-methylphenyl)azo]-5-dimethylaminophenol (3). This was pared by treating the 2-amino-4-methylphenol (0.65 g) with *m*-dimethylaminonol (0.7 g) in the above manner. The orange-red needles obtained sublimed at °. *Analysis.* $C_{15}H_{17}N_3O_2$ requires: 66.4% C, 6.3% H, 15.5% N; found: 66.1% C, % H, 15.6% N.

2-[1-(2-Hydroxy-5-nitrophenyl)azo]-5-dimethylaminophenol (4). 2-Amino-4-ophenol (0.7 g) was dissolved in 10 ml of 1 *M* sodium hydroxide solution 20 ml of 1 *M* hydrochloric acid solution was added with vigorous stirring; ne precipitate was formed. Diazotization and coupling were almost the same as cribed for (1). Dark yellow-brown needles were formed. *Analysis.* $C_{14}H_{14}N_4O_4$ uires: 55.6% C, 4.7% H, 18.5% N; found: 54.6% C, 4.5% H, 16.0% N.

2-[1-(2-Hydroxy-3,5-dinitrophenyl)azo]-5-dimethylaminophenol (5). Sodium ite (0.7 g) was dissolved in 10 ml of concentrated sulfuric acid and 2-amino-dinitrophenol (2 g) was added at 0–5°. After diazotization, the yellowish zo solution was poured on to ice and the precipitated diazonium compound filtered. This diazonium salt was suspended in a small amount of water. The pling procedure was the same as for (1). A dark brown amorphous precipitate formed. *Analysis.* $C_{14}H_{13}N_5O_6$ requires: 48.4% C, 3.8% H, 20.2% N; found: % C, 3.3% H, 18.4% N.

2-[1-(2-Carboxyphenyl)azo]-5-dimethylaminophenol (6). This was prepared treating the *o*-aminobenzoic acid (0.68 g) with *m*-dimethylaminophenol (0.7 g) as cribed for (1). The crude precipitate was reprecipitated from concentrated hydroric acid; the dark red needles sublimed at 250°. *Analysis.* $C_{15}H_{15}N_3O_3 \cdot 2HCl$ uires: 50.3% C, 4.25% H, 11.7% N; found: 48.7% C, 5.8% H, 11.5% N.

2-[1-(2-Carboxymethoxyphenyl)azo]-5-dimethylaminophenol (7). 2-Nitronoxyacetic acid (3 g) was dissolved in 25 ml of 0.5 *M* sodium hydroxide ution, and the mixture was heated on a water bath. Iron(II) sulfate (6 g) was led and the mixture was heated for 2 h. Iron was precipitated by addition of anol and filtered, and the filtrate was then evaporated to remove the ethanol. cipitated 2-aminophenoxyacetic acid was filtered off. The reagent was prepared treating the 2-aminophenoxyacetic acid (1.6 g) with *m*-dimethylaminophenol g) as described for (1). A dark brown amorphous powder was formed. *Analysis.* $H_{17}N_3O_4$ requires: 60.9% C, 5.4% N, 13.3% N; found: 57.8% C, 5.4% H, 12.4% N.

2-[1-(2-Arsonophenyl)azo]-5-dimethylaminophenol (8). This was prepared by treating the *o*-aminobenzenearsonic acid (1.08 g) with *m*-dimethylaminophenol (1. g) as described for (1). Brown needles were formed. *Analysis.* $C_{14}H_{16}N_3O_4$ requires: 46.0% C, 4.4% H, 11.5% N; found: 39.2% C, 4.3% H, 9.8% N.

[2-[1-(2-Hydroxy-4-sulfonaphthyl)azo]-5-dimethylaminophenol (9). Sm amounts of water were added to 1-amino-2-naphthol-4-sulfonic acid (1.2 g) to for a paste, and copper sulfate (0.12 g) in small amounts of water was added to th paste, which was then diazotized by sodium nitrite (0.7 g) solution. The diazotiz mixture was filtered, concentrated hydrochloric acid was added to the filtrate, a the precipitated diazonium salt was filtered. The coupling procedure was the sa as described for (1). Dark brown amorphous crystals were formed. *Analys* $C_{18}H_{17}N_3O_5S$ requires: 55.8% C, 4.4% H, 10.8% N; found: 48.9% C, 4.7% 8.5% N.

2-[8-Quinolylazo]-5-dimethylaminophenol (DMQAP; 10). This was prepar by treating the 8-aminoquinoline (0.9 g) with *m*-dimethylphenol (0.7 g) as describ for (1). The crystals obtained sublimed at 205°. *Analysis.* $C_{17}H_{16}N_4O$ require 69.8% C, 5.5% H, 19.2% N; found: 70.0% C, 5.5% H, 19.4% N.

2-(2-Thiazolylazo)-5-dimethylaminophenol (DMTAP; 11)[12]. Sodium nitri (0.7 g) was dissolved in 10 ml of concentrated sulfuric acid, and the solution w cooled to 0–5°. Glacial acetic acid (8.5 ml) and propionic acid (1.5 ml) were add to this solution followed by 2-aminothiazole (1.0 g). *m*-Dimethylaminophenol (1.4 was dissolved in 20 ml of ethanol, and coupling was done with the above diazoniu mixture at 0–5°. The dark purple needles obtained sublimed at 175°. *Analys* $C_{11}H_{12}N_4OS$ requires: 53.2% C, 4.9% H, 22.6% N; found: 53.4% C, 4.8% 22.6% N.

2-[2-(5-Nitrothiazolyl)azo]-5-dimethylaminophenol (12). This was prepar by treating the 2-amino-5-nitrothiazole (1.4 g) with *m*-dimethylaminophenol (1.4 g) described for (11)(m.p. 172°, dark purple amorphous crystals). *Analysis.* $C_{11}H_{11}N$ O_3S requires: 45.0% C, 3.8% H, 23.9% N; found: 43.6% C, 4.2% H, 16.7%

2-(2-Pyridylazo)-5-dimethylaminophenol (DMPAP; 13). To a solution of 2.1 of clean sodium in 10 ml of absolute ethanol, 2-aminopyridine (5 g) in 30 ml absolute ether was added, and the mixture was refluxed for 1 h under an atmosphe of nitrogen. Then, 5 ml of isopentyl nitrite was added, and refluxing was continu for an additional 2 h. On cooling, the diazonium salt precipitated and was filter off and dried in a vacuum desiccator. To a solution of *m*-dimethylaminophen (0.7 g) in 20 ml of absolute ethanol, the diazonium salt (2.2 g) in 10 ml of absolu ethanol was added at 0–5°, and carbon dioxide was passed through the solutio The crude material was recrystallized from ethanol–water mixture. The dark r needles obtained sublimed at 174°. *Analysis.* $C_{13}H_{14}N_4O$ requires: 64.5% C, 5.8% 23.1% N; found: 64.5% C, 5.8% H, 21.1% N.

2-[2-(5-Chloropyridyl)azo]-5-dimethylaminophenol (5-Cl-DMPAP; 14). To solution of 2.1 g of sodium amide in 30 ml of absolute ethanol, 2-amino-5-chlor pyridine (6.5 g) was added, and the mixture was refluxed for 1 h under atmosphere of nitrogen. Then, 5 ml of isopentyl nitrite was added to t mixture and refluxing was continued for an additional 2 h. On cooling, t diazonium salt precipitated and was filtered off and dried in a vacuum desiccat To a solution of *m*-dimethylaminophenol (1.4 g) in 20 ml of absolute ethanol, t diazonium salt (1.7 g) in 10 ml of absolute ethanol was added at 0–5° in a strea carbon dioxide. The crude material was recrystallized from ethanol–water mixture +1). The dark red needles obtained sublimed at 190°. *Analysis.* $C_{13}H_{13}N_4OCl$ quires: 56.4% C, 4.7% H, 20.2% N; found: 56.7% C, 4.7% H, 20.1% N.

2-[2-(5-Bromopyridyl)azo]-5-dimethylaminophenol (5-Br-DMPAP; 15). This as prepared by treating the 2-amino-5-bromopyridine (10 g) with the *m*-dimethylninophenol (0.7 g) as described for (14). The dark red needles obtained sublimed at 0°. *Analysis.* $C_{13}H_{13}N_4OBr$ requires: 48.6% C, 4.1% H, 17.4% N; found: 48.6% C, 9% H, 17.2% N.

SULTS AND DISCUSSION

olour reactions with some metals

The chelate compounds are easily prepared by adding a few drops of a lution of the reagent in alcohol or water to a solution of a heavy metal. The lour reactions with some metals at the optimal pH values are listed in Table I. e chelating reactions of reagents 6, 7 and 8 could not be detected visually.

BLE I

LOUR REACTIONS WITH SOME METAL IONS[a]

agent	Reagent	Al^{3+}	Cd^{2+}	Co^{2+}	Cu^{2+}	Fe^{3+}	La^{3+}	Mg^{2+}	Mn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
	y-O	—	O	r-P	r-P	Br	O	O	r-P	r-P	r-P	r-P
	y-O	R	O	p-R	y-R	Y	—	—	R	O	r-P	O
	y-O	R	y-R	R	r-P	Br	r-P	y-R	P	p-R	r-P	R
	p-R	r-P	r-P	r-P	r-P	Br	r-P	r-P	P	O	r-P	r-P
	R	p-R	p-R	p-R	p-R	Br	—	—	p-R	p-R	p-R	p-R
	Y	—	—	—	—	—	—	—	—	—	—	—
	y-O	—	—	—	—	—	—	—	—	—	—	—
	Y	—	—	—	—	—	—	—	—	—	—	—
	r-P	—	—	b-P	P	b-P	b-P	—	b-P	P	—	P
	y-O	—	r-O	r-P	r-P	Br	—	—	r-P	r-P	—	r-P
	O	—	r-P	P	P	P	P	—	r-P	r-P	—	r-P
	p-B	—	b-P	b-P	b-P	b-P	b-P	—	b-P	P	b-P	b-P
	Y	—	r-P	P	r-P	r-P	r-O	r-O	R	r-P	r-P	r-P
	Y	—	r-P	P	r-P	r-P	r-P	r-P	r-P	r-P	r-P	r-P
	Y	—	r-P	P	r-P	r-P	r-P	r-P	r-P	r-P	r-P	r-P

= Orange, P = Purple, R = Red, Y = Yellow, B = Blue, Br = Brown, b = bluish, p = purplish, r = reddish, = yellowish, — not detectable.

The detection limits of some reagents were then studied more quantitatively. he colours of a series of solutions containing known amounts of metals (added a Eppendorf micropipette), a drop of dye solution, 0.5 ml of pH 10 buffer lution and 0.5 ml of water, were observed visually against a reagent blank. The tection limits obtained are shown in Table II. From these results, subsequent udies were carried out with reagents 10, 11, 13, 14 and 15.

cid dissociation behaviour

All the reagents were sparingly soluble in water, but soluble in various

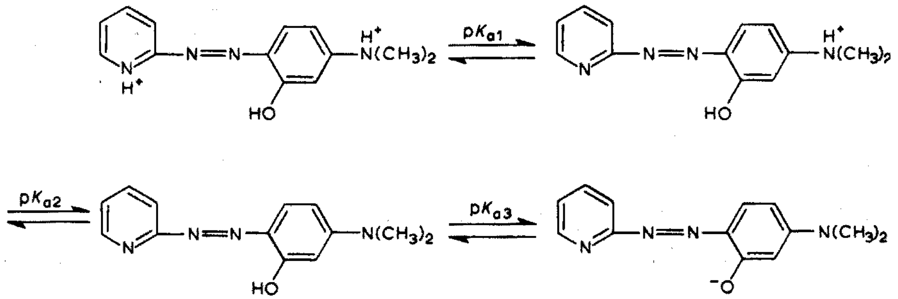
TABLE II

THE DETECTION LIMITS FOR SOME METALS[a]

Reagents	*Co(II)*	*Cu(II)*	*Ni(II)*	*Zn(II)*
1	0.3	0.3	0.3	0.6
2	0.6	0.6	0.6	0.9
3	0.3	0.3	0.6	0.6
4	1.2	0.6	0.6	1.2
5	0.3	0.3	0.3	0.3
9	0.3	0.3	0.3	0.6
10	0.3	0.9	0.3	0.9
11	0.3	0.3	0.3	0.3
12	0.3	0.6	0.3	2.1
13	0.03	0.03	0.03	0.03
14	0.09	0.06	0.03	0.06
15	0.09	0.06	0.03	0.06

[a] Concentrations are given in $\mu g\ ml^{-1}$.

organic solvents, including ethanol, methanol, MIBK, benzene and chloroform. Thes reagents showed acid–base indicator properties and were yellow in weak acidic an neutral solution but orange–red in strongly alkaline solution. Four species of thes reagents, H_3L^{2+}, H_2L^+, HL and L^-, are involved in its acid–base behaviour. Fo example, the four forms of DMPAP involved in its acid–base behaviour ar related by the following equilibria:



The acid–base equilibria of DMPAP may be formulated:

$$H_3L^{2+} \xrightleftharpoons{K_{a1}} H_2L^+ + H^+$$ (1

$$H_2L^+ \xrightleftharpoons{K_{a2}} HL + H^+$$ (2

$$HL \xrightleftharpoons{K_{a3}} L^- + H^+.$$ (3

The three acidity constants for DMPAP are then defined by

$$K_{a1} = \frac{[H_2L^+][H^+]}{[H_3L^{2+}]}$$ (4)

$$K_{a2} = \frac{[HL][H^+]}{[H_2L^+]} \tag{5}$$

$$K_{a3} = \frac{[L^-][H^+]}{[HL]} \tag{6}$$

ese associated equilibria can be calculated independently because the steps were fficiently separated. The acid dissociation constants determined are reported in ble III, where pK_{a2} refers to the dissociation of the dimethylamino group, and K_{a3} refers to the dissociation of the hydroxy group. The pK_{a1} value is below H 1. The pK_{a2} values of the dimethylamino group increase in the order DMTAP < MQAP < 5-Cl-DMPAP ≡ 5-Br-DMPAP < DMPAP, and the pK_{a3} values of the droxy group increase in the order DMTAP < 5-Cl-DMPAP ≡ 5-Br-DMPAP < MPAP < DMQAP. The wavelength of maximal absorbance and the molar ab-rptivity of each species in aqueous 40% (v/v) methanol solution are shown in ble IV. The shift of maximum wavelength from neutral to basic species increases the order DMQAP < DMTAP < DMPAP < 5-Cl-DMPAP < 5-Br-DMPAP. erefore, among these reagents 5-Br-DMPAP would be expected to be the best romogenic reagent for metals.

BLE III

ID DISSOCIATION CONSTANTS OF REAGENTS IN AQUEOUS 40% (v/v) METHANOL LUTION

=0.1 KCl, 25°)

agents	pK_{a1}	pK_{a2}	pK_{a3}
MTAP (11)	< 1	2.8	9.9
MQAP (10)	< 1	3.1	13.1
MPAP (13)	< 1	3.6	12.1
l-DMPAP (14)	< 1	3.4	11.6
r-DMPAP (15)	< 1	3.4	11.6

BLE IV

SORPTION MAXIMA OF REAGENTS AND MOLAR ABSORPTIVITIES[a]

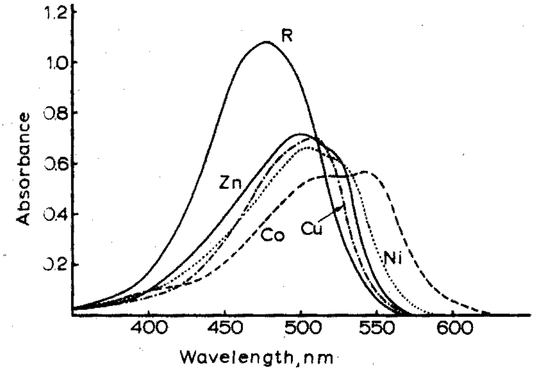
queous 40% (v/v) methanol solutions)

agents	*pH ~ 1*		*pH ~ 6*		*NaOH ~ 0.1 M*	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
MQAP	504	4.6	478	4.5	490	2.6
MTAP	540	6.1	502	4.6	524	4.1
MPAP	524	2.2	435	3.0	494	3.0
l-DMPAP	465	4.7	440	4.6	508	4.6
r-DMPAP	466	4.7	444	4.7	510	4.7

$_{max}$ is given in nm. All molar absorptivities are given as $\cdot 10^4$ l mol^{-1} cm^{-1}.

Absorption spectra

The complexes of these reagents with metals are not soluble in water soluble in aqueous organic solvents. In this paper, the absorption spectra aqueous 50% (v/v) ethanol solution were studied. The absorption spectra of copper, nickel, cobalt, and zinc chelates of the five reagents are shown in Fi 1–5. The absorption maxima of each metal chelate are also shown in Table



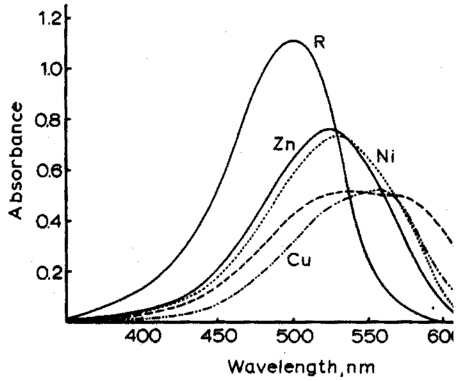
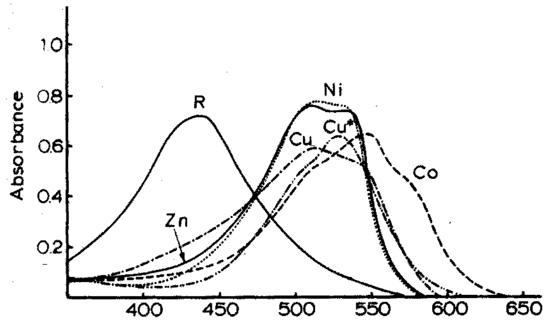


Fig. 1. Absorption spectra of DMQAP–metal chelates in aqueous 50% (v/v) ethanol. Reagent $2.5\cdot10^{-5}$ (Ni pH 8, Zn pH 10, Co pH 8.5) $1.75\cdot10^{-5}$ *M* reagent plus $0.75\cdot10^{-5}$ *M* metal. (Cu pH 8) $1.5\cdot10^{-5}$ reagent plus $1.0\cdot10^{-5}$ *M* copper *vs.* water blank. 1-cm cells.

Fig. 2. Absorption spectra of DMTAP–metal chelates in aqueous 50% (v/v) ethanol. Reagent $2.5\cdot10^{-5}$ (Ni, Zn, Co pH 8) $1.75\cdot10^{-5}$ *M* reagent plus $0.75\cdot10^{-5}$ *M* metal. (Cu, pH 8) $1.25\cdot10^{-5}$ *M* reag plus $1.25\cdot10^{-5}$ *M* copper *vs.* water blank. 1-cm cells.



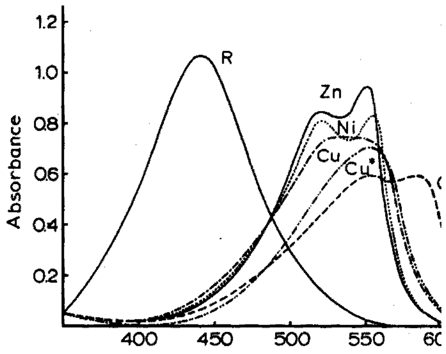
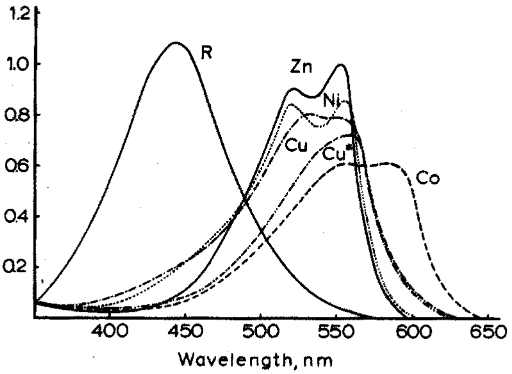


Fig. 3. Absorption spectra of DMPAP–metal chelates in aqueous 50% (v/v) ethanol. Reagent $2.5\cdot10^{-5}$ (Zn pH 11, Ni pH 9) $1.75\cdot10^{-5}$ *M* reagent plus $0.75\cdot10^{-5}$ *M* metal. (Cu pH 11, Co pH $1.875\cdot10^{-5}$ *M* reagent plus $0.625\cdot10^{-5}$ *M* metal. (Cu* pH 6) $1.25\cdot10^{-5}$ *M* reagent plus $1.25\cdot10^{-5}$ copper *vs.* water blank. 1-cm cells.

Fig. 4. Absorption spectra of 5-Cl-DMPAP–metal chelates in aqueous 50% (v/v) ethanol. Reag $2.5\cdot10^{-5}$ *M*. (Zn pH 11, Ni pH 10, Co pH 10, Cu pH 11) $1.75\cdot10^{-5}$ *M* reagent plus $0.75\cdot10^{-5}$ metal. (Cu* pH 4.5) $1.25\cdot10^{-5}$ *M* reagent and metal *vs.* water blank. 1-cm cells.



ig. 5. Absorption spectra of 5-Br-DMPAP–metal chelates in aqueous 50% (v/v) ethanol. Reagent $5 \cdot 10^{-5}$ *M*. (Zn, Ni, Co, pH 8, Cu pH 10) $1.75 \cdot 10^{-5}$ *M* reagent plus $0.75 \cdot 10^{-5}$ *M* metal. (Cu* pH 4) $25 \cdot 10^{-5}$ *M* reagent and metal *vs.* water blank. 1-cm cells.

ABLE V

BSORPTION MAXIMA OF CHELATES (nm)[a]

eagents	*Cu*	*Co*	*Ni*	*Zn*
MQAP	515	545, 515	535, 505	528, 505
MTAP	560	570	535	535
MPAP	515, 540, (530)[b]	546, 570	520	510, 534
Cl-DMPAP	530, 550, (555)	550, 585	520, 552	518, 550
Br-DMPAP	530, 550, (555)	555, 590	520, 552	570, 552

In aqueous 50% (v/v) ethanol solution measured against water. [b] Between brackets 1:1 chelate.

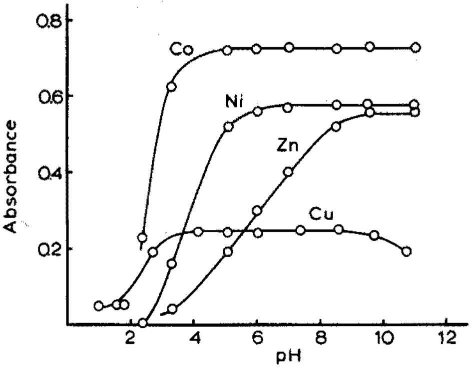
Although the wavelength shifts on chelation of the quinolylazo and thia-olylazo reagents are small (50–60 nm), those for the pyridylazo reagents are very rge (110–120 nm). The absorption spectra of the halogen-substituted pyridylazo agents show two absorption peaks clearly, except in the case of copper. The 1:1 opper chelate has only one absorption peak, although the 1:2 copper chelate has vo peaks.

ffect of pH

For evaluation of the optimal pH values for determinations of copper, nickel, obalt and zinc, the effects of pH on the absorbance were studied with the results hown in Figs. 6–10. In the cases of cobalt, zinc and nickel, the absorption pectra did not change over the whole range, so that obviously only one type of helate is formed. Copper chelates of DMPAP and its halogen-substituted reagents aving 1:1 and 1:2 copper–ligand ratios were assumed to be formed at low pH and t high pH, respectively. The optimal pH and wavelength with molar absorptivity nd sensitivity for the determination of cobalt, nickel, zinc and copper are shown Table VI.

ature of complex

The empirical formulae of the coloured complexes were determined by the



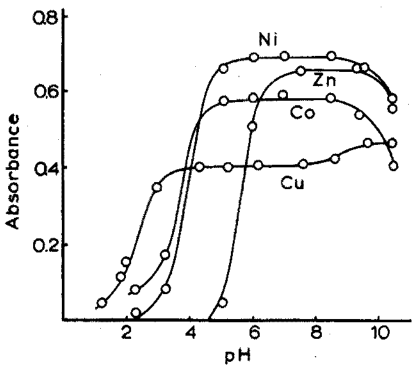
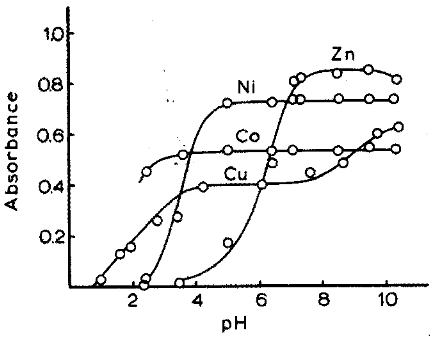


Fig. 6. Effect of pH on absorbance of DMQAP–metal chelates. Reagent $4.4 \cdot 10^{-5}$ *M*. Co, Zn and $1 \cdot 10^{-5}$ *M*, Cu $0.75 \cdot 10^{-5}$ *M vs.* reagent blank. 1-cm cells.

Fig. 7. Effect of pH on absorbance of DMTAP–metal chelates. Reagent $1 \cdot 10^{-3}$ *M*. Zn, Ni and $1 \cdot 10^{-5}$ *M*, Co $0.8 \cdot 10^{-5}$ *M vs.* reagent blank. 1-cm cells.



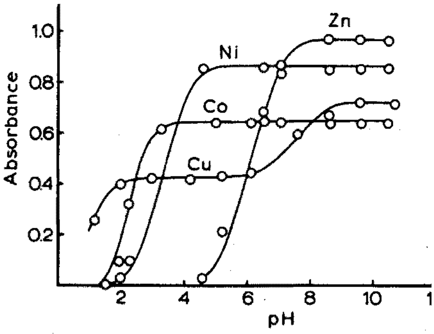


Fig. 8. Effect of pH on absorbance of DMPAP–metal chelates. Reagent $5.1 \cdot 10^{-5}$ *M*. Metals $7.5 \cdot 10^{-6}$ *vs.* reagent blank. 1-cm cells.

Fig. 9. Effect of pH on absorbance of 5-Cl-DMPAP–metal chelates. Reagent $5 \cdot 10^{-5}$ *M*. Meta $7.5 \cdot 10^{-6}$ *M vs.* reagent blank. 1-cm cells.

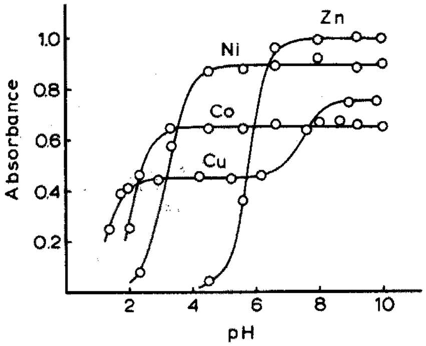


Fig. 10. Effect of pH on absorbance of 5-Br-DMPAP–metal chelates. Reagent $4.0 \cdot 10^{-5}$ *M*. Meta $7.5 \cdot 10^{-6}$ *M vs.* reagent blank. 1-cm cells.

ABLE VI

HE OPTIMAL pH VALUES AND WAVELENGTHS WITH MOLAR ABSORPTIVITIES OF OME METALS IN AQUEOUS 50% (v/v) ETHANOL

eagent	*Metal*	*Optimal pH*	*Molar absorptivity* ($\cdot 10^4$ *l mol*$^{-1}$ *cm*$^{-1}$)	*Sensitivity* (*μg cm*$^{-2}$)	*Optimal analytical wavelength*[a] (*nm*)
MQAP	Co	5.0–11.0	7.2	0.00082	547
	Ni	6.0–11.0	5.6	0.0011	535
	Cu	4.0–9.0	3.4	0.0019	520
	Zn	9.5–11.0	5.6	0.0012	528
MTAP	Co	5.5–8.5	7.4	0.00080	575
	Ni	5.5–8.5	6.9	0.00084	558
	Cu	4.0–8.0	4.1	0.0015	564
	Zn	7.5–9.5	6.7	0.00097	556
MPAP	Co	5.0–10.0	7.7	0.00077	574
	Ni	5.0–10.5	9.8	0.00060	545
	Cu[b]	4.0–6.0	5.3	0.0012	555
	Cu	10.0–10.5	8.3	0.00077	545
	Zn	7.0–9.5	*11.2*	*0.00058*	538
Cl-DMPAP	Co	3.0–10.5	8.5	0.00069	586
	Ni	4.5–10.0	*12.1*	*0.00049*	556
	Cu[b]	2.0–6.0	6.1	0.0010	556
	Cu	9.5–10.5	*10.2*	*0.00062*	554
	Zn	8.5–10.5	*12.2*	*0.00054*	550
Br-DMPAP	Co	3.0–10.0	8.8	0.00067	588
	Ni	4.5–10.0	*12.8*	*0.00046*	558
	Cu[b]	2.0–6.0	6.1	0.0010	558
	Cu	9.0–10.0	*10.0*	*0.00064*	555
	Zn	7.5–10.0	*13.3*	*0.00049*	552

gainst reagent blank. [b] 1:1 complex.

ntinuous variations method at the optimal pH and wavelength. In the case of pper, the curves indicated the formation of a 1:1 complex at pH 3 and a 1:2 mplex at pH 10 except with DMQAP, which formed only a 1:2 complex with pper. In the cases of nickel, cobalt and zinc, only 1:2 complexes were formed ith all reagents.

olvent extraction

The highly coloured complexes formed with metals under various conditions e useful for the determination of certain metals. These coloured complexes are luble in various organic solvents. Some results are shown in Table VII.

onclusions

Although these reagents are rather unselective, analytical conditions can be proved by a judicious choice of pH, solvent, or masking agents. Anyway, as otometric reagents, these compounds seem to be promising because of the re-arkably high molar absorptivity and large bathochromic shifts produced on

TABLE VII

EXTRACTABILITY OF METAL CHELATES IN VARIOUS ORGANIC SOLVENTS[a]

Metals	*Solvents*	*DMTAP*	*DMQAP*	*DMPAP*	*5-Cl-DMPAP*	*5-Br-DMPAP*
Co	MIBK	+	∓	∓	+	+
	1,2-Dichloroethane	−	−	+	+	+
	Benzene	+	+	∓	∓	±
Cu	MIBK	+	+	−	−	±
	1,2-Dichloroethane	+	+	±	±	±
	Benzene	±	+	−	−	−
Ni	MIBK	+	+	±	+	+
	1,2-Dichloroethane	+	+	+	+	+
	Benzene	+	+	+	+	+
Zn	MIBK	+	+	+	+	∓
	1,2-Dichloroethane	+	+	+	+	∓
	Benzene.	+	+	+	+	∓

[a] + very well, ± well, ∓ not well, − bad.

chelation. Further work on the solvent extraction and analytical application these reagents for determination of metals is now in progress.

SUMMARY

Fifteen azo dyes containing the *m*-dimethylaminophenol group were sy thesized, and their analytical potential for the determination of metals was studi spectrophotometrically. Among these reagents, the heterocyclic azo derivatives a most suitable as chromogenic reagents. The best reagents are the 2-pyridyla compounds. These complexes with copper, zinc and nickel show molar absorptiviti of the order of 100,000. For example, the 2-[2-(5-bromopyridyl)-azo]-5-dimethy aminophenol complexes with copper, zinc and nickel show molar absorptivities 1.0, 1.33 and $1.28 \cdot 10^5$ l mol^{-1} cm^{-1}, respectively. In these reagents, the *par* substituted dimethylamino group next to the azo group seems to play an importa role in achieving high molar absorptivity and stability of the metal complexes.

RÉSUMÉ

Quinze colorants azoïques renfermant le groupement *m*-diméthylamin phénol ont été synthétisés; on examine au spectrophotomètre leur possibili d'utilisation pour le dosage des métaux. Les composés 2-pyridylazo constituent l meilleurs réactifs; les complexes obtenus avec cuivre, zinc et nickel présentent d coefficients d'extinction molaire de l'ordre de 100,000; on a par exemple des valeu de 1.0, 1.33 et $1.28 \cdot 10^5$ l mol^{-1} cm^{-1} respectivement pour les complexes du cuivr du zinc et du nickel avec le 2-[2-(bromo-5-pyridil)azo]-5-diméthylaminophénol. L groupe diméthylamino en *para* par rapport au groupe azo semble jouer un rô important sur l'extinction molaire élevée et la stabilité des complexes métallique

USAMMENFASSUNG

Es wurden fünfzehn Azofarbstoffe dargestellt, die die *m*-Dimethylamino-
enol-Gruppe enthielten; ihre analytische Anwendbarkeit für die Bestimmung von
etallen wurde spektrophotometrisch untersucht. Von diesen Reagenzien eignen
ch die heterocyclischen Azoderivate besonders als chromogene Reagenzien. Die
sten sind die 2-Pyridylazo-Verbindungen. Deren Komplexe mit Kupfer, Zink und
ickel haben molare Extinktionskoeffizienten in der Grössenordnung von 100,000.
ie molaren Extinktionskoeffizienten der Komplexe von z.B. 2-[2-(5-Brompyridyl)-
o]-5-dimethylaminophenol mit Kupfer, Zink und Nickel sind resp. 1.0, 1.33 und
$28 \cdot 10^5$ l mol^{-1} cm^{-1}. Bei diesen Reagenzien scheint die *p*-substituierte Dimethyl-
nino-Gruppe gegenüber der Azo-Gruppe eine wichtige Rolle hinsichtlich eines
hen molaren Extinktionskoeffizienten und der Stabilität der Metallkomplexe zu
ielen.

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EPARATION, IDENTIFICATION AND DETERMINATION OF HORT-CHAINED CALCIUM POLYPHOSPHATES FROM PYROLYZED ALCIUM-DEFICIENT HYDROXYAPATITE

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eceived 21st March 1973)

Several workers have shown the existence of condensed phosphate in pyroyzed hydroxyapatite[1–5]. However, their presence was established indirectly by omparing the amount of orthophosphate in samples before and after acid hydrolysis. No identification or determination of these moieties was attempted, probably ecause methods for the separation of calcium polyphosphates from orthophoshate were not available. This paper describes a procedure for thin-layer separation f short-chained calcium polyphosphates and their determination in the presence f orthophosphate in preparations derived from pyrolyzed synthetic hydroxyapatite eficient in calcium. The data also suggest that the major condensation product f the pyrolysis of synthetic apatite is pyrophosphate.

XPERIMENTAL

reparation of labelled calcium-deficient hydroxyapatite and calcium polyphosphates

Calcium-deficient hydroxyapatite was prepared by the two-step procedure f Eanes[5]. First, radioactive amorphous tricalcium phosphate ($Ca_3(PO_4)_2 \cdot 3H_2O$) as prepared as follows: 350 ml of 257 m*M* ammonium monohydrogenphosphate ontaining 2.5 mCi of carrier-free disodium hydrogen(^{32}P)phosphate (New England Nuclear Corp., Boston, Mass.) were added rapidly to 200 ml of stirred 75 m*M* alcium nitrate, after adjustment of both solutions to pH 10.5 with fresh 7.4 *M* mmonia solution under an atmosphere of nitrogen. Precipitation was instantaneous. fter 5 min the mixture was filtered and the amorphous residue thoroughly ashed with ammoniacal water (pH 10.5). Chemical analyses of freeze-dried samples f the amorphous residue gave a Ca/PO_4 molar ratio of 1.5. In the second step, alcium-deficient hydroxyapatite, which had the same Ca/PO_4 molar ratio (1.5), as prepared by hydrolyzing the freshly washed amorphous tricalcium phosphate n ammoniacal distilled water (pH 10.5) for 20 h at 30°. The entire mixture was hen lyophilized.

The amorphous nature of the precipitated salt and the crystalline apatite dentity of the hydrolyzed product were established by X-ray powder diffraction. -Ray photographs were taken with a 57.3-mm diameter Debye–Scherrer powder amera under nickel-filtered copper radiation.

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Polyphosphates were produced in the hydrolyzed salt by ignition in a m furnace for 4–23 h at 600 ± 5°.

Chemical analyses

To establish Ca/PO_4 molar ratios, calcium was determined gravimetric by the method of Kolthoff and Sandell[6] and by atomic absorption spectrome orthophosphate was determined by the differential spectrophotometric metho Gee and Deitz[7]. Condensed phosphates were chemically determined as the differe between orthophosphate values before and after hydrolysis for 1 h in 5 *M* perchl acid at 100°. Sodium was determined by atomic absorption spectrometry.

Chromatography

Separation of ortho- and short-chained polyphosphates of divalent cati by anion-exchange thin-layer chromatography with polyethyleneimine-impregn microcrystalline cellulose[8] was not feasible, apparently because of the diva cations. Consequently, methods of separation of calcium ortho- and polyphosph based on ascending liquid–liquid partition were attempted. Thin-layer plates co with microcrystalline cellulose (Avicel (250 μm thickness)) were employed (Anal Inc., Wilmington, Del.). Aqueous solutions of trichloroacetic acid containing calc or sodium phosphates (250 mg ml^{-1}) were spotted and developed either in solution of Ebel[9] containing 15 ml of isopropanol, 0.5 g of trichloroacetic 0.08 ml of ammonia liquor and 5 ml of water, or in a modification of solution of Clesceri and Lee[10] which contained 71 ml of dioxane, 5.0 g of trichl acetic acid, 0.25 ml of ammonia liquor and 21.5 ml of water. The phospho containing spots were located as previously detailed[8].

In order to establish that the behavior of calcium phosphate on thin la could be ascribed to their identity as ortho- and short-chained polyphosph and not to calcium–orthophosphate complexes, they were converted into sodium forms by cation exchange on AG50W-X8 (sodium form) (BioRad Lab tories, Richmond, Calif.). Resulting phosphate solutions were found to be calci free, as judged by atomic absorption spectrometry.

To establish whether the developing solutions mobilized the sodium calcium counterions along with the phosphates of interest, thin-layer chrom graphy was carried out and the thin layers were dried and scraped. The scrap were analyzed for sodium, calcium and phosphate. The Ca/PO_4 and Na/ molar ratios were compared with those of the compounds chromatographed.

Chromatographic standards of disodium hydrogenphosphate and t sodium pyrophosphate decahydrate were commercial analytical-reagent g Standards of sodium tripolyphosphate ($Na_5P_3O_{10} \cdot 6H_2O$), trimetaphosp ($Na_3P_3O_9$) and calcium hydrogenphosphate were kindly donated by E. J. Gri Monsanto Co., St. Louis, Mo., while highly purified dicalcium pyrophosphate kindly donated by B. Fowler, National Institute of Dental Research, Nati Institutes of Health, Bethesda, Md. The purity of the calcium pyrophosphate been established by infrared spectroscopy. Calcium tripolyphosphate, of unes lished empirical formula, was made by passing sodium tripolyphosphate thr a column of AG50W-X8 (calcium form). The eluate contained small amoun calcium tripolyphosphate, although most of the highly insoluble product occluded in the interstices of the resin.

etermination of ortho- and polyphosphates

After radioactive samples had been chromatographed, thin-layer plates were ither scanned with a Model 7201 radiochromatogram scanner (Packard Instrument o., Downers Grove, Ill.), or thin layers were scraped from plates and placed into cintillation fluid[11] containing a thixotropic gel[12] for counting in a Model 3375 quid scintillation counter.

ESULTS

Sodium and calcium ortho-, pyro-, and tripolyphosphates and sodium tri- etaphosphate could be readily separated by liquid–liquid partition thin-layer hromatography with either the modified developing solution of Clesceri and Lee[10] r that of Ebel[9] (Table I). The chromatographic behavior of the calcium and odium salts was indistinguishable. By contrast, condensed calcium phosphates, nlike the corresponding sodium phosphates[8], were not mobilized from the origin f anion-exchange thin layers of polyethyleneimine-impregnated microcrystalline ellulose by aqueous solutions of lithium chloride. This behavior was not due erely to the anion-exchange quality of polyethyleneimine, because condensed alcium phosphates were not mobilized from the origin of microcrystalline cellulose in layers which had not been impregnated with the anion exchanger.

ABLE I

VERAGE R_F VALUES FOR PHOSPHATES WITH DIFFERENT DEVELOPING SOLUTIONS

hosphate salt	*Modified solution of Clesceri and Lee*[10]	*Solution of Ebel*[9]
rthophosphate	0.73	0.68
yrophosphate	0.44	0.29
ripolyphosphate	0.24	0.15
rimetaphosphate	0.14	0.12

Comparison of the amounts of phosphate and sodium or calcium in rapings of thin layers developed by liquid–liquid partition showed that less than ne tenth of the expected calcium was found associated with either of the obilized phosphates, calcium orthophosphate or calcium pyrophosphate. About alf of the sodium remained associated with the mobilized sodium pyrophosphate nd essentially all of it remained associated with sodium orthophosphate. This ggested that the hydrogen ion functioned as the major counterion for the hromatography of the calcium phosphates and for sodium pyrophosphate.

Differential spectrochemical analysis of pyrolyzed calcium-deficient hydroxypatite indicated that 84.9% of the total phosphate was in the form of orthohosphate while 15.1% appeared as condensed phosphate. By contrast, 100% of e non-pyrolyzed cacium-deficient hydroxyapatite was in the form of orthophoshate.

Chromatography indicated that while *ca.* 85% of the pyrolyzed hydroxypatite behaved as though it were orthophosphate, about 14% had an R_F value

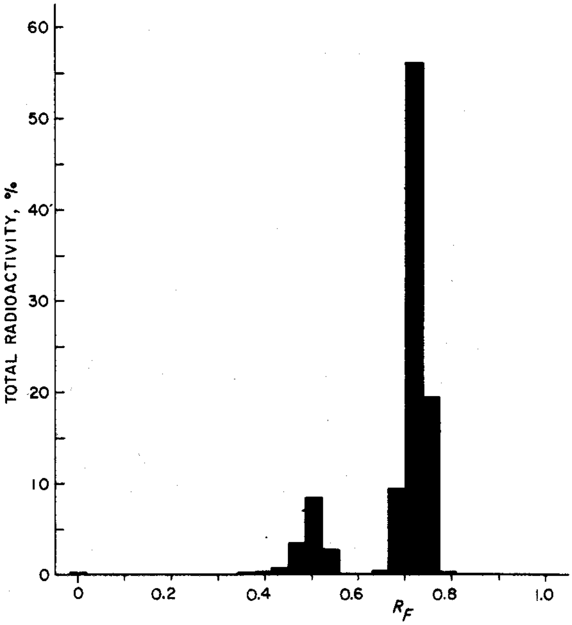


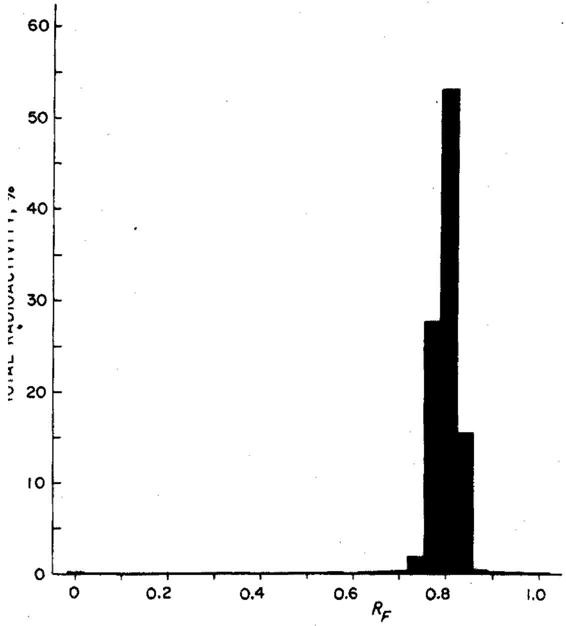
Fig. 1. Thin-layer radiochromatogram of ^{32}P-labelled pyrolyzed calcium-deficient hydroxyapatite Avicel using modified developing solution of Clesceri and Lee[10]. Standards of sodium and calci ortho-, pyro- and tripolyphosphate were simultaneously chromatographed and gave R_F values of 0. 0.50 and 0.30, respectively.

consistent with its identification as pyrophosphate and about 1% could not characterized (Fig. 1). By contrast, all of the hydroxyapatite in the non-pyrolyz material appeared to be orthophosphate (Fig. 2). On conversion of the pyrolyz and non-pyrolyzed calcium phosphates into sodium phosphates by cation exchan with AG50W-X8 (sodium form) and repeated chromatography, identical chromat graphic behavior was observed. Thus, the components migrating with R_F valu lower than that of calcium orthophosphate could not have represented calciur phosphate complexes. Comparison of the chemically determined condensed ph phate content of the pyrolyzed sample with its composition, as determin chromatographically, indicated that about 95% of the condensed phosphate w calcium pyrophosphate. The data are summarized in Table II.

TABLE II

COMPOSITION OF PYROLYZED CALCIUM-DEFICIENT HYDROXYAPATITE

Method	*Orthophosphate (%)*	*Pyrophosphate (%)*	*Other phosphate (%)*
Differential spectrochemical	84.9	15.1	
^{32}P-Radiochromatography			
Modified Clesceri and Lee[10]	84.6	14.6	0.8
Ebel[9]	85.2	13.9	0.9



ig. 2. Thin-layer radiochromatogram of ^{32}P-labelled calcium-deficient hydroxyapatite on Avicel using odified developing solution of Clesceri and Lee[10]. Standards of sodium and calcium ortho-, pyro- nd tripolyphosphate were simultaneously chromatographed and gave R_F values of 0.78, 0.44 and 0.18, espectively.

ISCUSSION

It was possible to separate calcium ortho-, pyro- and tripolyphosphates by iquid–liquid partition chromatography and to establish, by the conversion of alcium phosphates to the corresponding sodium salts, that the chromatographic ehavior of these moieties could not be due to their existence as calcium–hosphate complexes. In addition, the dissociation of calcium from the various hosphates and its apparent replacement by hydrogen ions upon chromatography re consistent with the indistinguishable R_F values observed on chromatographing he corresponding sodium and calcium phosphates. In other experiments not eported in detail here, the chromatographic behavior of various monovalent salts hydrogen, lithium, sodium and potassium) of ortho-, pyro- and tripolyphosphate vere seen to be identical.

The results of this study support the hypotheses of Winand[13] and of Berry nd Leach[4] that a possible formula for the chemical composition of calcium-leficient apatite prepared in aqueous systems is $Ca_{(10-x)}H_x(PO_4)_6(OH)_{(2-x)}$. If, as n the case of the apatite used in this study, the Ca/PO$_4$ molar ratio for this ompound is 1.5, the above compositional formula must reduce to $Ca_9H(PO_4)_6(OH)$ vith $\frac{1}{6}$ of the total phosphate as acid phosphate. On heating, then the theoretical xpectation of the total phosphate converted into condensed phosphate is likewise or 16.7%, a value closely supported by the experimentally determined 15%. The resent data also indicate that the principal polyphosphate condensation product is pyrophosphate, thereby suggesting that the condensation reaction may b presented as:

$$2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$$

and that reactions of the form:

$$2HPO_4^{2-} + H_2PO_4^{-} \rightarrow P_3O_{10}^{5-} + 2H_2O$$

play only a minor role in the total reaction process. The compositional formul for calcium-deficient apatite may then be written, as a first approximation, a follows: $Ca_{(10-x)}(HPO_4)_x(PO_4)_{(6-x)}(OH)_{(2-x)}$.

SUMMARY

Two liquid–liquid partition chromatography systems were employed t separate calcium ortho-, pyro- and tripolyphosphates on thin layers of micro crystalline cellulose. Chromatography on anion-exchange thin layers of polyethy eneimine was unsuccessful. The liquid–liquid partition system was used t demonstrate that the major condensation product produced on pyrolysis of calciu deficient hydroxyapatite is calcium pyrophosphate.

RÉSUMÉ

Une chromatographie de partage liquide–liquide est utilisée pour la séparatio d'ortho-, pyro-, et tripolyphosphates de calcium, sur couches minces de cellulos microcristalline. La chromatographie sur couches minces échangeuses d'anions d polyéthylèneimine n'a pas donné de bons résultats. Ce système de partage liquide liquide a permis de démontrer que la plus grande partie du produit condensé, lo de la pyrolyse d'hydroxyapatite pauvre calcium est constituée de pyrophosphat de calcium.

ZUSAMMENFASSUNG

Zwei Verteilungschromatographie-Systeme wurden zur Trennung von Cal ciumsalzen der Ortho-, Pyro- und Tripolyphosphorsäure an dünnen Schichte mikrokristalliner Cellulose angewendet. Die Chromatographie an anionenaustau schenden Polyäthylenimin-Dünnschichten zeigte keinen Erfolg. Mit Hilfe de Verteilungssystems wurde bewiesen, dass das wesentliche Kondensationsproduk das bei der Pyrolyse von Hydroxylapatit mit Calciumdefizit entsteht, Calcium pyrophosphat ist.

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HE RECOVERY OF GOLD FROM THIOUREA SOLUTIONS WITH PEN-CELL POLYURETHANE FOAMS

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eceived 23rd March 1973)

Several procedures for the dissolution of gold in ground ore bodies using idic thiourea solution have been described[1,2]. The application of thiourea solution r the selective desorption of gold cyanide complexes absorbed on anion-exchange sins has also been reported[3–5]. Various attempts have been made to recover gold om such aqueous thiourea solutions[6,7]. Lodeishchikov and Panchenko[6] described e adsorption of the gold–thiourea complex on active carbon in industrial plications; the different types of active carbon examined retained gold from queous thiourea solution (containing *ca.* 1 mg Au^{3+} l^{-1}) to approximately the me degree, and gold-free solution was obtained on using carbon charges ranging tween 450 and 600 mg l^{-1}. After the complete adsorption of gold, carbon was parated from the suspension by filtration or screening.

In a recent publication[8], a systematic investigation was made of the factors hich control the retention of the gold–thiourea complex on open-cell polyurethane am loaded with tri-*n*-butyl phosphate (TBP). It was demonstrated that trace ounts of gold were successfully separated on short foam columns at fast flow-rates 0–60 ml min^{-1}) even in the presence of high concentrations of various interfering ements. It was also shown[8] that the binding of gold–thiourea complex was quite pid and that the interfering elements studied had only a slight effect on the rate adsorption of gold on the loaded foam.

The present investigation is a continuation of previous work on the use of llular plastics for chemical separations; the aim was to apply polyurethane foam place of active carbon as a convenient adsorbent for gold–thiourea complex from re and ion-exchange leach solutions. Obviously, the use of the cheap foam aterial would eliminate the troublesome filtration process and should also decrease e time required for adsorption.

XPERIMENTAL

eagents and materials

All the reagents used were of analytical grade unless otherwise specified. ri-*n*-butyl phosphate (TBP) was purified as described by Hamlin *et al.*[9]. Gold loride solution was prepared by dissolving the chloride salt in distilled water. efore use, the gold solution was spiked with ^{198}Au (Institute of Isotopes, Budapest).

Two samples of polyurethane foam—a polyether of open-cell type—(H.1 and

H.2) were supplied by the North Hungarian Chemical Works, Sajóbábony, Hungary Three samples of polyurethane foam of a similar type (W8100, W8300 and W8600 were supplied by the Kunststoffbüro GmbH, München. One sample of polyurethane foam—a polyester of open-cell type—(PPI 80nFR) was supplied by Eurofoam Damstraat, 9200 Wetteren. Voltalef (polytrifluorochloroethylene) powder grade 300LDCHR (Plastimer, 5 Rue Général Foy, Paris) was sieved to 0.25-mm particle diameter by means of a series of standard sieves before use. Active carbon (E. Merck) was used.

The TBP-loaded polyurethane foams were prepared as previously described[10,11]. Voltalef powder was treated with the purified TBP exactly as described previously[12]

Apparatus

Stoppered flasks of 25-ml and 100-ml capacity were used in batch retention experiments.

For activity measurement, a NaI(Tl) detector and an energy-selective counting device (type NK-107/B, Gamma, Budapest) were employed.

Procedures

Charge determination of foam and Voltalef. Various amounts of TBP-loaded foam, unloaded foam or TBP-loaded Voltalef powder, were shaken with 50 ml o gold–thiourea complex ($5 \cdot 10^{-6}$ *M* gold(III)) in 100-ml flasks for 90 min. Gold concentrations were then determined in the aqueous solutions by radioactivity measurement.

RESULTS AND DISCUSSION

TBP-loading properties of different foams

Detailed studies were initially made on the loading properties of different types of polyurethane foams for the organic extractant (TBP). Various samples of foam material of different cell size, chemical composition and manufacture were used The TBP uptake of the different foams was determined by allowing 5 g of each washed and dried foam sample to equilibrate with 15 ml of TBP with efficient stirring, and then keeping it in contact with TBP overnight to ensure saturation The loaded foams were dried between two sheets of filter paper to remove excess o TBP and then weighed. The amount of TBP absorbed by the foam was determined by difference. The results (Table I) showed that polyurethane foams of the polyether type retain TBP much more efficiently than the polyester foam. Moreover the uptake of TBP by polyether foams was slightly increased by decreasing the cel dimensions of the foam material. In Table I, the cell dimensions of sample 1 > sample 2 and sample 3 > sample 4 > sample 5.

Obviously, the higher the uptake of the organic extractant, the higher wil be the retention capacity of the loaded foam, supposing that foams of 100% open-cel composition are used.

Extraction capacity and rate of adsorption

Since the aim of this investigation was to develop a suitable procedure for

BLE I

E TBP-LOADING CAPACITY OF VARIOUS TYPES OF POLYURETHANE FOAM

each case, 5 g of dry foam was taken)

nple no.	*Type of foam*	*Weight of loaded foam (g)*	*Weight of TBP absorbed/5 g of foam*
	Polyurethane foam, polyether, more than 95% open cell (H.1)	14.9516	9.9516
	Polyurethane foam, polyether, more than 95% open cell (H.2)	15.9490	10.9490
	Polyurethane foam, polyether, *ca.* 100% open cell (W8100)	14.4372	9.4372
	Polyurethane foam, polyether, *ca.* 100% open cell (W8300)	14.5991	9.5991
	Polyurethane foam, polyether, *ca.* 100% open cell (W8600)	15.8234	10.8234
	Polyurethane foam, polyester, *ca.* 100% open cell (PPI 80nFR)	10.3270	5.3270

he recovery of gold from aqueous solution of thiourea with foam material by a atch technique, detailed studies of the extraction capacities and rates of adsorption f the gold–thiourea complex with the different samples of TBP-loaded foams were arried out.

During preliminary experiments, it was observed that unloaded polyurethane oams themselves retained the gold complex. It was therefore necessary to investigate he possibility of using unloaded foam, for this would simplify the procedure, specially for industrial purposes.

In comparative experiments, the sorption capacity of the gold–thiourea omplex on TBP-loaded and unloaded foams was determined. Aliquots (10 ml) of old complex ($5 \cdot 10^{-6}$ *M*) were shaken with 0.1 g of each foam sample, in 25-ml toppered glass flasks for 90 min. After equilibration the activity of the aqueous olution was measured and the concentration of gold determined. The amount of old adsorbed on the foam material was calculated by difference.

The results (Table II) showed that the uptake of gold–thiourea complex by he different types of unloaded foam depends to some extent on cell dimension; he uptake decreased as the cell size decreased. However, both TBP-loaded and nloaded foam retain the gold complex to about the same extent (Table II), although he mechanism of retention seems to be quite different. In the case of loaded foam, he retention is probably analogous to a liquid–liquid partition mechanism (between

TABLE II

THE RECOVERY OF GOLD FROM ACIDIC SOLUTIONS OF THIOUREA WITH DIFFEREN POLYURETHANE FOAMS, VOLTALEF POWDER AND ACTIVE CARBON

(The sorbent charge was 10 g per liter of 0.1 *M* perchloric acid containing 3% thiourea and 1 sodium perchlorate. In all cases, the gold content of the initial solution was 1.00 mg l^{-1})

Sorbent	*Recovery of gold on sorbent after separation (%)*	
	Unloaded material	*TBP-loaded material*
Foam sample 1	93.2	93.5
Foam sample 2	91.3	92.5
Foam sample 3	89.0	91.5
Foam sample 4	87.8	91.5
Foam sample 5	85.2	90.0
Foam sample 6	77.2	88.3
Voltalef powder	0	87.8
Active carbon[a]	95.0	—

[a] 0.2 g of active carbon per liter.

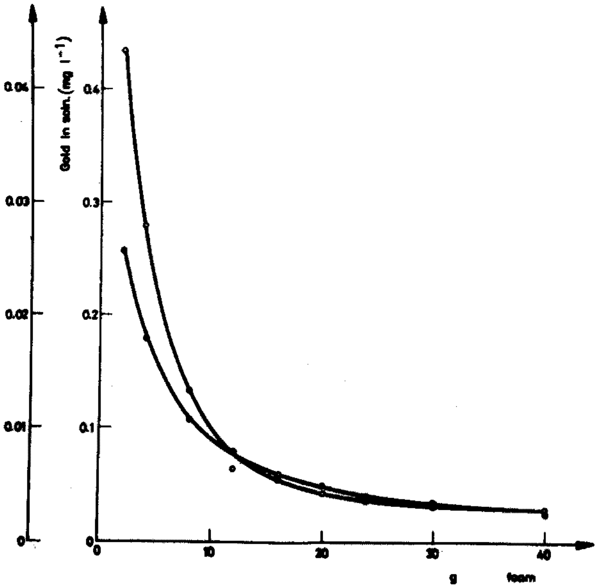
the aqueous and TBP phases) while in the case of unloaded foam, the mechanisı is probably mixed.

This was confirmed by an observation made during the extraction of tł palladium–thiourea complex by TBP-loaded[11] and unloaded foam: the palladiuı complex was completely retained on passing its solution through both loaded an unloaded foam columns. With TBP-loaded foam columns, the palladium comple was quantitatively eluted by 100 ml of distilled water in a similar way as in tł liquid–liquid extraction of palladium in a TBP–perchloric acid–thiourea system. I contrast, the palladium complex previously adsorbed on an unloaded foam colum was not eluted completely even by 300 ml of distilled water. This experiment show also that the foam material behaves as an inert support in the loaded state.

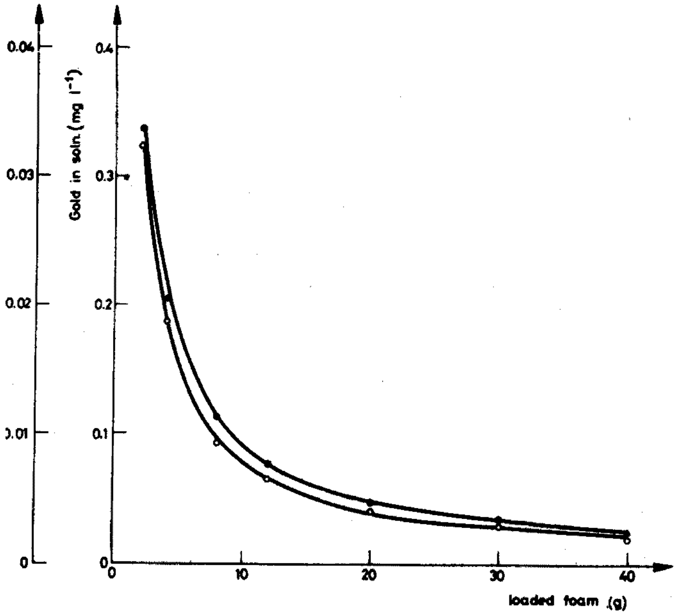
Further support for the inert behaviour of the foam itself in the loade state was found in the results obtained with foam sample no. 6 and Voltal powder; these retain TBP to the same extent, and adsorb the gold–thioure complex equally (Table II). Yet the unloaded Voltalef powder was inert towards tł gold–thiourea complex under the experimental conditions used.

It was found that the uptake of the gold–thiourea complex by 10 g of foaı material (loaded or unloaded) from 1 l of 0.1 *M* perchloric acid containing 3 thiourea, 1% sodium perchlorate and 1 mg of gold(III) was approximately equ to the uptake of 0.2 g of active carbon under the same experimental conditioı (Table II).

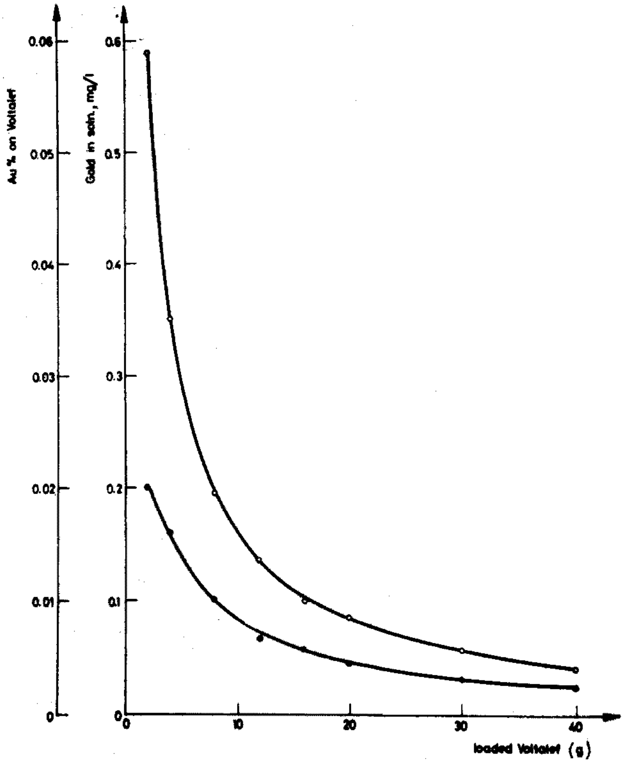
Similar results were also obtained for the determination of foam charg under identical conditions as those previously described for active carbon[6] bı ing foam weights ranging between 2 and 40 g l^{-1}. The results are shown in igs. 1, 2 and 3 for unloaded foam sample no. 1, TBP-loaded foam sample no. 1, d loaded Voltalef powder, respectively. The curves obtained are very similar to



. 1. Effect of foam charge (unloaded sample no. 1) on the sorption of gold from acidic thiourea ution. [Au]$=5\cdot10^{-6}$ *M*. [Thiourea]$=3\%$. [$NaClO_4$]$=1\%$. [$HClO_4$]$=0.1$ *M*. (○) Gold in soln.;) gold on foam.



. 2. Effect of foam charge (TBP-loaded sample no. 1) on the sorption of gold from acidic thiourea ition. Conditions as in Fig. 1. (○) Gold in soln.; (●) gold on foam.



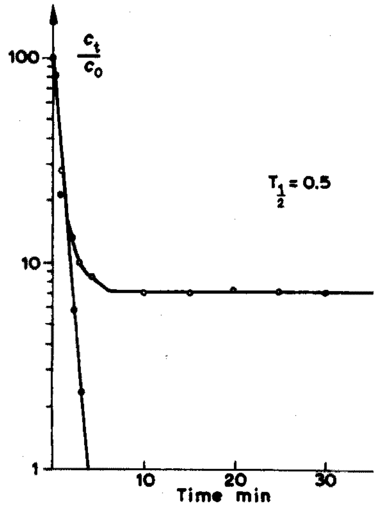


Fig. 3. Effect of Voltalef charge (TBP-loaded) on the sorption of gold from acidic thiourea soluti Conditions as in Fig. 1. (○) Gold in soln.; (●) gold on Voltalef.

Fig. 4. Rate of adsorption of the gold–thiourea complex on TBP-loaded polyurethane foam (sam no. 2) at room temperature. $[\mathrm{Au}]=5\cdot10^{-6}$ *M*. [Thiourea] = 3%. $[\mathrm{NaClO_4}]=1\%$. $[\mathrm{HClO_4}]=0.1$ *M*.

those previously published for carbon[6]. A gold-free solution can be obtain only on using foam charges of *ca.* 30 g $\mathrm{l^{-1}}$, which is about 50 times grea than the amount of carbon required.

In order to compare the retention rates of the gold–thiourea complex the different foam samples (loaded and unloaded) and loaded Voltalef with that active carbon, it was convenient to carry out a series of kinetic experiments[8] As an example, the results obtained with TBP-loaded foam sample no. 2, a shown in Fig. 4. The half-lives of adsorption of the gold–thiourea complex on the samples of foam materials (loaded and unloaded), loaded Voltalef and acti carbon are summarized in Table III. As expected, the retention rate of gold loaded foam material was, generally, better than that obtained with loaded Voltal The rate of adsorption of gold on loaded foam material was found to be the same that obtained with active carbon ($T_{\frac{1}{2}}$ was about 0.6 min ±5%).

In conclusion, unloaded polyurethane foams (open-cell polyethers) can used in place of carbon for the recovery of the gold–thiourea complex fro aqueous solutions, the method being especially useful for industrial purposes. F analytical application in the laboratory, the separation of gold should be done wi

ABLE III

HE HALF-LIVES OF ADSORPTION OF GOLD–THIOUREA COMPLEX ON VARIOUS YPES OF FOAMS AND POWDERS

orbent	*$T_{\frac{1}{2}}$ (min)*	
	Unloaded sorbent	*TBP-loaded sorbent*
oam sample 1	1.5	1.0
oam sample 2	1.3	0.5
oam sample 3	2.0	0.6
oam sample 4	1.5	0.6
oam sample 5	1.6	0.6
oam sample 6	1.8	0.4
oltalef powder	—	0.8
ctive carbon	0.6	—

BP-loaded foam. Under the latter conditions, the elimination of many interfering lements is more easily controlled[8].

The authors thank the Kunststoffbüro GmbH, München, and the Eurofoam, amstraat, 9200 Wetteren, for donating some foam samples used in this work.

UMMARY

The recovery of the gold–thiourea complex from aqueous solutions with BP-loaded and unloaded polyurethane foams was investigated in batch experiments. he rates of adsorption of the gold complex on various types of loaded and unaded foams were studied in detail and compared with the rate of adsorption on ctive carbon. Loaded and unloaded polyurethane foams of the polyether or olyester type behaved similarly to active carbon. The adsorption capacity of the ams was lower than that of active carbon but the use of foam simplifies the rocedure by eliminating the filtration process which is necessary with carbon.

ÉSUMÉ

Une étude est effectuée sur la récupération de l'or sous forme de complexe iourée, en solution aqueuse, au moyen de mousses polyuréthane, chargées de BP et non chargées. Les vitesses d'adsorption du complexe d'or sont déterminées comparées avec les vitesses d'adsorption sur charbon actif. L'utilisation des ousses présente l'avantage d'éviter la filtration, nécessaire avec le charbon.

USAMMENFASSUNG

Die Wiedergewinnung des Gold–Thioharnstoff-Komplexes aus wässrigen

Lösungen mittels TBP-beladenen und unbeladenen Polyurethan-Schäumen wu
untersucht. Die Geschwindigkeit der Adsorption des Gold-Komplexes an versc
denen Arten von beladenen und unbeladenen Schäumen wurde eingehend un
sucht und mit der Geschwindigkeit der Adsorption an Aktivkohle verglich
Beladene und unbeladene Polyurethan-Schäume vom Polyäther- oder Polyester
verhielten sich ähnlich Aktivkohle. Die Adsorptionskapazität der Schäume w
geringer als die von Aktivkohle, jedoch vereinfacht die Verwendung von Scha
das Verfahren, da der bei Aktivkohle notwendige Filtrationsprozess wegfällt.

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'HE POLAROGRAPHIC BEHAVIOUR OF THE 1,4-BENZODIAZEPINES,)XAZEPAM AND LORAZEPAM, AND A METHOD FOR QUALITY :ONTROL*

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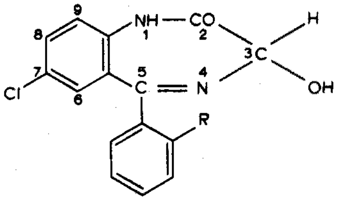
.eceived 12th March 1973)

Oxazepam (Serenid-D) and lorazepam (Ativan) are members of the benzodiazpine group of tranquillisers and have the structures (I) and (II) respectively:



(I) R = H

(II) R = Cl

)xazepam and lorazepam can be assayed by various methods. In the u.v. spectrohotometric procedure^{1,2} the active ingredient is extracted with a suitable solvent nd the absorbance of the resulting diluted solution is measured at 229 nm; nfortunately, this method cannot differentiate between the active constituent and ny degradation product present in the formulation. Non-aqueous acid–base itrations can be used for the pure substance$^{1-3}$, but the presence of certain xcipients in tablet formulations which have acidic or basic properties leads to rroneous results. Oelschläger *et al.* have studied the polarographic reduction nechanism of oxazepam^{4,5} and have produced a method of assay in acetate uffer pH 4.7 containing 20% dimethylformamide^{6}. Fazzari and Riggleman^{7} have xtracted oxazepam from dosage forms and determined it polarographically in a nethanol–methylene chloride solvent system. A methanolic extraction of the active ngredient followed by polarography in an acetate buffer at pH 4.7 has been used 'outinely for a number of years^{8}.

In this paper, a detailed study of the polarographic behaviour of oxazepam nd lorazepam over a wide pH range is described. This provides complementary

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* This paper was presented at *Analysis 72*, a conference held at Imperial College, London, in ieptember 1972.

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information to earlier spectral work[9] on the acid–base equilibria existing in aqueo solutions of these compounds. After selection of ideal pH ranges for analyti determinations, the variation of the limiting current with concentration w ascertained with varying percentages of non-aqueous solvent present; the solvent necessary to obtain dissolution of the active constituent before polarograph determination. These findings were then applied to the assay of oxazepam a lorazepam in different formulations.

EXPERIMENTAL

Apparatus

The polarographic behaviour of oxazepam and lorazepam in aqueous buffe was studied with a Polariter PO4 (Radiometer) in conjunction with a Kalous vessel and a saturated calomel electrode. Oxazepam in dimethylsulphoxide, methan and aqueous mixtures with these solvents, was studied with a Davis Cathode-R Polarograph A1660 (Southern Analytical) with a mercury pool as reference electro The H-cell was thermostatted at 25° and was designed so that a very fine strea of nitrogen could be bubbled through the sample solution to enable rapid deaerati of non-aqueous solutions.

The on-line stability and quality control method utilized a Cambrid polarograph and an H-cell with a calomel reference electrode separated from t sample solution by a 1-cm agar–KCl bridge. This cell was thermostatted at 25°.

Chemicals and reagents

Oxazepam and lorazepam (J. Wyeth and Brother, Ltd.) were used for t basic studies. Serenid-D and Ativan capsules or tablets were assayed polar graphically. Stable stock solutions (10^{-2}–10^{-3} *M*) of oxazepam and lorazepam we made up in AnalaR methanol or dimethylsulphoxide and appropriately diluted.

Variation of the half-wave potential ($E_{\frac{1}{2}}$) and the limiting current with p was studied with Britton–Robinson buffers in the pH range 1.8–12.0 and wi hydrochloric acid and sodium hydroxide at the extremes of this range. Spectr copically pure dimethylsulphoxide, acetonitrile and AnalaR methanol were used conjunction with 0.1 *M* tetraethylammonium perchlorate or Britton–Robins buffers for the non-aqueous studies. Sodium acetate–acetic acid buffer was used f the quality control method; a mixture of 8.2 g of anhydrous sodium acetate a 5.9 ml of anhydrous acetic acid in 200 ml of distilled water was diluted to 1 l.

Experimental techniques

For the theoretical studies in aqueous buffers, 10 ml of 10^{-4} *M* oxazepa in an appropriate supporting electrolyte was deaerated by a stream of nitroge the *i–E* curves were recorded at a slow rate of scanning (100 mV min^{-1}) reduce the effects of hysteresis of the recording instrument, and the $E_{\frac{1}{2}}$ value a limiting current were measured.

For the plots of limiting current against concentration, a continuous additi method was used with brief flushes of nitrogen for deaeration and stirring betwe successive additions, the *i–E* curves being recorded after each addition.

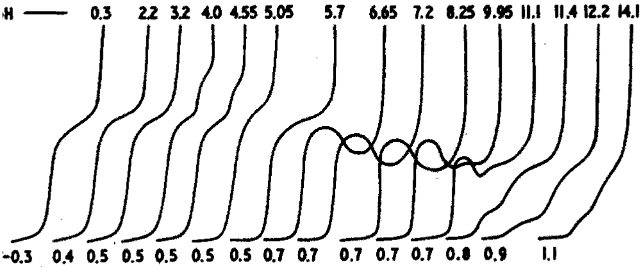
Rapid single tablet assays were attempted by grinding 15-mg Serenidblets to a fine powder in a mortar, adding 10 ml of dimethylsulphoxide and inding for a further 5 min; the suspension was allowed to settle and an iquot (0.1 ml) was transferred to a 10-ml volumetric flask and diluted to the ark with supporting electrolyte. This solution was used for polarography.

The stability and quality control method is described on p. 432.

ESULTS AND DISCUSSION

eduction process

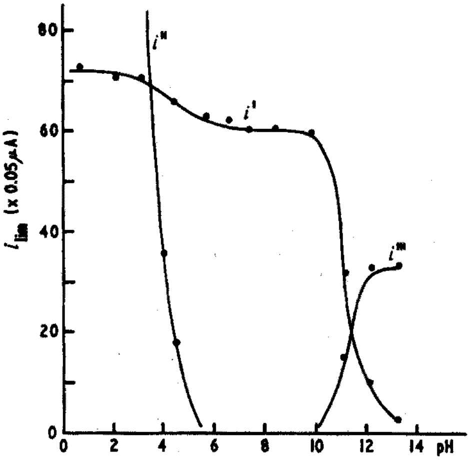
Oxazepam and lorazepam are reduced similarily over a wide pH range igs. 1 and 2). The main wave (i') is a 4-electron step, corresponding to imultaneous reduction of the 4,5-azomethine group and reductive splitting of the arbon–hydroxyl bond in the diazepine ring[5]. This wave is well defined and is iffusion-controlled in the pH range 0–6, but becomes strongly affected by adsorption f the reducible species on the mercury electrode above pH 6.0[4], the wave is then o distorted that it becomes useless analytically. A catalytic wave (i'') is observed t pH 4–5. Above pH 10 the main wave begins to decay, and another wave merges at more negative potential (i''') which reaches a maximum height orresponding to a 2-electron reduction at pH 12. This reflects an acid–base quilibrium with $pK_1' = 11.1$. At pH 10.8 the wave i''' is a small fraction of wave i'; ts wave height is practically independent of mercury pressure and is therefore inetically controlled. The wave pattern changed rather rapidly on repeated scanning bove pH 13, owing to alkaline hydrolysis of the benzodiazepine and/or subsequent eduction of the rearranged product of the first reduction at this pH.



ig. 1. Polarogram of 10^{-4} *M* oxazepam in Britton–Robinson buffers.

The variation of half-wave potential with pH (Figs. 3 and 4) showed three inear portions for the main wave i' with slopes of 50 mV/pH, 90 mV/pH and 0 mV/pH, for oxazepam, and 40 mV/pH, 90 mV/pH and 35 mV/pH for lorazepam. he first break corresponds to pK_1 2.0 for oxazepam and pK_1 1.8 for lorazepam, hich is in reasonable agreement with the spectroscopically determined values of .7 and 1.3, respectively[9].

The second break occurs at pH 5–6 for both species and is due to the ifficulty in measuring the $E_{\frac{1}{2}}$ values when the wave shape is distorted. The $E_{\frac{1}{2}}$ alue of wave i'' is independent of pH in the narrow range within which it appears. he values of $dE_{\frac{1}{2}}/dpH$ of i''' are 60 mV/pH for oxazepam, and 90 mV/pH for orazepam.



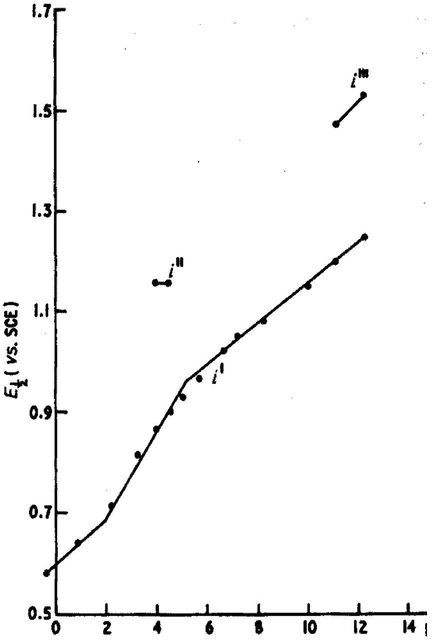
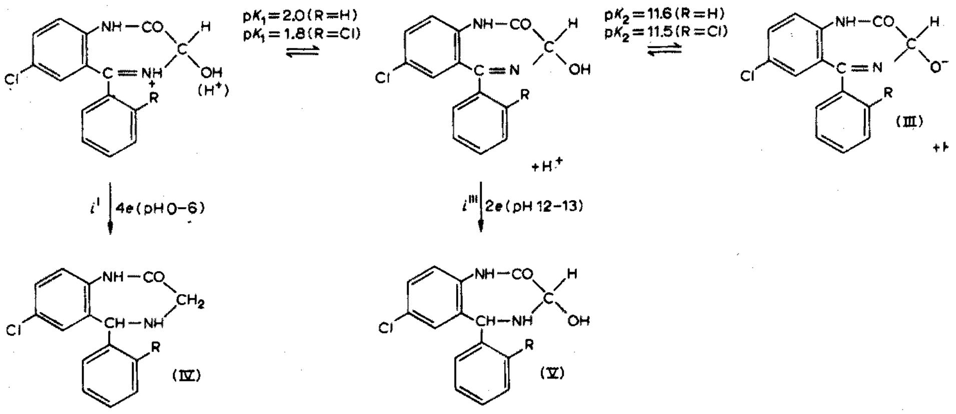


Fig. 2. Variation of the limiting currents of 10^{-4} *M* oxazepam and lorazepam with pH in Britton Robinson buffers.

Fig. 3. Variation of the half-wave potential of 10^{-4} *M* oxazepam with pH in Britton–Robinson buffer

The following scheme is a possible interpretation of the polarographi reduction waves of oxazepam and lorazepam.



In this scheme, no reduction of species III was observed in the available pl range. Species IV has been identified by i.r. and n.m.r. spectroscopy[5]; species could rearrange and be reduced further above pH 14. The pK_2 values wei determined spectroscopically[9].

Earlier spectroscopic studies[9] indicated that three species predominate in th bulk of the solution in the pH range 0–14 *i.e.* the singly protonated, neutral and anionic forms. This agrees with the pH range of extractability of the neutral form from biological fluids as collected in a recent review[10]. However, to explain why waves *i′* and *i‴* correspond to 4-electron and 2-electron reductions, respectively, it must be assumed that the hydroxyl group on carbon atom 3 is protonated before polarographic reduction in acid and mildly alkaline solution, whereas at pH 12–13, this group is not protonated and there is only a 2-electron reduction of the azomethine linkage.

Variation of limiting current with concentration and the effect of non-aqueous solvents

When cathode-ray polarography was used, well defined waves suitable for analytical purposes were produced in the pH range 0–6. The Ilkovic equation was therefore tested in acetate buffer pH 4.7, where the wave height corresponded to a 4-electron process and where acid hydrolysis would not affect the analytical accuracy. Oxazepam and lorazepam obeyed the equation in the concentration range 10^{-5}–10^{-4} *M* but above *ca.* 10^{-4} *M*, the relationship was invalidated by adsorption of the benzodiazepines or their reduction products on the mercury drop. This limitation was avoided, as is frequently the case for organic heterocyclic substances exhibiting adsorption in aqueous media, by the use of 0.1 *M* tetraethylammonium perchlorate in dimethylsulphoxide containing 10% water as the supporting electrolyte (Fig. 5 for oxazepam). The peak potential measured against a mercury pool was

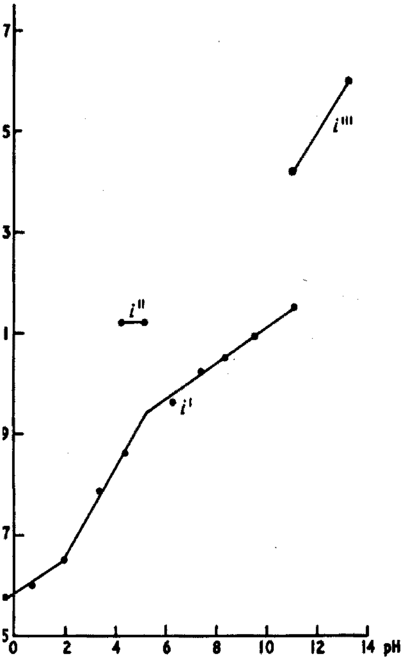


Fig. 4. Variation of the half-wave potentials of 10^{-4} *M* lorazepam with pH in Britton–Robinson buffers.

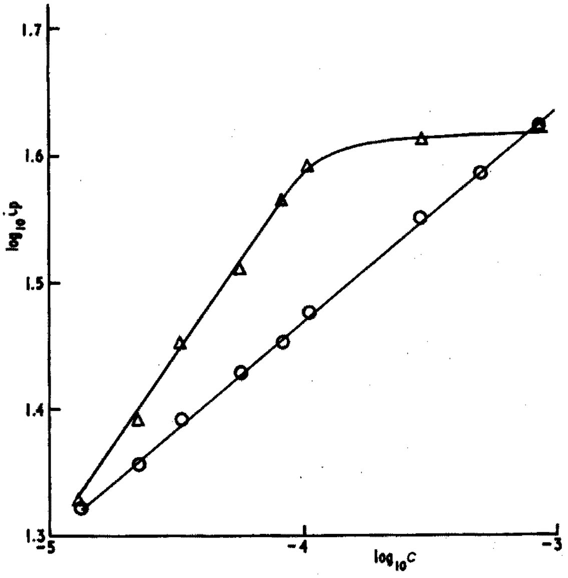


Fig. 5. Calibration plots for oxazepam. (○) In DMSO/10% H_2O; (△) in aqueous pH 4.7 acetate buffer.

considerably more negative than in aqueous media, −1.84 V (starting voltag −1.5 V), and not as well defined. A similar behaviour was observed in supportin electrolytes containing 90% acetonitrile and 90% methanol, the former giving to large a blank to be analytically desirable.

The linearity of response over a wider concentration range in predominantl non-aqueous media is obviously an advantage in rapid and direct formulatio assay by polarographic means, but this is counterbalanced by factors such as th lengthy deaeration of non-aqueous solvents and the irreproducible wave pattern negative potentials owing to erratic falling of mercury drops.

ANALYTICAL APPLICATIONS

A rapid method of quality control on single tablets was attempted b grinding up 15-mg Serenid-D tablets to a fine powder, dissolving the activ constituent in 10 ml of dimethylsulphoxide, and cathode-ray polarographic analysi of a sample of the supernate diluted with supporting electrolyte (0.1 *M* tetra ethylammonium perchlorate in 90% DMSO:10% H_2O). The height of the wave wa referred to a predetermined calibration plot. Because of the rapid-scanning cathod ray polarography and the avoidance of separation procedures, the method prove very rapid (5–10 min) and precise, but was not accurate enough for pharmaceutic control. Only 87% of oxazepam appeared to be extracted, and this was independer of the time of grinding and shaking of the sample with dimethylsulphoxide. Seve assays were carried out on the 15-mg formulations with a mean value of 13.05 m and a standard deviation of $4.5 \cdot 10^{-5}$.

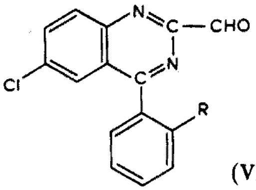
The final method selected for on-line stability trials and quality control oxazepam and lorazepam formulations employs methanol as solvent; this is mor time-consuming but much more accurate.

Recommended method

Weigh a quantity of the finely powdered capsule contents or tablets equivaler to about 20 mg of oxazepam or 8 mg of lorazepam, into a 30-ml stoppere centrifuge tube. Pipette 25 ml of absolute methanol on to the sample of oxazepar (10 ml for lorazepam), stopper the tube and shake vigorously for 30 min. The centrifuge at 2,500 r.p.m. until the supernatant solution is clear. Pipette an aliquc (5 ml) of the clear supernatant solution into a 100-ml graduated flask, dilute to th mark with acetate buffer pH 4.7 and then subject to d.c. polarography. Compar the height of this wave to a suitable standard on the same linear portion of th limiting current–concentration relationship. Calculate the weight of active constituer in the capsule or tablet from: mg of active constituent $= i_{\text{sample}}/i_{\text{standard}} \cdot x \cdot$ averag weight of capsule or tablet/weight taken where i_{sample} = limiting current of sampl i_{standard} = limiting current of standard, and $x = 20$ for oxazepam, or 8 for lorazepan

Results

The results of 10 polarographic assays of Serenid-D tablets containing 10 m of oxazepam gave a mean value of 9.896 mg/tablet with a standard deviation ±0.2323; the relative standard deviation was 2.325%. However, one assay gave value of 9.28 mg, which was probably due to inefficient extraction after "caking f the sample in the centrifuge tube. If this value is omitted, the mean result of assays was 9.96 mg/tablet, with a standard deviation of ±0.091 and a relative tandard deviation of 0.91%. Similar assays were carried out on Ativan containing .5 mg and 0.5 mg of lorazepam per tablet, (100 tablets of each concentration vere taken, the average weight was determined, the tablets were powdered finely, and liquots equivalent to 8 mg of lorazepam were taken for each assay). Ten assays vere performed on the tablets containing 2.5 mg of lorazepam per tablet; the nean value found was 2.500 mg/tablet with a standard deviation of ±0.041, and a elative standard deviation of 1.64%. Twelve assays on tablets containing 0.5 mg of orazepam per tablet gave a mean result of 0.514 mg/tablet, with a standard leviation of ±0.0088 and a relative standard deviation of 1.71%.



(VI)

The mean decomposition product formed on shelf storage of formulations containing oxazepam and lorazepam is the quinazolinecarboxaldehyde (VI), which is polarographically reduced in acetate buffer pH 4.7 at $E_{\frac{1}{2}} = -0.72$ V (*vs.* S.C.E.), compared with $E_{\frac{1}{2}} = -0.92$ V for the parent compounds. This difference in potential was used to monitor gross contaminations (2–10%) of the impurity in the formulations by conventional d.c. polarography. Lower levels (< 1%) could be measured by using more sensitive polarographic equipment in the region of −0.7 V; the parent compound is reduced at a more negative potential so that compensation for a large pre-wave is unnecessary.

Work is in progress to utilize the sensitivity of the method in single tablet assays which are becoming increasingly important in pharmaceutical control.

CONCLUSION

The changes of the polarographic reduction waves of oxazepan and lorazepam with pH, together with the corresponding u.v. spectral changes[9], suggest the presence of three species in aqueous solutions: the monoprotonated, the neutral and the anionic forms. pK_1 values were determined by study of the variation of $E_{\frac{1}{2}}$ with pH and such values are in reasonable agreement with those obtained by u.v. spectroscopy[9]. It is the monoprotonated species that is reducible over a wide range of pH and whose reduction waves are most suitable for analytical measurement, particularly in the pH range 3–6.

The polarographic method was applied to the assay of four formulations, containing 0.5–15 mg benzodiazepine/tablet, one of the assays being carried out in a supporting electrolyte containing 90% dimethylsulphoxide. The results in this dimethylsulphoxide medium were precise but inaccurate, whereas determinations carried out in buffered methanolic media were both precise and accurate.

SUMMARY

The polarographic behaviour of the drugs, oxazepam and lorazepam, has been investigated over a wide pH range. Different types of wave are obtained depending on the pH. The pK_a values calculated are in good agreement with those obtained from u.v. spectroscopic measurements. For analytical purposes, the optimal pH is 4.7 (acetate supporting electrolyte), the 4-electron reduction wave being measured. A quality control method for the two drugs in different formulations containing 0.5–15 mg of active constituent is described.

RESUMÉ

On examine le comportement polarographique de deux drogues (oxazepam et lorazepam) en fonction du pH. Les valeurs pK_a calculées correspondent bien à celles obtenues par des mesures spectroscopiques u.v. Le pH optimal pour l'analyse est 4.7, en utilisant un acétate comme électrolyte de base. On décrit une méthode d'analyse pour ces deux drogues, dans différentes formules contenant 0.5–15 mg de constituant actif.

ZUSAMMENFASSUNG

Das polarographische Verhalten der Arzneimittel Oxazepam und Lorazepam wurde über einen grossen pH-Bereich untersucht. In Abhängigkeit vom pH-Wert traten verschiedene Arten von Wellen auf. Die berechneten pK_a-Werte stimmen mit denen, die aus u.v.-spektroskopischen Messungen erhalten worden sind, gut überein. Für analytische Zwecke ist der optimale pH-Wert 4.7 (Acetat-Trägerelektrolyt), wobei die 4-Elektronen-Reduktionswelle gemessen wird. Eine qualitative Kontrollmethode für die beiden Arzneimittel in verschiedenen Formulierungen mit einem Gehalt von 0.5–15 mg an aktivem Bestandteil wird beschrieben.

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VOLTAMMETRIC BEHAVIOUR OF COPPER(III) AND ITS ANALYTICAL APPLICATIONS

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Received 18th March 1973)

Very few oxidizing agents which are satisfactory in alkaline media are known; among these copper(III) is of particular interest. Its history up to 1925 has been reviewed by Vrtis[1]. The presence of stable complexes in solutions containing copper(III), periodate or tellurate ions and hydroxide ions has been established beyond doubt[2–4]. The chemical and electrochemical properties of copper(III) complexes of biuret and oxamide[5] and of some cyclic amines[6] have been studied in nonaqueous solvent. Copper(II) has been oxidized to copper(III) in alkaline solution by electrolysis[1,7], with hypochlorite[2], with persulfate[1,3,4,8,9] and with periodate tself which can both oxidize and act as a stabilizing ligand[10,11].

Potassium diperiodatocuprate(III) and ditelluratocuprate(III) prepared by he persulfate method have been applied as analytical reagents by Beck[12] and more recently by Chandra and Yadava[13,14] and by Jaiswal[15]. Since some difficulties were encountered in the direct end-point detection recommended by Beck[12], Keyworth and Stone[16] adopted a potentiometric dead-stop end-point detection; Chandra and Yadava[13,14] used a method involving iodimetric back-titration of excess of arsenite solution.

In the work described here the voltammetric behaviour of diperiodatocuprate(III) and ditelluratocuprate(III) complexes was investigated in aqueous solution at a platinum microelectrode for which the diffusion layer was periodically renewed[17]. Analytical applications arising from this investigation are:

(*a*) an amperometric method for the standardization of copper(III) solutions, which represents a convenient alternative to the existing techniques;

(*b*) a voltammetric determination of microamounts of copper in the presence of different ions in hydroxide ion media and in potassium and sodium metals.

Both methods are sensitive, rapid and give good reproducibility.

EXPERIMENTAL

Apparatus

The voltammetric behaviour of copper(III) complexes and the voltammetric determination of copper(II) were investigated in a cell with the periodically renewed diffusion-layer platinum microelectrode. The polarographic currents were recorded at 25 ± 0.1° with a three-electrode system and a Metrohm polarograph E261 modified

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to allow a slow change of the applied potential and connected to an IR compensat Type E446 (Metrohm). The potentiostatic current–time curves were measured o the screen of a Tektronix Type 502 dual-beam oscilloscope with a 68-TS Wenking potentiostat for the control of the applied potential.

Both the reference and the auxiliary electrodes were saturated mercury(sulfate electrodes, connected to the polarographic cell by bridges consisting of solid mixture of silica gel and sodium sulfate (3:2). The amperometric titration copper(III) solutions was carried out also by means of the above-mention Metrohm equipment with a Beckman rotating platinum electrode as worki electrode (the 188501 variable speed drive unit and the 188551 rotating electro body).

The solution was deoxygenated, when necessary, by passing pure nitrog gas for 10 min.

All potential values are referred to the saturated calomel electrode.

The pH values of the supporting electrolytes were measured with a Metroh E388 potentiometer and a glass electrode except for the 0.1–1 *M* potassium hydroxid solutions. In this range the pH was calculated from the corresponding hydroxid ion concentration. The ionic strength was kept at 1 by adding potassium nitrat whenever necessary.

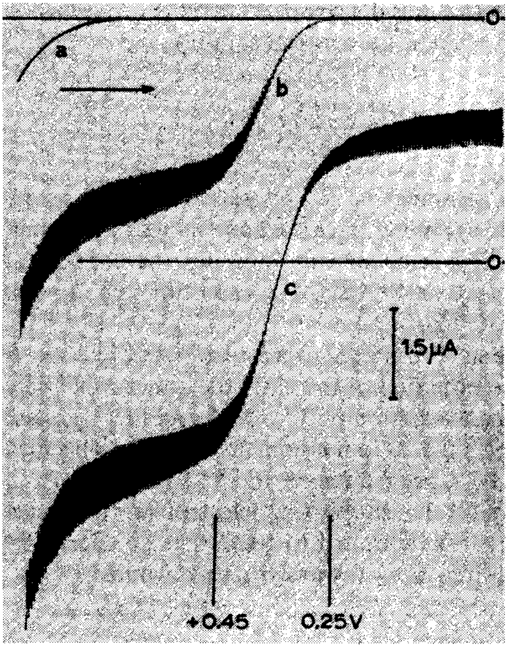
Reagents

"Pro analysi" chemicals were used. Copper(III) solutions were made by th persulfate method as described previously[12,15]. Ditelluratocuprate(III) solution were standardized by the method of Chandra and Yadava[13] or by the ampero metric method proposed in this paper. Standard diperiodatocuprate(III) solution were prepared by exhaustive electrolytic oxidation of copper(II) periodate in 1 potassium hydroxide solutions at a platinum anode (7.5 cm^2) polarized at +0.60

RESULTS AND DISCUSSION

Periodate complexes of copper(II) and copper(III)

Hydroxocuprate(II) ions are not electroactive on a platinum electrode. Th copper(II)–periodate complex, which is sufficiently soluble in alkaline media (p 13–14), investigated in a cell with the periodically renewed diffusion-layer platinu electrode, shows a well formed anodic wave, independently of the direction o recording, in the interval between +0.1 and +0.6 V (Fig. 1, curve b), even i the absence of special treatments of the electrode such as preoxidation or platinizin The best shaped anodic waves were obtained in the presence of a potassiu periodate concentration at least ten times greater than the copper(II) concentration the $E_{\frac{1}{2}}$ value is substantially unaffected by higher concentrations of the ligand. Th proportionality between the mean limiting anodic current and the copper(II) concen tration is maintained down to a concentration of $1 \cdot 10^{-5}$ *M* (Table I). Th copper(III) complex, obtained both by chemical oxidation and by electrolysis, give a cathodic wave, the mean limiting current of which is proportional to the comple concentration (Table I) and with an $E_{\frac{1}{2}}$ value of +0.370 V quite similar to th preceding anodic one. Mixtures of the oxidized and reduced forms of the periodat complex yield cathanodic waves (Fig. 1, curve c).



ig. 1. Voltammetric curves of: (a) supporting electrolyte alone; (b) $5\cdot10^{-4}$ *M* copper(II) and $5\cdot10^{-3}$ *M* otassium periodate in 1 *M* KOH solution; (c) $5\cdot10^{-4}$ copper(II), $5\cdot10^{-4}$ *M* diperiodatocuprate(III) nd $5\cdot10^{-3}$ *M* potassium periodate in 1 *M* KOH solution.

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LIMITING CURRENTS AS A FUNCTION OF THE COPPER CONCENTRATION

lyte: 1 *M* KOH, $1\cdot10^{-2}$ *M* complexing agent)

ation)	*Copper(II) complex oxidation process*				*Copper(III) complex reduction process*			
	Periodate		*Tellurate*		*Periodate*		*Tellurate*	
	$\bar{i}_d$ *(µA)*	$\bar{i}_d/C$ *(µA mmol^{-1})*	$\bar{i}_d$ *(µA)*	$\bar{i}_d/C$ *(µA mmol^{-1})*	$\bar{i}_d$ *(µA)*	$\bar{i}_d/C$ *(µA mmol^{-1})*	$\bar{i}_d$ *(µA)*	$\bar{i}_d/C$ *(µA mmol^{-1})*
	0.15	7.5	0.15	7.5	—	—	—	—
	0.50	6.6	0.50	6.6	0.35	4.6	0.35	4.6
	0.72	6.6	0.71	6.6	0.51	4.6	0.50	4.5
	1.60	6.4	1.60	6.4	1.12	4.5	1.11	4.4
	2.60	6.5	2.54	6.4	1.80	4.5	1.80	4.5
	4.20	6.4	4.16	6.3	2.98	4.5	2.95	4.5
	6.35	6.4	6.30	6.3	4.51	4.5	4.45	4.4

The process, which involves the participation of 1 electron per molecule, is olarographically reversible at the electrode, as shown by logarithmic analysis of the nodic and cathodic waves, which gave a value of near 60 mV for the ratio $E/\Delta \log(i/i_H - i)$. Quantitative examination of the instantaneous potentiostatic currents confirmed that the cathodic and the anodic limiting currents are diffusio controlled. The mean limiting diffusion current follows the equation[17]:

$$\bar{i}_\mathrm{d} = KC, \text{ where } K = \frac{nFAD}{r} + \frac{nFAD^{\frac{1}{2}}}{\pi^{\frac{1}{2}} t_\mathrm{tot}} \left(2t_\mathrm{tot}^{\frac{1}{2}} - 1.5t_\mathrm{p}^{\frac{1}{2}}\right)$$

where *n*, *F*, *A*, *D*, *C*, *r* have their usual meaning, t_rnj is the pulse period (5 s), a t_f is the electrode washing period (0.025 s). When the measured values of $\bar{i}$, *A* and were inserted in this expression, the diffusion coefficient value for the copper(II periodate complex was found to be $0.70 \cdot 10^{-5}$ cm^2 s^{-1}, and for the diperi datocuprate(III) complex to be $0.36 \cdot 10^{-5}$ cm^2 s^{-1}.

Voltammetric curves of the cited complexes were also recorded in t temperature range 5–55°: the half-wave potential of the cathodic and anodic wa shifts to a more negative value with a mean variation of 0.7 mV/degree ($E_{\frac{1}{2}}$ decreas from +0.385 V at 5° to +0.350 V at 55° in 1 *M* potassium hydroxide). The me limiting diffusion current increases by 1.7% per degree.

A change in the concentration of the supporting electrolyte (potassiu hydroxide from 1 to 7 *M*, and sodium hydroxide from 1 to 10 *M*) has no effect up the shape of waves, but causes a slight shift in $E_{\frac{1}{2}}$ toward negative values.

Tellurate complexes of copper(II) and copper(III)

As expected from the similarity of chemical behaviour between the perioda and tellurate complexes, the voltammetric behaviour also proved to be similar.

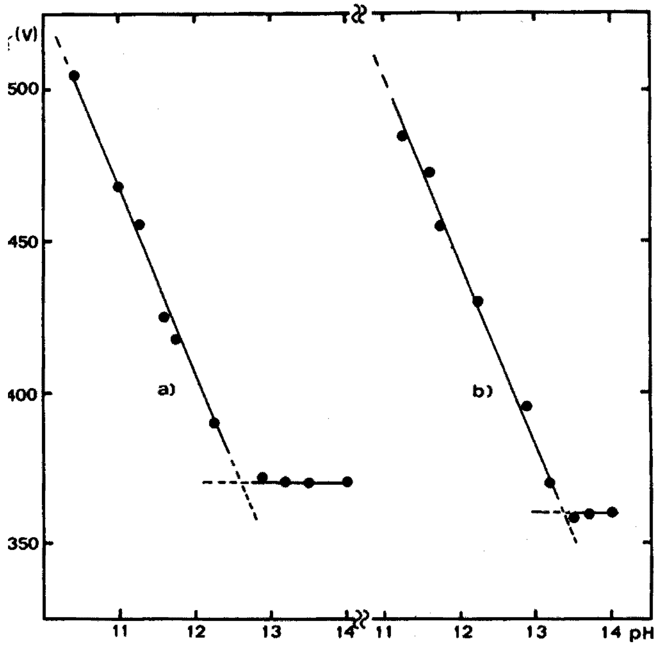
In 1 *M* potassium hydroxide the half-wave potential of the cathodic wa ($E_{\frac{1}{2}} = +0.360$ V), corresponding to the reduction of copper(III) complex, lies at t same potential as the anodic and cathanodic waves, related to the oxidation of t copper(II)–tellurate complex and the copper(II)/(III) tellurate mixtures, respectivel The shapes of these waves are quite similar to those in Fig. 1. Pretreatments of t electrode are again unnecessary in this case. The solubility of the copper(II tellurate complex is substantially limited to the concentrations in Table I. Exhausti electrolytic oxidation at a large platinum electrode caused an anodic deposit of t ditelluratocuprate(III) complex. As indicated in Table I, the height of the anodic a cathodic waves is strictly proportional to the complex concentration and does n differ much from that of the periodate complex.

The slope of the log plot corresponds to one-electron reaction. The temper ture coefficient of $\bar{i}_\mathrm{d}$ is 1.8% per degree in the temperature range 5–55°. Dependi on the reversibility of the wave, no appreciable variation of $E_{\frac{1}{2}}$ with temperature w noted.

As previously specified for the copper–periodate complexes, potentiostat measurements showed the limiting currents to be diffusion-controlled for the coppe tellurate complexes; the diffusion coefficient values were quite similar to the corr sponding ones for the copper–periodate complexes.

Effect of pH

The effect of the pH of the solution on the redox potential of the copper(II copper(III) complex couple was further investigated. Periodate and tellura complexes were tested in the pH ranges 10–14 and 11.5–14, respectively, wi



g. 2. Variation with pH of the $E_{\frac{1}{2}}$ value of the reversible copper(III)/copper(II) wave obtained with 10^{-5} M copper(II) in buffer solutions, at $\mu = 1$, containing $5 \cdot 10^{-4}$ M periodate (a) or tellurate (b) ions.

otassium hydroxide or carbonate mixtures as buffers at unit ionic strength. The riation of the $E_{\frac{1}{2}}$ for the oxidation of the copper(II) complex with pH is reported Fig. 2, where curve (a) refers to the copper(II)–periodate complex and curve (b) the copper(II)–tellurate complex. The reported data were obtained under the same perimental conditions, for either the periodate or tellurate complex, with regard buffer mixtures, ionic strength ($\mu = 1$), concentration of copper(II) ($5 \cdot 10^{-5}$ M) d ligand ($5 \cdot 10^{-4}$ M). The slight solubility of both complexes at pH values lower an 13 necessitated the use of the indicated concentrations of metal and ligand, and ndered the voltammetric investigation at pH values lower than those cited. It is oteworthy that an anodic red-orange deposit of the ditelluratocuprate complex as formed on the electrode in solutions of the copper(II)–tellurate complex below H 11.5.

The experimental data showed that the ratio $\Delta E_{\frac{1}{2}}/\Delta$pH, for both complexes, is out 60 mV in the pH range 10.5–12.5 for the copper(II)–periodate complex, and .5–13.5 for the copper(II)–tellurate complex, which indicates a one-proton elec- ode reaction, rather than the reaction described by Jenšovský[18].

NALYTICAL APPLICATIONS

mperometric titration of copper(III) solutions

The commonest established procedure for the standardization of copper(III) lutions is that described by Chandra and Yadava[13], but the method is laborious d time-consuming. As shown above, a platinum microelectrode allows the duction of copper(III) complexes to be studied in alkaline hydroxide solutions.

The corresponding wave is well shaped and its limiting current is diffusion-controll This is the basis of the proposed amperometric method. Since the periodate mi compete with copper(III) as oxidant, ditelluratocuprate(III) solutions are norma used. Owing to the low solubility of sodium periodatocuprate(III), it is conveni to use potassium hydroxide solutions. Results obtained for copper(III) solutions reported in Table II, in which the results obtained by the method of Chan and Yadava are given for comparison. All samples were run in duplicate.

TABLE II

ANALYSIS OF COPPER(III) SOLUTIONS

Sample	*Copper(III) concn. (mol l⁻¹)*	
	Recommended procedure	*Reference 13*
1	0.0157	0.0152
2	0.0240	0.0245
3	0.0510	0.0510

Procedure. Prepare a copper(III) solution by the persulfate oxidati method[13]; as reported previously[13], it is very important to remove completely excess of persulfate by boiling, because of its interference in the determinati Transfer 1 ml of copper(III) solution to the titration vessel and add about 20 ml 1 *M* potassium hydroxide solution; deaeration is unnecessary. Apply +0.15 V to working platinum electrode and titrate with a 0.002 *N* neutral arsenite soluti prepared from primary-standard arsenic trioxide. The resulting titration curve is an "L-form" shape. The method is suitable for copper(III) concentrations down $5 \cdot 10^{-4}$ *M*. The rotating platinum electrode should be adjusted so that it rotates about 800 rev min⁻¹.

Voltammetric determination of microamounts of copper(II)

As mentioned earlier, when copper(II) ions are present in an alkaline soluti containing tellurate or periodate ligands, a well shaped anodic wave occurs a platinum electrode, and the limiting current is strictly proportional to the copper(concentration. This offers the possibility of a voltammetric determination of copp Potassium periodate is more convenient than tellurate because the solid comp with copper(II) quickly dissolves in hydroxide solutions. The proposed method gi reproducible results for copper concentrations down to $1 \cdot 10^{-5}$ *M*. The effects foreign ions on the determination of copper are summarized in Table III.

Cations which form a precipitate may coprecipitate some copper. As sho in Table III, potassium fluoride may be used as complexing agent when iron(I is present; other reagents, such as ammonia, tartrate, citrate, EDTA, etc., comp with periodate ions in the copper(II) complex formation.

The method was applied to the analysis of sodium and potassium metals a alkaline hydroxide, because of their importance as heat-transfer media in nucl

BLE III

FECTS OF DIVERSE IONS ON THE DETERMINATION OF COPPER

itial solutions: volume 25 ml, Cu(II) 25 μg ml^{-1}, $5 \cdot 10^{-3}$ *M* KIO_4, 1 *M* KOH or NaOH)

tion	*Highest level studied without interference (mg present)*	*Anion*	*Highest level studied without interference (mg present)*
uminum	100	Arsenate	75
n(III)[a]	10	Chloride	150
thium	100	Chromate	100
dium	600	Nitrate	150
tassium	1000	Molybdate	100
nc	5	Sulfate	150
		Vanadate	50

n the presence of 1 *M* KF as complexing agent.

actors. Suitable standard alkali metal samples were not available, hence synthetic andards were prepared by adding weighed amounts of standard copper solution the dissolved metal samples. The method offers significant advantages over existing ies because of its simplicity and the elimination of the neutralization and pH ljustment.

Procedure for determination of copper in sodium and potassium metals. Dissolve accurately weighed sample of sodium or potassium metal in methanol, drive off e alcohol and dilute with distilled water, using established methods[19]. The highest sulting concentration of potassium hydroxide or sodium hydroxide must be 7 *M* or *M*, respectively. Make 25 ml of this solution $3 \cdot 10^{-3}$ *M* in periodic acid and cord the polarogram from +0.5 to +0.1 V. The removal of oxygen is unnecessary. etermine the concentration of copper by the standard addition method. In the treme conditions of alkalinity, copper can be determined in the concentration nge $3 \cdot 10^{-4}$–$3 \cdot 10^{-5}$ *M*.

JMMARY

Copper(II) and copper(III) complexes with periodate or tellurate ligands are ectroactive at a smooth platinum electrode, giving an anodic, cathodic or cathanodic ave in the presence of alkaline hydroxide solutions containing copper(II), copper- II), or copper(II)–copper(III) species, respectively. The corresponding limiting rrents are diffusion-controlled. The following analytical applications are proposed:) amperometric titration of copper(III) solutions; (*b*) voltammetric determination copper. Results of amperometric titrations of copper(III) were similar to those an established procedure. Voltammetry of copper(II) allows the metal to be termined down to concentrations of $1 \cdot 10^{-5}$ *M*, even in the presence of different ns; the procedure can be applied to such heat-transfer media for nuclear reactors as dium and potassium metals and their hydroxides.

SUMÉ

Une étude est effectuée sur le comportement voltammétrique, à l'électrode

de platine, des complexes de cuivre(III) et de cuivre(II), avec periodate et tellura Les vagues polarographiques correspondantes sont bien formées et contrôlées p diffusion. On propose comme applications analytiques: (*a*) le titrage ampèrométriq de solutions de cuivre(III); (*b*) le dosage voltammétrique de microquantités cuivre, en présence de divers ions.

ZUSAMMENFASSUNG

Kupfer(II)- und Kupfer(III)-Komplexe mit Perjodat oder Tellurat Liganden sind an einer glatten Platinelektrode elektroaktiv und ergeben ei anodische, kathodische oder kathanodische Welle in Gegenwart von Alkalihydroxi lösungen, die resp. Kupfer(II)-, Kupfer(III)- oder Kupfer(II)–Kupfer(III)-Spezi enthalten. Die zugehörigen Grenzströme sind diffusionskontrolliert. Folgende an lytische Anwendungen werden vorgeschlagen: (*a*) amperometrische Titration v Kupfer(III)-Lösungen; (*b*) voltammetrische Bestimmung von Kupfer. Die Ergebnis der amperometrischen Titrationen von Kupfer(III) sind ähnlich denen, die nach ein eingeführten Methode erhalten werden. Die Voltammetrie von Kupfer(II) erlau die Bestimmung des Metalls bis zu Konzentrationen von $1 \cdot 10^{-5}$ M herab, auch Gegenwart von verschiedenen Ionen. Das Verfahren kann auf metallisches Natriu und Kalium und deren Hydroxide angewendet werden, die als Kühlmittel für Ker reaktoren Verwendung finden.

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NZYME ELECTRODE FOR GLUCOSE BASED ON AN IODIDE 1EMBRANE SENSOR

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Spectrophotometric[1,2] and electrochemical[3–6] methods are most frequently sef for the determination of glucose in biological fluids. Some of these procedures mploy an enzymatic approach, *i.e.*, glucose oxidase catalyzes the oxidation of lucose to gluconic acid. The hydrogen peroxide produced is either measured irectly[7] or reacts quantitatively with another indicating reagent:

$$\text{glucose} + O_2 \xrightarrow[\text{oxidase}]{\text{glucose}} \text{gluconic acid} + H_2O_2 \qquad (1)$$

ome electrochemical methods[5,6] use iodide ion as an indicator which reacts with ydrogen peroxide according to the equation:

$$H_2O_2 + 2I^- + 2H^+ \xrightarrow{\text{catalyst}} I_2 + 2H_2O \qquad (2)$$

he iodine produced is subsequently monitored by electrochemical techniques. epending on the oxygen concentration and the pH, however, the iodine formed reaction (2) can take part in various reactions: formation of iodide and hypoiodide, nd reduction of hydrogen peroxide by the hypoiodide can occur[8]. Although olybdate ions have been used[5,6] as catalysts for reaction (2), peroxidase enzyme n also be employed and has the advantage of higher efficiency at low (10^{-4} *M*) dide concentrations.

In this investigation the concept of measuring glucose activity via two concutive reactions was used, *i.e.*, hydrogen peroxide produced in the enzymatic xidation of glucose liberates iodine in a peroxidase-catalyzed second reaction. he decrease in iodide activity was monitored with iodide-selective electrodes, both flow streams as well as in stationary solutions. Two iodide-selective electrodes eference and indicating electrode) separated by a delay reaction coil were laced in the flow stream, whereas an enzyme electrode was prepared for measureents in stationary solutions.

The construction of enzyme electrodes for measurement of different organic ubstrates has been reported earlier. Most of them incorporate a potentiometric nsor, *e.g.* oxygen[9,10], carbon dioxide[11], or ammonium ion[12–14] electrodes, but ome use voltammetric measuring techniques[15]. The potentiometric-type enzyme lectrode described in this paper was fabricated by placing a thin reaction layer ontaining a mixture of immobilized glucose oxidase and peroxidase over an iodidensitive membrane electrode. The iodide-selective electrode is one of the most elective and sensitive of all potentiometric detectors[16].

EXPERIMENTAL

Apparatus

Potentiometric measurements were made with a high impedance inp differential amplifier[17,18]. The amplified signal was fed into an Orion digital p meter (Model 801) and displayed on a potentiometric recorder (Sargent Mod 5RLG).

For application in flow streams, iodide-sensitive membranes were prepare from pressed silver sulfide–silver iodide in the ratio 1 : 1. Plexiglas tubes were use as the electrode body onto which pressed pellets and flow-through caps we fitted. A silver wire immersed into a 10^{-2} M silver nitrate solution served as intern reference. The electrode bodies were dyed black in order to avoid photodeco position of the internal reference solution.

The flow system is shown in Fig. 1. The enzyme solution, a mixture glucose oxidase and peroxidase, was introduced from e into the substrate (from via a mixing chamber (b) directly after the first electrode (a′, reference electrode The reaction mixture then passed through a delay coil (c) which was kept at consta temperature and permitted a certain reaction time (1 min at the flow rate 2 min^{-1}). The ratio of the substrate solution to enzyme solution was 3 : 1. The decrea in iodide activity was subsequently monitored at the indicating electrode (a). T outflow from this system was gravity-fed to waste at f.

A peristaltic pump (Sage Model 375) was used and provided various flo rates for enzyme and substrate solution, respectively. Thus, the reaction time cou be varied from 40 s to 250 s.

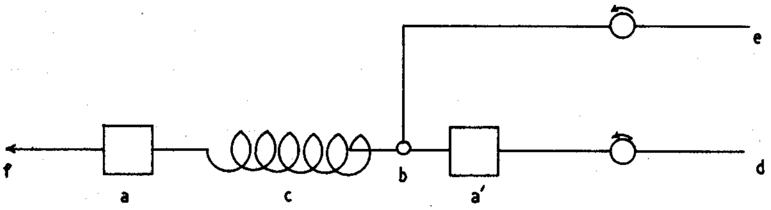


Fig. 1. Flow stream system for assay of glucose.

Immobilized enzyme

For the fabrication of the glucose-sensitive enzyme electrode for measure ments in stationary solutions, three different procedures were used.

(*a*) The enzyme layer consisted of a solution of enzymes at concentratio of 100 mg ml^{-1} for glucose oxidase and 50 mg ml^{-1} for peroxidase.

(*b*) The enzyme mixture was physically entrapped in polyacrylamide whic was allowed to polymerize by light on a nylon netting[12].

(*c*) The enzyme mixture was chemically bound to a polyacrylic acid derivati by a modification of an earlier procedure[19].

Polymerization of acrylic acid. Approximately 50 ml of reagent grade acryl acid were dissolved in 20 ml of hexane and placed into a 3-neck round-botto flask; a few milligrams of ammonium persulfate were added as an initiator. T reaction was carried out under a nitrogen atmosphere by replacing the air with d trogen through one of the necks. The flask was heated in a heating jacket until pid polymerization was observed; then it was quickly removed from the heating ket and cooled to room temperature. This polymer was kept in a desiccator til use.

Preparation of copolymer. To neutralize polyacrylic acid, calculated amounts 0.1 *M* sodium hydroxide were mixed with polymer crumbs and stirred overnight. e liquid sodium salt was evaporated in the Rotovap until brittle and porous, and s then ground to fine powder. The powder (3.6 g) was suspended in 6 ml of hexane a small flask which was precooled to about 4°. The reaction was started by the dition of 2.8 ml of sulfonyl chloride with stirring and kept cool in an ice bath for h. The gases generated during reaction were removed by suction. The product s washed with ether and dried under vacuum; then 0.5 g of *p*-nitroaniline d 6 ml of ether were added and the mixture was stirred overnight. The resulting llow granules were filtered, washed with ether to remove the unreacted *p*-nitroiline and air-dried. These granules were used as starting material for the coupling enzymes.

Binding of enzymes. The general procedure used for preparing an active atrix was to dissolve 150 mg of the above preparation in 10 ml of distilled water. The lution was adjusted to pH 5 with dilute acetic acid, and then 0.5% triethylenetramine was added slowly with stirring until white insoluble fine particles were served. The insoluble particles were washed three times and collected by centrifugan. The precipitate was resuspended in 5 ml of distilled water and reduced by the dition of titanium(III) chloride. The precipitate was washed several times with stilled water and centrifuged. Precooled nitrous acid (0.5 *M*, 10 ml) was then ded with agitation for 2 min. The precipitate was flushed with cold distilled water, ntrifuged several times and then added immediately to 10 mg of glucose oxidase zyme, or glucose oxidase–peroxidase enzyme mixture, dissolved in 3 ml of 0.05 *M*, etate buffer pH 5 with stirring in an ice bath for 1 h. The sediment was centrifuged d washed well with distilled water several times. The final gel was resuspended in all amounts of 0.01 *M* phosphate buffer pH 7 and stored at 4° until used.

In all cases the enzyme layer on the iodide-sensitive membrane was covered ith a tight cap made from dialysis paper. The electrodes were stored in phosphate ffer solutions pH 6.

Saturated calomel electrodes or iodide-sensitive electrodes served as re-rences. The measurements with the glucose electrode were carried out in stirred ermostated solutions. Readings were obtained after allowing sufficient time to ach steady-state values.

ther reagents

All chemicals used were reagent grade. Glucose oxidase solutions were prered from *Asparagillus niger* (Sigma Chemical Co., activity 18 units per mg solid; e unit will oxidize 1 μM of glucose to gluconic acid and H_2O_2 per min at H 5.1 and 35°); lactoperoxidase and peroxidase were prepared from horseradish igma Chemical Co., activity 100 purpurogallin units per mg; one unit forms one g of purpurogallin in 20 s from pyrogallol at pH 6 and 20°).

Substrate solutions were prepared with 1.0 *M* and 0.1 *M* phosphate buffer at H 6 and 5, respectively.

RESULTS AND DISCUSSION

Measurements in flow streams

Measurements were done to determine the dependence of the rate of t consecutive reactions[1,2] on the oxygen concentration of the substrate solution. N difference was observed in the reaction rate with air-saturated or atmospher oxygen-saturated substrate solutions in both flow streams and stationary solution

From a batch of iodide-selective electrodes, two electrodes with simil response characteristics, such as slope of calibration graph and zero potenti (E_0), were selected and subsequently modified for application in flow stream Potential oscillations at the electrodes which were in sequence with the surges the peristaltic pump were found to be sufficiently suppressed by using a solutic of high ionic strength (0.1 *M* phosphate buffer) at pH 6.0.

Optimal ratio of glucose oxidase peroxidase. Because of the unknown kineti of the enzyme-catalyzed reactions involved, it was necessary to determine t optimal concentration ratio of the two enzymes. Measurements were carried out flow streams with a buffered glucose–potassium iodide solution as substrate solutio In one case, the glucose oxidase concentration in the enzyme solution was ke constant and the amount of peroxidase was varied (Fig. 2, curve a) while in t other the concentration of peroxidase was constant and the glucose oxidase conte was altered (Fig. 2, curve b). An optimal ratio of 1:2 (peroxidase:glucose oxidas was obtained in both investigations (for the activities mentioned in the Experiment section).

Temperature dependence. The temperature dependence of the enzym catalyzed reaction is governed both by the temperature-dependent reaction rate a

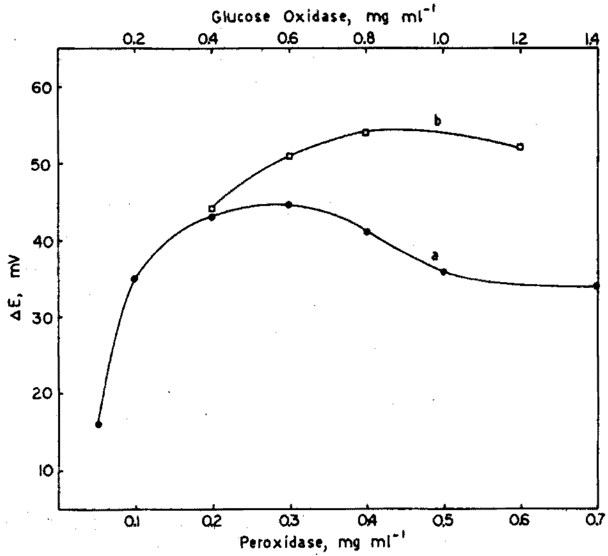


Fig. 2. The dependence of the reaction rate (represented by ΔE) on the peroxidase (curve a) or gluco oxidase (curve b) concentration in the case of constant concentration (0.4 mg ml^{-1}) of the oth enzyme. KI concentration, 10^{-4} *M*; pH, 6.00; reaction time, 77 s; glucose concentration, 10^{-3} *M*; ten perature, 26°.

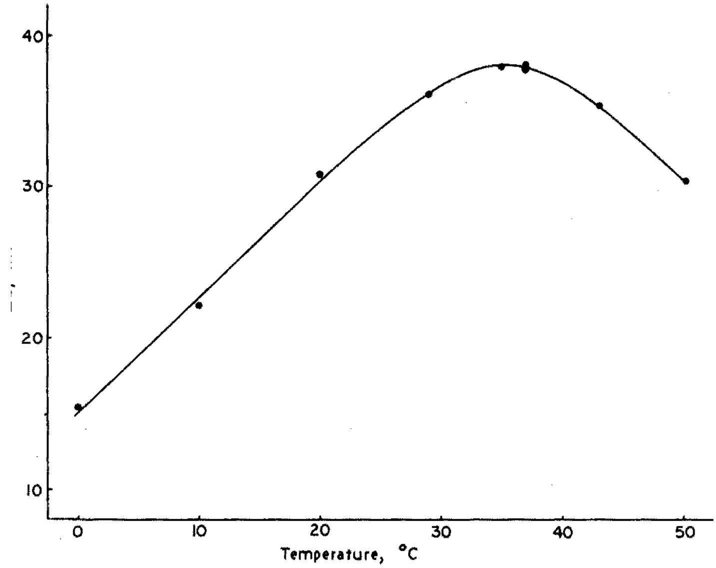


Fig. 3. The influence of temperature on the reaction rate. Peroxidase, 0.3 mg ml^{-1}; glucose oxidase, 0.6 mg ml^{-1}; reaction time, 235 s; pH, 6.00; glucose concentration, 10^{-3} *M*; KI concentration, 10^{-4} *M*.

by enzyme denaturation. The temperature dependence of the overall reaction was taken as the potential difference between reference and indicating electrodes at a constant glucose concentration. A maximal response was observed between 35° and 38°, when the temperature was varied from 0° to 50° (Fig. 3)

Electrode potential dependence on reaction time and glucose/iodide concentrations. The dependence of the electrode on the flow rate and consequently, the reaction time, is shown in Fig. 4. The reaction times shorter than 60 s did not provide satisfactory sensitivity. The time-consuming long reaction time is also disadvantageous. Reaction times of 77 s and 235 s were chosen and were applied according to practical requirements.

Increasing potential response was obtained with decreasing concentration of iodide ions (Fig. 5), and results in a higher sensitivity of the system described. This effect, however, is limited by the applicable concentration range for the iodide-sensitive membrance electrode.

Glucose calibration. The electrode response towards glucose concentration was calibrated under the following conditions: 10^{-4} *M* potassium iodide, 1.0 *M* phosphate buffer, pH 6.0, enzymes in the ratio 1:2 (peroxidase, 0.3 mg ml^{-1}; glucose oxidase, 0.6 mg ml^{-1}) and temperature 26°. The calibration graph is shown in Fig. 6. A potential step of 40 mV was obtained in the concentration range 10^{-3} *M*–10^{-4} *M* glucose. The average response time for a reaction time of 235 s was 3–4 min.

Measurements in stationary solutions

The potentiometric response of the glucose electrode is due to the decrease of iodide activity in the enzyme reaction layer. On immersion of the glucose electrode into glucose solution, the consecutive reactions (1, 2) begin to occur at the sensor surface. The reaction yields a growing gradient between the iodide activity in the

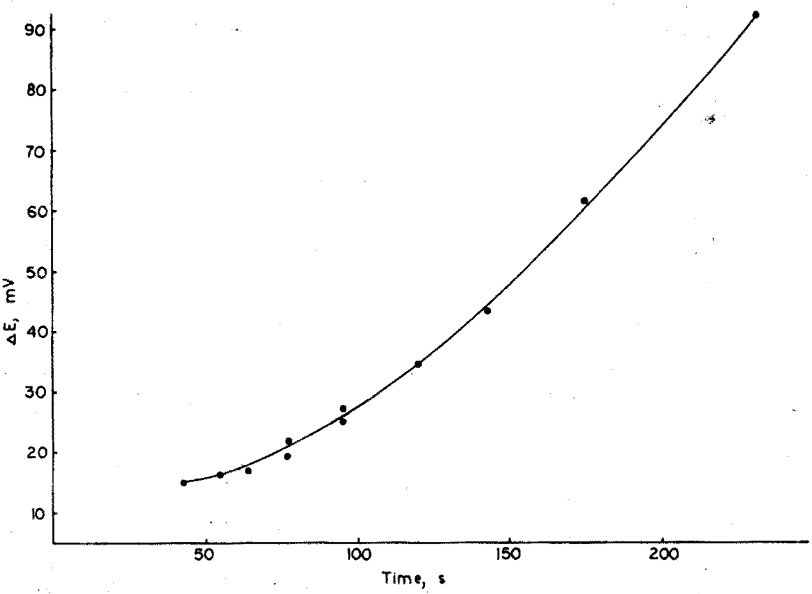


Fig. 4. The dependence of electrode potential change on the reaction time. Temperature, 26°; othe conditions as in Fig. 3, except for reaction time.

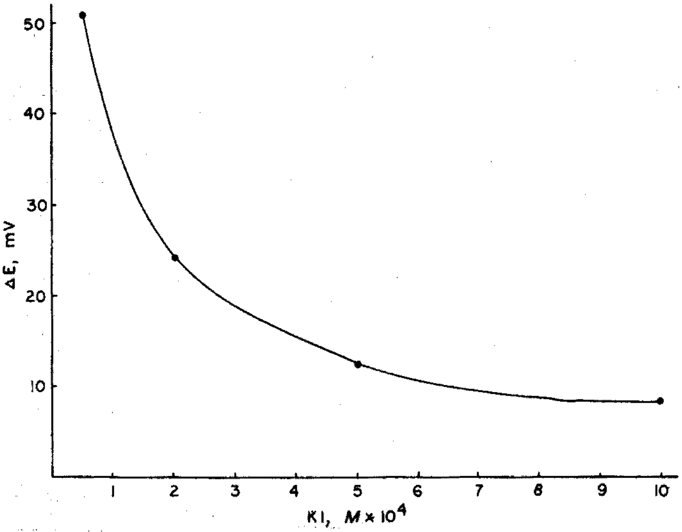


Fig. 5. The effect of iodide concentration on the electrode potential change, ΔE, in a flow stream. pH 6.0; temperature, 26°; reaction time, 77 s; enzyme solution concentrations as above; glucose concen tration, 10^{-3} *M*.

bulk solution and the enzyme layer. Because this concentration gradient is th driving force of the diffusion process under constant bulk conditions, a steady stat is soon established.

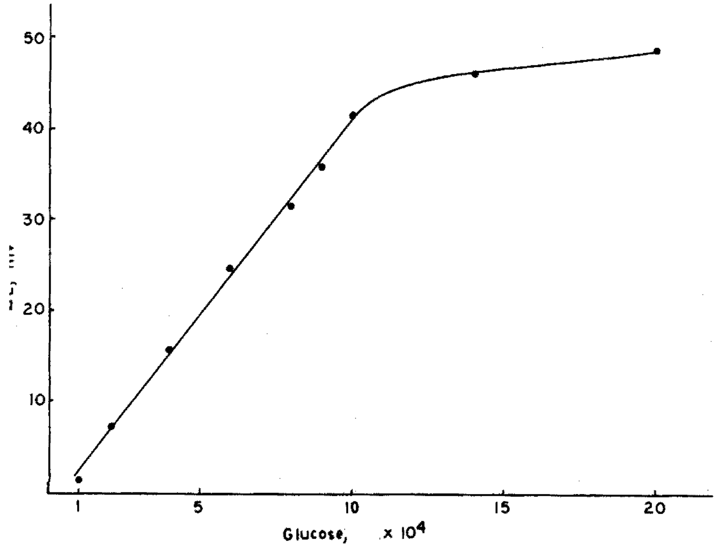


Fig. 6. Calibration graph for glucose in the case of 10^{-4} *M* iodide concentration at pH 6.00 and 26°. The concentration of the enzyme solution is 0.6 mg ml^{-1} for glucose oxidase and 0.3 mg ml^{-1} for peroxidase; reaction time 235 s.

A relatively simple model can be produced if the following assumptions are made.

1. The reaction rate does not depend on the oxygen concentration. (This is in a good agreement with experimental observation. The saturation of the sample solution with oxygen did not affect the electrode function.) Alternatively, the oxygen concentration is constant in the reaction layer.

2. The thickness of the reaction layer is very small and constant.

3. The concentration of the bulk solution is constant, and not affected by the reaction. (The analytical detector is not supposed to change the system to be measured.)

4. Reaction (2) is not significantly slower than reaction (1). In this case the steady-state condition is achieved in not too long a time, as was observed in the experiments.

5. The substrate concentrations are much smaller than the Michaelis constant.

6. The "concentration" and the "activity" terms can be used interchangeably.

The electrode function can be considered with the aid of the following terminology:

$[G]$ = the glucose concentration in the bulk solution;
$[G]-X$ = the glucose concentration in the reaction layer;
$[H_2O_2]$ = the hydrogen peroxide concentration in the reaction layer;
$[I^-]$ = the iodide activity in the bulk solution;
$[I]-Y$ = the iodide activity in the reaction layer;
k_1 and k_2 = the rate constants of reactions (1) and (2), respectively;
a = the order of reaction (2) for iodide.

The change of peroxide concentration can be expressed as:

$$\frac{d[H_2O_2]}{dt} = -k_1([G]-X)+k_2[H_2O_2]([I^-]-Y)^a \qquad (3$$

$$D_I = \frac{D_{0I}}{\Delta l} \text{ and } D_G = \frac{D_{0G}}{\Delta l}$$

where D_{0I} and D_{0G} are the diffusion constants of iodide and glucose, respectivel and Δl is the thickness of the diffusion layer.

From assumption (3) at steady state, $d[H_2O_2]/dt=0$, thus:

$$[H_2O_2] = \frac{k_1([G]-X)}{k_2([I^-]-Y)^a} \qquad (4$$

It is obvious that

$$d[I^-]/dt = -k_2[H_2O_2]([I^-]-Y)^a+D_IY \qquad (5$$

In the steady state $d[I^-]/dt=0$, and substituting the value of $[H_2O_2]$ from eqn. (4)

$$D_IY = k_1([G]-X)$$

The change of the glucose concentration in the reaction layer can be expresse as

$$d[G]/dt = -k_1([G]-X)+D_GX \qquad (6$$

For the steady-state conditions ($t\rightarrow\infty$; $d[G]/dt=0$), $X=k_1[G]/(D_G+k_1)$.

The electrode potential in absence of glucose is:

$$E_1 = E_0-(RT/nF)\ln[I^-] \qquad (7$$

In the presence of a constant glucose concentration in the bulk solution:

$$E_G = E_0 - \frac{RT}{nF}\ln([I^-]-Y) = E_0 - \frac{RT}{nF}\ln\left[[I^-] - \frac{k_1}{D_1}\left([G] - \frac{k_1[G]}{D_G+k_1}\right)\right]$$

$$= E_0 - \frac{RT}{nF}\ln\left[[I^-] - \frac{k_1}{D_1}\,\frac{D_G[G]+k_1[G]-k_1[G]}{D_G+k_1}\right]$$

$$E_G = E_0 - \frac{RT}{nF}\ln\left[[I^-] - \frac{k_1}{D_1}\cdot\frac{D_G[G]}{D_G+k_1}\right] \qquad (8$$

From eqns. (7) and (8):

$$\Delta E = -\frac{RT}{nF}\ln\frac{[I^-]}{[I^-] - \frac{k_1}{D_1}\cdot\frac{D_G[G]}{D_G+k_1}} \qquad (9$$

From this equation it is obvious that the lower the concentration of iodide, th higher is the electrode response to a constant glucose concentration. Howeve the lower limit of iodide concentration depends on the properties of the iodide selective electrode in the lower concentration range. The optimal iodide concentration for measuring glucose concentration in the range 10^{-3}–10^{-4} M was foun to be 10^{-4} M.

For the sensitive measurement of glucose concentration [G], it is advantageous for the k_1/D_1 ratio to be very high. The value $D_1 = D_{01}/\Delta l$ can be decreased by increasing the thickness of the reaction layer, or by using a cover around the electrode which retards the diffusion of iodide ions into the enzyme layer. The value of k_1 can be increased by using a high concentration of a very active enzyme mixture.

A plot of the steady-state potential [ΔE] *vs.* −log glucose is an S-shaped curve (Fig. 7). The deviation of the readings from theory at high glucose concentrations could originate either from the non-Nernstian properties of the iodide electrode in the range 10^{-5}–10^{-7} *M*, or from the fact that in this glucose concentration range assumption (4) is not valid.

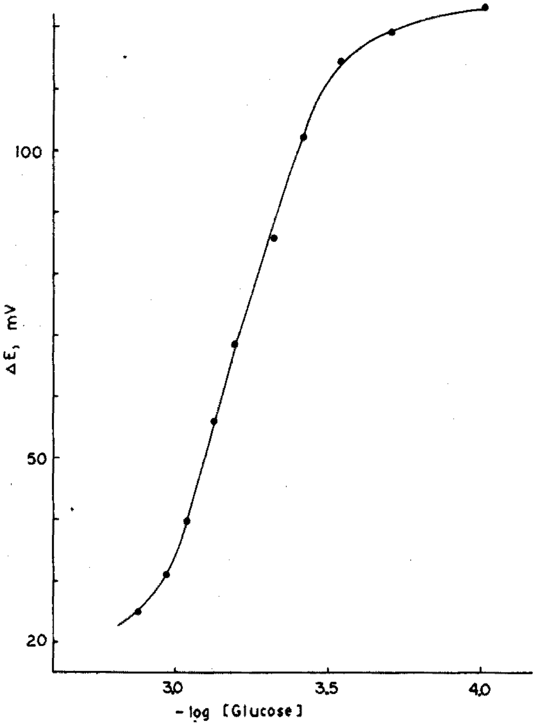


Fig. 7. Dependence of the glucose enzyme electrode potential on the glucose concentration. pH, 6.0; KI concentration, 10^{-4} *M*; temperature, 26°.

Electrodes made from the various preparations of the enzyme layer (*i.e.*, methods *a* to *c*, Experimental) did not show different shapes of the calibration graph. Higher enzyme activities, however, resulted in steeper slopes and best results were obtained with an enzyme solution as the reaction layer (method *a*). The lifetime of the electrode on the other hand, increased with immobilization of the enzyme mixture either physically or chemically. In order to determine the stability of the glucose oxidase–peroxidase coating on the surface of the iodide electrode, the electrode potential was measured at periodic intervals following the addition of a definite amount of glucose to the iodide buffer solution at room temperature. The stability of the electrodes varied from 40 h (solution type) to 3 days (immobilized type). The electrode was considered to be inactive if it los 10% of the original response measured in 10^{-3} *M* glucose solutions.

The response time of the various electrodes was found to be between 2 an 8 min, depending on the temperature, the glucose concentration and the thicknes of the enzyme layer.

The optimal pH of the buffer solution was found to be 5–6.

Interferences

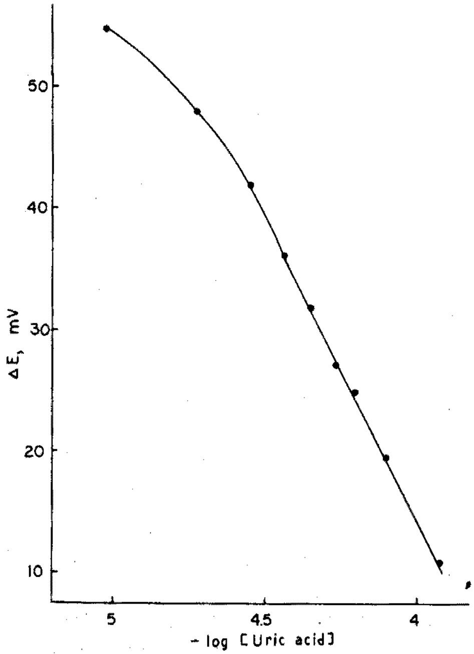
Interferences in the measurement of glucose with a glucose electrode can b categorized in three groups.

(*a*) Interferences at the iodide electrode: thiocyanate, sulfide, cyanide an silver(I) were found to be serious interferences[16].

(*b*) Interference in the glucose–glucose oxidase and hydrogen peroxide peroxidase reaction. The selectivity of the first reaction has been studied[6,20–22].

(*c*) Interferences which arise from the change of the diffusion pattern in th enzyme layer, *i.e.*, effect of constituents of the examined solution.

No interference was observed from anions like chloride, fluoride and phos phate, or from cations like Ca^{2+}, Mg^{2+}, Fe^{3+}, K^{+} and Na^{+}. Proteins (egg albumin and urea did not interfere. Strong interference was observed from uric acid (Fig. 8 tyrosine, ascorbic acid and iron(II), because of a competing reaction in the oxidatio



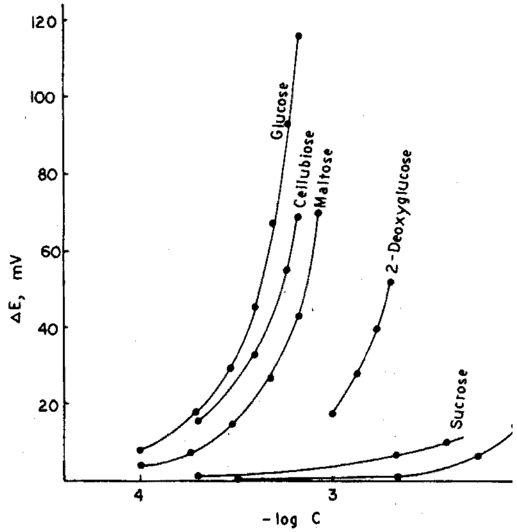


Fig. 8. Interference of uric acid on glucose electrode. Glucose concentration, $5.65 \cdot 10^{-4}$ *M*; pH, 5.0 KI concentration, 10^{-4} *M*.

Fig. 9. Potentiometric response of glucose electrode to sugars. pH, 5.0; KI concentration, 10^{-4} *M*.

of iodide to iodine in the hydrogen peroxide–peroxidase system. It is obvious that oxidizing and reducing agents can affect reaction (2). They can provide another pathway for the decomposition of the peroxide formed in reaction (1).

The response of the glucose electrode toward cellobiose, maltose, sucrose, mannose and 2-deoxy-glucose is shown in Fig. 9.

The interference of uric acid was removed by sample pretreatment. Hydrogen peroxide and peroxidase were added to the sample followed by addition of catalase after incubation for 20 min at room temperature. However, the concentration of hydrogen peroxide must not exceed 0.003‰, as irreversible inhibition of peroxidase takes place. Catalase catalyses the decomposition of the excess of hydrogen peroxide and does not interfere in the measurement because it cannot pass the dialysis membrane. An alternative method for the removal of uric acid would be by precipitation with zinc sulfate and barium hydroxide[23].

Measurement of glucose in blood serum

Glucose measurements in artificial blood samples (Dade Labtrol and Pathtrol) are shown in Table I. Untreated samples gave lower potentiometric response than the equimolar glucose solution, owing to interference from uric acid. The same effect was observed for fluorimetric methods[24]. However, no interference was observed with the spectrophotometric method with *o*-toluidine and the method of Guilbault and Lubrano[15].

Upon treatment of the blood sample with hydrogen peroxide, peroxidase and catalase, the removal of the interference from uric acid and other possible reducing agents was achieved (Table I).

TABLE I

MEASUREMENT OF GLUCOSE IN ARTIFICIAL BLOOD

(All results are given as mg/100 ml)

Method	*Glucose concentration of*	
	Artificial blood serum (Labtrol)	*Artificial blood serum (Pathtrol)*
Reported	102	255
Determined by *o*-toluidine method[25]	97.5	250
Determined by glucose electrode without pretreatment	73.8	143
Determined by glucose electrode after pretreatment	97	245

Conclusions

The potentiometric determination of glucose by means of the enzymes glucose oxidase and peroxidase with iodide as indicating substance and an iodide electrode as sensor, can be applied in flow streams and stationary solutions. Glucose oxidase is highly selective for glucose, and only maltose and cellibiose interfere.

Reducing agents, however, such as ascorbic acid, tyrosine and uric acid interfer strongly, and glucose measurements in samples containing them are only accurat after suitable pre-treatment.

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SUMMARY

The construction of a new type of enzyme electrode for the potentiometri determination of glucose is reported. The electrode response is based on the enzyme-catalyzed reactions:

$$\text{Glucose} + O_2 \xrightarrow{\text{glucose oxidase}} \text{gluconic acid} + H_2O_2$$

$$H_2O_2 + 2I^- + 2H^+ \xrightarrow{\text{peroxidase}} 2H_2O + I_2$$

The highly selective iodide sensor monitors the local decrease in the iodide activit at the electrode surface. The properties of the above reactions were examine kinetically, with flow-stream techniques and potentiometric detection. The glucos electrode constructed and the use of flow-stream experiments with two iodid sensors provided accurate and convenient glucose determinations in the absenc of some oxidizing and reducing agents.

RÉSUMÉ

On décrit un nouveau type d'électrode enzymatique pour le dosage potentiométrique du glucose. La réponse de l'électrode est basée sur les réactions de catalys enzymatique:

$$\text{glucose} + O_2 \xrightarrow{\text{glucose oxydase}} \text{acide gluconique} + H_2O_2$$

$$H_2O_2 + 2I^- + 2H^+ \xrightarrow{\text{peroxydase}} 2H_2O + I_2$$

Cette électrode permet des dosages de glucose exacts, en l'absence de certain oxydants et réducteurs.

ZUSAMMENFASSUNG

Die Herstellung einer neuartigen Enzymelektrode für die potentiometrisch Bestimmung von Glucose wird beschrieben. Die Wirkungsweise der Elektrode beruht auf den enzymkatalysierten Reaktionen:

$$\text{Glucose} + O_2 \xrightarrow{\text{Glucose Oxidase}} \text{Gluconsäure} + H_2O_2$$

$$H_2O_2 + 2J^- + 2H^+ \xrightarrow{\text{Peroxidase}} 2H_2O + J_2$$

Der hochselektive Jodidsensor misst die lokale Abnahme der Jodidaktivität an der Elektrodenoberfläche. Die Eigenschaften der obigen Reaktionen wurden mit Strömungsverfahren und potentiometrischem Nachweis kinetisch untersucht. Die hergetellte Glucose-Elektrode und die Anwendung von Strömungsversuchen mit zwei odidsensoren ermöglichten genaue und bequeme Glucosebestimmungen in Abwesenheit einiger Oxidations- und Reduktionsmittel.

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SHORT COMMUNICATION

Arsenic and antimony in laundry aids by instrumental neutron activation analysi

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Considerable attention has been focused on work reported by Angino *et al.* where the conclusion was drawn that arsenic from detergents (or more generall laundry aids) are perhaps contaminating the rivers and drinking sources in Kansa and possibly other areas in the United States. As part of the Food and Dru Administration's heavy metal surveillance program, arsenic levels in laundry aid were measured. This paper describes the measurement of trace amounts of arseni and antimony (which is also a toxic element) in laundry aids by neutron activatio analysis (n.a.a.). The results for arsenic by n.a.a. are compared with those obtaine by other analytical techniques. The concentrations in the various laundry aids teste ranged from 5 to 51 p.p.m. of arsenic and from 1 to 8 p.p.m. of antimony.

Experimental

Seven phosphate-based laundry aids (without boron) were purchased in th Kansas City District of the Food and Drug Administration. The samples include three enzyme presoaks, one detergent, two heavy-duty enzyme detergents, and on heavy-duty detergent, and were assumed to be representative of laundry aids ob tainable elsewhere in the United States.

Samples of the laundry aids (*ca.* 500 mg) and standards of arsenic(II oxide and metallic antimony were weighed directly into clean quartz vials, whic were then sealed by using an oxygen–methane torch. Great care was taken t treat samples and standards alike and to avoid contamination of the quartz vial before neutron irradiation. After the samples and standards had been sealed i quartz, they were irradiated for 20 min in the high neutron flux position (*c* $1 \cdot 10^{13}$ n cm^{-2} s^{-1}) of the 1-MW reactor at the Naval Research Laboratory. Th vials were rotated during the irradiation to insure a uniform neutron exposur After the samples had been irradiated, they were allowed to undergo radioactiv decay for 3–5 days to allow the 15.4-h ^{24}Na to decrease in intensity relative to th 2.7-day ^{122}Sb and 26.4-h ^{76}As. At the end of that time the samples were analyze for arsenic and antimony.

The analyses were made with a high-resolution Nuclear Diodes Ge(L detector, which had a resolution of 2.09 keV at 1.33 MeV and an efficiency of 5 ith respect to NaI(Tl), and a Nuclear Data 4096 channel analyzer. Figure 1 is a ortion of the γ-ray spectrum obtained. By using a high-resolution detector, the 59-keV ^{76}As γ-ray was separated from the 564-keV γ-ray of ^{122}Sb.

The amount of arsenic or antimony in the samples was calculated from the llowing equation:

$$\text{p.p.m. As (or Sb)} = \frac{[\mu\text{g As (or Sb) in std.}]\ (\text{activity of sample})}{(\text{weight of sample})\ (\text{activity of std.})}$$

he ratio of the activity of the sample to that of the standard was computed by e total peak area method[2].

esults and discussion

The results of the arsenic and antimony determinations by n.a.a. are shown Table I. The results for arsenic obtained by n.a.a. are also compared with those btained by X-ray fluorescence and by a colorimetric determination with arsine eneration as reported by Schick and Watlington[3]. No data for antimony by other chniques were available.

ABLE I

RSENIC AND ANTIMONY CONCENTRATIONS IN LAUNDRY AIDS DETERMINED BY a.a. AND COMPARATIVE ARSENIC RESULTS

rand	*Type*[a]	*p.p.m. Sb by n.a.a.*[b]		*p.p.m. As*					
				N.a.a.[c]		*X-ray*[d]		*Arsine*[e]	
		Mean	*s*	*Mean*	*s*	*Mean*	*s*	*Mean*	*s*
	EP	1	0.5	5	0.7	6	5	5	0.7
	EP	2	0.5	17	2	11	3	15	2
	EP	7	0.9	51	4	47	5	57	5
	D	5	1	33	5	28	4	28	5
	HDED	8	1	48	11	36	4	51	8
	HDED	3	0.1	10	2	12	3	11	2
	HDD	6	0.4	43	3	34	7	38	4

EP, enzyme presoak; D, detergent; HDED, heavy-duty enzyme detergent; HDD, heavy-duty detergent.
Mean and standard deviation from 3 determinations.
Mean and standard deviation from 5 determinations.
Mean and standard deviation from 3 determinations; data from Schick and Watlington[3].
Mean and standard deviation from 3–6 determinations; data from Schick and Watlington[3].

Several problems were encountered in the early phases of this work. riginally, arsenic was determined radiochemically after neutron activation by a lfide precipitation technique. However, because the detergent solution foamed cessively, results were unsatisfactory. The second and most critical problem was e non-resolution of the 559-keV γ-ray from arsenic and the 564-keV γ-ray from ntimony. The radiochemical procedure originally used did not separate antimony om arsenic, and the NaI(Tl) detector originally used did not resolve the two rays. The first determinations were unrealistically high for arsenic because of this

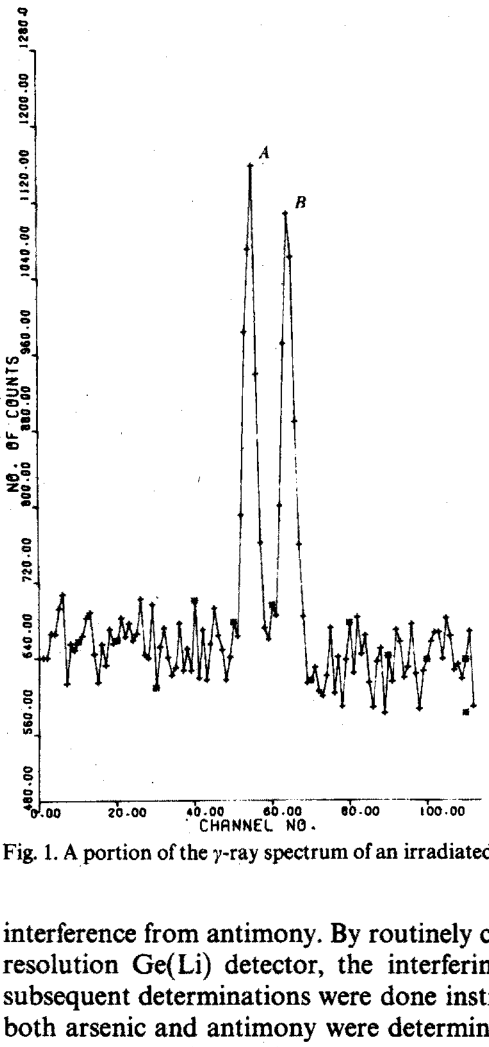

Fig. 1. A portion of the γ-ray spectrum of an irradiated laundry aid. (A) 559-keV ^{76}As; (B) 564-keV ^{12}

interference from antimony. By routinely checking the arsenic samples with a hig resolution Ge(Li) detector, the interfering γ-ray of antimony was resolved. subsequent determinations were done instrumentally with the Ge(Li) detector, a both arsenic and antimony were determined.

The precision of the analyses may be estimated from Table I. Visual i spection of the samples and the variation between replicate analyses led us believe that the samples may not have been homogeneous, which makes int comparison of the different techniques difficult. However, such a comparis showed that the results for arsenic by n.a.a. agreed with those by the arsine a X-ray techniques within about 15%.

Other neutron-induced nuclear reactions leading to ^{76}As besides ^{75}As(n,γ)^{76} have small cross-sections and do not interfere with the arsenic determinations[4] The ^{122}Te(n,p)^{122}Sb reaction leads to ^{122}Sb but unless gross amounts of telluriu are present this interference is negligible[4]. Neither ^{122}Sb or ^{76}As is a fission produ so that trace amounts of fissionable material would not interfere with the measurements. For the small sample size used and the phosphate matrix, se shielding is negligible.

Neutron activation has certain advantages as a means of analysis for arse nd antimony in laundry aids. Since the sample is sealed in a quartz vial at the eginning of the irradiation and the seal is not broken during the analysis, there s no chance of arsenic losses by volatilization. Because no reagents are used, lank errors from reagent contamination cannot occur. The technique used does ot exploit special properties of the laundry aids and so would be applicable to variety of matrices. Arsenic and antimony were not detected in the quartz vials. he analysis was done instrumentally so that the time expended per sample was brief (less than 15 min for the analysis of both elements).

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Analytica Chimica Acta, 66 (1973) 460–4

SHORT COMMUNICATION

Spectrophotometric determination of platinum(IV) with *o*-hydroxythiobenzhydrazi

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Numerous reagents have been proposed for the spectrophotometric dete
mination of platinum, but Beamish[1] recommended only the tin(II) chloride[2] an
p-nitrosodimethylaniline[3] methods for the purpose. Of these two methods, th
former lacks sensitivity whereas the latter is liable to serious interference fro
other platinum metals and associated base metals. Sur and Shome[4] used thi
salicylamide for the gravimetric and spectrophotometric determination of platinu
but even traces of palladium and copper interfered.

Recently, Shome and Gangopadhyay[5] proposed *o*-hydroxythiobenzhydrazi
as a reagent for the spectrophotometric determination of ruthenium. This reagent
also very sensitive for the photometric determination of platinum(IV), and h
the advantage that, under the optimal conditions for platinum, moderately lar
amounts of the other platinum metals and the associated base metals (exce
copper) do not interfere. Interference from copper can be masked by addition
magnesium(II)–EDTA complex.

Platinum(IV) forms two types of complexes with HTBH: a colorless comple
which is formed in 1–6 *M* hydrochloric acid medium and can be extracted wi
methyl isobutyl ketone; and a blue complex, which is readily obtained from h
solutions at pH 5.5–6.5 and can be extracted with chloroform or methyl isobu
ketone. At intermediate acidity a mixture of both these complexes is formed. T
colorless complex extracted with methyl isobutyl ketone is slowly converted to t
blue form, the rate of conversion being increased by the presence of some pyridi
The extract of the blue platinum complex shows maximal absorbance at 690 n
Beer's law is obeyed in the concentration range 0.46–9.2 μg Pt ml^{-1} and t
absorbance is stable for more than 24 h.

In view of the high sensitivity and selectivity of the reagent and the wi
permissible range of experimental conditions, the method can be recommended
preference to other procedures for the spectrophotometric determination
platinum(IV). It may be mentioned that the success of *o*-hydroxythiobenzhydrazi
as a reagent for platinum is due to the fact that the complexes formed by a
other elements have practically no absorption at 690 nm.

Experimental

Apparatus. A Carl Zeiss PMQ II spectrophotometer with 1-cm quartz ce was used for the absorbance measurements. pH was measured with a Cambridge pH meter.

Reagents and chemicals. Chloroplatinic acid (E. Merck) was dissolved in dilute hydrochloric acid, and the solution was standardized by the formic acid method. The stock solution was diluted with distilled water as required.

Standard solutions of diverse ions were obtained by dissolving A. R.-grade reagents in distilled water or dilute hydrochloric acid.

The reagent was prepared as described previously[5] and used as a 0.01 *M* solution in ethanol.

Procedure

Place a measured amount of platinum(IV) solution and 1 ml of a 5% solution of sodium potassium tartrate in a 100-ml separatory funnel, and adjust the pH of the solution to 2.0–6.5. Add an excess (2.0 ml) of ethanolic 0.01 *M* reagent solution. Heat on a boiling water bath for 15 min. Cool and extract with 5-ml portions of methyl isobutyl ketone. Collect the combined extracts in a 50-ml volumetric flask. Add *ca.* 0.2 ml of pyridine and dilute to volume with the solvent. Dry the extract with anhydrous sodium sulphate and allow to stand for at least 3 h. Measure the absorbance of the extract at 690 nm against an appropriate reagent blank.

If the complex is extracted from a solution of pH 5.5–6.5, the absorbance measurements can be carried out immediately after the extraction and no addition of pyridine is necessary.

Absorbance curves

The absorbance curves of the platinum(IV)–hydroxythiobenzhydrazide complex in methyl isobutyl ketone medium are shown in Fig. 1.

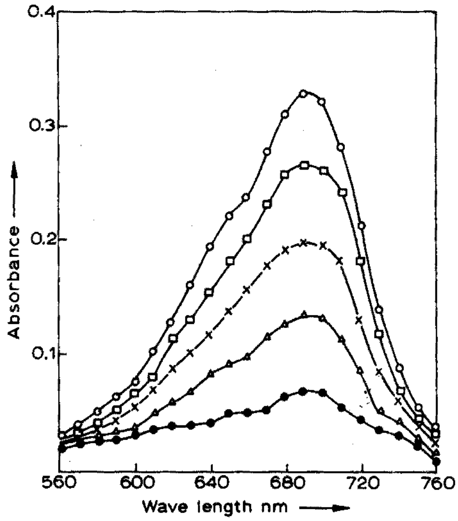

Fig. 1. Absorbance curve for the platinum-*o*-hydroxythiobenzhydrazide complex. Pt(IV), (●) 0.46 μg ml^{-1}; (△) 0.92 μg ml^{-1}; (×) 1.38 μg ml^{-1}; (□) 1.84 μg ml^{-1}; (○) 2.30 μg ml^{-1}.

Effect of variables

The optimal pH range for the complete extraction of the platinum(IV)-*o*-hydroxythiobenzhydrazide complex was determined by adjusting the pH of the solution with 10% sodium acetate solution and dilute hydrochloric acid, and then extracting with methyl isobutyl ketone. The absorbances of the extracts were measured at 690 nm against an appropriate reagent blank. The pH values of the aqueous layers were determined immediately after the extraction of the complex. The results indicated that the formation and extraction of the blue platinum complex was complete in the pH range 5.5–6.5. Below pH 5.5, a mixture of blue and colorless forms of the complex was obtained. When the acidity exceeded 1 *M* in hydrochloric acid only the colorless complex was formed.

Only the blue form of the complex was extractable in chloroform or carbon tetrachloride. Both the blue and colorless complexes could be extracted with either methyl isobutyl ketone or isoamyl alcohol. The colorless complex after extraction slowly changed to the blue form and the rate of conversion was accelerated by pyridine. When the platinum(IV) complex was extracted from a solution at pH 2.0 with methyl isobutyl ketone, the addition of 0.2 ml of pyridine per 50 ml of extract was necessary to develop the blue color completely in 3 h; larger amounts of pyridine did not enhance the rate of conversion.

The platinum complex was fully developed when the reagent–metal ratio exceeded 8:1.

Effect of diverse ions

In the study of the effect of diverse ions, a standard solution containing 115.0 μg of platinum(IV) was mixed with the required amount of the solution of the ion examined, and the recommended procedure was followed, a waiting time of 3 h being allowed. When copper(II) was examined, 5 ml of 0.05 *M* magnesium–EDTA complex was added to avoid interference; EDTA alone produced slightly low results.

The following amounts of diverse ions could be tolerated, *i.e.* the error caused was less than 2%: 2000 μg of Fe^{3+}, Co^{2+}, Cu^{2+} (with Mg–EDTA added), Se^{6+}, Mo^{6+}, Te^{6+}, W^{6+}, Hg^{2+}, Re^{7+}, Au^{3+}, Os^{6+}, Pd^{2+}, Ru^{3+}; 3000 μg of Ti^{4+}, V^{5+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, U^{6+}, Ir^{3+}, Rh^{3+}; 5000 μg Zn^{2+}, Ga^{3+}, Cd^{2+}, In^{3+}.

Nature of the complex

The empirical formula of the blue form of the platinum(IV)–*o*-hydroxythiobenzhydrazide was determined by the mole-ratio method as described by Meyer and Ayres[6]. A series of solutions containing $1.18 \cdot 10^{-5}$ *M* platinum(IV) were mixed with various concentrations of the reagent ranging from $2.95 \cdot 10^{-6}$ *M* to $7.08 \cdot 10^{-5}$ *M*, heated and extracted with methyl isobutyl ketone as described before. The absorbances of the extracts were measured and plotted against the mole ratio of the ligand to metal ions. The results clearly indicated that a 1:2 metal–ligand complex was formed. The composition of the complex was verified by the conventional slope-ratio method.

The blue and colorless complexes were also prepared in the solid state and analysed for platinum, nitrogen, sulphur, and chlorine. The results for the blue complex (35.80% Pt, 10.09% N, 11.78% S) corresponded to the formula $(C_7H_7N_2OS)_2$-

PtO. The results for the colorless complex (32.64% Pt, 9.42% N, 11.01% S, 11.52% Cl) were in fair agreement with the formula $(C_7H_7N_2OS)_2PtCl_2$. A spectroscopic study to elucidate the structure of the complexes is in progress.

Molar absorptivity, sensitivity and optimal range

The molar absorptivity of the platinum(IV) complex at 690 nm was found to be $2.78 \cdot 10^4$ l mole^{-1} cm^{-1}. The sensitivity[7] of the colour reaction was 0.007 μg cm^{-2}. The optimal range of concentration for absorbances between 0.2 and 0.7 was 1.44–5.04 μg Pt ml^{-1}.

The relative mean error and the coefficient of variation of the method were found to be 0.24% and 0.64%, respectively.

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SHORT COMMUNICATION

Purification of silver halides

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It is well known that impurities, even at very low concentrations, can greatly affect the physical properties of many materials. Much work has been done in this field, particularly on organic and inorganic semiconductors[1–3].

Silver halides, too, have been the object of basic research. It has long been recognized that it is possible to detect effects on the photolytic behaviour of silver chloride by copper(I) ions at the 0.01-p.p.m. level[4]. Recently, there has been a great increase in both experimental and theoretical studies intended to clarify the effect of single impurities on the intrinsic physical characteristics of silver halide crystals. And, because of the development of more refined and sensitive techniques, extremely pure silver halide samples are needed.

This paper deals with the adaptation for preparative purposes of a recent analytical procedure[5] for the separation and determination of trace metallic impurities in silver halides, based on solvent extraction with chelating agents. Concentrated aqueous potassium iodide solution was used as the solvent for silver halides. The solution was extracted with dithizone and 8-hydroxyquinoline (oxine), successively. On addition of water to the iodide solution of silver halide, pure silver iodide precipitated. The solubility of silver iodide *vs.* potassium iodide concentration is reported in Fig. 1.

Pure silver iodide, carefully washed and dried, can be converted to silver chloride or bromide by bubbling chlorine or bromine through the molten salt.

Apparatus and reagents

Pear-shaped separating funnels with teflon stopcocks were used for extractions.

Absorbances were measured with a Bausch & Lomb recording spectrophotometer model Spectronic 505, with quartz or glass cells having a light path of 10 mm.

Potassium iodide solution (4.5 M; 100 g/100 ml). To the solution add a few drops of 85% hydrazine hydrate, in order to reduce any iodine present. After several extractions with $5\cdot10^{-4}$ *M* dithizone in carbon tetrachloride, extract further with $2.5\cdot10^{-5}$ *M* dithizone until the spectrum of the extracting agent remains constant. To the aqueous solution, add extrapure hydrochloric acid to give pH *ca.* 5, and then shake with carbon tetrachloride to eliminate all residual dithizone, *i.e.* until the organic solvent remains colourless.

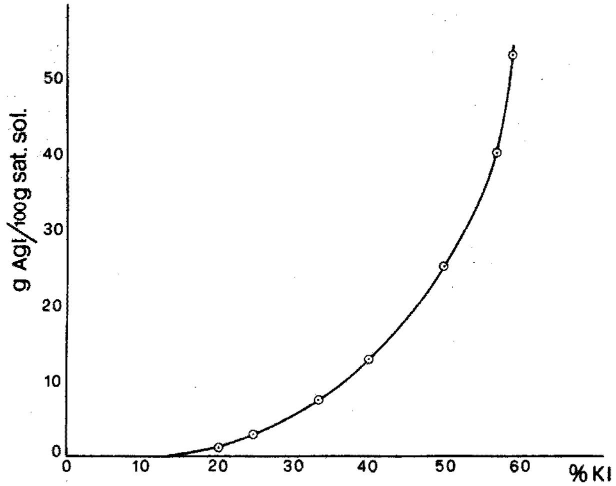

Fig. 1. Solubility of silver iodide in potassium iodide solutions at 25°.

Store the purified iodide solution in neutral glass vessels over dithizone in carbon tetrachloride.

Ammonia solution. Dissolve gaseous ammonia in water previously extracted with dithizone and oxine.

Hydrochloric acid. Merck extra-pure (maximum declared impurities: Fe $\leqslant$ 0.5 p.p.m.; Zn $\leqslant$ 0.1 p.p.m.; Pb $\leqslant$ 0.05 p.p.m.) was used.

Dithizone (diphenylthiocarbazone; C. Erba). Use without purification as solutions ($5 \cdot 10^{-4}$ M and $2.5 \cdot 10^{-5}$ M) in carbon tetrachloride, checking the absorption spectrum.

Oxine (8-hydroxyquinoline; C. Erba). Use as 0.01 M and 0.1 M solutions in carbon tetrachloride.

Water. Deionized water was twice distilled in Pyrex apparatus and further treated with dithizone and oxine. After purification the water was stored in neutral glass vessels over dithizone solution.

Bromine (C. Erba, R.P.). Distil several times, until no residue remains after distillation.

Chlorine (I. T. Baker) was used without any treatment.

Procedure for the purification of silver halides

Sample dissolution and extraction of impurities. Dissolve 100 g of silver iodide in 300 ml of the 4.5 M potassium iodide solution and add 2–3 drops of hydrazine hydrate. Extract this solution several times with 10-ml portions of $2.5 \cdot 10^{-5}$ M dithizone, shaking for 15 min each time, until the spectrum of the organic phase coincides with the spectrum of a fresh solution of dithizone. In order to confirm the complete removal of all dithizone-extractable impurities, wash the organic phase of the last extraction in a separating funnel twice with 5-ml portions of 4.5 M potassium iodide to remove traces of silver(I) and then with 0.5 M ammonia solution. If dithizonates are still present, the organic phase has a pink colour; otherwise it is colourless.

After finishing the extractions with dithizone, adjust the pH of the aqueous phase to *ca.* pH 5 with hydrochloric acid and wash the solution with carbon tetrachloride to remove dissolved or dispersed dithizone. Readjust the pH to 9 by adding 0.5 *M* ammonia solution and extract several times with 0.01 *M* oxine until all complexable impurities are removed.

Precipitation of pure silver iodide. To the above aqueous solution of silver iodide, add slowly and with continuous agitation, *ca.* 2 l of distilled water, working in the dark. Separate the yellow precipitate of silver iodide by decantation and wash thoroughly with distilled water on a fritted glass filter, until no iodide remains. Dry the product *in vacuo* at 50°. (Yield: 99.1 g of pure silver iodide.)

Recovery of potassium iodide. The dilute potassium iodide solution from the filtration of silver iodide is very pure and can be used again after concentration. For this purpose, evaporate the solution under reduced pressure in order to reach the initial concentration (50% w/w, d = 1.545 at 20°). Then filter the solution and store over dithizone.

Solvent recovery. Recover carbon tetrachloride by successive washings with concentrated sulphuric acid, water, 10% sodium hydroxide, and water. Finally distil the solvent over lime[6].

Purification of silver chloride and silver bromide. The described procedure is directly applicable to the purification of silver chloride or silver bromide. It is advisable, however, to convert the starting samples of silver chloride or bromide to silver iodide, in order to avoid the introduction of chloride or bromide ions which could make the recovery of potassium iodide more difficult. This is easily achieved by suspending silver bromide or chloride in a potassium iodide solution (*ca.* 0.1 *M*) in slight excess with respect to the required stoichiometry. The conversion is fast and quantitative. After filtration and washing, the silver iodide is dissolved in the 4.5 *M* potassium iodide solution.

Conversion of silver iodide to silver bromide or chloride

Silver iodide was converted to the other halides by treating the molten silver iodide (m.p. 552°) with a stream of chlorine or bromine. Use a quartz reaction vessel and a quartz tube for introducing the gaseous reagents. Because of the exothermic nature of the reaction, pass the gas over the salt initially without heating. Then, after about 1 h, heat the reaction vessel in order to melt the silver iodide and to facilitate the removal of I_2, ICl and ICl_3. When no more vapours of iodine and iodine chlorides are visible, bubble chlorine through the molten mass again to complete the conversion of silver iodide to the chloride. After complete reaction, quickly pour the molten salt into a beaker containing purified water. (The product so obtained is a dispersed phase and not a compact mass; accordingly, any danger of contamination in grinding is eliminated.). Then filter the silver chloride and dry under reduced pressure at 50°. From 35 g of silver iodide, an almost quantitative yield of 21.3 g of silver chloride was obtained.

To convert silver iodide to silver bromide, a similar method was used, by bubbling bromine-saturated air through the molten salt. From 15 g of silver iodide, 10.8 g of silver bromide (90% yield) were obtained. The non-quantitative yield in this case was due to mechanical losses in the incomplete transfer of the molten salt from the quartz vessel.

Analytical evaluation of the products

The analytical check was based on the evaluation of the impurities extracted by dithizone and by oxine. A blank was carried out for a solution of 4.5 *M* potassium iodide without silver halide.

Procedure. Dissolve 5 g of the sample (silver chloride, bromide or iodide) in 40 ml of 4.5 *M* potassium iodide and extract the solution with 10 ml of $2.5 \cdot 10^{-5}$ *M* dithizone in carbon tetrachloride at pH 8. Wash the organic phase twice with 2–3 ml of 4.5 *M* potassium iodide to remove silver dithizonate, and record the spectrum between 400 and 700 nm. Compare this spectrum with the spectrum obtained from the blank solution.

The impurities contained in the sample can be approximately evaluated from the lowering in the absorbance at 620 nm, where dithizone shows a maximum in the spectrum and most metal dithizonates do not absorb. If it is assumed that the impurities have an average atomic weight of 100 and complex two moles of dithizone per ion, and if 10 ml of dithizone is used to extract the solution containing 5 g of the sample, then a lowering in absorbance of 0.02 corresponds to a total impurities content of less than 0.05 p.p.m.

In a further step, wash the aqueous phase with carbon tetrachloride at pH 5 to remove the dissolved dithizone, and after adjusting the pH to 8–9 with ammonia solution, extract with 0.01 *M* oxine. In this case also, evaluate the impurities by comparison with a blank solution.

The samples purified by the described procedure contained no more than 0.1–0.3 p.p.m. of total dithizone-extractable impurities and no impurities extractable by oxine.

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SHORT COMMUNICATION

Spot test for hydroxytriazenes with picric acid

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(Received 20th October 1972)

Hydroxytriazenes act as versatile ligands forming chelates with many met ions[1], and their spectroscopic and magnetic properties are also of interest^{2-} However, there is a surprising paucity of methods for detection of this class compounds. The present author[5] reported a test based on the formation of a pir colour when hydroxytriazenes reacted with α-naphthylamine. In the prese communication, the development of a red colour by heating the solid hydrox triazene or a drop of ethanolic solution with 2–5 drops of a saturated ethanol solution of picric acid is the basis of detection.

Experimental

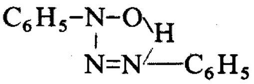
Preparation of hydroxytriazenes. All the hydroxytriazenes were prepared the action of diazonium salts on corresponding hydroxylamines, by Sogani a Bhattacharya's method[6]. These are listed in Table I, along with their melting poin and the colour reactions with picric acid.

Procedure. Treat a pinch of solid hydroxytriazene or a drop of te solution (0.001% w/v in ethanol) with 2–5 drops of a saturated ethanolic solutic of picric acid and heat for 1 min over a water bath at 55–60°. A red colo develops if a hydroxytriazene group is present. In some cases the colour developme takes place even in cold, but heating is recommended.

Results and discussion

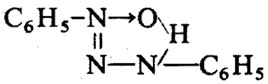
This reaction was tested for 35 compounds; all gave a positive test (Table

In the case of 3-hydroxy-1,3-diphenyltriazene, on the basis of its dissociatic constant and ultraviolet spectra, Purohit and Sogani[7] postulated an intra-molecul hydrogen-bonded structure "A" and a tautomeric form "B". On the basis infrared studies, an intra-molecular hydrogen-bonded structure of the tautomer form was also proposed[8], and Mitsuhashi *et al.*[9] supported this view on the bas of infrared studies of the ^{15}N-substituted product.



$C_6H_5{-}N(O{\cdots}H){-}N{=}N{-}C_6H_5$

"A"



$C_6H_5{-}N(\rightarrow O{\cdots}H){=}N{-}N{-}C_6H_5$

"B"

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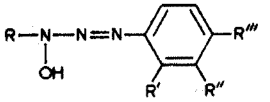
BLE I

ACTION OF HYDROXYTRIAZENES WITH PICRIC ACID



o.	*Compound* *R*	*R′*	*R″*	*R‴*	*M.p.* (°)	*Colour given on heating with picric acid solution*
	CH_3	H	H	H	69	Dark reddish brown colour
	CH_3	COOH	H	H	193	Dark reddish brown colour
	CH_3	H	H	Cl	149	Orange red colour
	CH_3	H	H	CH_3	116	Intense red colour even in cold which intensifies on heating
	CH_3	H	H	NO_2	231	Colour remains yellow. Test not given
	CH_3	CH_3	H	H	51	Light red colour in cold, on heating first dark red and then intense reddish brown
	CH_3	H	H	COOH	214	Light brown red colour
	CH_3	OCH_3	H	H	82	Dark red colour in cold, which intensifies on heating
	CH_3	H	Cl	Cl	149	Dark red colour
	CH_3	Cl	H	H	62	Dark red colour
	CH_3	NO_2	H	H	143	Reddish brown colour
	C_2H_5	H	H	H	45	In cold reddish brown colour, which on heating becomes intense red
	C_2H_5	H	H	CH_3	78	In cold reddish brown colour, which on heating becomes intense red
	C_2H_5	H	H	OCH_3	73	In cold reddish brown colour, which on heating becomes intense red
	C_2H_5	H	H	Cl	103	Intense red colour
	C_3H_7	H	H	H	61	Intense red colour
	C_3H_7	H	H	CH_3	45	Intense red colour
	C_3H_7	H	H	Cl	82	Intense red colour
	C_6H_5	H	H	H	125	Intense red colour
	C_6H_5	Cl	H	H	78	Intense red colour
	C_6H_5	H	H	SO_3Na	157	Intense red colour
	C_6H_5	H	H	$COCH_3$	154	Intense red colour
	C_6H_5	H	H	Cl	148	Intense red colour
	C_6H_5	H	H	Br	154	Intense red colour
	C_6H_5	H	H	COOH	184	Colour development is slow and heating for 5 min is needed
	C_6H_5	COOH	H	H	167	Intense red colour
	C_6H_5	H	H	$NHCOCH_3$	147	Intense red colour
	C_6H_5	H	H	CH_3	130	Intense brown red colour
	C_6H_5	H	OH	COOH	194	Brown red colour
	p-$CH_3C_6H_4$	H	H	H	127	Intense red colour
	p-$CH_3C_6H_4$	Cl	H	H	101	Intense red colour
	p-$CH_3C_6H_4$	H	H	CH_3	131	Intense red colour
	p-$CH_3C_6H_4$	Br	H	H	93	Intense red colour
	p-$CH_3C_6H_4$	H	Br	H	173	Intense red colour
	p-$CH_3C_6H_4$	H	H	Br	162	Intense red colour

The reaction of α-naphthylamine with hydroxytriazenes[5] can be interprete as evidence for form "A". However, the present report provides support for th contribution of the tautomeric form "B". Both amine oxide ($\equiv N \rightarrow O$) and secondar amino ($= N{-}H$) groups are known to form picrates and the development of a re colour by hydroxytriazenes with picric acid is due to the formation of picrate which is indicative of the presence of these groups. A preliminary study of soli picrates has been made, which indicates that the picrates formed are of the donor-acceptor type of molecular complexes rather than salts.

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SHORT COMMUNICATION

Iodimetric analysis of formate ion in the presence of nitrate ion

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Work undertaken in this laboratory on the kinetics of formate ion oxidation by an alkali metal nitrate melt required an analytical procedure for the determination of small amounts of formate ion in samples containing variable, unknown amounts of carbonate and nitrite ions and a large amount of nitrate ion. A method suitable or large numbers of samples with a short working time was also desirable.

Acid–base titrimetric methods were obviously unsuitable, while redox methods in acidic media could not be used because of possible oxidation of formate on by nitrate ion[1]. In a preliminary evaluation, Stamm's method[2] did not give an easily detectable end-point. However, by considerable modification of an iodimetric method reported by Verma and Bose[3], a titrimetric method was developed which enabled 4–10 micromole of formate to be determined with a precision of *ca.* 1%. The method was applicable in the presence of high concentrations of nitrate and also permitted the prior destruction of nitrite ion with excess sulphamic acid without interference. The method was lengthy but required little actual working time so that it was convenient for large numbers of samples.

Experimental

Standard 0.0025 M arsenic(III) solution. Dissolve an accurately weighed amount of dried AnalaR arsenic(III) oxide in sodium hydroxide solution in the usual way, then just acidify with dilute hydrochloric acid and neutralize with sodium hydrogencarbonate before diluting to the desired volume.

Standard 0.005 M iodine solution. Prepare the iodine solution, add sufficient AnalaR potassium iodide to give an iodide concentration of 0.5 *M*, and standardize against the arsenic(III) solution using a hydrogenphosphate–dihydrogenphosphate buffer (pH 7.2) and starch indicator.

Phosphate buffer solution. Prepare from the sodium or potassium salts to give 0.5 *M* concentrations of hydrogenphosphate and dihydrogenphosphate.

Other solutions. Prepare in the usual way, 0.5 *M* sulphuric acid, 1 *M* sodium hydrogencarbonate, and 0.5 *M* sulphamic acid.

Recommended procedure. Dissolve the sample to be analyzed in the minimal amount of water in a 10-ml volumetric flask and neutralize by dropwise addition of 0.5 *M* sulphuric acid, if necessary. Add, in this order, 1 ml of 0.5 *M* sulphamic acid, 0.5 ml of 1 *M* sodium hydrogencarbonate, and 2 ml of the phosphate buffer, mixing well between additions. Finally, pipette in exactly 2 ml of the standard 0.005 *M* iodine solution, which is sufficient for the analysis of 10 μmole of formate Dilute to 10 ml, and stopper the flask tightly. Heat the prepared solution in a steam bath for 5 h, cool, and determine the excess of iodine by titrating with the standard arsenic(III) solution using starch indicator. It is not necessary to adjust the pH of the solution before titration because the phosphate buffer is already present. For a sample originally containing 4 μmole of formate (0.18 mg of formic acid), the titration volume will be *ca.* 2.4 ml.

Before adapting this procedure for the determination of larger amounts of formate ion, take proper precautions against an explosion, because carbon dioxide is a reaction product and the flask must be tightly sealed.

Results and discussion

The method is based on the oxidation of formate ion when heated with an excess of iodine

$$HCO_2^- + I_3^- = H^+ + CO_2 + 3I^- \qquad (1$$

but differs from that of Verma and Bose[3] in the manner by which iodine is retained during the heating of the sample, in the use of sulphamic acid to destroy nitrite ion, and in the use of a phosphate buffer. Rather than vaporized iodine being recovered from a condenser[3], the vapor pressure of the iodine was lowered by the addition of a high concentration of iodide. The formation of the triiodide ion wa very effective in stabilizing iodine; no loss of iodine could be detected from a solution which was 0.002 *M* in iodine and 0.1 *M* in iodide ion after heating for 1.5 h in a stoppered 10-ml volumetric flask. By contrast, when the iodide ion concentration was also 0.002 *M*, more than 50% of the iodine was lost within 45 min. As pointed ou below, any loss of iodine from a solution which is 0.1 *M* in iodide ion and contained in a stoppered 10-ml volumetric flask is within experimental erro even after 5 h of heating in a steam bath.

Though nitrite ion is normally destroyed before iodimetry in acidic solution to prevent the oxidation of iodide ion[4], it was found necessary here to destroy nitrite by sulphamic acid to prevent its oxidation by iodine. (Thermodynamic calculation also indicates the latter oxidation in a neutral solution at high nitrite concentrations.) The possibility of the reverse reaction, *i.e.*, the oxidation of iodide by nitrate in a neutral solution, was checked and found not to occur, though this reaction is thermodynamically favorable in the absence of nitrite ion.

The heating time required for the completion of reaction (1) was determined using two sets of solutions containing known aliquots of a 0.004 *M* sodium formate solution, 2 ml of the standard 0.005 *M* iodine solution, and 2 ml of the phosphate buffer solution. One of the sets contained, in addition, 20 mmole of nitrate ion (1.7 g of sodium nitrate) and 0.5 mmole of sulphamate (neutralized sulphamic acid). The formate solution was prepared from recrystallized BDH laboratory reagen grade sodium formate. After diluting in 10-ml volumetric flasks and stoppering the flasks were heated in a steam bath for varying lengths of time, cooled, and the excess of iodine determined. After 5 h of heating, there were no furthe changes detected in the volume of arsenic(III) required for the titration of any test solutions initially containing the same aliquot of formate solution. The signifi antly longer heating time required for the present method compared to that of erma and Bose[3] is probably due, in part, to the inverse relationship between the ate of reaction (1) and the iodide ion concentration[5].

To ascertain the validity of the method developed for the determination of icromole amounts of formate ion, sets of solutions were analyzed after heating r 5 h. Since neither the exact concentration of formate nor the absence of a ystematic error were known, the nitrate-free data were used to determine the erpendicular least-squares fit of the following equation:

$$V_F = (V_T - V_t) M_{As(III)}/M_F \qquad (2)$$

here V_F is the volume of the formate ion solution, V_T is the volume of the rsenic(III) solution required for the titration of 2 ml of the standard iodine solution, $_t$ is the volume of the arsenic(III) required for the titration of the iodine in xcess, and $M_{As(III)}$ and M_F are the respective molarities of the arsenic(III) and rmate ion solutions. $M_{As(III)}$ was considered to be a known constant and M_F and $_T$ the constants to be determined. Ten sets of data points (V_F, V_t) were used n the calculation to give a value for V_T of 4.25 ml. Direct determination of V_T tandardization of the iodine solution) gave a value of 4.29 ml for the average of 5 trations with a standard deviation of 0.04 ml. The 1% smaller value calculated for $_T$ could reflect a slight loss of iodine during the heating period; however, this annot be said with certainty, because the two values are within one standard eviation. The reliability of the analytical method developed is also supported by e fact that M_F was calculated to be 0.00408 *M*, and the solution was prepared be *ca.* 0.004 *M* by dilution of a 0.1 *M* formate solution.

To determine the precision of the method developed, values for V_F were alculated from eqn. (2) by means of the least-squares determined constants and e titration volumes, and compared with the experimental volumes of formate olution used. For the nitrate-free samples, to which the least-squares line was tted, this comparison showed an average deviation of 0.002 ml and a standard eviation of 0.03 ml. For the samples containing nitrate ion and sulphamate ion, e average deviation was 0.05 ml and the standard deviation was 0.05 ml. The verage error for samples containing high nitrate ion and 4–10 μmole of formate ion as +1.2%.

We wish to thank the Science Research Council for awarding a research llowship to one of us (J.D.B.).

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SHORT COMMUNICATION

Diagrammes potentiel/pO^{2-} du neptunium et du plutonium dans l'eutectique LiCl–K

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(Reçu le 24 février 1973)

Le diagramme d'équilibre potentiel rédox/pO^{2-} pour l'uranium a été étab récemment dans notre laboratoire[1]. En continuation de ces travaux, nous avo établi les diagrammes relatifs au neptunium et au plutonium. Nous avons utili les divers potentiels standards que nous avons publiés précédemment (potentie du neptunium[2,3], potentiels du plutonium[4]) et nous avons mesuré les produits solubilité de NpO_2 et PuO_2 dans l'eutectique LiCl–KCl à 400°. Cette déterminati a été effectuée par comptage-α en tenant compte des données récentes pour l'activi spécifique du neptunium et du plutonium[5].

Les diagrammes sont établis à 400°. A cette température, le neptunium pe se présenter aux états d'oxydation 3+, 4+, 5+ et le plutonium aux états 3+, 4 A des températures supérieures à 400° ($\simeq$425°) le neptunium (V) n'est plus stabl Les potentiels standards sont rapportés au système Cl_2/Cl^- ($E^0_{Cl_2/2\,Cl^-}=0.00$) et to les potentiels calculés sont pris négativement de façon à obtenir un diagram correspondant au mode de représentation de Trémillon[6].

Nous avons employé les donnés suivants:

$L_{PuO_2} = 10^{-11}$ $\quad$ $L_{NpO_2} = 10^{-10.5}$

$E^0_{Pu(III)/Pu(O)} = -2.062$ V $\quad$ $E^0_{Np(III)/Np(O)} = -2.378$ V

$E^0_{Pu(IV)/Pu(O)} = -1.959$ V $\quad$ $E^0_{Np(IV)/Np(O)} = -2.197$ V

$E^0_{Pu(IV)/Pu(III)} = -1.649$ V $\quad$ $E^0_{Np(IV)/Np(III)} = -1.594$ V

$E^0_{NpO_2(V)/NpO_2\downarrow} = 0.119$ V

Pour une solution telle que $[NpO_2(V)]=[Np(IV)]=[Np(III)]=10^{-2}$ la précipitation de NpO_2 a lieu pour p$O^{2-}\leqslant 4.25$ puisque $[Np(IV)]\ [O^{2-}]^2$ $10^{-10.5}$. De la même façon, pour $[Pu(IV)]=[Pu(III)]=10^{-2}$ *M* on déduit que précipitation de PuO_2 commence à p$O^{2-}=4.5$. Les pO^{2-} de début de précipitati étant fixés on peut tracer les diagrammes de la Fig. 1.

Neptunium

L'examen du diagramme montre que le pouvoir oxydant de $NpO_2($ vis-à-vis du bain augmente avec le pO^{2-} de 4.5 à 5.7; lorsque p$O^{2-}>5.7$ il e

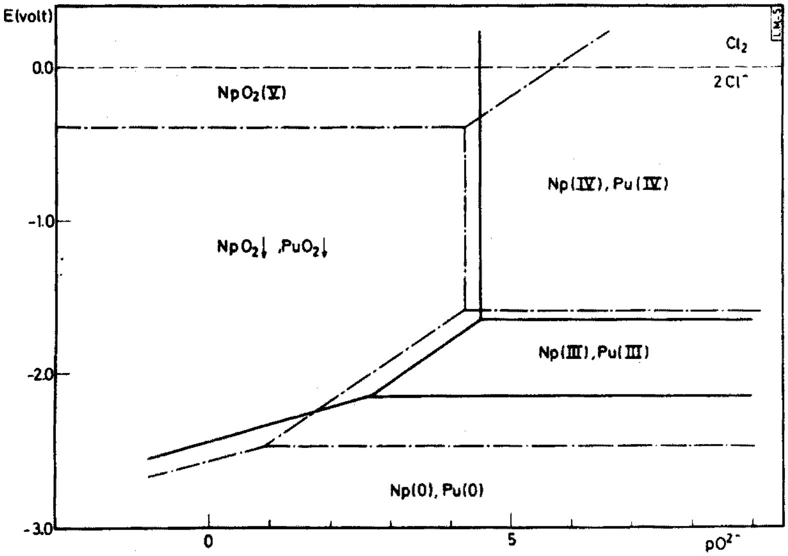

Fig. 1. Diagrammes E/pO^{2-} du neptunium et du plutonium dans l'eutectique LiCl–KCl à 400°. (——) Pu. $[\mathrm{Pu(IV)}]=[\mathrm{Pu(III)}]=10^{-2}\ M$. (–––) Np. $[\mathrm{NpO_2(V)}]=[\mathrm{Np(IV)}]=[\mathrm{Np(III)}]=10^{-2}\ M$.

donc impossible de stabiliser le neptunium (V). Le calcul de la constante d'équilibre de la réaction $\mathrm{NpO_2(V)+Cl^-} \rightleftharpoons \mathrm{NpO_2}+\frac{1}{2}\ \mathrm{Cl_2}$ est immédiat. En égalant les expressions

$$E_{\text{éq}} = -0.119+0.134 \log\ [\mathrm{NpO_2^+}] = 0.134 \log\ (P_{\mathrm{Cl_2}})^{\frac{1}{2}}\ ,$$

on obtient $K=(P_{\mathrm{Cl_2}})^{\frac{1}{2}}/[\mathrm{NpO_2^+}]=10^{-0.89}$ atm$^{\frac{1}{2}}$ mole^{-1} l^{-1}.

Plutonium

Le comportement du plutonium est plus simple car les ions plutonyles n'existent pas à l'équilibre dans les chlorures fondus. En passant du neptunium au plutonium, la zone de stabilité du bioxyde s'élargit vers le potentiel de référence et la zone de stabilité de l'ion 3+ diminue.

Uranium, plutonium et neptunium

Si l'on compare les diagrammes de ces trois actinides, (voir ref. 1), on constate que le domaine de potentiel dans lequel les ions $\mathrm{UO_2(VI)}$ et $\mathrm{NpO_2(V)}$ sont stables, est identique; la stabilité de l'ion trivalent vis-à-vis du bain diminue en passant de l'uranium au plutonium. En réalité, il est cependant difficile de faire une comparaison tout à fait pertinente, étant donné que toutes les données, pour l'uranium, n'existent pas à 400°.

Nous remercions l'Institut Interuniversitaire des Sciences Nucléaires pour le soutien apporté à notre laboratoire. Nos remerciements vont également à G. Landresse pour la discussion du manuscript.

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SHORT COMMUNICATION

Utilisation des propriétés électrochimiques du système Fe^{2+}/Fe^{3+} en présence de chlorures pour le contrôle en continu de bain d'usinage chimique

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(Reçu le 17 mars 1973)

Au cours de l'usinage chimique de métaux ferreux à l'aide d'une solution aqueuse de chlorure ferrique, la qualité des pièces obtenues diminue régulièrement au fur et à mesure que le bain perd son "agressivité". Cet inconvénient peut être évité par un contrôle continu de l'état de vieillissement de la solution ferrique; mais les méthodes utilisées jusqu'à présent (mesures de densité, de viscosité, de conductivité ou d'absorbance) n'ont pu mener à un contrôle satisfaisant du milieu. Nous avons pensé qu'en utilisant les propriétés électrochimiques du système Fe^{2+}/Fe^{3+} il serait possible d'obtenir un meilleur contrôle du bain.

En effet, l'usinage des pièces correspond théoriquement à une réaction d'oxydoréduction. En fait, le bain étant constitué par une solution de chlorure ferrique, la réaction complète s'écrit:

$$2\,FeCl_3 + Fe \rightarrow 3\,FeCl_2 \qquad (1)$$

Au cours de l'usinage, le milieu s'enrichit donc en chlorure ferreux, ce qui correspond à une diminution du pouvoir oxydant de la solution et à une diminution de l'agressivité. Il est alors nécessaire de régénérer la solution d'attaque; pour ce, on utilise un oxydant qui réagit sur Fe^{2+} pour redonner Fe^{3+} selon:

$$FeCl_2 + HCl + Ox \rightarrow FeCl_3 + RedH \qquad (2)$$

Cette réaction montre qu'en plus de l'oxydant il faut introduire dans la solution de l'acide chlorhydrique. Finalement il s'agit de suivre la concentration du bain en ions ferreux pour effectuer la régénération dès que cette teneur devient incompatible avec un bon usinage.

Aucune étude électrochimique n'ayant—à notre connaissance—été effectuée dans un tel milieu, nous avons été conduits à tracer les courbes intensité–potentiel caractéristiques du système Fe^{2+}/Fe^{3+} en présence de chlorures.

Courbes intensité–potentiel du système Fe^{2+}/Fe^{3+} en présence de chlorures

Le bain neuf est constitué par du perchlorure de fer du commerce ($FeCl_3$RP) en solution aqueuse de densité 1.26. Sa teneur en acide chlorhydrique est voisine de 0.1 *M*. Le milieu est suffisamment conducteur pour qu'on puisse opérer san addition d'électrolyte-support. L'électrode de référence est une électrode au sulfat mercureux (ESS). Nous avons d'abord utilisé une micro-électrode de platine poli les courbes obtenues manquaient totalement de reproductibilité et étaient in exploitables. Nous avons alors opéré avec une micro-électrode de carbone vitreu (V 25 de Carbone-Lorraine) qui nous a donné des résultats très reproductible

La courbe 1 (Fig. 1) correspond à la réduction des ions fer(III) d'un bai neuf: $E_{\frac{1}{2}\mathrm{cat}} = -0.17$ V/ESS. Si l'on réduit totalement une aliquote de ce bain pa du fer en poudre, la solution ferreuse obtenue est caractérisée par la courbe 2 $E_{\frac{1}{2}\mathrm{an}} = +0.18$ V/ESS. Le système Fe^{2+}/Fe^{3+} n'est donc pas un système rapide e présence de chlorures. Cependant, la courbe-somme (courbe 3, Fig. 1) travers sans inflexion l'axe des abscisses ($E_{\text{éq}} = 0.03$ V/ESS); cette courbe a été tracée dans l mélange à volumes égaux des deux solutions ferreuses et ferriques précédemmen analysées. Le domaine de potentiel utilisable est limité vers -1.5 V/ESS par l réduction des protons de la solution et vers $+1.4$ V/ESS par l'oxydation de chlorures.

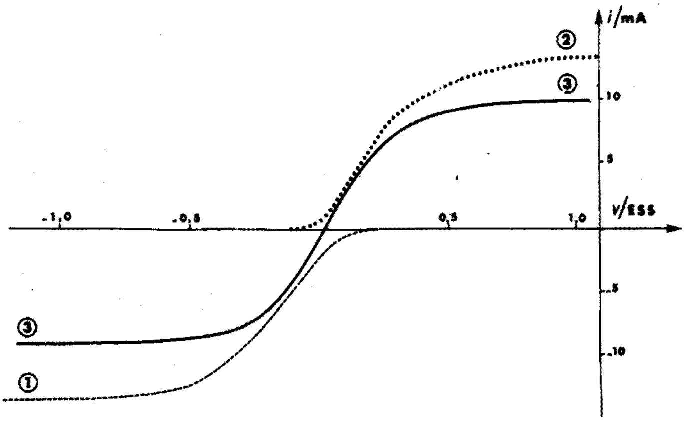

Fig. 1. Courbes intensité–potentiel du système Fe^{2+}/Fe^{3+} en présence de chlorures. (1) Fe^{3+}, (2) Fe^{2+} (3) $Fe^{2+} + Fe^{3+}$.

Réactions indicatrices de la concentration en ions fer(II)

A partir du faisceau de courbes de la Fig. 1, on peut concevoir plusieur méthodes électrochimiques permettant de suivre en continu l'évolution du bai d'usinage[1,2], c'est-à-dire son enrichissement en fer(II). Nous avons éliminé les techniques faisant intervenir une électrode indicatrice et une électrode de référence l'expérience montre que cette dernière ne résiste pas à l'attaque du bain alors qu les électrodes de carbone vitreux ont fonctionné durant quinze jours consécutifs a laboratoire et plusieurs mois en usine sans que leur réponse varie.

Nous avons donc examiné les deux méthodes basées sur l'emploi de deu électrodes indicatrices (de carbone vitreux) et choisi l'ampérométrie plutôt que l potentiométrie pour des raisons d'appareillage: il était plus facile d'imposer un différence de potentiel entre les électrodes et d'observer le courant résultant qu d'imposer un courant et d'utiliser les variations de potentiel produites.

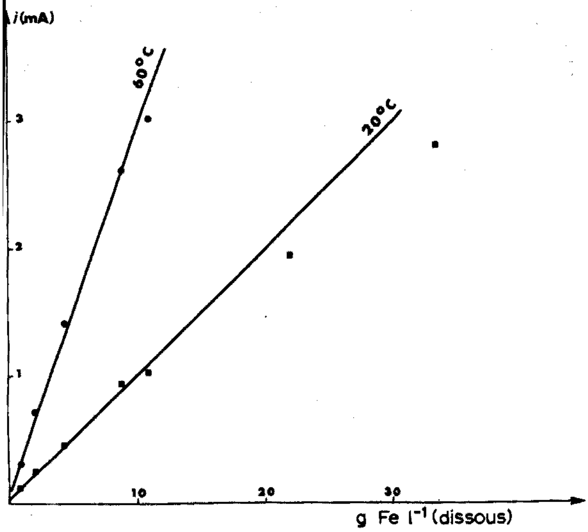

Fig. 2. Intensité du courant circulant entre deux micro-électrodes de carbone vitreux (surface voisines de 1.1 mm^2) en fonction de la quantité de fer dissoute par le bain d'usinage.

L'examen de la Fig. 1 montre que l'on doit obtenir un courant proportionnel à [Fe^{2+}] si l'on impose entre les deux électrodes une différence de potentiel de l'ordre de 0.8 V. C'est effectivement ce que nous avons constaté (Fig. 2) en mesurant les variations du courant entre les deux micro-électrodes en fonction de la quantité de fer dissoute par le bain, grandeur proportionnelle à [Fe^{2+}]. La courbe représentative est une droite de 0 à 10 g l^{-1} de fer dissous aussi bien à température ambiante (20°) qu'à 60°, températures imposées au bain en cours d'usinage.

Contrôle et régénération du bain

Le contrôle continu du bain est obtenu par immersion d'une cellule[3] reproduite Fig. 3 et dont l'élément essentiel est le couple d'électrodes de carbone vitreux. Ces électrodes sont logées dans un compartiment de mesure qui définit la géométrie du système. Une turbine entraînée par un moteur asynchrone assure dans ce compartiment un régime hydrodynamique stable. Ces deux dispositions permettent d'affranchir la cellule des conditions extérieures comme son degré d'immersion où l'agitation du bain à tester et d'obtenir des résultats identiques pour des mesures effectuées d'une part en bécher, d'autre part, dans un bac de quelques centaines de litres sur des solutions identiques agitées ou non.

Le bain, muni de cette cellule, peut être mené de façon continue ou discontinue. En fonctionnement discontinu, on traite successivement les pièces jusqu'à ce que le courant circulant entre les électrodes de carbone indique une teneur en fer(II) incompatible avec un bon usinage. Les opérations sont alors arrêtées et le bain réoxydé et réacidifié par d'acide chlorhydrique. Ce procédé fonctionne en usine de façon satisfaisante.

Une utilisation plus rationnelle de la cellule consiste à maintenir en permanence la teneur du bain en fer(II) à la valeur donnant les meilleures conditions d'usinage, ce qui correspond à un bain ayant dissous 2 à 3 g Fe l^{-1}. Soit i_r la

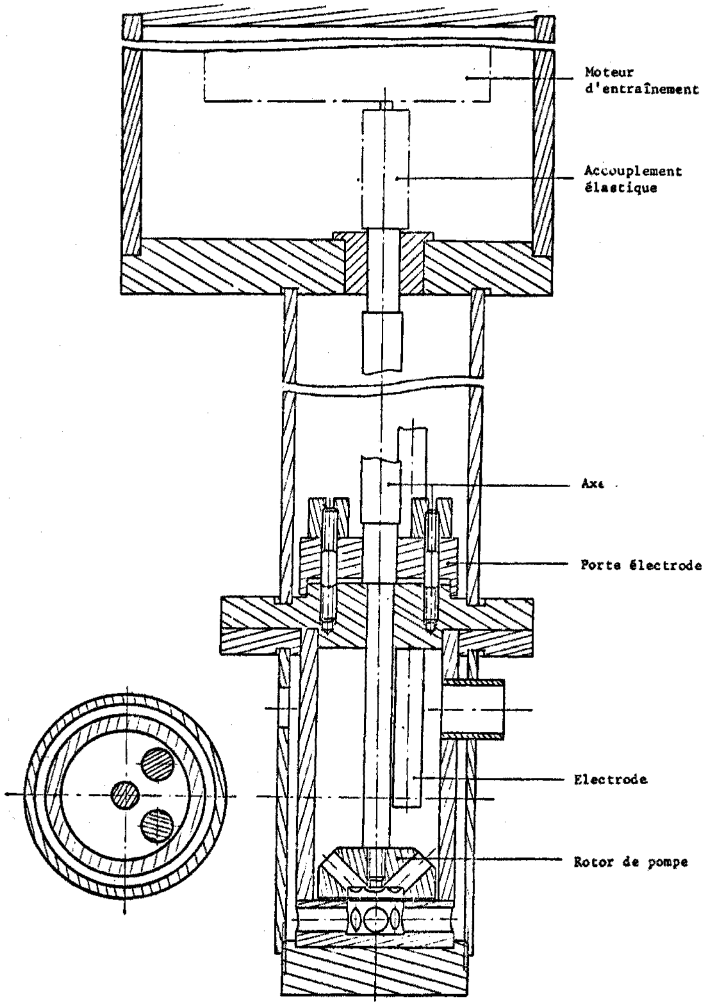

Fig. 3. Coupe longitudinale de la cellule de contrôle.

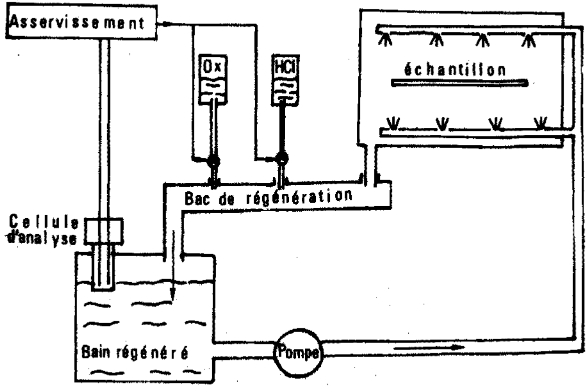

Fig. 4. Schéma d'ensemble du prototype réalisé en laboratoire.

valeur correspondante du courant. La régénération du bain est alors effectuée sans interrompre l'usinage en comparant électroniquement à i_r le courant qui circule entre les deux électrodes indicatrices. Le dispositif de comparaison alimente un relais qui commande l'addition d'oxydant et d'acide chlorhydrique, de telle manière que l'échauffement local du bain par suite de son oxydation ne soit pas prohibitif.

Le schéma de principe d'une telle installation est reproduit Fig. 4.

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SHORT COMMUNICATION

Impervious barrier-ring oven technique

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(Received 12th February 1973)

The ring oven developed by Weisz[1] is coming into greater use for the stud and determination of traces of materials in the environment. The difficulties i obtaining sharp, well-defined rings for quantitative analyses with the ring oven hav long been recognized. The problem can be avoided by supplemental use of a impervious barrier ring embedded in the filter paper, and centered 1–2 mm insid the heated ring of the oven. This takes advantage of evaporation and heat induced reactions provided by the heated ring zone. The impervious barrier permit more rapid addition of reagents, and enables the formation of sharp, intens colors, and reproducible ring thickness by elimination of overrunning at the heate ring zone.

Yagoda[2] developed a barrier ring for confined spot tests on filter paper i 1937, which consisted of an 11-mm i.d. ring made with a paraffin wax. The wa used was not suitable for use with heat as it diffused through the paper whe placed on the heated ring oven. In this laboratory, numerous synthetic product were evaluated and Bareco Polywax 2000*, a low molecular weight homopolyme of ethylene, was found to meet the requirements for use on the ring oven.

Impervious barrier rings may be prepared by melting the prilled wax in petri dish on a hot plate. As the wax melts to form a thin layer, a heate Pyrex or metal tube of the desired i.d. is placed in the wax melt, removed, an immediately stamped on a single filter paper resting on a heated glass plate. A absorbent material such as blotter paper should first be placed on the glass t absorb the excess wax. Immediate removal of the stamped filter paper from the hea yields a colorless, semi-transparent ring which is chemically inert and stable up to temperature of 125°. Convenient lengths of Pyrex tubes were satisfactory fo producing 31 mm or 20 mm i.d. stamped rings. The outer circle of the wax rin rests on the heated surface of the ring oven, with 1–2 mm of the embedded wa

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* Bareco Division, Petrolite Corporation, P. O. Drawer K, Tulsa, Okla., 74115. Crayford, Ken England/Petrowaxes Limited/Thames Road. Tokyo, Japan/Royo Ink Mfg. Co., Ltd./6,2-Chome Kyobash Chuo-Ku, P.O. Box 355.

Prepared barrier rings are now available from the Arthur H. Thomas Company, Philadelphi Pa. 19105. They are produced on S and S filter paper No. 595 with a choice of 20 mm or 31 mm i. barriers.

ring protruding into the lighted area of the annular space of the ring oven. As the barrier material is semi-transparent, easier visual evidence of solution migration is obtained.

Observations were made, with a 200 × magnification, of nickel dimethylglyoximate precipitated against the barrier material. The red precipitate was found to be abutted to the wax barrier and there was no penetration of color. With a normal rate of solutions addition to the filter paper, nickel was deposited in a fine, sharp ring immediately adjacent to the barrier. Whenever gross flooding was deliberately induced, the metal solution diffused back from the barrier rather than flooding over the barrier ring.

In related ring oven research now being conducted, isotopes are being used. These isotope studies have emphasized the absolute necessity of adding all samples, solutions, and reagents to the exact center of the ring. Failure to do so produced activities varying as much as 30% between different quadrants of the same ring. For this reason, it was found helpful to use a guide, in the form of a metal or thick plastic circle, for marking the exact center of the barrier ring. A tiny hole drilled in the exact center of the guide permits the use of a pencil for marking the center of the ring before use.

This work was supported in part by the National Science Foundation RANN Program, Grant GP-35114X.

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BOOK REVIEWS

Handbuch der analytischen Chemie, Herausgegeben von W. Fresenius und G Jander†, *Teil III. Quantitative Analyse. Band IIIaα 2. Elemente der dritten Hauptgruppe: Aluminium*, Bearbeitet von H. Bensch, Springer-Verlag, Berlin, 1972 xix+716 S., Gebunden DM 198.–.

Comme tous les ouvrages édités dans cette série *Handbuch der analytischen Chemie* de W. Fresenius et G. Jander†, le volume III aα 2 traitant de la séparation et du dosage de l'aluminium représente un travail de grande qualité, offre un intérêt particulier pour les chimistes analystes et inorganiciens.

Ce volume (2ème édition) a été préparé par H. Bensch de l'Institut de Recherche en Matière de Métaux Légers de la "Vereinigte Aluminium-Werke AG" de Bonn (Allemagne).

Dans une première partie (19 p.), l'auteur introduit les bases fondamentales de la chimie de l'ion aluminium en solution aqueuse (hydratation, complexation par ligands minéraux et organiques, influence de la constitution du milieu sur la stabilité des complexes).

La seconde partie est consacrée à la méthodologie du dosage proprement dit (557 p.). Les techniques sont groupées de la façon suivante: méthodes gravimétriques, méthodes volumétriques, méthodes optométriques (photométrie d'absorption, spectrofluorimétrie, spectrométrie d'émission de flamme, d'absorption atomique, spectrométrie d'émission: arc et étincelle, fluorescence X), méthodes électrométriques (polarographie directe, indirecte et inverse, titrage ampérométrique) méthodes radiométriques (analyse par activation, échange isotopique).

La dernière partie de l'ouvrage (128 p.) traite des méthodes de séparation de cet élément (précipitation, masquage par complexation, extraction liquide–liquide électrolyse, échangeurs d'ions, chromatographie sur papier, électrochromatographie gaz chromatographie et autres).

On doit reconnaître que tous les chapitres sont fort bien présentés et en relation avec leur importance. Dans chaque cas, le principe de la détermination est donné, les domaines d'applications, les conditions opératoires, les sensibilités et les précisions sont décrits.

Cet ouvrage est donc parfaitement réalisé, jusque dans les détails, et sera indispensable à tous ceux qui doivent mettre en oeuvre une méthode de séparation et d'analyse de l'aluminium.

Werner Haerdi (Genève)

P. G. Jeffery and P. J. Kipping, *Gas Analysis by Gas Chromatography*, International Series of Monographs in Analytical Chemistry, Vol. 17, Pergamon Press, Oxford, 2nd Ed., 1972, x + 196 pp., price £5.50.

The preface of this new edition is perhaps a little unfair to book reviewers in that no indication is given of the rapid advances in the particular field which have necessitated its production. A close perusal of the text shows that few remarkable advances have in fact been made in the eight years which have passed since the first edition appeared. However, the first edition has been out of print for some time, and the authors have taken the opportunity to bring it up to date. New information has been added to many sections of the book, in which the original pattern of general information, determination of individual gases, and applications, is retained. The most important new material covers column packings and flame-photometric and coulometric detectors As an exposition of the use of g.c. methods in gas analysis of all kinds, the text remains unrivalled.

A. M. G. Macdonald (Birmingham)

Handbuch der analytischen Chemie, Herausgegeben von W. Fresenius, *Teil III. Quantitative Analyse. Band VI bβ. Elemente der sechsten Nebengruppe: Uran*, Bearbeitet von J. Korkisch und F. Hecht, unter Mitarbeit von H. Sorantin, Springer-Verlag, Berlin, 1972, xii + 524 S., Gebunden DM 168.–.

D'aucuns pourraient encore penser que l'analyse de l'uranium n'est pas "monnaie courante". Toutefois, depuis le développement des réacteurs nucléaires, son importance ne cesse de croître, ce qui vient d'ailleurs confirmer—par la variété des méthodes de séparation et de dosage resencées—le volume VI bβ du *Handbuch der analytischen Chemie*, édité par W. Fresenius et consacré à cet élément (lère édition).

Cet ouvrage a été préparé par trois spécialistes en la matière, soit les professeurs J. Korkisch et F. Hecht de l'Institut de Chimie Analytique de l'Université de Vienne, et H. Sorantin, ingénieur au Centre de Recherche du Réacteur de Siebensdorf (Autriche).

Ainsi que j'ai eu l'occasion de le mentionner précédemment à propos de la parution du volume III aα 2 (aluminium), la série des *Handbuch* représente un travail de grande qualité auquel ce volume lui aussi ne fait pas exception.

Les lignes maîtresses de la table des matières sont celles adoptées dans tous les ouvrages de cette série: méthodes gravimétriques (réactifs minéraux et organiques), méthodes volumétriques (redox, complexométrie), méthodes optométriques (photométrie d'absorption dans solvants variés, fluorimétrie, spectrographie d'émission et d'absorption des rayons-X), méthodes électrométriques (polarographie, coulométrie, électrolyse), méthodes de séparation (échangeurs d'ions, chromatographie de partage, extraction liquide–liquide).

Il est évident qu'une attention toute particulière (173 p.) est portée sur les techniques de dosages isotopiques (radiochimique, spectrométrie de masse). Dans la première partie de ce chapitre, les auteurs traitent de la préparation des échantillons pour l'analyse (alliages, minerais, prélèvements biologiques, combustibles nucléaires ceramo-métalliques). Il est évident que ce chapitre s'adresse à des spécialistes. Néanmoins, les auteurs auraient pu parfois insister plus sur les précautions à prendre en matière de radioprotection, qui font elles aussi partie en quelque sorte de la méthodologie.

La seconde partie est consacrée à la description des méthodes de dosage radiochimique (activité α, β, γ; activation neutronique, dilution isotopique) des isotopes naturels et artificiels de l'uranium et ceux de leur famille. Dans chaque cas, le principe de la technique est rappelé, les conditions opératoires sont décrites et les interférences mentionnées.

Le problème de l'analyse des éléments combustibles irradiés est traité dans un dernier chapitre.

En résumé, ce volume ne s'écarte pas de la ligne de conduite logique, rationnelle et intelligente imposée par l'éditeur d'une façon générale à tous ses ouvrages. Il permet de se documenter rapidement sur la méthode à utiliser pour un dosage et de compléter, si nécessaire, cette documentation en consultant les références bibliographiques, but d'une telle encyclopédie.

Werner Haerdi (Genève)

F. E. Beamish and J. C. Van Loon, *Recent Advances in the Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford, 1972, xvi+511 pp., price £14.00.

The analysis of the noble metals has been since ancient times more of an art than a science. The methods of analysis are based on some of the longest standing classical techniques, and were developed with little reference to scientific interpretation. One man, F. E. Beamish has devoted a lifetime's work to changing this situation, both by his extensive investigations based on providing improved classical methods of noble metal analysis, on a reasonable scientific basis, and by collecting and evaluating the work of others in this field. His previous book on the analytical chemistry of the noble metals summarized his findings in this respect.

With the advent of modern instrumental methods, analysis of noble metals no longer occupies such a unique position. In general, the noble metals can be determined by such techniques with the same general facility as other metals. This is well brought out in the present text. The extensive references (1609) bear witness to the great effort that has been made in this area. The instrumental methods covered are atomic absorption spectrometry, neutron activation analysis, emission spectroscopy, various electrochemical techniques and spectrophotometry. Recent advances in gravimetry, titrimetry and separations are also included. The treatment of each section is comprehensive, and, together with its precursor, this is an essential source book for all who are involved in the analysis of the noble metals.

A.Townshend (Birmingham)

LeRoy F. Johnson and William C. Jankowski, *Carbon-13 NMR Spectra. A Collection of Assigned, Coded and Indexed Spectra*, Wiley–Interscience, New York, 1972, price £11.25.

This book by Johnson and Jankowski of Varian Associates contains a compilation of 500 carbon-13 n.m.r. spectra recorded in natural abundance with concomitant proton noise decoupling. The presentation is excellent, each spectrum being a high-quality full-page reproduction of the original trace. Signal positions and assignments are provided, and there is a useful code index which enables the shift of a carbon-13 nucleus in a given environment to be readily located.

The book is very timely as Fourier transform carbon-13 n.m.r. spectroscopy is rapidly becoming a major method for routine structural investigation of organic compounds. The Varian proton n.m.r. catalogues have proved to be very useful reference books, and this companion volume on carbon spectra should find a place in most n.m.r. laboratories as a reference book for spectral assignments and perhaps as a source of undergraduate problems.

W. B. Jennings (Birmingham)

D. De Soete, R. Gijbels and J. Hoste, *Neutron Activation Analysis*, John Wiley, New York, 1972, xx+836 pp., price £14.00.

Over the last few years, there has appeared a fairly large number of text-books, long reviews or substantial chapters in more general analytical texts, dealing with some field of radioactivation analysis. Consequently, one now tends—quite unfairly—to be slightly prejudiced against any new text-book on the subject. The sad fact is that with book prices soaring it is now nearly impossible to produce a definitive text on even one aspect of activation analysis at a price individuals can be expected to afford.

It was therefore delightful to find so many worthwhile topics and such a wealth of practical detail included in *Neutron Activation Analysis*. The treatment throughout is clear and the illustrations are abundant. There is an excellent chapter on radiochemical separations (82 pp.) and about half the chapter entitled "Analysis without chemical separation" comprises a valuable sub-section (26 pp.) on the use of computers. Non-specialists will find the chapter on sample and standard preparation (62 pp.) most helpful.

There are also sizable chapters on such topics as neutron induced reactions (72 pp.), the growth and decay of radioactivity (37 pp.), systematic errors (57 pp.), and the statistical interpretation of results (65 pp.). Many may think it quite proper that about one quarter of the book should be devoted to these subjects; but, with an eye on the price, my own feeling is that these chapters—although undeniably useful—need not have been so long.

The authors have wisely decided not to attempt to provide a selection of detailed methods. Instead, they have prepared a long table of applications, the list being arranged according to the element determined and the matrix. From this, the reader is referred back to a compilation of some 3000 references, the latest of which would appear to be dated 1968. The tabulation and reference list together make up a chapter (~180 pp.).

All in all, this is a very readable book and the comprehensive nature of its contents is impressive. It should appeal, for totally different reasons, to both specialists and non-specialists. I have no hesitation in suggesting that those who can afford it should buy it.

C. L. Graham (Birmingham)

PUBLICATIONS RECEIVED

ICSU Abstracting Board, *Proceedings of the Full Board Meeting, June 1972, Ustaoset, Norway*, 286 pp., US $ 15.00 plus postage from ICSU Abstracting Board Secretariat, 17 rue Mirabeau, 75016 Paris, France.

Contents:
1. A detailed description of the activities of the Board.
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