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Vol. 64, No. 3	May 1973	**(completing Vol. 64)**
Vol. 65, No. 1	June 1973	
Vol. 65, No. 2	July 1973	**(completing Vol. 65)**
Vol. 66, No. 1	August 1973	
Vol. 66, No. 2	September 1973	
Vol. 66, No. 3	October 1973	**(completing Vol. 66)**
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By J. FOUCHIER, F. BILLET and H. EPSTEIN

1970. 1488 pages. Dfl. 130.00 (about US$45.60)

Since the first edition appeared in 1953, this dictionary has become known to almost every scientist working in the field of chemical and industrial engineering. Although the emphasis is on the industrial and engineering side of chemistry, this work has proved to be of great value to each chemist in general and also to many physicists.

As the greater proportion of chemical publications is written in English, French or German, this dictionary has been kept trilingual. Another practical point is that the authors, in order to solve the difficulties involved in nomenclature, sometimes refer to commercial names (trade marks) or to a chemical formula, which should permit the reader to recognize the product as such.

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– Scientia –

Man darf überzeugt sein dass auch diese Auflage bei den Chemikern und auch bei Übersetzungsabteilungen viele Freunde finden wird.

– Seifen-Öle-Fette-Wachse –

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The Vapour Pressures of Pure Substances

Selected Values of the Temperature Dependence of the Vapour Pressures of Some Pure Substances in the Normal and Low Pressure Region.

by TOMÁS BOUBLÍK, *Czechoslovak Academy of Sciences, Prague,*
VOJTECH FRIED, *Brooklyn College of the City University of New York,*
and ERUARD HÁLA, *Czechoslovak Academy of Sciences, Prague.*

1973. 632 pages. Dfl. 75.00 (about US$26.30). ISBN 0-444-41097-X

The saturated vapour pressure is one of the more important physicochemical properties of pure compounds. In this book an extensive set of experimental vapour pressure data is collected; in addition smoothed values of the vapour pressures, as obtained by fitting the data to the Antoine equation, are presented together with the calculated boiling points and sets of the Antoine constants for each compound.

These constants provide in themselves condensed information on the phase behaviour, very suitable for practical application, while deviations of the smoothed from the experimental pressures and standard deviations (also listed) indicate the accuracy of measurements and the reliability of the equation with the given set of constants.

The choice of systems presented in the tables was governed by the availability and quality of the experimental data, and partly by the practical importance of the system in question.

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Developments in Inorganic Nitrogen Chemistry, Volume 2

edited by CHARLES B. COLBURN, *Department of Chemistry, School of Arts and Sciences, Auburn University, Alabama, U.S.A.*

1973. 238 pages. Dfl. 100.00 (about US$35.10) ISBN 0-444-40962-9

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Analytica Chimica Acta, 66 (1973) 1–3

ANDERS RINGBOM

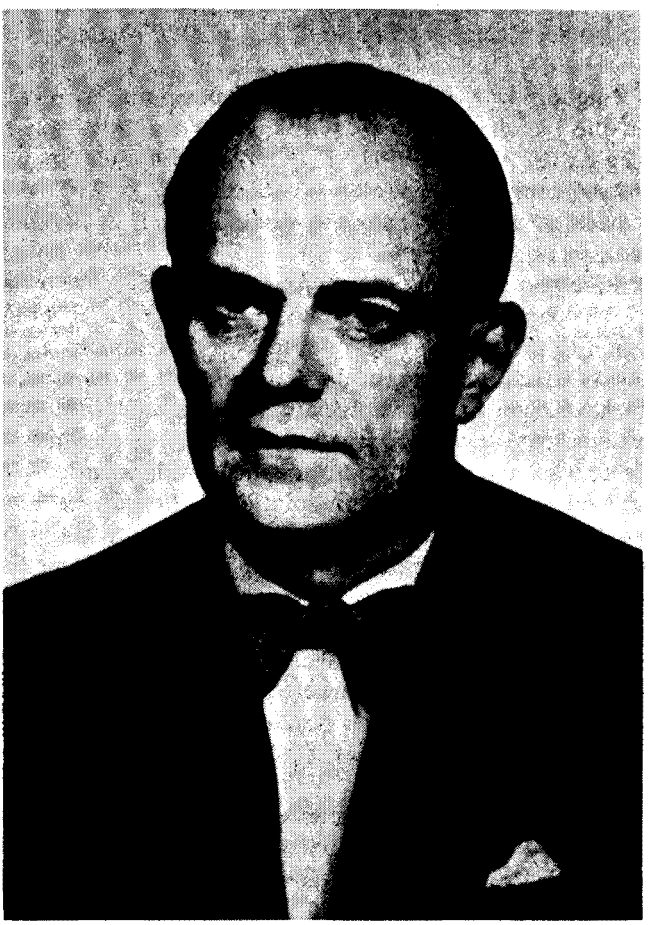
1903–1972

Professor Anders Ringbom died suddenly in Åbo, Finland, on December 21, 1972.

Anders Ringbom was born in Åbo 1903. After going to school in the same city, he entered the Faculty of Chemical Engineering at Åbo Akademi where he received the degrees of M.Sc. in 1925 and Dr.Sc. in 1936. When he retired on January 1, 1969, he could look back on 42 active years at Åbo Akademi, first as research and teaching assistant, later as lecturer and finally as Professor of Analytical and Inorganic Chemistry.

His scientific contributions bear witness to his deep knowledge and outstanding ability. His papers are characterized by clarity of thought and presentation and by a rare ability for finding elegant solutions to complicated problems. The treatment is always based on theoretical calculations. It is therefore not surprising that his papers have been highly appreciated among analytical chemists. Several of his contributions may now be considered classics. The greatest achievement of Anders Ringbom was his contribution to the development of the theory of complexiметric analysis of metal ions in solution. He began his research work in this field about 1950 and was soon able to show how the mathematical problems could be solved in a simple and elegant way. He presented his method in the form of a paper and later as a chapter in a large compilatory work. Both received much favorable attention, and Professor Ringbom was invited to several countries to give lectures about the new technique. In 1963 he published the monograph *Complexation in Analytical Chemistry* where different types of chemical analysis were treated according to the principles developed for the complexiметric analysis of metal ions. The book has greatly affected theoretical analytical chemistry all over the world.

In 1966 Finska Vetenskapssocieteten selected Anders Ringbom for the E. J. Nyström award for outstanding scientific contributions. In the same year Abo Akademi awarded him the Harry Elving teacher's grant. In 1969 Svenska Kemistsamfundet honored him with the Torbern Bergman medal for excellent scientific work. He was also a honorary member of the Finnish Chemical Societies, Finska Kemistsamfundet and Suomalaisten Kemistien Seura. At Åbo Akademi, he took an active part in the administration as Vice-president during 1954–57 and as Dean of the Faculty of Chemical Engineering during 1962–66. During the period 1961–65, he was a member of the State Commission for Technological Research, and he was appointed as a permanent adviser on technical education for the period 1965–67 by the Ministry of Education. Professor Ringbom also took an active interest in student organizations. He was president of the student corporation at Åbo Akademi 1953–57 and was elected an honorary member of the corporation in 1957.



After his retirement in 1969 Anders Ringbom remained active in research. He was particularly interested in the determination of equilibrium constants for complexation reactions and was also working on a new edition of his monograph.

Anders Ringbom's ability was often utilized by international organizations. As a member of the Analytical Section of the International Union of Pure and Applied Chemistry, he took an active part in the compilation of solubility product tables for metal sulfides. He was a member of the Editorial Advisory Board of Analytica Chimica Acta from 1961 until his death.

Anders Ringbom was highly regarded as a friend and colleague, not only in Finland but in many countries throughout the world. His pleasant and cheerful personality made everybody enjoy his company. His memory will live among those who had the privilege of being his friends.

Erkki Wänninen

Analytica Chimica Acta, 66 (1973) 5–11

DETERMINATION OF TRACE AMOUNTS OF CHROMIUM BY ATOMIC ABSORPTION SPECTROMETRY WITH A TANTALUM FILAMENT ATOMIZER

TOSHIHISA MARUTA and TSUGIO TAKEUCHI

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya (Japan)

(Received 9th January 1973)

Many attempts have recently been made to use various types of non-flame devices in order to overcome the disadvantages of conventional flame atomizers in atomic absorption spectrometry. Atomizers have been based on carbon furnaces, carbon filaments, carbon rods, platinum loops, tungsten loops and tantalum loops[1]. Papers describing the applications of such techniques now appear constantly. However, although non-flame atomization systems have certain advantages, various problems have still to be solved. One of these is poor accuracy caused by appreciable matrix interferences. In a previous paper in this series[2] the interfering effects of various acids on chromium absorption in atomic absorption spectrometry with a tantalum filament atomizer were reported.

In the present study, the effect of various foreign ions on the chromium absorption in atomic absorption spectrometry with a modified tantalum filament atomizer was examined. The mechanism of the interferences observed is discussed below. The tantalum filament atomizer was evaluated as a practical means of determining traces of chromium in aqueous solution, and the determination of chromium in standard steels was studied to evaluate the proposed method.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash AA-1E emission and atomic absorption spectrometer fitted with a Hitachi Model QPD-54 recorder and an HTV R-106 photomultiplier tube was employed. The burner assembly of the system was replaced by a tantalum filament atomizer.

The tantalum filament atomizer and the pyrex glass chamber used are shown in Fig. 1. The chamber, with optical-quality silica windows, was used to enclose the tantalum filament and two electrodes ensuring an argon atmosphere. A small recess was made in the middle of the filament to locate the sample solution. Tantalum was preferred because of its resistivity to most reagents at high temperature and its high melting point. Argon gas was employed as the inert gas sheath. The filament was mounted between two electrodes, and was heated by passing an electric current. The temperature of the filament was controlled by varying the voltage supply to a low voltage transformer by means of a continuously variable transformer.

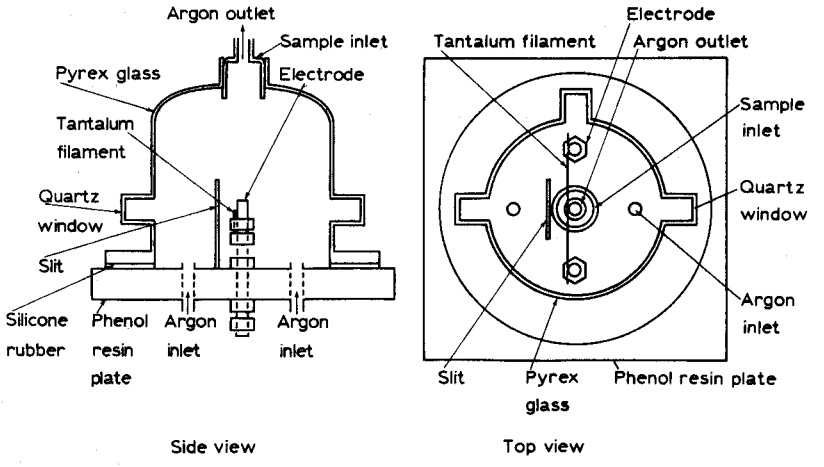


Fig. 1. Tantalum filament atomizer and chamber.

The light source was a chromium hollow-cathode lamp (Hamamatsu TV Co., Ltd.). The radiation from the lamp was electronically modulated at 60 Hz. The optical arrangement was similar to that used for previous atomic absorption spectrometric studies[2] in which the beam of radiation from the hollow-cathode lamp was focused about midway, immediately above the heated filament, and then refocused at the entrance slit of the monochromator. The optimal monochromator slit width for chromium was 150 μm. The 357.9-nm chromium resonance line was used.

Reagents

Stock solutions of chromium(VI) and (III) were prepared as described previously[3]. Stock solutions of iron, cobalt, nickel, copper, aluminum and manganese were prepared from the high-purity metals. Magnesium, calcium and strontium stock solutions were prepared from their metal carbonates dissolved in hydrochloric acid. Stock solutions of molybdenum and vanadium were prepared from ammonium molybdate and ammonium metavanadate, respectively.

All the reagents were of analytical-reagent grade, and the water was distilled and then de-ionized.

Solutions of lower concentrations were prepared by successive dilution with water just before use. Each dilute solution was 0.02 *M* in hydrochloric acid.

Procedure

The filament was heated to 2150° in an atmosphere of argon for about 2 s to remove any unwanted contamination on its surface.

The sample solution (0.5 μl) was placed in the recess of the filament by means of a Hamilton microsyringe. The absorption chamber was freed of air by argon flowing through it for 1 min. By passing a low current (*ca.* 3 A at 0.4 V) through the filament, the solvent was completely vaporized in 20 s without vaporization of the sample salts. The power was switched off, and the filament was allowed to cool for 30 s. This stage was necessary to obtain high absorption signals. Atomization of the sample was effected at high power levels (35–80 W). All atomic absorption signals

were recorded. The height of the absorption signal was used to determine the concentration of chromium. Details of other manipulation procedures are given elsewhere[2]. Argon was supplied to the chamber at a flow rate of 2 l min^{-1}.

RESULTS AND DISCUSSION

Relation between power level and filament temperature

The relationship between the power level supplied to the tantalum filament and the temperature attained by the filament is shown in Table I. The power supplied to the filament was estimated from current–voltage measurements and the temperature attained by the filament was measured with an optical pyrometer. The high power level (80 W) was sufficient to heat the filament to 2400° in less than 1 s after switching on.

TABLE I

RELATION BETWEEN POWER LEVEL AND FILAMENT TEMPERATURE

Power level (W)	35	50	65	80
Filament temp. (°)	1650	1900	2150	2400

Effect of filament temperature on chromium absorption signal

The manner in which the signal strength varies with the filament temperature is shown in Fig. 2. The absorption signal observed was transient: the rise of the absorption signal from its background noise level to the maximum was achieved in about 0.5 s. The highest absorption signal was obtained when the filament temperature level (1650°) was the lowest. A certain drop in peak height was observed at the higher filament temperature levels, and this can be attributed to the sluggish response of the detection amplification systems used for measuring transient signals. At high temperature levels, the chromium atoms came off so rapidly that the amplifier used lagged behind the atomization process, yielding absorption peak distortion.

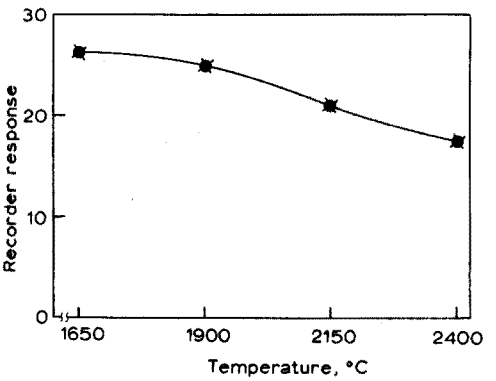


Fig. 2. Effect of tantalum filament temperature on chromium absorption signal. (●) 3 ng Cr(III); (×) 3 ng Cr(VI).

Analytical calibration curves and detection limit

The chromium absorption obtained at two filament temperature levels (1900° and 2150°) is plotted against the weight of chromium taken in Fig. 3. It can be seen that the graphs are linear up to 4 ng, but then curve with increasing amounts of chromium. This is probably mainly due to a sluggish response of the amplifier to a transient signal, for the distortion of the peak height will increase with increasing height of the peak. Figures 2 and 3 also show that the height of the absorption peak for chromium was independent of valency state (III) or (VI) for these ranges.

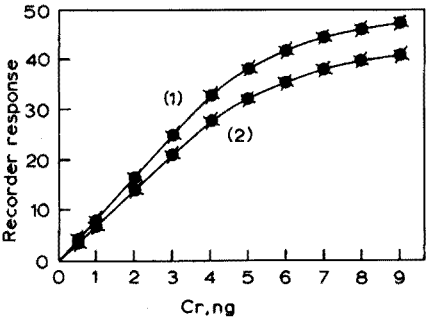


Fig. 3. Analytical calibration curves for chromium. (●) Cr(III); (×) Cr(VI). (1) Filament temperature of 1900°; (2) filament temperature of 2150°. Flow rate of argon, 2 l min^{-1}.

The detection limit is defined as the amount of chromium at which the peak height is equal to twice the background noise. The detection limit in this method was $9.4 \cdot 10^{-11}$ g. Sensitivity is taken as the amount of chromium which would produce a 1% change in absorption over the linear part of the calibration curve. The sensitivity in this technique was $5.2 \cdot 10^{-11}$ g.

The proposed technique is very rapid as the time for a complete single analysis of the aqueous sample was only 2 min. There are no memory effects between determinations. The most prominent advantages of the proposed method of atomization are its high sensitivity, simplicity and rapidity.

Reproducibility

Aliquots (0.5 μl) of a 6-p.p.m. chromium solution were repeatedly analyzed under optimized conditions to estimate the reproducibility of the method. The coefficient of variation calculated from ten determinations was 2.8%. It is reasonable to suppose that this technique should lend itself to routine analysis, if interferences could be eliminated under suitable conditions.

Interferences studies

The effects of various metals on the absorption signal from a 6-p.p.m. chromium solution were measured at various temperatures. Solutions of chromium (6 p.p.m.) containing 100-, 50- or 10-fold weights of 12 different foreign ions were employed. The results obtained are summarized in Table II. Only interferences which resulted in a change of absorption signal of more than 5% were taken to be significant.

TABLE II

INTERFERENCES OF VARIOUS FOREIGN IONS ON CHROMIUM(III) ABSORPTION[a]

($3 \cdot 10^{-9}$ g Cr were used with 100-, 50- and 10-fold weight amounts of added ion)

Ion added	*Temp. (°)*	*% Change in signal*[b]			*Ion added*	*Temp. (°)*	*% Change in signal*[b]		
		100	*50*	*10*			*100*	*50*	*10*
Na	1900	0	0	0	Mo	1650	+33	0	0
	2400	0	0	0		1900	+23	0	0
Mg	1650	− 71	−65	−10		2150	+18	0	0
	1900	− 61	−56	0		2400	0	0	0
	2150	− 40	−33	0	Mn	1900	0	0	0
	2400	− 22	−16	0		2400	0	0	0
Ca	1650	−100	−86	−19	Fe	1900	0	0	0
	1900	−100	−84	−16		2400	0	0	0
	2150	−100	−70	−14	Co	1650	−55	−24	0
	2400	− 93	−65	−11		1900	−48	−20	0
Sr	1650	−100	−81	−17		2150	−36	−15	0
	1900	−100	−71	−15		2400	−25	−10	0
	2150	−100	−67	−12	Ni	1650	−49	−20	0
	2400	− 88	−48	−9		1900	−40	−15	0
Al	1900	0	0	0		2150	−27	−12	0
	2400	0	0	0		2400	−18	−8	0
V	1650	+65	+55	+42	Cu	1900	0	0	0
	1900	+40	+37	+25		2400	0	0	0
	2150	+31	+26	+18					
	2400	0	0	0					

[a] Interferences of various foreign ions on chromium(VI) absorption were essentially the same.
[b] Each value represents the average of five values.

No interferences of iron, copper, manganese, aluminum or sodium on either chromium(III) or chromium(VI) absorptions were observed in the atomizer, irrespective both of concentrations of these foreign ions and of the filament temperature levels. Iron did not interfere even at a 300-fold amount. Yanagisawa *et al.*[4] reported that iron, copper, manganese, aluminum and sodium caused serious interferences on chromium absorption in the air–acetylene flame. The interferences obtained with the tantalum filament atomizer are widely different from those observed with the conventional flame. It seems reasonable to consider that in the atmosphere of argon gas in the atomizer there will be little difficulty in producing atoms of elements such as aluminium, iron, etc., which form refractory oxides in flame media.

It can be seen from Table II that no interference was observed from any of the metal ions investigated at the 10-fold level with the exception of alkaline earth elements and vanadium. The degree of the interferences observed decreased with increasing temperature level attained by the filament. At high temperature (2150°), no interference of vanadium on chromium absorption was observed at 2-fold concentrations. Vanadium and molybdenum gave marked enhancing effects on chromium absorption at low filament temperatures, but at the high temperature (2400°) no interferences were observed from these ions even in 100-fold amounts. The enhancing effects may be explained by a greatly increased rate of dissociation

of chromium compounds in the presence of vanadium or molybdenum at relatively low filament temperatures. The high temperature level (2400°) may be effective in dissociating chromium salts even in the absence of vanadium or molybdenum.

Talmi and Morrison[5] reported that calcium chloride caused light losses at the wavelength measured with the graphite crucible atomizer; the losses were attributed to Rayleigh light scattering. Ebdon *et al.*[6] found that relatively volatile elements such as magnesium gave serious depressing effects on manganese absorption with the carbon filament atom reservoir. In this work, the depressing effects of magnesium, calcium, strontium, cobalt and nickel in the tantalum filament atomizer cannot be explained by a simple theory at the present time.

So further study is necessary to explain the mechanism by a coherent theory. From a practical standpoint, it is evident that interferences may be minimized by using the high filament temperature level. However, the loss of signal intensity which results from high filament temperatures must be balanced against the benefits of lower interference.

Determination of chromium in steel

The sample (0.1000 g) was dissolved in hydrochloric and nitric acids, and the solution was boiled to remove all oxides of nitrogen; enough hydrochloric acid was added to make the final acidity about 0.02 *M* and the solution was diluted to 200 ml with water. Volumes of 0.5 μl of each sample were atomized at a filament temperature of 2150°. The results obtained are shown in Table III together with the certificate values. It can be seen that this method is quite satisfactory from the point of view of accuracy and precision. At least for the steels studied, the method was free from matrix effects.

TABLE III

DETERMINATION OF CHROMIUM IN STEEL

No.	*Sample*[a]	*Certificate value (%)*	*Found*[b] *(%)*	*Coefficient of variation (%)*
1	500-2 Cr–Mo steel	1.10	1.08 ± 0.04	3.7
2	507-2 Cr–Mo steel	0.98	0.96 ± 0.04	4.2
3	501-2 Cr–Mo steel	1.03	1.00 ± 0.03	3.0
4	508-2 Ni–Cr steel	0.76	0.80 ± 0.03	3.8
5	510-2 Ni–Cr–Mo steel	0.44	0.48 ± 0.02	4.2
6	515-2 SNC 21	0.36	0.33 ± 0.01	3.0
7	514-2 SCM 22	1.07	1.03 ± 0.04	3.9
8	153-2 Alloy steel	1.01	1.06 ± 0.03	2.8
9	152-2 Alloy steel	0.52	0.50 ± 0.02	4.0

[a] Japan Standards for iron and steel.
[b] Average of five analyses.

SUMMARY

The sample solution containing chromium was vaporized and atomized from a tantalum filament by electrical heating into an argon stream within an absorp-

tion chamber. The interference of various metals on the atomic absorption spectrometry of chromium was investigated. Interferences were minimized by using a high filament temperature. The flameless atomizer was used for the determination of chromium in steel at a filament temperature of 2150°; with the steels investigated no matrix effect was observed, and the accuracy and precision were satisfactory.

RÉSUMÉ

On propose une méthode de dosage du chrome à l'état de traces, par spectrométrie par absorption atomique, avec atomiseur à filament de tantale. On examine l'influence de divers métaux. Les interférences sont réduites au minimum en portant le filament à des températures élevées. L'atomiseur sans flamme a été utilisé pour le dosage du chrome dans l'acier à une température de filament de 2150°. Aucun effet de matrice n'a été observé avec les aciers examinés; exactitude et précision sont satisfaisantes.

ZUSAMMENFASSUNG

Die chromhaltige Probenlösung wurde mittels eines elektrisch geheitzten Tantalfadens in einem Argonstrom innerhalb einer Absorptionskammer verdampft und atomisiert. Die Störungen verschiedener Metalle bei der Atomabsorptionsspektrometrie von Chrom wurden untersucht. Die geringsten Störungen traten bei hoher Heizfadentemperatur auf. Der flammenlose Atomisator wurde auf die Bestimmung von Chrom in Stahl bei einer Heizfadentemperatur von 2150° angewendet. Bei den untersuchten Stählen wurde kein Matrixeffekt beobachtet, und die Genauigkeit und Reproduzierbarkeit waren zufriedenstellend.

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1 See, *e.g.* G. F. Kirkbright, *Analyst*, 96 (1971) 609.
2 T. Maruta and T. Takeuchi, *Anal. Chim. Acta*, 62 (1972) 253.
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5 Y. Talmi and G. H. Morrison, *Anal. Chem.*, 44 (1972) 1455.
6 L. Ebdon, G. F. Kirkbright and T. S. West, *Anal. Chim. Acta*, 58 (1972) 39.

Analytica Chimica Acta, 66 (1973) 13–21

THE DETERMINATION OF CADMIUM BY ATOMIC ABSORPTION IN AIR, WATER, SEA WATER AND URINE WITH A R.F. CARBON BED ATOMIZER

J. W. ROBINSON*, D. K. WOLCOTT, P. J. SLEVIN and G. D. HINDMAN
Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)
(Received 18th November 1972)

In recent years, there has been a great deal of concern about the environmental and biological effects of heavy metal pollution. This concern has been so great as to generate interest even in the popular literature[1]. In order to evaluate the effects of heavy metal pollution it is necessary to measure the levels of these pollutants in the air, in fresh and salt water systems, in soils, and in biological systems.

There is a variety of analytical techniques available which can be used for these analyses individually, but there are few or none which can be applied to all of these varied sample types without extensive sample preparation (*i.e.*, dissolution, solvent extraction, etc.).

The object of this work was to develop a procedure capable of handling gas or liquid samples with the minimum of equipment modification and with an analytical sensitivity down to the p.p.b. range for sample volumes in the microliter range.

Atomic absorption has excellent selectivity, and the various flameless techniques recently introduced[2–6] have generally improved the sensitivity. However, most of these flameless techniques are limited to liquid samples.

The system used has been previously described[6–9]. It offers the advantages of higher sensitivity, and the capability to do direct air analysis[6–8]. This paper describes how the atomization system has been extended to liquid samples such as water, sea water and urine.

EXPERIMENTAL

Equipment

The following equipment was used: R.F. generator (Lepel Model); monochromator (Jarrell-Ash 0.5-m Ebert); optical pyrometer (Leeds-Northrup Company); filament transformer (General Electric 34J243 110 V input, 6.3 V output); variable transformer (Staco Inc. 2PF751 0–8 S rated).

The detector and readout system required a IP28A photomultiplier tube, a Jarrell-Ash broad-band a.c. amplifier, and a Beckman 10-in stripchart recorder. The optics were Suprasil Phano-convex quartz lenses, 10 cm focal length, and Suprasil 0.5-in diameter quartz flat cell windows.

* Address all correspondence to this author.

Air sampling network (Fig. 1). Compressed air tank, input rotameter, calcium chloride scrubber, activated charcoal scrubber, millipore filter, and constant-pressure sampling head.

Platinum loop liquid injector (Fig. 2). Variable transformer, ammeter, filament transformer, and 20 gauge platinum wire loop.

Direct drop liquid injector (Fig. 3). Hamilton 10-μl syringe with 3-in needle.

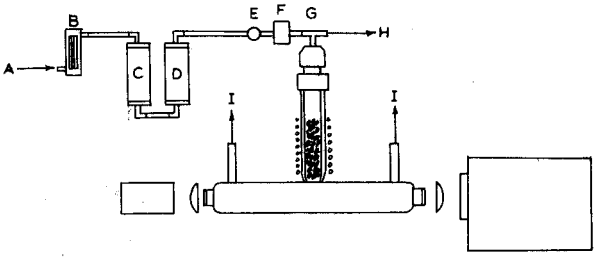

Fig. 1. Air sampling network. (A) Compressed air inlet, (B) flowmeter, (C) calcium chloride drying tube, (D) activated charcoal scrubber, (E) valve, (F) millipore filter, (G) "T" adapter, (H) excess clean air out or ambient air in, (I) exhaust ports.

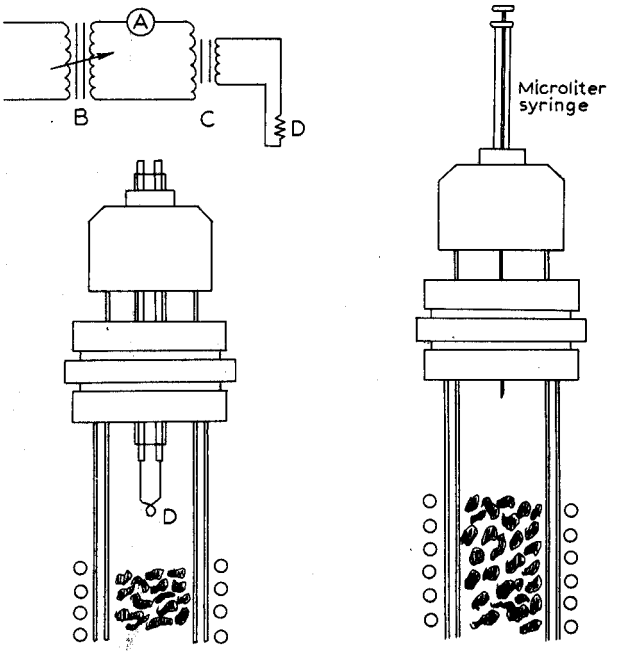

Fig. 2. Platinum loop injector. (A) Ammeter, (B) variable transformer, (C) filament transformer, (D) platinum loop.

Fig. 3. Direct drop injector.

Chemicals and solutions

Cadmium stock solution (1000 μg ml^{-1}). Dissolve 1.000 g of cadmium metal (A. D. Mackay and Co.) in the minimal volume of concentrated hydrochloric acid and dilute to 1 l with 1% (v/v) hydrochloric acid. Prepare more dilute solutions daily

by dilution of the stock solution with distilled water. All solutions were stored in polyethylene bottles and vials. No solutions were stored overnight in order to avoid plating-out problems.

Air samples

The system depicted in Fig. 1 was used for measurement of ambient air signals. To provide a source of cadmium-free air, compressed air was passed through calcium chloride to remove water vapor, and through activated charcoal and a millipore filter to remove molecular and particulate cadmium contamination. The clean air stream then passed through a "T" adapter at 1.5 l min^{-1}. The exhaust pump then pulled air from this stream when valve E was open at 0.5 l min^{-1}. When valve E was closed, ambient air was drawn into the atomizer at H.

After measurement of the total absorption signal at the cadmium 228.8-nm resonance line, the Barnes demountable hollow cathode was replaced by a hydrogen lamp to determine the degree of molecular background. The atomic absorption was the difference between the two signals.

The data obtained for ambient air are presented in Table I.

Liquid samples

Two systems of liquid sampling were used. The first utilized a platinum loop which was used only for vaporization of the sample. The more difficult step of atomization was accomplished by the bed of hot carbon (Fig. 2).

In operation, a 4-μl sample was syringed directly onto the platinum loop, which was then lowered to *ca.* 5 cm from the hot carbon. The loop was allowed to dry by radiant heating, then current was passed through to drive off the metal sample. The loop was maintained at incandescence (*ca.* 1600° as measured by optical pyrometer) until the absorbance signal had passed. A second burn was carried out to ensure that all cadmium had actually been removed from the loop. The results obtained with the platinum loop injector are given in Table II.

In the second system for liquid sampling (Fig. 3), a 4-μl sample drop was allowed to fall directly on to the top of the hot carbon, where vaporization and atomization occurred. The results of the direct drop injection technique are also given in Table II.

In both cases of liquid samples, replicate samples were run using the Barnes demountable hollow cathode and a hydrogen lamp to ascertain the degree of molecular absorption.

TABLE I

ANALYSIS OF AIR SAMPLES

Sample date	*Absorbance*	*Conc. ($\mu g/m^3$)*
Aug. 24, 1972[a]	$0.027 + 0.005$	0.020 ± 0.004
Aug. 25, 1972[b]	0.044 ± 0.008	0.035 ± 0.005

[a] Immediately after heavy rain.
[b] Weather hot, clear, sunny.

TABLE II

ANALYSIS OF LIQUID SAMPLES

Sample (4 μl)	*Absorbance measured*	
	Direct drop method	*Pt loop method*
Deionized water	0.131	0.014
Deionized water + 10^{-3} μg Cd ml^{-1}	0.242	0.050
Deionized water + $2.5 \cdot 10^{-3}$ μg Cd ml^{-1}	0.276	—
Deionized water + $7.0 \cdot 10^{-3}$ μg Cd ml^{-1}	0.346	—
Deionized water + 10^{-2} μg Cd ml^{-1}	0.432	0.130
Deionized water + 10^{-1} μg Cd ml^{-1}	1.301	0.167
Diluted sea water (9:1)	0.468	0.180
Diluted urine sample (9:1)	0.337	0.130

RESULTS AND DISCUSSION

Air samples

The direct determination of atmospheric cadmium has previously been reported by this laboratory[6]. However, there have been modifications to the atomization system which have resulted in a five-fold increase in sensitivity. Instead of using carbon rods in the atomizer, small carbon chips (0.25 × 0.5 in) were used, thus providing a greater surface area for atomization reactions. Also, because of the effect of geometrical size on the R.F. coupling efficiency, the smaller chips allowed the attainment of higher temperatures (1500° compared to 1350°). Further, lower air-flow rates were used (475 cm^3 min^{-1} compared to 1200 cm^3 min^{-1}). With these modifications, a 1% cadmium signal resulted from an ambient air concentration of 0.005 μg m^{-3} (previous limit = 0.02 μg m^{-3}).

Results of measurement of cadmium in air samples in Baton Rouge are shown in Table I. Of particular interest is the effect noted of cadmium pollution reduction by rainfall. Cadmium signals after a heavy rain were reduced almost 50%.

Liquid samples

Atomization. The results obtained with the platinum loop are indicated by Fig. 4. The characteristic concentration (1% absorption) was shown to be about 10^{-13} g Cd. However, the results were imprecise. It was felt that the major problem was the lack of ability to vaporize the sample off the loop in a reproducible manner. Some improvement in precision might result from better control of the loop heating cycle. However, the results illustrated the use of the platinum wire–carbon-bed combination for liquid analysis.

In an attempt to overcome problems involved in the platinum loop atomization step, liquid samples were dropped directly onto the hot carbon rods. The optimal sample size for the equipment used was 4 μl. Smaller samples would have been desirable to reduce the background but smaller samples could not be dropped reproducibly from the syringe.

The results attained were encouraging. The purest water available gave an absorption signal of 26%. Molecular absorption was shown to be no greater than

5%. Calibration curves were made up by adding known quantities of cadmium to "pure" water. The absorptions by the resultant solutions were measured and a calibration curve was obtained (Fig. 4).

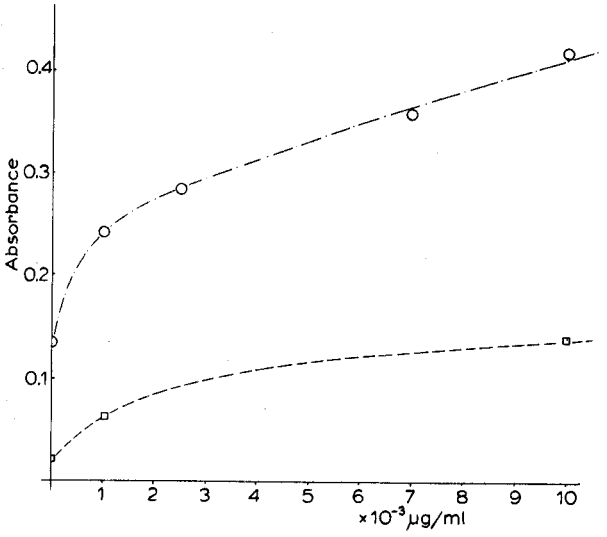

Fig. 4. Calibration curves. (○) Direct drop injection; (□) platinum loop injector.

Urine samples. The direct drop method was used to determine the cadmium level in urine. A 4-μl untreated sample was dropped directly on to the carbon bed. A typical absorption trace is shown in Fig. 5. The results showed that untreated samples were too concentrated to be analyzed directly. The absorption traces with a hollow-cathode source indicated total absorption by the sample. The absorption trace with a hydrogen lamp gave evidence of matrix effects from the high salt content of the sample. Both traces showed that the degree of absorption was too high to be useful. A (1+9) dilution with deionized water solved the problem.

The analysis of the sample used showed the presence of $1 \cdot 10^{-2}$ μg Cd ml^{-1} in the urine sample.

Sea water samples. Samples (4 μl) were dropped directly onto the hot carbon. The results are illustrated in Fig. 6. In a similar pattern to the urine samples, the absorption of the hydrogen lamp radiation showed considerable molecular absorption or scattering. But the atomic absorption signal (which includes molecular absorption) showed very high net atomic absorption. As with the urine sample, the sample was diluted (1+9) with deionized water and then analyzed by direct drop injection. The analysis of the sample showed the presence of $7 \cdot 10^{-2}$ μg Cd ml^{-1} in the sample.

Background correction

Molecular or broad-band absorption occurred for every type of sample tested. The method used for background correction in this laboratory was cumbersome, but more convenient methods have been published[10,11]

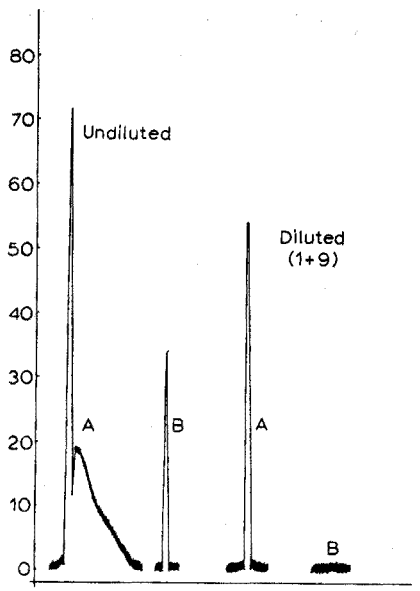

Fig. 5. Absorption traces for urine sample. (A) Demountable hollow cathode; (B) hydrogen continuum lamp.

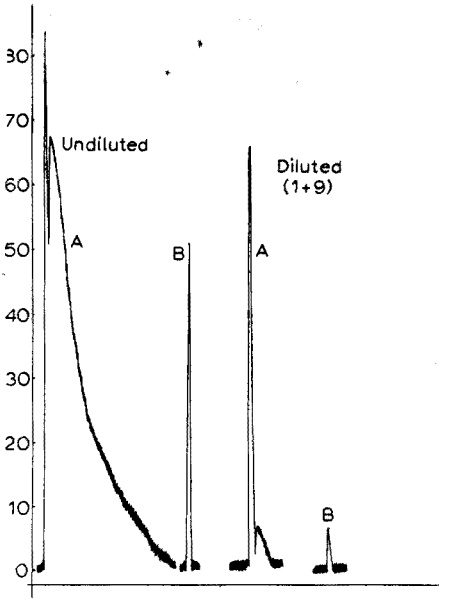

Fig. 6. Absorption traces for sea water sample. (A) Demountable hollow cathode; (B) hydrogen continuum lamp.

Chemical interferences

Chemical interferences were studied by making up solutions containing 10 ng Cd ml^{-1} and 1 p.p.m. of interferent, *i.e.* a 100-fold excess. All interfering ions were present as sodium salts.

No interferences were found from the following ions: MoO_4^{2-}, NO_3^-, SiO_3^{2-}, SO_4^{2-}, TeO_3^{2-}, VO_3^-, WO_4^{2-}, F^-, Br^-, I^- and Cl^-. A slight depression of the absorption signal was noted in the presence of perchlorate, and a more severe (30%) depression of signal was encountered when borate was present.

Removal of the solvent from the sample by preheating

When the carbon filament technique[4] is used, the sample is loaded and heated directly to drive off the solvent. A large molecular absorption signal is usually obtained from the solvent. This molecular signal is so great that the atomic absorption signal is not measurable if it is carried out simultaneously. Hence, preheating to drive off the solvent is necessary before atomic absorption measurements can be made.

In contrast to the carbon filament technique, when the R.F. heater and the carbon bed is used, the solvent is burned, usually to carbon monoxide and hydrogen which do not absorb at wavelengths below 200 nm. (Incomplete combustion would lead to molecular absorption by the fragments, so it is necessary to ensure complete combustion to obtain best results.)

In an attempt to emulate the carbon filament technique, liquid samples (5

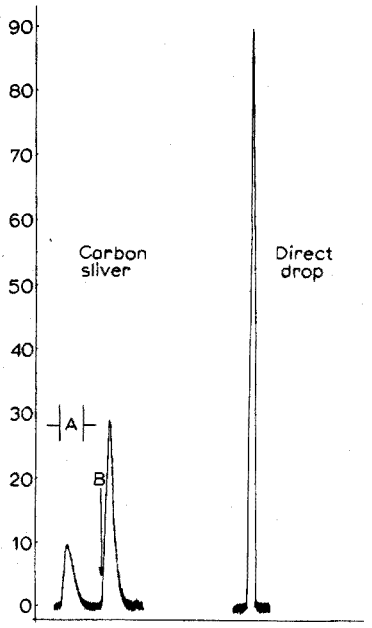

Fig. 7. Comparison of carbon sliver and direct drop injections. (A) Drying at 6 cm above carbon bed; (B) injection of dried sliver onto carbon bed.

μl) were loaded onto slivers of carbon and dropped directly onto the carbon bed. A typical absorption trace is shown in Fig. 7. Some molecular absorption was evident but the degree of absorption was not extensive, and with modified equipment might be corrected for without a drying step; this should lead to a significant increase in accuracy.

Similar slivers of carbon impregnated with the sample were preheated for various times and temperatures to dry off the solvent. Results showed that in every case, cadmium was lost in the drying stage. This illustrated that a very accurate heating and timing program of drying would be vital in order to get reproducible results by the carbon filament technique. It is conceded that if a constant percentage of the cadmium was lost in this operation that a calibration curve would correct the error. But, in practice, variation in carbon filament electrical resistance (and hence temperature), line voltage, program timing, etc., would lead to variations in the loss of cadmium during drying, and hence introduce an error.

The virtual removal of the molecular absorption signal permits analyses to be carried out without a preheating step. This greatly simplifies the technique and improves accuracy and precision.

In addition, the direct drop technique also provides an excellent opportunity for automating the non-flame atomic absorption system. The short time required for sampling, coupled with a device such as the Hamilton automatic injector, should allow completely automatic analysis of trace metals at the p.p.b. level. We intend to pursue this line of study with simultaneous background correction.

Relative sensitivity of direct drop and carbon sliver technique

Absorption traces obtained from cadmium in drops injected directly onto the carbon bed, and cadmium solution introduced using carbon slivers, are shown in Fig. 7. The concentrations of cadmium were equal in each case. The results show that the direct drop technique was more sensitive than the carbon sliver technique. Difficulty in recovering the cadmium from the carbon was probably the cause of the decreased sensitivity. The results for carbon filament were not obtained directly, but if the problem involves loss of cadmium on the carbon it would be expected that a similar loss would be encountered with a carbon filament. It should be emphasized that the results obtained in this work cannot be used as a direct measure of this loss in carbon filaments because the latter are operated at higher temperatures which would diminish the loss. However, they are indicative of basic sensitivity problems.

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SUMMARY 6

The analytical parameters are described for the determination of cadmium by atomic absorption in air, water, sea water, and urine. The technique involves the use of an R.F. generator which heats up a carbon bed to approximately 1400°. This sample is reduced to free metal atoms and is analyzed directly afterwards. The atomization step and the measuring step are separate steps in this procedure. Detection limits of 10^{-13} g were reached. Quantitative analyses were carried out on the types of samples indicated.

RÉSUMÉ

Les paramètres analytiques sont décrits pour le dosage du cadmium par absorption atomique, dans l'air, l'eau, l'eau de mer et l'urine. On utilise un support de carbone chauffé à 1400° environ. L'échantillon réduit en atomes métalliques libres est analysé ensuite directement. On peut atteindre des limites de détection de 10^{-13} g. Des analyses quantitatives ont été effectuées.

ZUSAMMENFASSUNG

Es werden die analytischen Parameter für die Bestimmung von Cadmium in Luft, Wasser, Meerwasser und Urin mittels Atomabsorption beschrieben. Bei dem Verfahren wird ein R.F.-Generator angewendet, der einen Kohlenstoffträger auf etwa 1400° erhitzt. Die Probe wird zu freien Metallatomen reduziert und unmittelbar anschliessend analysiert. Die Atomisierung und die Messung erfolgen bei diesem Verfahren in getrennten Stufen. Es wurden Nachweisgrenzen von 10^{-13} erzielt. Mit den angegebenen Arten von Proben wurden quantitative Analysen ausgeführt.

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THE DETERMINATION OF 2-HYDROXYNICOTINIC ACID AND ITS MAJOR METABOLITE IN BLOOD AND URINE BY SPECTROPHOTOFLUORIMETRY AND DIFFERENTIAL PULSE POLAROGRAPHY

J. ARTHUR, F. de SILVA, NORMAN STROJNY and NANCY MUNNO

Department of Biochemistry and Drug Metabolism, Hoffmann-La Roche Inc., Nutley, N.J. 07110 (U.S.A.)

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The pharmacology of nicotinic acid and its derivatives has been extensively studied and recently reviewed[1]. 2-Hydroxynicotinic acid (I) was first synthesized by Phillips[2] in 1895, and an improved synthesis in higher yields was reported more recently by Taylor and Crovetti[3]. It is one of a series of analogs of nicotinic acid that were synthesized[4] and showed significantly greater pharmacological activity than nicotinic acid in *in-vitro* screening[5,6]. It was also found to be more potent than nicotinic acid in rats as a hypolipidemic agent in the inhibition of cholesterol and fatty acid biosynthesis[7,8]. Studies on the metabolism of the compound in the dog and rat[9] indicated that the major product of biotransformation was the N-1-riboside (II) (Fig. 1).

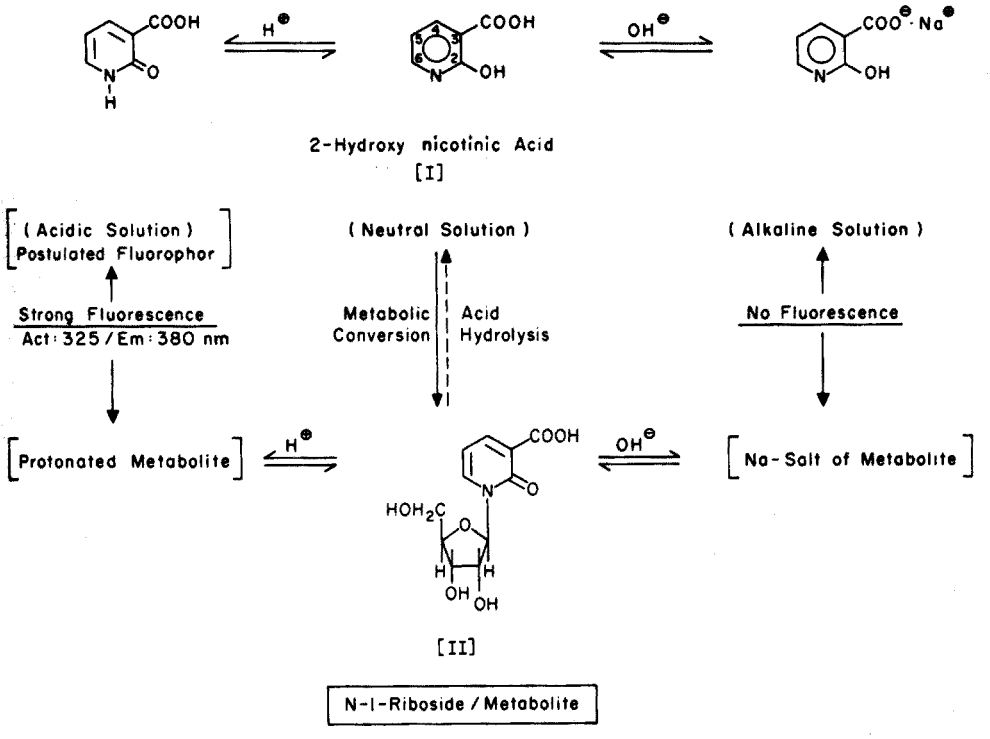

Fig. 1. Chemical reactions of 2-hydroxynicotinic acid (I) and its N-1-riboside (II).

2-Hydroxynicotinic acid is polar and exhibits amphoteric properties owing to the hydroxyl group in position 2 and the carboxyl group in position 3 (Fig. 1). The compound exhibits pK_a values of 5.3 and 12.3. The u.v. absorption spectra (Fig. 2) show strong absorption bands owing to the aromatic nature of the compound. The characteristic shifts seen in the absorption maxima at different pH values are due to the effect of pH on the degree of ionization of the molecule.

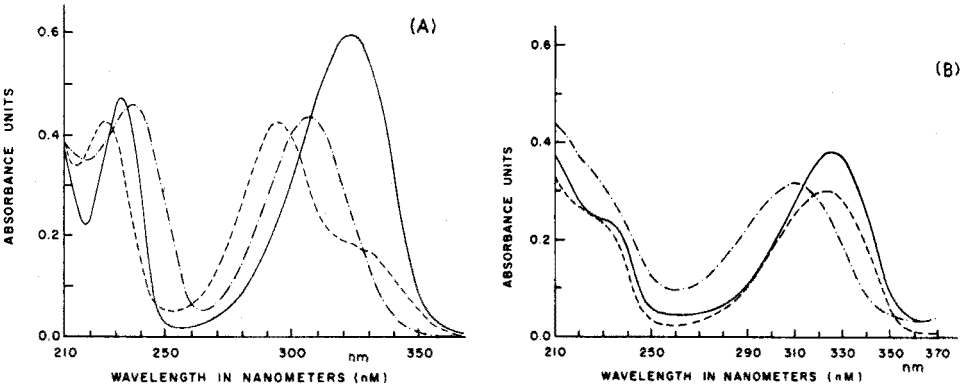

Fig. 2. Ultraviolet absorption spectra of (A) 2-hydroxynicotinic acid and (B) the N-1-riboside. Concentration, 10 μg ml^{-1}. (——) 0.1 *M* HCl; (–·–·) 0.1 *M* NaOH; (– – – –) methanol. A Coleman-Hitachi EPS-3 double-beam ratio-recording spectrophotometer was used.

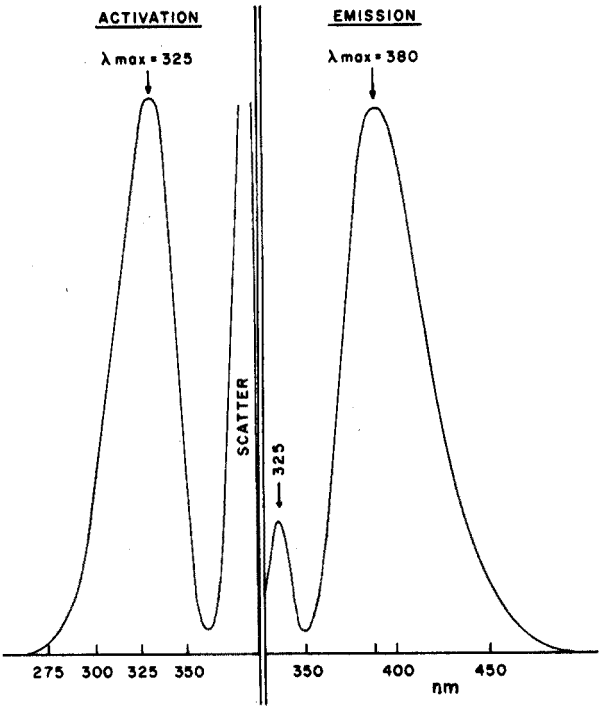

Fig. 3. Excitation/emission spectra of 2-hydroxynicotinic acid in methanol–0.1 *M* HCl (80+20).

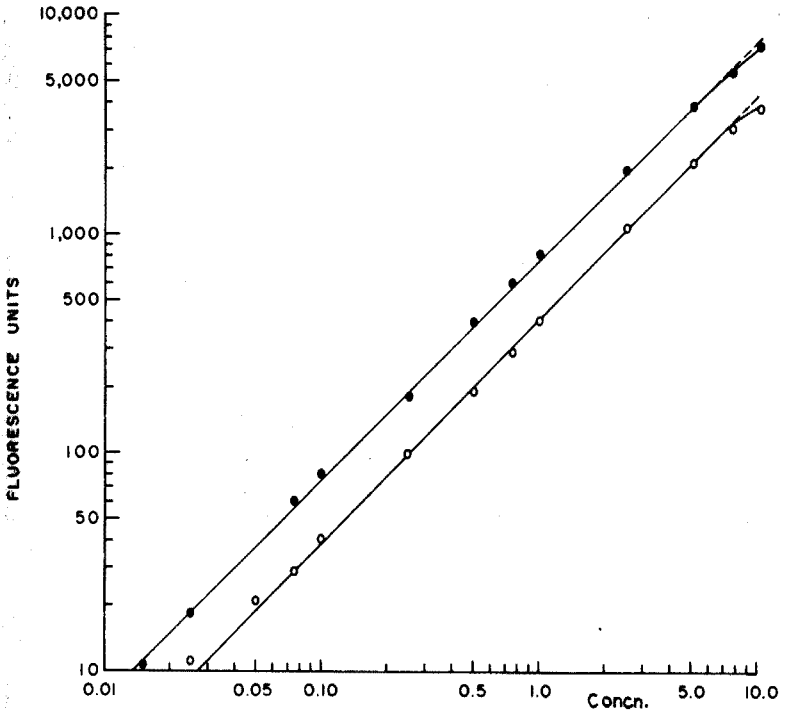

Fig. 4. Linear range of fluorescence *vs.* concentration of 2-hydroxynicotinic acid (●) and its N-1-riboside (○). Concentration is given as μg/5 ml of methanol 0.1 *M* HCl (80+20).

The compound fluoresces intensely in methanol–0.1 *M* hydrochloric acid (80+20) with excitation and emission maxima at 325 nm and 380 nm, respectively (Fig. 3). The fluorescence intensity (quantum yield) is sufficiently high to yield potential sensitivity limits in the nanogram range (Fig. 4). A fluorimetric assay was developed for 2-hydroxynicotinic acid and its major metabolite, the N-1-riboside, in blood and urine by using a thin-layer chromatographic separation step to ensure the specificity of the assay for the intact drug and its major metabolite.

The assay was used to determine the blood levels and the urinary excretion of the drug in man following the administration of single 500-mg oral doses.

EXPERIMENTAL

Standard solutions

2-Hydroxynicotinic acid. $C_6H_5NO_3$; m.w. = 139.1, m.p. = 258–260°; pharmaceutical grade purity, >99%. Weigh out 10.00 mg of the acid, transfer it to 100-ml volumetric flask, and dissolve in and make up to volume with absolute methanol to give a stock solution containing 100 μg ml^{-1}. Make a 1+9 dilution of this stock solution in methanol to yield a working solution containing 10 μg ml^{-1}.

1,2-Dihydro-1-β-D-ribofuranosyl-2-oxonicotinic acid. N-1-riboside metabolite of (I); m.w. = 271.23, m.p. = 212–214°; pharmaceutical grade purity, >99%. Prepare a stock solution and a working solution in methanol exactly as described for 2-hydroxynicotinic acid.

Reagents

All inorganic reagents were of analytical-grade purity (>99%) and were used without further purification. Aqueous solutions were prepared in double distilled water.

1.0 M Sodium phosphate buffer (pH 3.5). Weigh out 142.0 g of disodium hydrogenphosphate, dissolve and dilute to 1.0 l in distilled water. Also dilute 68.5 ml of 85% phosphoric acid to 1.0 l with distilled water. Titrate the phosphate solution with the diluted acid to pH 3.5 (pH meter).

Acetone and *n*-hexane were certified ACS reagent grade.

Instrumentation

All fluorescence measurements were made in a Farrand spectrofluorimeter equipped with a xenon arc energy source and an RCA IP-28 photomultiplier. The 10-nm slit arrangement was used in all four positions. The monochromators were corrected for the fundamental Hg lines, but the fluorescence measurements were not corrected for energy and other instrumental artefacts. The instrument sensitivity was adjusted for maximum energy for each day by means of a quartz reference rod and a standard solution of the compound to be analyzed.

For the polarographic analysis, a Princeton Applied Research Model 174 analyzer was used.

Assay in blood

Into a 15-ml conical glass-stoppered centrifuge tube add 1 ml of blood and 10 ml of acetone and shake on a reciprocating shaker for 10 min. Along with the samples run a control blood specimen and two separate 1-ml specimens of control blood containing internal standards of 1.0 μg of I and 2.0 μg of II (evaporate 100 μl of the working solution containing I and 200 μl of the working solution containing II under a stream of nitrogen at 60° to dryness and dissolve the residue by adding 1 ml of control blood) in parallel with the unknown samples. Centrifuge the samples (25°, 2000 rev min^{-1}) for 10 min, and transfer the supernate (acetone–aqueous layer of *ca.* 9 ml) to another 15-ml centrifuge tube. Concentrate the sample by evaporating off the acetone in the sample by heating at 60° in a water bath under a stream of nitrogen. Re-extract the precipitate by adding 1 ml of water and 5 ml of acetone, re-suspend the precipitate by slurrying it with a clean micro-spatula, shake for 10 min and centrifuge. Combine this extract with the first extraction and concentrate as before to a final volume of 1–2 ml.

To the concentrated supernates add 4 ml of pH 3.5 phosphate buffer, mix well and wash the buffered extract with two 5-ml portions of *n*-hexane by shaking for 10 min on a reciprocating shaker, centrifuging, and aspirating off the hexane. Extract the sample successively with three 5-ml portions of ethyl acetate–*n*-butanol (80+20), shaking for 10 min per extraction, centrifuge at 2000 rev min^{-1}, preferably in a refrigerated centrifuge at 0–5° and combine the extracts in a 15-ml tube by successive evaporation in a hot water bath (60°–65°); finally evaporate to dryness.

Dissolve the residues in 100 μl of isopropanol–chloroform (1+1) and transfer quantitatively onto a 20×20 cm silica gel G chromatoplate (prepared from Mallinckrodt SilicAR (TLC-7GF-5) as the adsorbent) which has been predeveloped in ethyl acetate to a height of 15 cm as a preparative "clean-up" step and re-activated

in a 40° oven for 2 h. To ensure quantitative transfer, re-elute the tubes with another 50 μl of isopropanol–chloroform (1+1) followed by a final elution with a mixture of methanol–water–concentrated ammonia liquor (90+5+5). Apply this solvent mixture with care, using a stream of nitrogen to volatilize the solvent off the plate, and taking care to minimize the spreading out of the spot over a 2-cm^2 area owing to the gelatinous lipid-like material present. The plate can be developed even though the spots are still wet. Develop the chromatoplate twice for 12–15 cm in the ascending mode in a vapor-saturated chamber containing benzene–acetone–glacial acetic acid–water (60+40+5+2.5). Air-dry the plate and then examine under long-wave u.v. light. A typical chromatogram is shown in Fig. 5.

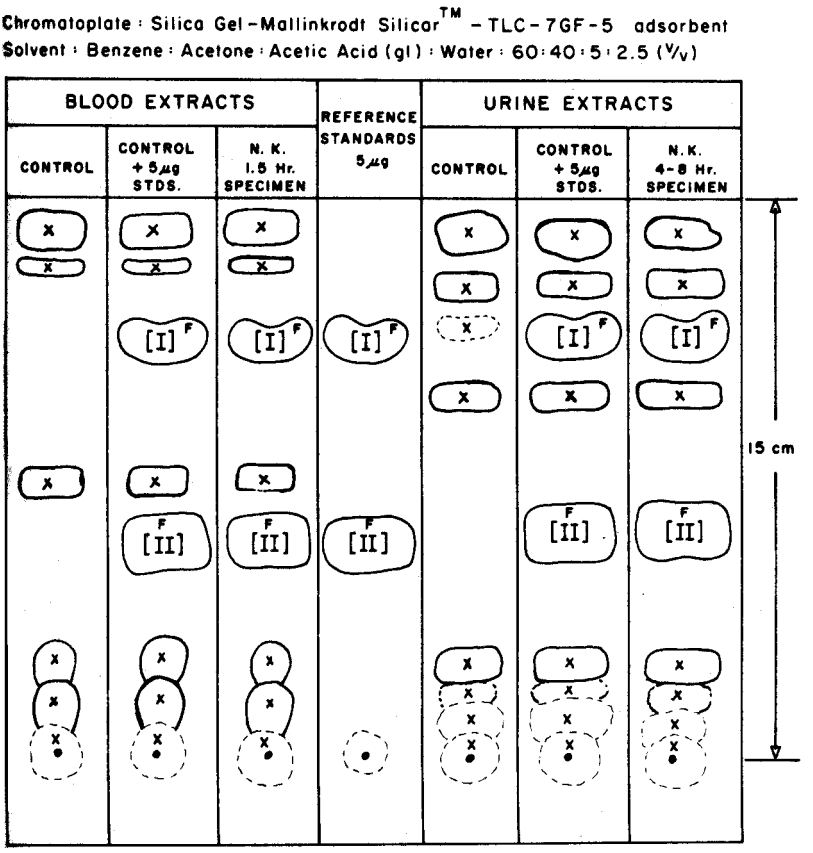

Fig. 5. Thin-layer chromatograms of the ethyl acetate–*n*-butanol (80+20) extracts of blood (acetone–P.F.F.) and of a (1+9) dilution of urine, from subject N.K. F=fluorescent under short- and long-wave u.v. X=u.v. absorbing under short-wave u.v. After double development, the R_F values of the reference standards were 0.76 for I and 0.35 for II.

Mark the silica gel areas (2 cm^2) corresponding in R_F values to 5 μg of reference standards of authentic I (R_F=0.6–0.8), and II (R_F=0.4–0.5) run alongside the sample extracts. Scrape off these areas, carefully transfer into 15-ml conical centrifuge tubes and elute directly with 10 ml of methanol–0.1 *M* hydrochloric acid

(80 + 20) by shaking vigorously on a reciprocating shaker for 10 min. Centrifuge the samples and transfer the supernate to a 1-cm quartz cell. Measure the fluorescence of the intact drug I at 380 nm, with excitation at 325 nm, and measure that of the metabolite II at 385 nm, with excitation at 330 nm. A further 1 + 9 dilution may be required if the initial fluorescence readings are above 1000 (TM) fluorescence units (T = transmittance and M = meter multiplier factor).

Calculations. All fluorescence readings (TM) are corrected for blood blank readings.

$$(a)\ \text{Determination of unknown}: \frac{[\text{TM}]\ \text{unknown}}{[\text{TM}]\ \text{int. std.}} \cdot \frac{\text{Conc. of int. std. } (\mu\text{g})}{\text{ml of sample}}$$

$$= \mu\text{g of I or II/ml of blood.}$$

$$(b)\ \text{Determination of \% recovery}: \frac{[\text{TM}/\mu\text{g ml}^{-1}]\ \text{int. std.}}{[\text{TM}/\mu\text{g ml}^{-1}]\ \text{ext. std.}} \cdot 100 = \text{\% recovery.}$$

Percent recovery of each compound is calculated routinely as a check on analytical precision and reproducibility.

Assay in urine

Procedure. Dilute 1 ml of the urine specimen* to 10 ml with distilled water, and transfer a 1-ml aliquot of this solution to a 15-ml glass-stoppered centrifuge tube. Add 4.0 ml of phosphate pH 3.5 buffer solution.

Along with the samples, run a 1-ml specimen of a (1 + 9) dilution of control urine (taken before medication or from a pooled control source) and three 1-ml specimens of diluted control urine containing respectively 0.5, 1.0 and 5.0 μg of both I and II added as internal standards, which are used to prepare a calibration curve for the determination of the unknowns and also for the determination of percent recovery. Extract the sample successively with three 5-ml portions of ethyl acetate–*n*-butanol (80 + 20) and combine the extracts as described in the blood assay. Dissolve the residue in 1 ml of ethyl acetate–*n*-butanol (80 + 20), and transfer an 0.5-ml aliquot into a separate set of 15-ml centrifuge tubes to be subsequently used if further dilution of the samples is required. Evaporate the remaining 0.5 ml to dryness and transfer quantitatively onto a 20 × 20 cm t.l.c. chromatoplate exactly as described for blood. Determine the fluorescence of each compound as described for blood, after correction for control (blank) fluorescence and making appropriate dilutions of the sample to correct for possible fluorescence quenching at high concentrations.

Calculations. Prepare a calibration curve of the corrected fluorescence *vs.* the concentration of the recovered internal standards (0.5, 1.0, and 5.0 μg) and read the concentrations in the unknowns directly off the standard curve or by direct comparison to the fluorescence of any given internal standard. These calculations and the determination of percent overall recovery of the added internal standards

* A second (1 + 9) dilution may be necessary in the analysis of the 0–24 h pooled urine specimen because the major percent of the dose is excreted during this period and the concentrations of both compounds depending on the total volume voided may be quite high (> 100–150 μg ml^{-1}).

are performed as described for the blood assay. Appropriate corrections for the aliquots and/or dilution factors involved must be made where necessary.

Polarographic determination of I and II in urine

Both compounds can be reduced in acidic buffer to give a reduction wave characteristic of substituted pyridines and pyridinium compounds[10]. Differential pulse polarography as previously described[11] permits the determination of about 8 μg of I and 15 μg of II per ml of the urine specimen as the limit of detectability. Owing to the extensive urinary excretion of both compounds after administration of I, the concentrations of both are sufficiently high to be readily measured. Because of the wide linear range possible with polarography, the technique is well suited to urine analysis where the concentrations may vary widely. It also eliminates the serial dilution of the sample required to circumvent quenching associated with measuring high concentrations fluorimetrically.

Ethanol–0.2 M potassium phosphate buffer. Mix absolute ethanol with 0.2 *M* potassium dihydrogenphosphate solution in a 1:1 ratio. Titrate potentiometrically to pH 5.0 with 0.2 *M* phosphoric acid, and mix well by inversion. This is the supporting electrolyte solution.

Procedure. Extract the urine specimen (1 ml of a (1+9) dilution of original sample) and separate by thin-layer chromatography exactly as described in the fluorimetric assay. Along with the samples, process a 1-ml specimen of control urine (1+9 dilution) and three specimens of control urine to which I and II are added as internal standards in the following amounts, 10 and 20 μg, 20 and 40 μg, 40 and 80 μg, respectively. After the t.l.c. separation, carefully scrape the silica gel areas corresponding in R_F values to authentic I and II (Fig. 5) into 15-ml centrifuge tubes and elute twice with 5 ml of ethyl acetate–*n*-butanol (80+20)*. Centrifuge the samples, combine the extracts in another 15-ml tube, and evaporate to dryness in a 75° water bath under a stream of nitrogen.

To the residue add 5 ml of the ethanol–phosphate buffer solution. Mix well on a mixer and deoxygenate the samples for 5 min with nitrogen (prepurified-Matheson) introduced through a sintered glass (fritted) tube. Transfer the degassed sample into the polarographic cell containing the 3 operational electrodes set up as described previously[11], pass a stream of nitrogen over the surface of the solution. Obtain a polarogram by scanning the sample from −1.10 V to −1.80 V (*vs.* S.C.E.), using the differential pulse mode of operation, and the polarographic parameters previously described[11].

The polarograms were recorded on an X-Y recorder and showed peaks at $E_p = -1.50$ V and −1.45 V *vs.* S.C.E. for compounds I and II, respectively (Fig. 6).

Calculations. Measure the peak current (Δi_{max}) produced by the external standards, the recovered internal standards and in the unknowns as indicated in Fig. 6. Prepare calibration curves of the external and internal standards by plotting Δi_{max} (μA) *vs.* concentration (μg ml^{-1}). Determine the amount of drug in the unknowns either by interpolation from the internal standard curve, or by direct comparison to a given internal standard[11].

* This solvent mixture has to be substituted for methanol–0.1 *M* HCl (80+20) to minimize contamination with the fluorescent indicator [Mn-activated $ZnSiO_3$] which severely interferes with the polarographic analysis of I and II.

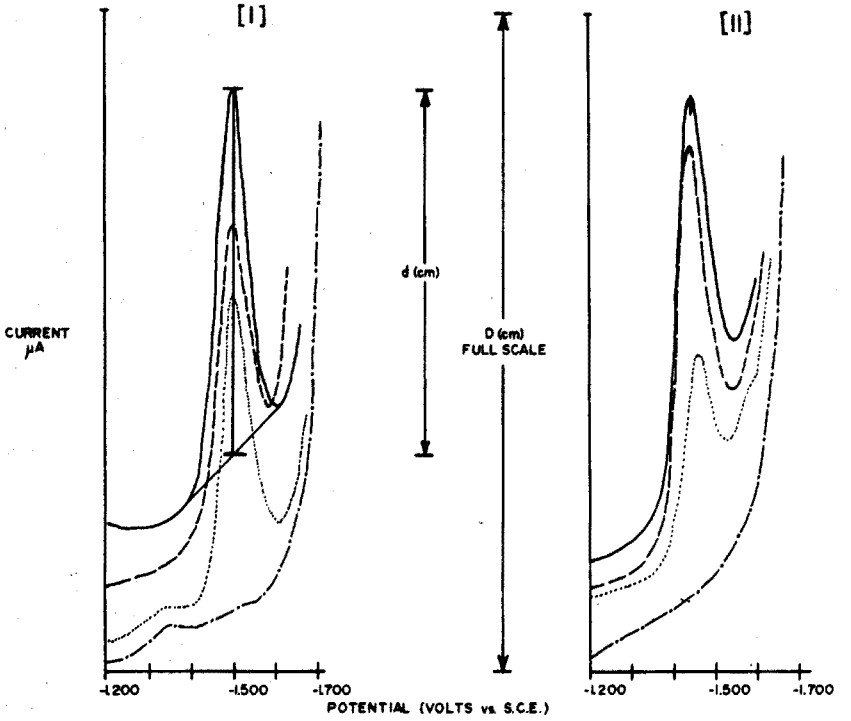

Fig. 6. Differential pulse polarograms of 2-hydroxynicotinic acid (I) and its N-1-riboside (II) determined in ethanol–phosphate buffer solution. (–·–·–) Control urine; (·····) control + 100 μg of I or II; (– – – –) patient urine 0–4 h sample; (——) reference standard, 100 μg of I or II. Peak height d (cm)/full scale height D (cm) · range of measurement (μA) = peak current (Δi_{max}) in μA. For I, full scale = 5 μA, and for II, full scale = 2 μA.

The overall % recovery is determined by direct comparison of the slope (μA μg^{-1} ml of final solution) of the internal standard curve to that of the external standard curve.

RESULTS AND DISCUSSION

2-Hydroxynicotinic acid (I) is a highly ionized compound exhibiting strong amphoteric properties. This fact complicates the extraction of the compound into organic solvents. An investigation of the physicochemical properties of the compound indicated that its strong ultraviolet absorption and intense luminescence properties had most potential for analytical purposes. The u.v. absorption spectra of I (Fig. 2A) indicated the strong aromatic nature of the molecule. In methanol (neutral pH) the compound exhibited maxima at 217 nm and 295 nm ($A_{295}/\mu g\ ml^{-1} = 0.042$). In alkaline solution (0.1 M sodium hydroxide) the maxima shifted to 238 nm and 307 nm ($A_{307}/\mu g\ ml^{-1} = 0.043$), while in acidic solution (0.1 M hydrochloric acid) the maxima were at 233 nm and 325 nm ($A_{325}/\mu g\ ml^{-1} = 0.059$), attesting to the high degree of ionization of the molecule in solution. Similar pH-dependent shifts in the absorption maxima of the metabolite (II) were also seen (Fig. 2B).

Although the absorbance of both I and II at 325 nm was sufficiently high, the potential limit of detection from blood was only of the order of 2–4 μg ml^{-1}, because of high absorbance values from biological specimens. Therefore this approach was not pursued further.

Both compounds also exhibited strong fluorescence in acidic solutions with excitation and emission at 325 and 380 nm for I (Fig. 3) and at 330 and 385 nm for II, respectively. The fluorescence intensity (quantum yield) of I in methanol–0.1 *M* hydrochloric acid (80+20) was sufficiently high [TM/μg ml^{-1}≃3900] to give a limit of detection of 0.04–0.05 μg of I per ml of blood or urine. The fluorescence [TM/μg ml^{-1}≃2000] of the metabolite (II) was about 0.53 times that of I, resulting in a lower limit of the order of 0.10–0.12 μg of [II] per ml of blood or urine. The linear range for determination for both compounds was about 0.01–5.0 μg of each compound per 5 ml of final solution (Fig. 4). Both compounds showed fluorescence quenching at concentrations greater than 5.0 μg. It is noteworthy that because the molecular weight ratio of the metabolite to the parent compound is 1.95, on a per mole basis the intrinsic fluorescence of the two compounds is approximately equal.

The determination of the pH for optimal extraction of the two compounds from aqueous media into organic solvents was investigated by means of the intrinsic fluorescence of the compounds. The compounds are virtually unextracted into organic solvents above pH 7.0, because water-soluble salts are formed. They are, however, extractable from aqueous solutions into polar organic solvent mixtures, especially ethyl acetate–*n*-butanol, at acidic pH values. The optimal pH for extraction was 3.5; sodium phosphate-buffered biological specimens gave cleaner extracts than did potassium phosphate-buffered samples.

Analysis of blood samples at acidic pH required a prior protein precipitation step followed by the extraction of the protein-free filtrate (PFF) buffered to pH 3.5. This procedure results in an unavoidable loss of compound in the protein precipitate. Several precipitants were investigated: the use of hot tungstic acid in sulfuric acid[12] gave promising results for I with an overall recovery of 64±3.0% (s_r). The metabolite, however, was partially hydrolyzed (*ca.* 10–20%) to I (see Fig. 1) under these conditions. Investigation of milder precipitation conditions to prevent this hydrolysis showed that acetone gave the best overall results.

Various polar solvents, either singly or in mixtures, were tested for their ability to extract both compounds from the acetone–water filtrate of blood. Ethyl acetate–ethanol (80+20) gave satisfactory recovery of I (*ca.* 65%) but yielded unsatisfactory and variable recovery of II (*ca.* 30%). The extracts also contained sufficient u.v.-absorbing material to cause spurious quenching effects, especially at low concentrations of I and II. This resulted in an anomalous low apparent recovery from blood of about 40–50% when the fluorescence was first measured in 4 ml of methanol–0.1 *M* hydrochloric acid (80+20). The recovery increased, however, to values of 60–70% on further dilution of the sample, indicating the need for further sample purification.

Back-washing the residue of the ethyl acetate–ethanol extract dissolved in pH 3.5 buffer with *n*-hexane removed significant amounts of the u.v.-absorbing material, thus reducing the overall sample blank while removing negligible amounts of the compounds (< 1%). Further investigation showed that ethyl acetate–*n*-butanol

(80+20) was an even better solvent mixture than ethyl acetate–ethanol, in that it increased the recovery of both I and II with a concomitant reduction of u.v.-absorbing contaminants.

The t.l.c. separation step presented certain problems of resolution of I from II, owing to the highly polar nature of these compounds. The commercially available chromatoplates such as Brinkman (F_{254}) were not suitable because of tailing in over a dozen solvent systems investigated. Chromatoplates made from Mallinckrodt SilicAR (TLC-7GF-5) silica gel of 250 μm thickness were the most satisfactory. Predevelopment and reactivation of the plate, as described in the procedure, were required in order to minimize tailing. It was also necessary to use very polar solvent systems for development to obtain the best resolution of the two compounds from each other and from coextracted polar gelatinous impurities. The capacity of these t.l.c. plates for these compounds was relatively high: up to 100 μg of I and 200 μg of II were resolved with only a 2% contamination of the area of the metabolite II from "tailing" of I. To compensate for this, it was found that the combined steps of protein precipitation, solvent extraction, solvent evaporation, and transfer onto the plate, required in the assay produced a 2% maximal overall breakdown of the metabolite to yield I which would contaminate the t.l.c. zone of authentic I. These two unavoidable factors have nevertheless been minimized, so that the errors caused by possible cross-contamination of I and II apparently cancel each other out and are not serious except when working at the absolute limit of sensitivity of the assay. The highly polar solvent mixtures used to transfer the residues of the ethyl acetate–*n*-butanol extracts of blood (PFF) and urine onto the t.l.c. plates are again necessary for the quantitative recovery of both compounds. Although the first solvent mixture, isopropanol–chloroform (1+1), yielded quantitative recovery of I, most of the more polar metabolite was not recovered. The second solvent mixture, methanol–water–ammonia (95+5+5) solubilized the lipid-like gelatinous residue adhering to the walls of the tube and effected a quantitative transfer of II. Elution of both compounds from the silica gel into methanol–0.1 *M* hydrochloric acid (80+20) was virtually quantitative (>95%).

The availability of 3-^{14}C-labeled I* (specific activity, $1.25 \cdot 10^5$ dis min^{-1} μg^{-1}) and of the labeled metabolite, 3-^{14}C-II (specific activity, $1.11 \cdot 10^3$ dis min^{-1} μg^{-1}), which was isolated and recrystallized from the urine of a dog treated with labeled I[9], enabled further verification of the recovery data obtained in blood and urine by the fluorimetric method.

The mean recovery of amounts of I ranging from 100 ng to 10.0 μg added to 1 ml of blood and determined fluorimetrically by the recommended method was $82 \pm 4.5\%$ (s_r; $n=21$). The mean recovery of II in amounts ranging from 250 ng to 25.0 μg added to 1 ml of blood was $58 \pm 6.0\%$ (s_r; $n=18$). These values are in good agreement with those obtained in parallel determinations using the 3-^{14}C-labeled drug and metabolite which gave mean recoveries of $80 \pm 3.0\%$ (s_r; $n=11$) for I, and $54 \pm 7.0\%$ (s_r; $n=11$) for II. The recovery of I and II from urine (including t.l.c.) was about 90% and 85%, respectively.

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* Synthesized by Dr. A. Liebman (1972), Department of Chemical Research, Hoffmann-La Roche Inc., Nutley, N.J. 07110.

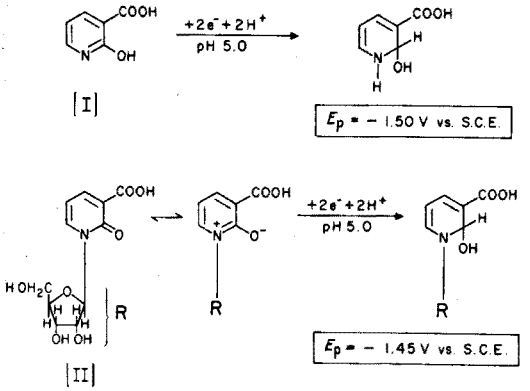

Fig. 7. Postulated mechanisms for the polarographic reduction peaks due to 2-hydroxynicotinic acid (I) and its N-1-riboside (II).

The polarographic assay has the advantage that it is simple. However, it is not as sensitive as the fluorimetric assay. The peak of I at −1.50 V *vs.* S.C.E. in pH 5.0 buffer is due to the reduction of the azomethine group (>C=N–) in the pyridine ring[10] (Fig. 7). The metabolite II is a pyridinium compound which gives a peak at −1.45 V *vs.* S.C.E.; this is probably also due to the reduction of an azomethine group produced by the enolate tautomer of the carbonyl group at pH 5.0. Therefore, the reaction mechanisms postulated in Fig. 7 are due to the same functional group which yields the same hemiacetal as the end-product. The separation of the two peaks by only 0.05 V is probably due to the substituent effects of the riboside moiety. Polarographic reduction waves for ribose (as a free pentose) have been reported[13] and occur around −1.70 V *vs.* S.C.E. at pH 5.0. The reaction is thought to be due to partial "opening" of the cyclic form, which results in an aldehyde group which is reduced to a secondary alcohol. Such a reaction does not occur in II because the ribose moiety is bound to the pyridine-nitrogen. The sensitivity limit for I is nearly twice that of II, *viz.*, 1.0 μg I and 2.0 μg of II per ml of final solution analyzed (total volume = 5 ml). The overall recovery of the assay, including the t.l.c. separation step is of the order of 75% for I and 50–55% for II, thus the effective limit of detection from urine is 5–8 μg of I and 15 μg of II per ml of urine. Comparative analysis of human urine by polarography and fluorimetry (Table I) showed acceptable agreement between the two methods.

The intense u.v. absorbance, fluorescence emission, the highly polar nature of these compounds, and the high concentrations usually found in urine, also favor the use of high-pressure liquid–liquid chromatography for their determination with commercially available instrumentation equipped with sensitive u.v. and fluorescence detectors. Various nucleic acids have been successfully analyzed by this technique[14].

Application of the method to biological specimens

The blood levels of I and II were determined in three male subjects after administration of a single 500-mg oral dose of the drug. Semi-logarithmic plots of the data for each subject are presented in Figs. 8–10. The blood level curves of the intact drug I in all three subjects show that it was rapidly absorbed; measurable

TABLE I

COMPARATIVE ANALYSIS OF HUMAN URINE FOR I AND II BY POLAROGRAPHY AND SPECTROFLUORIMETRY

(In $\mu g\ ml^{-1}$ of urine)

Sample	*I*		*II*	
	Polarography	*Fluorimetry*	*Polarography*	*Fluorimetry*
(N.K.)				
0–4 h	81	77	132	132
4–8	—[a]	—[a]	1298	1275
(J.S.)				
0–4 h	920	844	195	215
4–8	14	12	981	856
(D.H.)				
0–4 h	92	112	71	62

[a] Not measurable: Polarography = 8 μg of I or 15 μg of II per ml of urine. Fluorimetry = 0.05 μg of I or 0.10 μg of II per ml of urine.

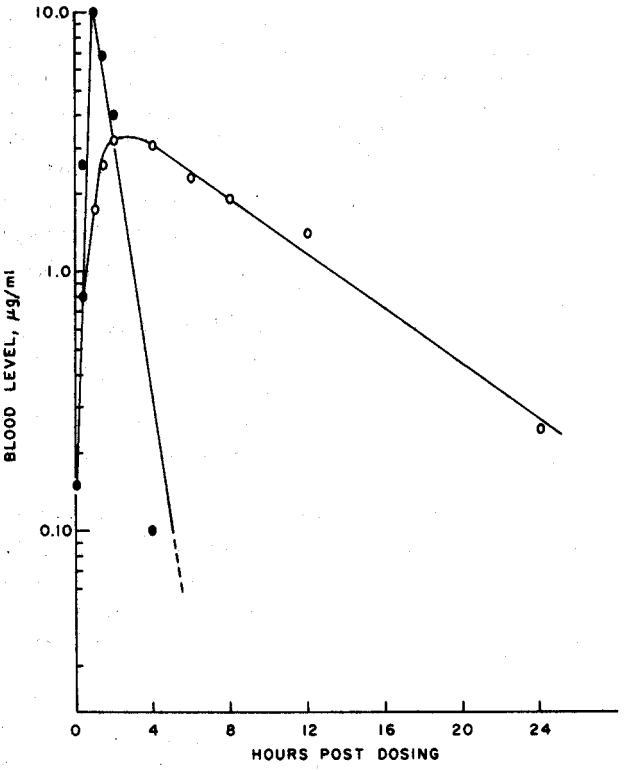

Fig. 8. Blood level fall-off curves of I (●) and II (○) in man after oral administration of a single 500-mg dose of I. Subject: D.H. (m); weight, 211 lbs (95.9 kg). Dose 5.21 mg kg^{-1}. The limit of detection was 0.04–0.05 $\mu g\ ml^{-1}$ for I and 0.10–0.12 $\mu g\ ml^{-1}$ for II.

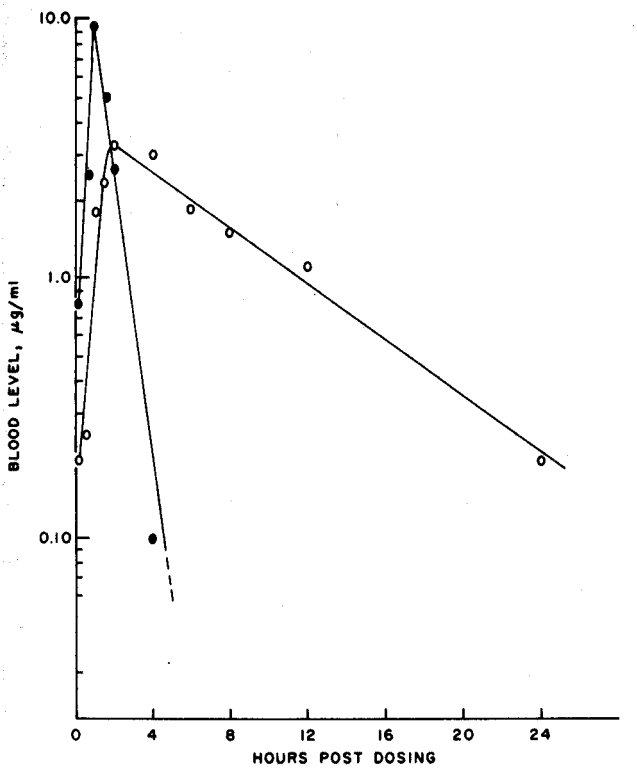

Fig. 9. Blood level fall-off curves for a second subject J.S. (m). Weight, 189 lbs (85.5 kg). Dose, 5.81 mg kg^{-1}. All other parameters as in Fig. 8.

levels were seen 15 min after dosing, rising to peak levels at 1 h of 5.9 μg I ml^{-1}, 9.3 μg I ml^{-1} and 9.9 μg I ml^{-1} in subjects N.K., J.S. and D.H., respectively. In all three subjects, the blood levels declined rapidly between 1 and 4 h in an exponential manner with an apparent half-life of 30 min. After 4 h, the blood levels of I were no longer measurable. Metabolite II was also measurable 15–30 min after dosing, indicating rapid biotransformation of the drug. The blood levels rose gradually to peak levels of 3.2–3.3 μg ml^{-1} at 2 h in subjects D.H. and J.S., and 6.0 μg ml^{-1} at 4 h in subject N.K. These blood levels declined exponentially to non-measurable amounts after 24 h, with an apparent half-life of elimination of 5.5, 5.4, and 4.0 h in subjects D.H., J.S., and N.K., respectively.

The urinary excretion of I and II by the three subjects is summarized in Table II. The data indicate that the parent drug is rapidly eliminated (paralleling the rapid decline in the blood levels which in all three subjects were not measurable after 4 h) with 31.6% of the dose in subject D.H., 19.5% of the dose in subject J.S., and 8.4% of the dose in subject N.K. excreted in the 0–4 h period. The rapid metabolism of I to the N-1-riboside (II) was also reflected in the urinary excretion of the metabolite, with the major percentage of the dose being excreted as this compound. The metabolite reached its peak excretion in all 3 subjects in the 4–24 h period, as shown in Table II. The total amount of the administered drug (500 mg)

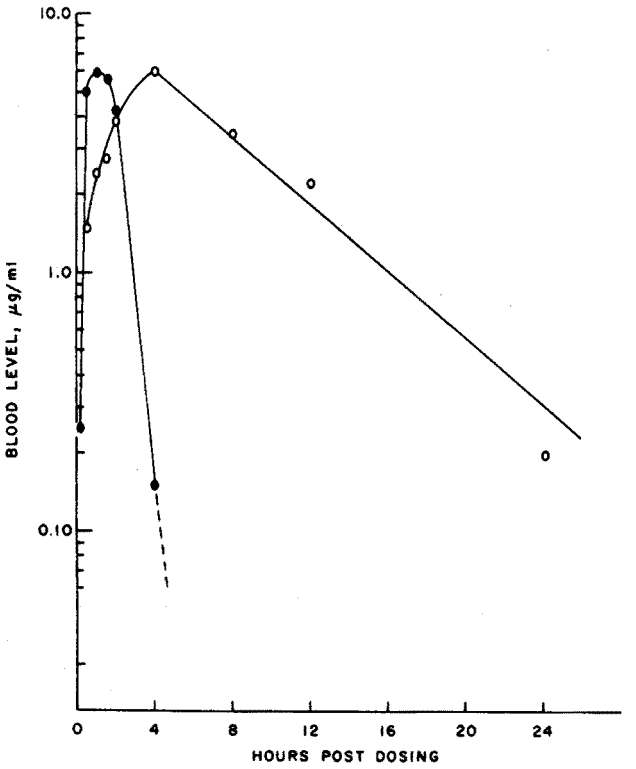

Fig. 10. Blood level fall-off curves for a third subject N.K. (m). Weight, 159 lbs (72.3 kg). Dose, 6.92 mg kg^{-1}. All other parameters as in Fig. 8.

TABLE II

URINARY EXCRETION OF I AND II IN MAN

(A single 500-mg dose of the drug was administered orally; determined by spectrofluorimetric analysis. Weights and dose ratios are given in the legends to Figs. 8–10)

Excretion period (h)	*D.H. (m)*			*J.S. (m)*			*N.K. (m)*		
	% of dose excreted as			*% of dose excreted as*			*% of dose excreted as*		
	I	*II*	*Total %*	*I*	*II*	*Total %*	*I*	*II*	*Total %*
0–4	31.6	11.9	43.5	19.5	8.5	28.0	8.4	6.6	15.0
4–8	1.3	24.5	25.8	0.6	19.9	20.5	0.3	13.7	14.0
8–24	0.5	24.1	24.6	0.1	21.2	21.3	0.1	5.6	5.7
24–48	—[a]	—[a]	—[a]	—[b]	—[b]	—[b]	0.4	0.8	1.2
% of dose recovered	33.4	60.5	93.9	20.2	49.6	69.8	9.2	26.7	35.9

[a] Not measurable *i.e.* <0.05 μg I and 0.10 μg II ml^{-1} of urine.
[b] No sample collected.

recovered in the overall 48-h period accounted for 36–94%, depending on the subject. The reason for the low recoveries in subject N.K. is not known.

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SUMMARY

A sensitive and specific spectrofluorimetric assay was developed for the determination of 2-hydroxynicotinic acid (I) and its major metabolite, the N-1-riboside (II) in blood and urine. Both compounds exhibit strong fluorescence in acidic media. Thin-layer chromatography is employed to separate the drug from its metabolite; the compounds are eluted from the silica gel into methanol–0.1 *M* hydrochloric acid (80 + 20). The sensitivity is 0.04–0.05 μg of I and 0.10–0.12 μg of II per ml of blood or urine. The two compounds can also be determined by differential pulse polarography, which is especially suitable for urine. The fluorimetric method was applied to the determination of blood levels and the urinary excretion of the drug in man after single oral 500-mg doses.

RESUME

Une méthode spectrofluorimétrique sensible et spécifique est proposée pour le dosage de l'acide hydroxy-2-nicotinique (I) et de son métabolite principal, le N-1-riboside (II), dans le sang et l'urine. Ces deux composés présentent une forte fluorescence en milieu acide. La chromatographie sur couche mince est utilisée pour séparer la drogue d'avec son métabolite. Ces composés sont élués du gel de silice avec un mélange méthanol–acide chlorhydrique 0.1 *M* (80:20). La sensibilité est de 0.04 à 0.05 μg de I et 0.1 à 0.12 μg de II par ml de sang ou d'urine. Ces deux composés peuvent également être dosés par polarographie différentielle, convenant particulièrement bien pour l'urine. La méthode fluorimétrique a été utilisée pour l'analyse du sang et de l'urine après des doses orales de 500 mg.

ZUSAMMENFASSUNG

Es wurde eine empfindliche und spezifische spektrofluorimetrische Methode für die Bestimmung von 2-Hydroxy-Nikotinsäure (I) und dessen Hauptmetaboliten, dem N-1-Ribosid (II), in Blut und Urin entwickelt. Beide Verbindungen zeigen in sauren Medien eine starke Fluoreszenz. Das Arzneimittel wird von seinem Metaboliten durch Dünnschichtchromatographie abgetrennt; die Verbindungen werden vom Silicagel mit Methanol–0.1 *M* Salzsäure (80–20) eluiert. Die Empfindlichkeit ist 0.04–0.05 μg I und 0.10–0.12 μg II pro ml Blut oder Urin. Die beiden Verbindungen können ebenfalls durch Differential-Pulse-Polarographie bestimmt werden, die sich besonders für Urin eignet. Die fluorimetrische Methode wurde auf die Bestimmung von Gehalten in Blut und auf die Harnausscheidung des Arzneimittels im Menschen nach einzelnen oralen Dosen von 500 mg angewendet.

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N-ARYLHYDROXAMIC ACIDS AS REAGENTS FOR VANADIUM(V)

SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH N-*m*-TOLYL-*p*-METHOXYBENZOHYDROXAMIC ACID

V. K. GUPTA and S. G. TANDON

Department of Chemistry, Ravishankar University, Raipur, M.P. (India)

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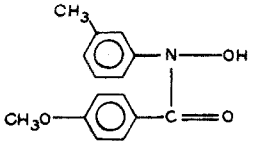
The use of N-phenylbenzohydroxamic acid and N-phenylcinnamohydroxamic acid as excellent reagents for determination and detection of vanadium(V), has led to systematic searches for better reagents in the family of hydroxamic acids[1–7] In recent years, many new N-arylhydroxamic acids have been synthesized and examined as vanadium reagents[2–4,7]. It has been found that the selectivity and sensitivity of a reagent can be altered by changing the substituent groups attached to the functional group.

In a further extension of this work, more new N-arylhydroxamic acids, with different substituent groups attached to the functional group have been synthesized[8]. In the work described here, the reactions of these synthesized N-arylhydroxamic acids with vanadium(V) in concentrated hydrochloric acid solutions were examined. The extraction behaviour of the coloured metal complexes obtained was studied qualitatively, and the absorption spectra of the chloroform extracts were compared. Of the N-arylhydroxamic acids examined, N-*m*-tolyl-*p*-methoxybenzohydroxamic acid, I, proved to be the most sensitive reagent for the



(I)

spectrophotometric determination of vanadium(V). The molar absorptivity of its bluish-violet complex is 5750 ± 50 l mole^{-1} cm^{-1}, compared to 4650 ± 50 l mole^{-1} cm^{-1} for the violet PBHA complex[1,6], both being calculated on the basis of vanadium and at their respective wavelengths of maximum absorption.

EXPERIMENTAL

Apparatus

A Unicam SP500 spectrophotometer with 10-mm matched corex or silica cells was employed for most of the measurements. A Beckman Model DK-2 ratio-recording spectrophotometer was also used.

Reagents

Solutions of N-arylhydroxamic acids (*ca.* 0.005 *M*) were prepared in ethanol-free chloroform. These solutions were stable for several days when stored in dark bottles. All the other chemicals were of AR or C.P. grade (BDH or E. Merck).

Ammonium metavanadate

A stock solution was prepared by dissolving analytical-grade ammonium metavanadate in glass-distilled water. The vanadium content was determined by standard methods.

Colour reaction

Chloroform solutions of N-arylhydroxamic acids react with vanadium(V), yielding extracts the colour of which depends on the hydrochloric acid concentration of the aqueous phase. Between pH 1 and 6.5 mahogany red extracts are usually obtained; when the aqueous solution contains more than 2 *M* hydrochloric acid, the extracts are reddish violet, violet or bluish violet. All the hydroxamic acids examined here reacted similarly. The complexes formed from concentrated hydrochloric acid solutions could be extracted by several organic solvents such as chloroform, benzene, carbon tetrachloride, 1,2-dichlorobenzene, ethyl acetate or diethyl ether. Chloroform was found to be the most suitable solvent for extraction, provided that it is free from ethanol; the small amounts of ethanol added to chloroform as a preservative cause a hypsochromic shift of the wavelength of maximal absorption.

Development of colour

For comparing the sensitivities of the hydroxamic acids as reagents for vanadium(V), the molar absorptivities of the coloured systems were determined at their respective wavelengths of maximal absorption. The stock solution of vanadium(V) was oxidized by potassium permanganate or bromine water to keep vanadium in the pentavalent state.

Procedure for preliminary tests

Transfer an aliquot of oxidized solution containing 0.02–0.2 mg of vanadium(V) to a separatory funnel, and add distilled water and hydrochloric acid until the volume is about 25 ml and the acidity between 2.8 and 7.5 *M*. Add 10 ml of a 0.005 *M* chloroform solution of N-arylhydroxamic acid and shake vigorously for a few minutes. Allow the two layers to separate for a few minutes and collect the coloured chloroform layer in a 50-ml beaker containing about 1.5 g of anhydrous sodium sulphate to remove moisture. Wash the aqueous layer three times with 3–5 ml of chloroform to remove any residual colour, and add the washings to the beaker. Decant the coloured solution into a 25-ml volumetric flask. Wash out the adhering colour from sodium sulphate crystals with small portions of chloroform. Combine the washings with the main solution, and dilute to the mark with chloroform.

Absorption spectra

The absorption spectra of the coloured chloroform extracts were determined

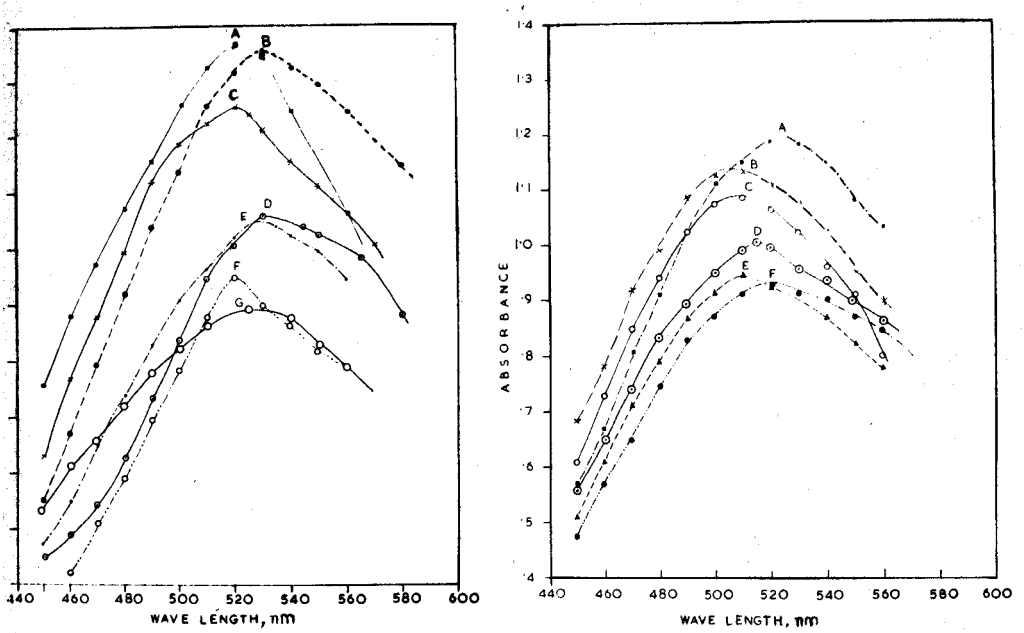


Fig. 1. Absorption spectra of vanadium(V) complexes from 4 *M* hydrochloric acid with chloroform containing, (A) N-1-naphthyl-*p*-methoxybenzo- (V, 12.92 mg l^{-1}); (B) N-*p*-tolyl-*o*-methoxybenzo- (V, 14.74 mg l^{-1}); (C) N-*o*-tolyl-*o*-methoxybenzo- (V, 12.78 mg l^{-1}); (D) N-phenyl-*o*-methoxybenzo- (V, 12.86 mg l^{-1}); (E) N-*m*-tolyl-*p*-methoxybenzo- (V, 9.35 mg l^{-1}); (F) N-*m*-tolyl-*o*-methoxybenzo- (V, 9.88 mg l^{-1}); (G) N-1-naphthyl-*o*-methoxybenzohydroxamic acid (V, 10.30 mg l^{-1}).

Fig. 2. Absorption spectra of vanadium(V) complexes from 4 *M* hydrochloric acid with chloroform containing, (A) N-*m*-tolylbenzo- (V, 12.55 mg l^{-1}); (B) N-*o*-tolyl-*p*-chlorobenzo- (V, 11.17 mg l^{-1}); (C) N-*o*-tolyl-*m*-methylbenzo- (V, 8.53 mg l^{-1}); (D) N-*p*-tolyl-*m*-nitrobenzo- (V, 10.85 mg l^{-1}); (E) N-*o*-tolyl-*o*-iodobenzo- (V, 10.14 mg l^{-1}); (F) N-*m*-tolyl-*m*-methylbenzohydroxamic acid (V, 9.67 mg l^{-1}).

in the visible region, against appropriate compensating blank solutions. The wavelength of maximal absorption of the coloured chloroform extract of a particular hydroxamic acid remained unaffected on increasing the hydrochloric acid concentration of the aqueous phase to more than 2 *M*.

In studies of the molar absorptivities of the hydroxamic acid complexes, the hydrochloric acid concentration of the aqueous phase was adjusted to 4 *M*. To ensure complete extraction of vanadium, the aqueous layer was repeatedly shaken with aliquots of reagent solution till it gave no colour. Adherence to Beer's law was confirmed for each system. The average molar absorptivities of the coloured systems were calculated at the wavelengths of their maximum absorption and on the basis of vanadium(V) content.

The results of the studies are given in Table I and the absorption spectra of a few typical coloured extracts are shown in Figs. 1 and 2.

DISCUSSION

All the N-arylhydroxamic acids react with vanadium(V) in concentrated

TABLE I: SPECTRAL CHARACTERISTICS OF COLOURED VANADIUM(V)–N-ARYL-HYDROXAMATES IN CHLOROFORM

S. no.	*Hydroxamic acid*	*Colour of extract*[a]	λ_{max} *(nm)*	ε *(l mole^{-1} cm^{-1})*
1.	N-phenyl-*n*-valero-	RV	505	4050
2.	N-*p*-tolyl-*n*-valero-	RV	510	4350
3.	N-1-naphthyl-*n*-valero-	RV	510	4220
4.	N-phenylcapro-	RV	505	4020
5.	N-*p*-tolylcapro-	RV	510	4350
6.	N-1-naphthylcapro-	RV	495	4250
7.	N-phenylcaprylo-	RV	510	4000
8.	N-*p*-tolylcaprylo-	RV	510	4200
9.	N-phenylcapri-	RV	500	4150
10.	N-*p*-tolylcapri-	RV	510	4450
11.	N-*m*-tolylcapri-	RV	510	4450
12.	N-1-naphthylcapri-	RV	495	4150
13.	N-1-naphthyllauro-	RV	500	3800
14.	N-phenylmyristo-	RV	510	4320
15.	N-*p*-tolylmyristo-	RV	515	4300
16.	N-1-naphthylmyristo-	RV	500	3850
17.	N-*p*-tolylbeheno-	RV	510	4150
18.	N-*o*-tolylphenoxyaceto-	RV	495	4230
19.	N-*o*-tolylphenylaceto-	RV	510	3900
20.	N-1-naphthylphenylaceto-	RV	505	4000
21.	N-phenyl-1-naphthylaceto-	RV	510	4300
22.	N-*p*-tolylphenoxyaceto-	RV	510	3950
23.	N-phenyl-2,4-dichlorophenoxyaceto-	RV	505	3050
24.	N-*p*-tolyl-2,4-dichlorophenoxyaceto-	RV	500	3250
25.	N-phenylundecyleno-	RV	500	4150
26.	N-*p*-tolylundecyleno-	RV	515	4500
27.	N-*p*-tolyl-*m*-nitrobenzo-	RV	515	4700
28.	N-1-naphthyl-*p*-nitrobenzo-	RV	505	4500
29.	N-*o*-tolyl-*o*-methylbenzo-	V	510	4500
30.	N-*m*-tolyl-*o*-methylbenzo-	BV	530	4700
31.	N-1-naphthyl-*o*-methylbenzo-	V	515	4300
32.	N-*o*-tolyl-*m*-methylbenzo-	V	510	5100
33.	N-*m*-tolyl-*m*-methylbenzo-	BV	520	4900
34.	N-*o*-tolyl-*p*-methylbenzo-	V	510	5500
35.	N-*m*-tolyl-*p*-methylbenzo-	BV	520	5350
36.	N-1-naphthyl-*p*-methylbenzo-	V	510	4900
37.	N-1-naphthyl-*p*-chlorobenzo-	V	510	4350
38.	N-*o*-tolyl-*p*-chlorobenzo-	V	505	5200
39.	N-*o*-tolylbenzo-	V	510[b]	5000
40.	N-*m*-tolylbenzo-	BV	525[c]	4850
41.	N-*o*-tolyl-*o*-chlorobenzo-	V	505	3800
42.	N-*m*-tolyl-*o*-chlorobenzo-	BV	530	4150
43.	N-*o*-tolyl-*o*-iodobenzo-	V	510	4750
44.	N-*m*-tolyl-*o*-iodobenzo-	BV	530	3800
45.	N-phenyl-*o*-methoxybenzo-	BV	530	4200
46.	N-*o*-tolyl-*o*-methoxybenzo-	BV	520	5000
47.	N-*m*-tolyl-*o*-methoxybenzo-	BV	520	4900
48.	N-*p*-tolyl-*o*-methoxybenzo-	BV	530	4700
49.	N-1-naphthyl-*o*-methoxybenzo-	BV	525	4400
50.	N-*m*-tolyl-*p*-methoxybenzo-	BV	530	5750
51.	N-1-naphthyl-*p*-methoxybenzo-	BV	520	5400
52.	N-phenylbenzo-	V	510, 530[d]	4650

[a] V = violet, BV = bluish violet, RV = reddish violet. [b] Reported[5], 510 nm. [c] Reported[5], 530 nm. [d] Reported, 510 nm[1], 530 nm[6]

hydrochloric acid media to form extractable coloured complexes (Table I). The colours of the extracts are violet, bluish-violet or reddish-violet with different hydroxamic acids. The absorption band is generally broad and is around 510 nm for most of the acids. A shift of absorption band to 495 nm occurs for N-1-naphthylcapro-, N-1-naphthylcapri-, and N-*o*-tolylphenoxyacetohydroxamic acids, while a shift to longer wavelengths (up to 530 nm) occurs for N-*m*-tolyl-*o*-iodobenzo-, N-*m*-tolyl-*o*-methylbenzo-, N-*m*-tolyl-*o*-chlorobenzo-, N-phenyl-*o*-methoxybenzo-, N-*p*-tolyl-*o*-methoxybenzo-, and N-*m*-tolyl-*p*-methoxybenzohydroxamic acids. The lowest molar absorptivity (3000 l $mole^{-1}$ cm^{-1}) was observed for N-phenyl-2,4-dichlorophenoxyacetohydroxamic acid, while the highest value (5750 l $mole^{-1}$ cm^{-1}) was for N-*m*-tolyl-*p*-methoxybenzohydroxamic acid.

Since quite a large number of compounds have now been examined, it is worthwhile to compare the changes brought about in the spectral characteristics of the coloured extracts of different hydroxamic acids with those of PBHA, which is an established reagent for vanadium(V)[1,6].

Hydroxamic acids derived from aliphatic carboxylic acids

Hydroxamic acids numbered 1 to 26 (Table I) fall under this head; these are derived from aliphatic carboxylic acids or from acetic acid in which one of the hydrogen atoms is replaced by a phenoxy, phenyl, or 1-naphthyl group, conjugation being absent.

Replacement of a methyl group in the *o*-, *m*- or *p*-positions of the N-phenyl ring by a N-1-naphthyl ring has little influence on the position and intensity of the absorption band of the vanadium(V) complex. All of these complexes are reddish-violet.

Replacement of the aromatic ring of PBHA, which is conjugated with the carbonyl group, by an aliphatic group leads to the expected decrease in the wavelength of maximum absorption. The colour of the complex also changes from violet to reddish-violet. Thus hypsochromic and hypochromic effects are observed. The length of the aliphatic chain does not appreciably affect the position and intensity of the absorption band. Similar observations were made for hydroxamic acids derived from phenoxyacetic acid, 1-naphthylacetic acid, 2,4-dichlorophenoxyacetic acid and phenylacetic acid, where a $-CH_2-$ or $-OCH_2-$ group separates the aromatic ring from the carbonyl group. Removal of conjugation is presumably responsible for this behaviour. It should be noted that these hydroxamic acids are unsuitable for solvent extraction and spectrophotometric determination of vanadium(V) because the full colour develops only slowly and after repeated extractions. These hydroxamic acids are relatively less soluble in benzene, chloroform and ethanol.

Hydroxamic acids derived from aromatic carboxylic acids

Hydroxamic acids numbered 27 to 52 fall under this head; these are derived from benzoic and substituted benzoic acids, substituents such as methoxy, methyl, nitro, chloro, and iodo, being attached at various positions in the benzene ring. In all these compounds the carbonyl group is in conjugation with the aromatic ring.

Substitution of a methyl group at the *o*- or *p*-position of the N-phenyl ring,

or replacement of the N-phenyl ring by N-1-naphthyl, has no marked effect on the position of the absorption band of the vanadium(V) complexes. However, *m*-methyl substitution in the N-phenyl ring results in a conspicuous bathochromic shift of the absorption band and the colour of the complex changes to bluish-violet. The effects on the intensity of the absorption are generally small and cannot be easily accounted for. The nature and position of substituents in the other ring seems to play an important role.

An examination of the hydroxamic acids numbered 29 to 36 shows that *m*- or *p*-substitution of a methyl group in the C-phenyl ring has a definite hyperchromic effect, while *o*-methyl substitution in this ring has a hypochromic influence on the corresponding complexes. The wavelength shifts are relatively small.

The vanadium(V) complexes of methoxy-substituted benzohydroxamic acids are characterized by a bluish-violet colour, with a bathochromic shift of the absorption band. Here the position of substitution seems to play an important role. *o*-Substitution in either ring, attached to the carbon or nitrogen atoms of the hydroxamic acid functional group, seems to oppose the bathochromic shift. The introduction of a methoxy group in the phenyl ring conjugated with the carbonyl group, increases the length of the resonance system and the consequent bathochromic shift of the absorption band is in accord with the well known rules of spectroscopy[9,10]. The hyperchromic effect of the methoxy group is most striking in the *p*-substituted hydroxamic acids where the resonance system is longest. In *o*-substituted methoxy derivatives, the resonance system is still present, but the steric effect of the *o*-group presumably partially annuls the resonance effect. This has also been observed in earlier studies of vanadium(V) complexes with other *p*-substituted methoxybenzohydroxamic acid[2].

On the basis of the above studies and previous studies reported from this[7,11,12] and other laboratories[4–6,13], a few broad concepts, which may prove extremely useful in examining new hydroxamic acids as reagents for vanadium(V), may be outlined.

(*a*) Hydroxamic acids derived from hydroxylamine (*i.e.* when R′=H, *cf.* general formula I) form complexes with vanadium(V) which are practically not extracted with hydrocarbon and nonoxygenated solvents such as benzene, toluene, chloroform, carbon tetrachloride and 1,2-dichlorobenzene. For this extraction, higher alcohols such as *n*-hexanol, and *n*-octanol have been recommended, but these are generally unsuitable as extractants because their purification is tedious, and complications arise from the hydrogen peroxide formed during storage[14]. These hydroxamic acids are, therefore, of limited practical importance for developing solvent extraction and colorimetric methods for the determination of vanadium(V).

(*b*) Hydroxamic acids derived from N-arylhydroxylamines (*i.e.* when R′ is phenyl, *o*-, *m*-, or *p*-tolyl, or 1-naphthyl) form complexes with vanadium(V) which are readily extracted with hydrocarbon and nonoxygenated solvents, chloroform being the best. Alcohols are not tolerated by these complexes even in trace amounts. Several of these hydroxamic acids have proved excellent reagents for the spectrophotometric determination of vanadium(V)[1,4–6,11].

It may be noted that N-arylhydroxamic acids derived from aliphatic and substituted aliphatic carboxylic acids are relatively less sensitive as reagents for vanadium(V). Hydroxamic acids with increased length of conjugation show greatly

enhanced sensitivity[7]. Methoxy or methyl substitution also deepens the colour. Hydroxamic acids containing electronegative substituents such as chloro, bromo, iodo or nitro groups, offer no special advantage.

In future work it would be of interest to examine the effects of the following changes on the general behaviour of the reagents: (*a*) replacement of R′ by groups containing electrophilic substituents such as halogen or nitro groups; (*b*) substitution of bulkier groups such as phenoxy and naphthoxy at the *o*-positions in the N- and C-phenyl rings, which might improve selectivity.

Composition of vanadium(V) complex

Attempts were made to establish the composition of the solid complexes. These could be isolated from the aqueous media by two methods: (*a*) precipitation of the complex by adding a saturated aqueous solution of N-arylhydroxamic acid to a vanadium(V) solution containing hydrochloric acid; (*b*) extraction with chloroform followed by evaporation of the solvent at room temperature and low pressure.

The solid violet complexes were unstable and turned green after a few months. Elemental analyses of even freshly prepared complexes did not settle their empirical formula unambiguously. Similar difficulties have been encountered by other workers[15]. Montenqui[16] obtained the solid complex of PBHA and vanadium(V) and assigned the formula $(C_{13}H_{10}O_2N)VO_2H \cdot HCl$ to it. Majumdar *et al.*[17] isolated 2 solid complexes of vanadium(V) and PBHA, and assigned to them the formulae $(C_{13}H_{10}O_2N)_2VOCl$ and $(C_{13}H_{10}O_2N)_4V_2O_3$. It is thus seen that there is no agreement in the findings of different workers.

In this laboratory, composition studies in solutions have been made[15,18] by applying Job's method of continuous variations as applicable to two-phase systems[19–21]. In all of the N-arylhydroxamic acid and vanadium(V) complexes formed in strong hydrochloric acid solutions, the metal to ligand ratio was found to be 1:2.

SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH N-*m*-TOLYL-*p*-METHOXYBENZOHYDROXAMIC ACID

Experimental

Reagent solution. N-*m*-Tolyl-*p*-methoxybenzohydroxamic acid is a white needle-shaped compound. A 0.1% (w/v) solution in ethanol-free chloroform was used for all extractions. This solution is stable for several days when stored in dark bottles. The absorption spectrum of the vanadium(V) complex is given in Fig. 1. The reagent blank is negligible at 530 nm.

Procedure. To ensure that vanadium in the sample solution is in the pentavalent state, add a few drops of dilute potassium permanganate solution until a faint pink colour persists. To a separatory funnel, transfer an aliquot of the sample solution containing less than 0.12 mg of vanadium(V) and add distilled water until the volume is about 25 ml and the acidity between 2.8 and 7.5 *M*. (In the present work the acidity was kept at about 4 *M*.) Add 8–10 ml of 0.1% reagent solution and shake the funnel vigorously for 2 min. Then proceed as in the General procedure given on p. 40. Measure the absorbance against chloroform as blank at

530 nm. Calculate the amount of vanadium(V) corresponding to the absorbance by reference to a calibration curve.

Colour reaction

In aqueous media which are 2–10 *M* in hydrochloric acid, N-*m*-tolyl-*p*-methoxybenzohydroxamic acid reacts with vanadium(V) to form a bluish-violet complex. If chloroform solutions of the reagent are employed, stable bluish-violet extracts are obtained. These extracts have a broad absorption band around 530 nm, with a molar absorptivity of 5750 ± 50 l mole^{-1} cm^{-1} (calculated on the basis of vanadium).

Many other organic solvents, such as carbon tetrachloride, benzene, 1,2-dichlorobenzene, ethyl acetate and diethyl ether, could be used instead of chloroform, but these give less favourable distribution ratios for both reagent and the complex. The behaviour of 1,2-dichlorobenzene was investigated in detail because this solvent is less soluble in water than chloroform, and is much less volatile, hence there are no losses of solvent by dissolution or evaporation. Unfortunately, extraction was found to be slow and incomplete even on repeated extractions.

It should be noted that there is no reaction between vanadium(IV) and N-*m*-tolyl-*p*-methoxybenzohydroxamic acid.

Effect of variables

Acidity. The optimal range of hydrochloric acid concentration in the aqueous phase is 2.8–7.5 *M*. The absorbance decreases by 4% in 2 *M* hydrochloric acid and by 15% in 9.0 *M* hydrochloric acid. Only hydrochloric acid is suitable for adjusting the acidity, but other common acids can be tolerated provided that their concentration in the aqueous phase is less than 1 *M*.

Stability of colour. Colour is extracted into the chloroform layer in less than 2 min and the extracts are stable for a few days if stored in a cool dark place. The absorbance of the extracts when stored for about 24 h remains practically unaltered.

Amount of reagent. The absorbances increase rapidly as the mole ratio of reagent to vanadium(V) is increased from 1:1 to 8:1; from ratios of 8:1 to 100:1, absorbances remain stable. In practice, for each milligram of vanadium, 70–80 mg of reagent were used. The order in which the reagents are mixed is not critical.

Beer's law

Beer's law is obeyed in the concentration range 26–182.5 μg of vanadium per 25 ml, hence the practical range for the determination of vanadium is computed to be 1.8–6.2 p.p.m.

Effect of other ions

The effects of various ions on this determination of vanadium(V) are almost the same as those found when PBHA is used. Results obtained in a few typical determinations of vanadium are given in Table II. The following ions do not interfere when the weight ratio of each to vanadium is 200:1: Al(III), Ba(II), Be(II), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mg(II)), Hg(II), Mn(II), Ni(II), Sn(IV), Sr(II), Th(IV), U(VI), Zn(II), acetate, nitrate, perchlorate, tartrate and sulphate.

TABLE II

EFFECT OF VARIOUS IONS

Ion[a]	*Amount added (mg)*	*Absorbance*[b] *530 nm*	*Ion*[a]	*Amount added (mg)*	*Absorbance*[b] *530 nm*
None	—	0.470[c]	Fe^{3+}	30	0.470
Al^{3+}	30	0.465	MoO_4^{2-}	20	0.450
Ba^{2+}	30	0.470	Mn^{2+}	30	0.465
Co^{2+}	30	0.475	Ti^{4+}	10	0.420
Cu^{2+}	30	0.465	Zr^{4+}	10	0.460
Cr^{3+}	30	0.470	UO_2^{2+}	30	0.475

[a] Ions were added as their nitrate salts, except for iron ($FeCl_3$), titanium ($TiOCl_2$) and molybdenum (NH_4^+ salt).
[b] Concentration of vanadium = 1.17 p.p.m.
[c] Mean of 3 analyses of the same sample.

Mo(VI), Ti(IV) and Zr(IV) interfere and their tolerance limit is generally small. It may be noted that these ions also interfere in the determination of vanadium(V) with PBHA.

The proposed method is quick and gives reproducible results. It is not affected by wide variation in factors such as temperature, ionic strength and the volume of the aqueous phase.

SUMMARY

A study of the coloured complexes of 51 N-arylhydroxamic acids with vanadium(V) in hydrochloric acid media is described. The absorption spectra of the coloured chloroform extracts and the molar absorptivities are compared. The effects of different substituents attached to the carbon and nitrogen atom of the hydroxamic acid functional group are discussed. A rapid extraction-spectrophotometric method for the determination of vanadium(V) is described, employing the most promising of these reagents, N-*m*-tolyl-*p*-methoxybenzohydroxamic acid. The method is highly selective and tolerates large amounts of diverse ions usually associated with vanadium-bearing materials including iron(III), aluminium(III), chromium(III), nickel(II), cobalt(II), zinc(II) and manganese(II).

RÉSUMÉ

Une étude est effectuée sur les complexes colorés de 51 acides N-aryl-hydroxamiques avec le vanadium(V) en milieu acide chlorhydrique. Une comparaison est effectuée entre les spectres d'absorption des extraits dans le chloroforme et les coefficients d'extinction molaire. On examine l'influence de divers groupements substitués sur le carbone et l'azote de l'acide hydroxamique. Une méthode spectrophotométrique, avec extraction, est décrite pour le dosage du vanadium(V), utilisant le plus prometteur de ces composés, l'acide N-*m*-tolyl-*p*-méthoxybenzohydroxamique. La méthode est très sélective; elle peut tolérer la présence de grandes quantités d'ions généralement présents: fer(III), aluminium(III), chrome(III), nickel(II), cobalt(II), zinc(II) et manganèse(II).

ZUSAMMENFASSUNG

Die gefärbten Komplexe von 51 N-Arylhydroxamsäuren mit Vanadin(V) in salzsauren Medien wurden untersucht. Die Absorptionsspektren der gefärbten Chloroformextrakte und die molaren Extinktionskoeffizienten werden miteinander verglichen. Die Einflüsse verschiedener Substituenten, die mit dem Kohlenstoff- und Stickstoffatom der funktionellen Gruppe der Hydroxamsäure verknüpft sind, werden diskutiert. Eine schnelle extraktions–spektrophotometrische Methode für die Bestimmung von Vanadin(V) unter Verwendung des am besten geeigneten Reagenzes, N-*m*-Tolyl-*p*-methoxybenzohydroxamsäure, wird beschrieben. Die Methode ist hoch selektiv und wird durch grosse Mengen verschiedener Ionen, die üblicherweise in vanadinhaltigen Proben vorkommen, wie Eisen(III), Aluminium-(III), Chrom(III), Nickel(II), Kobalt(II), Zink(II) und Mangan(II), nicht beeinflusst.

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DÜNNSCHICHT-CHROMATOGRAPHISCHE TRENNUNG UND SPEKTRALPHOTOMETRISCHE BESTIMMUNG EINIGER ÜBERGANGSMETALLE ALS MONOTHIO-β-DIKETONATE*

H. MÜLLER und R. ROTHER

Sektion Chemie, Karl-Marx-Universität, Leipzig (Deutsche Demokratische Republik)

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Monothio-β-diketone werden seit einigen Jahren in der analytischen Chemie besonders zur spektralphotometrischen Bestimmung von Metallspuren verwendet[1]. Nachteile beim Einsatz von Monothio-β-diketonen als Reagenzien zur extraktionsphotometrischen Metallspurenbestimmung liegen darin, dass die Metallchelate sich in ihren Absorptionseigenschaften nur wenig unterscheiden und sich so gegenseitig bei der Bestimmung stören. Es erschien deshalb aufschlussreich zu testen, inwieweit sich die Monothio-β-diketonate dünnschicht-chromatographisch trennen lassen und eine anschliessende photometrische Bestimmung der Metallspuren möglich ist.

Zur Adsorptionschromatographie auf Kieselgel- und Aluminiumoxidschichten sind nur wenige Metallkomplexe gut geeignet. Voraussetzung hierfür ist eine möglichst geringe Polarität der Metall–Ligand-Bindung, andernfalls erfolgt eine Spaltung des Komplexes während des Laufvorganges. Neben völlig homöopolaren Metallverbindungen, wie z.B. den Cyclopentadienylen und Carbonylen, eignen sich deshalb für diese Art der Chromatographie vor allem Chelate mit Metall–Schwefel-Bindungen, da diese weit weniger polar sind als vergleichsweise die Metall–Sauerstoff-Bindungen. Ausserdem sind die Metallkomplexe, deren Liganden Schwefel als Donoratome enthalten, durch starke Farbigkeit ausgewiesen, die bei Übergangsmetallen auf intensive Charge-transfer-Übergänge zurückzuführen ist. Diese Farbigkeit erweist sich für die Eigendetektion auf der DC-Platte und für eine anschliessende photometrische Bestimmung der Metallkomplexe als sehr vorteilhaft. Neben den schon bekannten Schwefel enthaltenden Chelaten, wie den Dithizonaten[2], Dialkyldithiocarbamaten[3–5], Dithiolaten[6] zur dünnschichtchromatographischen Trennung von Metallionen, konnten wir zeigen, dass auch die Monothio-β-diketonate hierfür gut geeignet sind. Die Monothio-β-diketone sind unter den Typ der "Breitband-Chelatbildner" einzuordnen, d.h. sie reagieren mit vielen Metallionen[1].

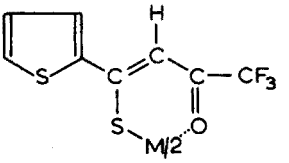
Die komplexchemischen Eigenschaften der Monothio-β-diketone werden dabei weitgehend durch das Schwefeldonoratom bestimmt. Daraus resultiert, dass diese Gruppe der Chelatbildner bevorzugt mit den "weichen", thiophilen Metallen stabile Metallchelate bildet und so namentlich zur Abtrennung von den "harten" Metallen geeignet ist. (Über die Einteilung in Metalle der Klasse (a) und (b), die

* Teilweise vorgetragen auf der Chemiedozententagung in Freiberg (DDR) vom 6.–8. April, 1971.

in erster Näherung identisch ist mit der Einteilung in "harte" und "weiche" Lewis-Säuren, siehe u.a. Ahrland und Mitarbeiter[7].)

Durch Einstellung bestimmter pH-Werte ist es ausserdem möglich, mehr oder weniger selektive Extraktionen einzelner Gruppen von Kationen vorzunehmen. Im vorliegenden Fall extrahierten wir Kupfer-, Kobalt- und Nickelionen bei einem pH-Wert von 6.5, Rhodium- und Palladiumionen aber bei einem pH-Wert von 4. Untereinander wurden die Metallchelate dann durch die DC getrennt. Es kam also eine Kombination von Solvensextraktion als Gruppentrennung und DC als Einzelnachweis zur Anwendung.

Die quantitative Bestimmung dünnschicht-chromatographisch getrennter Substanzgemische erfolgt entweder auf der DC-Platte selbst (direkte oder *in situ* Methoden) oder nach Entfernen und Eluieren der Sorptionsschicht[8]. Wir wählten die letztere Arbeitstechnik, die den Vorteil bietet, dass nach der Trennung und Isolierung der Substanzen für die Bestimmung präzise Mikroverfahren zur Verfügung stehen (z.B. Mikrophotometrie). Als Komplexbildner erwies sich Thiothenoyltrifluoraceton geeigneter als das ebenfalls untersuchte Thiodibenzoylmethan. Thiothenoyltrifluoraceton bildet mit Metallen Neutralchelate der allgemeinen Form



Diese Chelate sind elektrisch neutral und weitgehend hydrophob, so dass es möglich ist, apolare Fliessmittel als mobile Phase einzusetzen. Das erweist sich als nützlich, da die Gefahr des Ablösens der Sorptionsschicht weitgehend vermindert wird und die Entwicklungszeiten verkürzt werden.

EXPERIMENTELLES

Reagenzien

Komplexbildner. Thiothenoyltrifluoroaceton wurde nach den Angaben der Literatur[9] hergestellt und zeigte einen Schmelzpunkt von 73–74°. Zum Zwecke der Zuordnung wurden die Metallchelate nach den in der Literatur angegebenen Verfahren präpariert und durch Schmelzpunkt und Mikroanalyse auf ihre definierte Zusammensetzung überprüft.

Dünnschichtmaterialien. Als stationäre Phase war Kieselgel D (VEB Chemiewerk, Greiz-Dölau/DDR), Aluminiumoxid oder Gemischen aus Kieselgel und Aluminiumoxid überlegen. Die Sorptionsschicht wurde nach dem Auftragen (Schichtdicke 0.5 mm) 30 Minuten bei 110° aktiviert.

Laufmittel. Als Laufmittel dienten Lösungsmittel der Reinheit p.A. oder "zur Chromatographie".

Eichlösungen wurden entweder durch Auflösen bekannter Mengen der in Substanz hergestellten Metall–Thio-β-diketonate in Chloroform oder durch Extraktion der Metalle aus wässriger Phase mit in Chloroform gelöstem Thiothenoyltrifluoraceton gewonnen. Die Gehaltsbestimmungen der wässrigen Metallsalzlösungen erfolgte nach Standardmethoden.

Arbeitsweise

Zur *Trennung und Bestimmung von Cu, Ni und Co* wurde wie folgt verfahren: Aus der wässrigen Phase werden die Metallspuren bei einem pH-Wert von 6.5 (nichtkomplexierender Puffer nach[10]) durch kurzzeitiges, intensives Schütteln mit einer 10^{-4} *M* Lösung von Thiothenoyltrifluoraceton in Chloroform quantitativ extrahiert. Die organische Phase wird abgetrennt und störender Chelatbildnerüberschuss (Beeinflussung der Metallchelatflecken durch lange Schwanzbildung des Komplexbildners) mit 0.01 *M* KOH reextrahiert. Der organische Extrakt wird danach in kleinen hydrophobierten Glastiegeln bei *ca.* 40° unter Inertgas konzentriert. Die verbleibende organische Phase wird mit einer Mikropipette quantitativ auf die DC-Platte übertragen.

Zur Trennung der Chelatgemische kam die eindimensionale aufsteigende Technik unter Verwendung von "Sandwich-Kammern" zur Anwendung.

Nach Beendigung des Chromatographievorganges erfolgte die Entfernung der durch die Eigendetektion erkennbaren Substanzflecken von der DC-Platte. Getestet wurde hierzu auch die von Gagliardi und Likussar[11] vorgeschlagene Apparatur zum Absaugen und Extrahieren der Trägersubstanz, die sich jedoch in unserem Falle nicht bewährte. Deshalb wurde im weiteren die Trägersubstanz einfach manuell entfernt. Dabei traten, wie durch systematische Versuche bewiesen wurde, praktisch keine Substanzverluste auf.

Zwischen den einzelnen Substanzflecken war, wie aus den hR_F-Werten ersichtlich ist, genügend Zwischenraum, dass eine in gewissen Grenzen störungsfreie Entfernung erfolgen konnte. Das Sorptionsmittel mit dem adsorbierten Metallchelat wird in verschliessbare Mikrozentrifugenröhrchen überführt und exakt 0.150 ml Chloroform hinzugefügt. Mittels eines Mikromischers wird intensiv durchmischt. Anschliessend wird zentrifugiert und die überstehende klare Lösung entweder in Mikroküvetten des "Beckman Spectro-Colorimeter Model 151" (Schichtdicke etwa 0.3 cm) oder in Mikroküvetten des "Spekols" (Schichtdicke 1.000 cm) photometriert. Unterschiedliche Mengen an Trägermaterial haben im untersuchten Bereich bis 40 mg keinen Einfluss auf die Extinktion.

Zur *Trennung und Bestimmung von Pd und Rh* wird folgende Arbeitsvorschrift vorgeschlagen: Die Rhodium und Palladium enthaltende wässrige Lösung wird mit Puffer (siehe vorher) auf einen pH-Wert von 4 eingestellt (aus Vorversuchen ergab sich, dass Rh in einem pH-Bereich von 2–6 extrahierbar ist). Dann werden 3 ml einer $4 \cdot 10^{-3}$ *M* Lösung von Thiothenoyltrifluoraceton in Chloroform hinzugegeben. Anschliessend fügt man soviel Äthanol hinzu, dass sich beide Phasen vermischen. Die Lösung wird 60 min bis fast zum Sieden erhitzt. Nach 30 min erfolgt eine abermalige Zugabe von 5 ml Äthanol. Nach dem Erkalten wird zweimal 3 min mit je 5 ml Chloroform extrahiert. Die Extrakte vereinigt man und schüttelt sie zur Entfernung des überschüssigen Komplexbildners mit 0.01 *M* KOH. Der verbleibende organische Extrakt wird wie vorher angegeben weiterbehandelt.

Geräte

Beckman Ultramicro Analytical System Model 150.

Spektral-Kolorimeter "Spekol" des VEB Carl Zeiss, Jena mit Zusatzverstärker "ZV" und Messansatz EKMi.

Wechselspannungsregler "Statron 220/2.25".

ERGEBNISSE

Abbildung 1 zeigt typische Chromatogramme für die Trennung von Co-, Cu- und Ni-thiothenoyltrifluoracetonaten bzw. Rh- und Pd-thiothenoyltrifluoracetonaten. Die daraus resultierenden hR_F-Werte (R_F-Werte · 100) ergeben sich zu

$Rh(STTA)_3 = 9$
$Co(STTA)_3 = 11$
$Cu(STTA)_2 = 27$
$Pd(STTA)_2 = 33$
$Ni(STTA)_2 = 41$
$HSTTA = 80$

Die praktischen Erfassungsgrenzen sind dadurch gegeben, dass unterhalb einer gewissen Konzentration die Metallchelate auf der DC-Platte nicht mehr erkennbar sind. Sie liegen bei Anwendung der angegebenen Technik für Kobalt bei 10 ng, für Kupfer, Nickel, Rhodium sowie Palladium bei 50 ng. Die bei der Bestimmung von Kobalt in Gegenwart von Nickel und Kupfer in etwa gleichen Verhältnissen ermittelten Eichkurven zeigt die Abb. 2. Von den untersuchten Fremdionen stören die Bestimmung von Kobaltspuren (Extraktion des Kobalts bei pH-Wert 6.5) bis zu den nachfolgend angegebenen Mengen nicht: 20 μg Fe^{3+}, 2 μg Pd^{2+}, Mn^{2+} oder Rh^{3+}, 0.6 μg Cu^{2+} oder Ni^{2+}. Ausserdem rufen auch grössere Überschüsse an Alkali- und Erdalkaliionen keine Störung der Bestimmung hervor.

Es ist natürlich auch möglich, Kupfer in Gegenwart von Nickel- und Kobaltspuren bzw. Nickel in Gegenwart von Kupfer- und Kobaltspuren zu bestimmen.

Aus dem Chromatogramm der Abbildung 1(b) ist ersichtlich, dass sich Rh und Pd als Thiothenoyltrifluoracetonate gut trennen lassen. Extrahiert man die in etwa gleichen Konzentrationen vorliegenden Rh- bzw. Pd-Chelate, ergibt die photometrische Bestimmung nach der dünnschicht-chromatographischen Trennung folgende Ergebnisse (Tabelle I). Eine nach einem Rechenprogramm auf dem Kleinrechner "Cellatron 82-05" ausgeführte statistische Fehlerauswertung aller ermittelten Werte liefert für die angegebenen Bestimmungen von Rhodium und Palladium folgende Parameter.

TABELLE I

ERGEBNISSE DER PHOTOMETRISCHEN BESTIMMUNG VON Rh UND Pd

Pd (ng)	*E*[a]	*Rh (ng)*	*E*[a]
100	0.043	100	0.065
200	0.072	200	0.153
300	0.133	300	0.259
400	0.170	500	0.487
500	0.225	700	0.630
800	0.360	1000	0.930

[a] Mittelwerte aus 3 Bestimmungen. $d = 1.000$ cm; Messansatz EKMi. Messwellenlängen $\lambda_{Pd(STTA)_2} = 388$ nm; $\lambda_{Rh(STTA)_3} = 396$ nm.

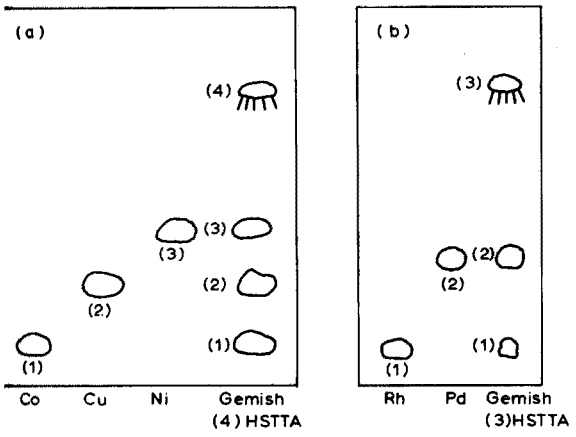


Abb. 1. (a) DC-Trennung von Co(III)-, Cu(II)- und Ni(II)-thiothenoyltrifluoracetonaten. (b) DC-Trennung von Rh(III)- und Pd(II)-thiothenoyltrifluoracetonaten. Sorbens, SiO_2; Schichtdicke, 0.5 mm; Fliessmittel, $CHCl_3$/*n*-Hexan (30+70); Trennstrecke, 10 cm; Laufzeit, *ca.* 45 min.

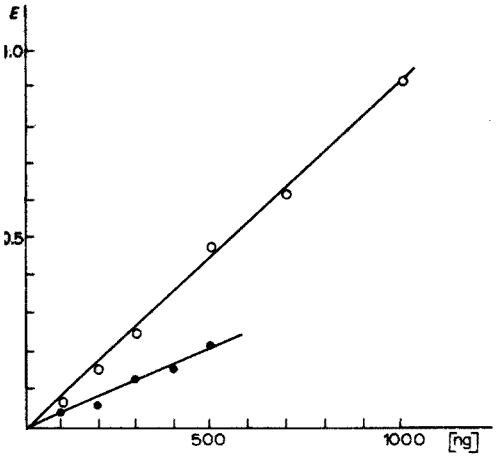


Abb. 2. Photometrische Kobaltbestimmung nach DC-Trennung der Chelatgemische (Co, Ni, Cu). (○) Mikroküvetten, $d=1.000$ cm; (●) Mikroabsaugküvetten, $d=0.3$ cm. Messwellenlänge $\lambda=375$ nm.

Rhodiumbestimmung: Gesamtstandardabweichung der Extinktion = 0.040 mit N = 12 Freiheitsgraden. Die resultierende Geradengleichung für die Eichkurve hat die Form $y=0.00096x-0.027$ mit einem Korrelationskoeffizienten von 0.9939.

Palladiumbestimmung: Gesamtstandardabweichung der Extinktion = 0.025 mit N = 12 Freiheitsgraden. Die daraus resultierende Geradengleichung für die Eichkurve hat die Form $y=0.000463\ x-0.010$ mit einem Korrelationskoeffizienten von 0.9816.

DISKUSSION

Unsere Untersuchungen zeigten, dass die M–Thiothenoyltrifluoracetonate günstige physikalisch-chemische Eigenschaften für eine dünnschicht-chromatogra-

phische Trennung mit nachfolgender photometrischer Bestimmung besitzen.

Während des Laufvorganges wurden keinerlei Zersetzungserscheinungen an den Metallchelaten beobachtet. Die hohen molaren Extinktionskoeffizienten dieser Chelate[12] ermöglichen eine Bestimmung von Cu, Ni, Co, Rh und Pd im Nanogrammbereich. Diese hohen molaren Extinktionskoeffizienten im sichtbaren Spektralbereich und das weitgehend hydrophobe Verhalten dieser Metallchelate mit den damit verbundenen Vorteilen bei der dünnschicht-chromatographischen Trennung sind auch die Hauptunterschiede zu den in der letzten Zeit untersuchten Metall–Thenoyltrifluoracetonaten[13].

Besonders geeignet erscheint die von uns untersuchte Methode zur Abtrennung "thiophiler" Metallspuren von Alkali- bzw. Erdalkalimetallionen durch Extraktion (Gruppentrennung) und nachfolgender dünnschicht-chromatographischer Trennung der extrahierten Metallspuren (Einzelnachweis).

Die Methode lässt sich auch auf andere als die in der vorliegenden Arbeit untersuchten Metall–Thio-β-diketonate anwenden. Durch Variation der Extraktionsbedingungen (pH-Wert, Maskierungsmittel u.a.) sowie durch geeignete Wahl der Trennbedingungen (Trennschicht und Laufmittel) sind weitere Möglichkeiten zur Lösung von Trennproblemen gegeben.

ZUSAMMENFASSUNG

Die dünnschicht-chromatographische Trennung von Cu, Co, Ni sowie Pd und Rh in Form ihrer Monothio-β-diketonate wurde untersucht. Als Beispiel ist die Trennung der mit Thiothenoyltrifluoraceton in Chloroform extrahierten Co-, Ni- und Cu-Chelate sowie der Pd- und Rh-Chelate auf Kieselgel mit $CHCl_3$/*n*-Hexan (30 + 70) beschrieben. Die ermittelten R_F-Werte zeigen, dass eine saubere Trennung möglich ist, so dass eine mikrophotometrische Bestimmung nach Elution der Metallchelate mit $CHCl_3$ erfolgen kann. Die Bestimmung hat dabei praktische Erfassungsgrenzen für Kobalt von 10 ng und für Kupfer, Nickel, Rhodium und Palladium von 50 ng. Die Bestimmung von Kobaltspuren in Gegenwart von Kupfer und Nickel sowie die Trennung und Bestimmung von Rhodium- und Palladiumspuren ist beschrieben.

SUMMARY

The thin-layer chromatographic separation of Cu, Co, Ni, Pd and Rh as monothio-β-diketonates was investigated. As examples the separation of the thiothenoyltrifluoracetonates of Co, Ni and Cu, and of Pd and Rh on silica gel with $CHCl_3$/*n*-hexane (30 + 70) after extraction with chloroform is described. The obtained R_F-values show a good separation. The metal chelates can be determined microphotometrically after their elution with chloroform. The practical limit of the determinations is 10 ng for cobalt and 50 ng for Cu, Ni, Rh, Pd. The determination of traces of Co in presence of Cu and Ni, and the separation and determination of traces of Rh and Pd are described.

RÉSUMÉ

Une étude est effectuée sur la séparation chromatographique sur couche

mince de Cu, Co, Ni, Pd et Rh, sous forme de monothio-β-dicétonates. On donne comme exemples, la séparation de Co, Ni et Cu et la séparation Pd et Rh sous forme de thiothénoyltrifluoracétonates sur silicagel et $CHCl_3$/n-hexane(30 + 70), après extraction dans le chloroforme. Les valeurs de R_F obtenues montrent qu'une bonne séparation est possible. Les chélates métalliques peuvent être dosés par microphotométrie après avoir été élués au moyen de chloroforme. Les limites pratiques de ces dosages est de 10 ng pour le cobalt et 50 ng pour Cu, Ni, Rh et Pd. On décrit une méthode de dosage de traces de cobalt, en présence de cuivre et de nickel, ainsi qu'une séparation et dosage de traces de rhodium et de palladium.

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REVERSED PHASE FOAM CHROMATOGRAPHY

SEPARATION OF IRON FROM COPPER, COBALT AND NICKEL IN THE TRI-*n*-BUTYL PHOSPHATE–HYDROCHLORIC ACID SYSTEM

T. BRAUN, L. BAKOS* and ZS SZABÓ

Institute of Inorganic and Analytical Chemistry, L. Eötvös University, 1443 Budapest (Hungary)

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Tri-*n*-butyl phosphate (TBP) is extensively applied in analytical chemistry for the separation of metals in systems with different compositions. Several papers have been published on the separation of metal chlorides, including iron and nickel chlorides, with TBP. Different methods have been used in these studies, but for the present purpose, the results obtained by extraction and reversed-phase chromatography methods were of greatest interest.

Specker and Cremer[1] were the first to report data on the extraction of iron(III) chloride with TBP. They used TBP dissolved in benzene and extended their studies, in addition to the parameters important for separation, to the establishment of the composition of complexes present in the system. Majumdar and De[2] reported distribution coefficients which differed substantially from the data given by Specker and Cremer and later by other authors.

Gindin and Ivanov[3] investigated the separation of cobalt and nickel chlorides and demonstrated that although the distribution coefficient of cobalt chloride in the hydrochloric acid–TBP system is small, separation is nevertheless feasible, because the value for nickel chloride is only about one hundredth of that for cobalt chloride. Eshovska and Kopakh[4] determined the dependence of cobalt chloride distribution on hydrochloric acid concentration and determined the composition of the complex taking part in the extraction which they found to be $CoCl_2 \cdot 2$ TBP. Günzler and Mühl[5] extracted copper(II) ions from hydrochloric acid solutions with TBP and found that the distribution coefficient is of the order of 0.1. They also stated that the presence of iron(II) ions may increase the partition coefficient of copper by two orders of magnitude. They explained this finding by the formation of a readily extractable copper–iron double complex having the composition $(FeCu)Cl_4 \cdot$ TBP. Specker and Shirondker[6] studied the extraction of trace amounts of copper, cobalt, nickel and other metals in the presence of iron(II) ions.

Partition chromatography may be interpreted as an extraction process repeated many times. It is therefore obvious why liquids well-proven as extracting agents have often been tried for application as stationary phases. Hayes and Hamlin[7] studied the chromatographic behaviour of iron(III), cobalt(II), nickel(II) and copper(II) ions. The stationary phase was TBP, supported on granular PTFE. Mikulski

* Central Research Institute for Physics, Budapest, Hungary.

and Stronski[8] used a column filled with TBP on a silicate-based support for the separation of cobalt, iron and manganese. Preobrazhensky and Katykhin[9], as well as Alimarin *et al.*[10] also used TBP supported on PTFE. They separated iron(III) ions from other metals by feeding the mixture of metal ions in >2 *M* hydrochloric acid solution onto the column. Iron was bound selectively, while the other metals passed through the column at such hydrochloric acid concentrations. Iron was eluted with <0.5 *M* hydrochloric acid. According to their data, the procedure lends itself to the removal of iron traces.

After such antecedents, it appeared interesting to test the applicability of the foam chromatographic method discussed in detail in previous papers[11–13] for the separation of some metal chlorides in the TBP–hydrochloric acid system. This study included repeated measurement of the distribution ratio of iron, since the literature data are not in full agreement, and the separation of iron from nickel, cobalt and copper by foam chromatography. This separation is a current analytical problem in the investigation of different alloy types. Moreover, the separation of iron from cobalt is of importance in the production of radiochemical preparations, primarily in the production of carrier-free ^{59}Fe. Cobalt contaminations can arise not only during production, but relative enrichment of ^{60}Co activity can occur during the life of the preparation from the ^{59}Fe, so that repeated purification of the radioactive preparation may become necessary.

Tri-*n*-butyl phosphate is capable of extracting hydrochloric acid too, at least up to a definite hydrochloric acid concentration in the organic phase. At hydrochloric acid concentrations exceeding a well-defined value (which, however, varies with the diluent used for TBP), a new phase may separate from the organic phase:

$$TBP_O + HCl \rightarrow TBP \cdot HCl_O$$

Metals are usually extracted in the form of ion associates. It is characteristic for such systems that the composition of the associate is largely dependent on the components of the system. Thus, for example, according to Specker and Cremer[1], the compounds in the extraction of iron salts are described by the following equations:

$$3\ TBP_O + FeCl_3 \rightarrow FeCl_3 \cdot 3\ TBP_O$$

in the case of aqueous phases which are 4 *M* in hydrochloric acid, and

$$2\ TBP_O + FeCl_3 + HCl \rightarrow HFeCl_4 \cdot 2\ TBP_O$$

in the case of aqueous phases which are 7.9 *M* in hydrochloric acid. In these processes TBP usually partly or wholly replaces hydrate water.

EXPERIMENTAL

Reagents and materials

Unless otherwise stated, reagent-grade chemicals were used. EDTA, copper sulphate, hydrochloric acid and nitric acid were of analytical-reagent grade.

Tri-n-butyl phosphate. Technical grade TBP was washed with a 5% sodium carbonate solution and subsequently with water, and distilled in vacuum. The fraction boiling at 168° at 15 torr was used.

Metal chlorides. Analytical grade $NiCl_2 \cdot 6\ H_2O$, $CuCl_2 \cdot 2\ H_2O$, $FeCl_3 \cdot 6\ H_2O$ and $CoCl_2 \cdot 6\ H_2O$ (Reanal, Hungary) were used.

Polyurethane foam. Open-cell polyether type (Északmagyarországi Vegyimüvek, Sajóbábony, Hungary) was used.

Isotopes. Carrier-free ^{58}Co was used in the form of its chloride. ^{59}Fe (specific activity 9.9 Ci g^{-1}) was used in the form of 0.05 *M* $FeCl_3$ solution. Both isotopes were produced in the Isotope Institute of the Hungarian Academy of Sciences.

Twice-distilled water was used in all experiments.

Analytical procedures

Hydrochloric acid was determined by potentiometric titration with a Radiometer Titrigraph. Titration of the organic phase was carried out in a 2:1 mixture of alcohol and water.

Metals were determined—after suitable preparation—by complexometry. Solutions containing copper were directly titrated with EDTA. Nickel, cobalt and iron—when not radiometrically determined—were determined by back-titration of excess of EDTA. In all cases the indicator was PAN[14].

For activity measurements, a NaI(Tl) scintillation detector or a Ge/Li semiconductor detector, coupled with a 1024-channel analyzer (KFKI NTA 512-B) was used.

All measurements were carried out at ambient temperature (26° ± 1°).

Equipment

The chromatographic columns used were 20 cm long and 10 mm in diameter. In batch experiments glass-stoppered flasks and a shaking machine were applied. The column was filled as described earlier[12], with the difference that columns were equipped with short effluent spouts in order to reduce dead space[13].

RESULTS AND DISCUSSION

Extraction of metal chlorides

It is well known that some metals form readily extractable chloride complexes in aqueous solutions at low hydrochloric acid concentrations, while others require high acid concentration. Thus, the partition coefficient and the migration of the individual metals along a TBP-loaded chromatographic column depend on the hydrochloric acid content of the system. In order to influence the migration of the metal ions, it is expedient to know the dependence of their partition coefficients on hydrochloric acid concentration. Accordingly, the distribution of hydrochloric acid was first determined between TBP and water. The results are presented in Fig. 1. Contact time before measurements was 15 min, this period being sufficient for equilibration; preliminary measurements indicated that establishment of the equilibrium requires only 30 s. The measured data are in good agreement with data from the literature.

The distribution of nickel chloride was not investigated, since it does not form chloride complexes extractable with TBP.

In studies on the distribution of cobalt, copper and iron chlorides between TBP and hydrochloric acid varying in concentration from 1 to 8.4 *M*, 5 ml of a

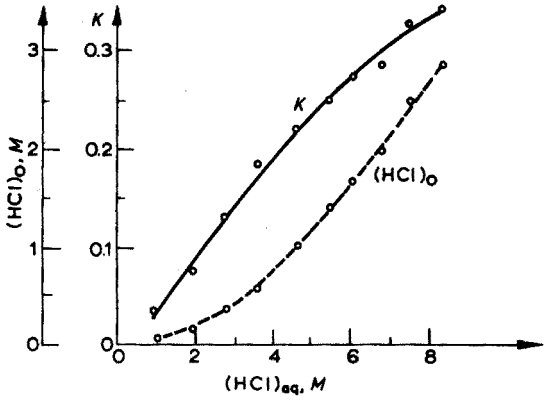

Fig. 1. Distribution of hydrochloric acid between tributyl phosphate and water *vs.* hydrochloric acid concentration.

solution containing 1 mg ml^{-1} of the respective metal was used. The ratio of the organic and aqueous phases was 1 : 1. Preliminary experiments indicated that the distribution equilibria were reached within 30 s, therefore measurements were made after 20 min of agitation. After separation of the phases, the metal content of the aqueous phase was determined directly, while that of the organic phase was determined after re-extraction with distilled water. The distribution of iron(III) chloride was determined by means of solutions containing ^{59}Fe. The results are presented in Fig. 2. The values for copper(II) chloride are in good agreement with the data

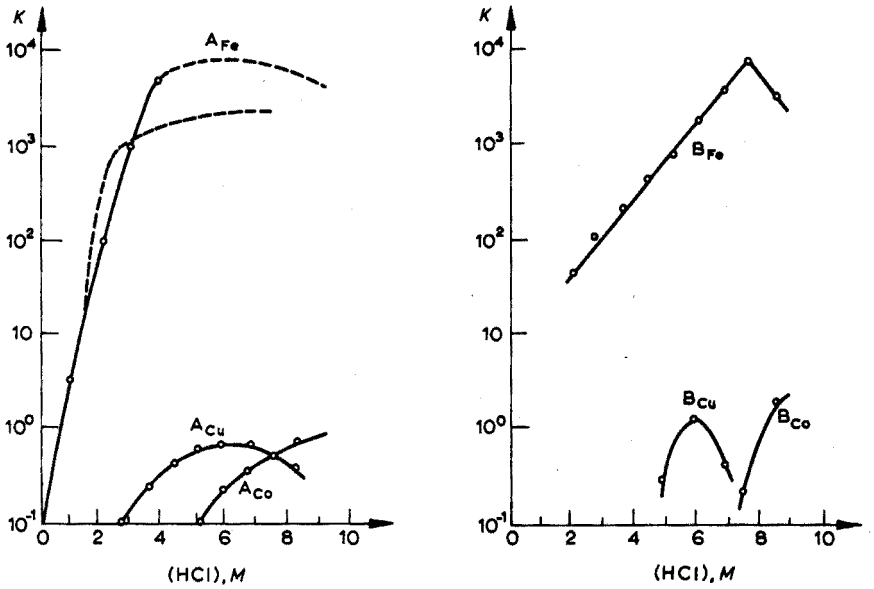

Fig. 2. Distribution ratios of cobalt, copper and iron in the TBP–HCl system *vs.* hydrochloric acid concentration in the aqueous phase.

Fig. 3. Distribution ratios of cobalt, copper and iron in the TBP (polyurethane foam)–HCl system *vs.* hydrochloric acid concentration in the aqueous phase.

reported by Weidmann[15]. The dashed portion of the plot representing the partition coefficients of iron(III) chloride indicates the minimum value calculated from the experimental data, because the exact value could not be determined.

Determination of partition coefficients by the batch method

In batch measurements, the organic phase was TBP supported on polyurethane foam; 1 g of the foam saturated with TBP (*ca.* 67% TBP) was agitated with 10 ml of the aqueous solution. In this work, the distribution ratio was defined as

$$K_d = \frac{g_o/V_o}{g_a/V_a}$$

where g is the amount of the investigated metal and V is the volume of the organic phase, the suffix o indicates the organic phase, and a indicates the aqueous phase. The initial metal concentration was 1 mg ml^{-1} as in extraction experiments, and the equilibration time was 30 min. The results (Fig. 3) indicate that the optimal hydrochloric acid concentrations found in liquid–liquid extraction do not change significantly in the case of TBP on polyurethane foam support for batch extraction. Batch measurements were also preceded by measurements of time dependence. For cobalt and copper chlorides, the equilibrium was established within 1 min, while equilibration was slower for iron(III) chloride, particularly in the case of diluted solutions ($\leqslant 0.1$ mg ml^{-1}).

Column experiments

The chromatographic behaviour of metal ions was studied on columns filled with cylindrical pieces of polyurethane foam pretreated with TBP. The data of the column were as follows: diameter 1 cm, height of packing 11.5 cm, weight of packing 2.92 g, TBP content 91.2%, flow rate 1 ml min^{-1}.

The volume of the sample was 1 ml in all cases. Before use, the eluting solutions were equilibrated with TBP.

The object of these experiments was to find optimal concentrations for column preparation and hydrochloric acid concentration in order to obtain good resolution at high flow rates. The shape of the foam pieces had an important effect on the quality of the column. In Fig. 4 breakthrough plots of iron(III) chloride obtained with two differently prepared columns are shown. Plot I corresponds to the column filled with 1–1.5 cm foam cubes, while plot II corresponds to the column filled with foam pieces of similar size, but of cylindrical shape. It may be seen from the figure that cube-shaped packing leads to greater inhomogeneity and consequently to significantly worse breakthrough characteristics. The best column properties were obtained by cutting the foam pieces already impregnated with TBP into smaller pieces with average lengths of 2 to 5 mm and using these pieces to fill the column.

Figure 5 shows the elution peak of 4 mg of nickel(II) chloride obtained with 4 *M* hydrochloric acid as eluent. From this measurement, the interstitial volume of the column was calculated to be 6.5 ml, *i.e.* 71%. Figures 6 and 7 show the elution curves of iron and copper chlorides. The results indicate that in this system it is possible to separate iron from cobalt, nickel and copper chlorides, but that the latter three cannot be separated from each other. The retention of iron(III) ions is

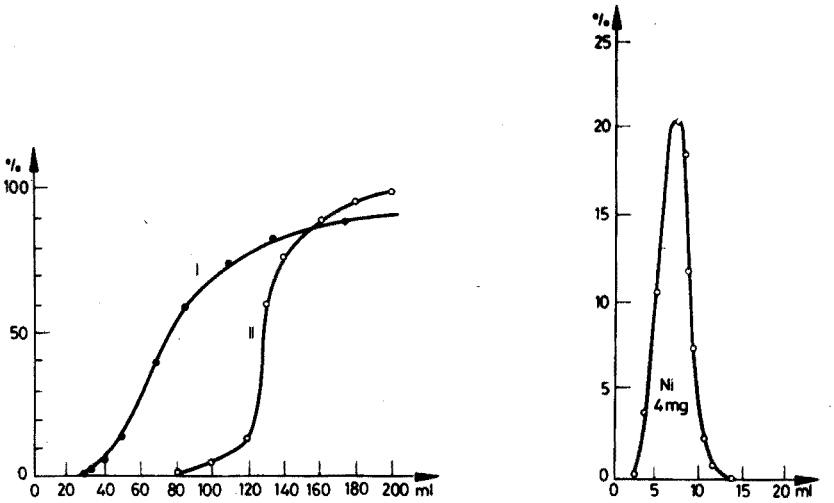

Fig. 4. Breakthrough curves for iron. Support, polyurethane foam. Weight of packing, 2.13 g (curve I) and 2.33 g (curve II). Stationary phase, TBP saturated with hydrochloric acid. Iron concentration, 4 mg ml^{-1}. Hydrochloric acid concentration, 4 *M*.

Fig. 5. Elution of nickel chloride. Eluent, 4 *M* hydrochloric acid.

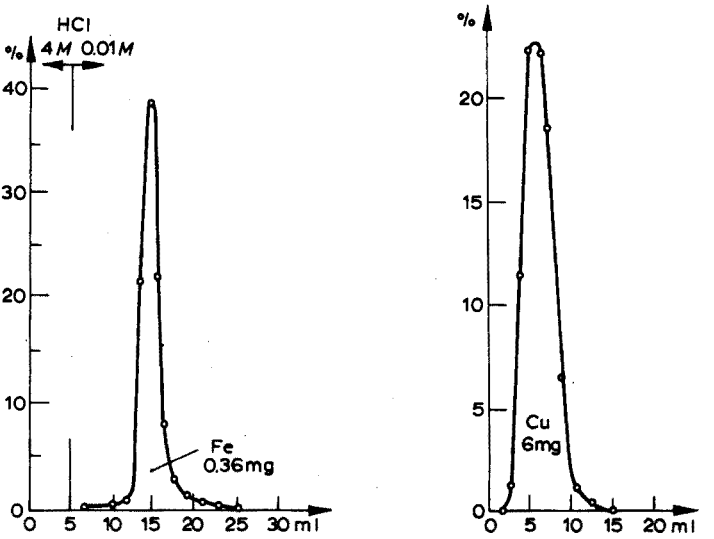

Fig. 6. Elution of iron(III) chloride. Eluent, 0.01 *M* hydrochloric acid.

Fig. 7. Elution of copper(II) chloride. Eluent, 4 *M* hydrochloric acid.

practically infinite in 4 *M* hydrochloric acid, whereas at this acid concentration nickel, copper and cobalt pass through the column quantitatively. As shown in Fig. 6, the iron bound on the column can be eluted with 0.01 *M* hydrochloric acid. Chromatographic data for the iron–nickel separation carried out in this way are presented in Fig. 8.

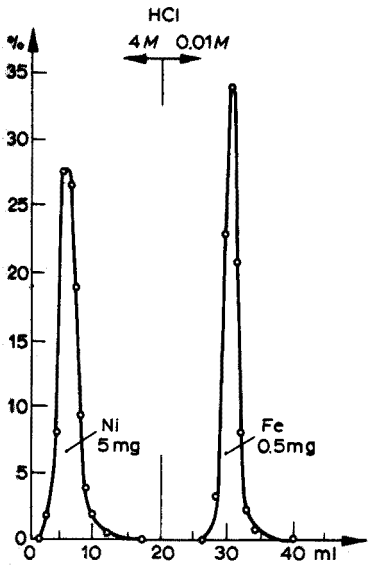

Fig. 8. Separation of nickel and iron. Support, polyurethane foam. Stationary phase, TBP. Flow rate, 1 ml min^{-1}. Eluent for nickel, 4 *M* hydrochloric acid. Eluent for iron, 0.01 *M* hydrochloric acid.

TABLE I

SEPARATION OF IRON(III) AND COPPER(II) CHLORIDES AT DIFFERENT METAL RATIOS BY FOAM CHROMATOGRAPHY IN THE HYDROCHLORIC ACID–TRIBUTYL PHOSPHATE SYSTEM

Fe:Cu ratio	*Taken (mg)*		*Found (%)*	
	Fe	*Cu*	*Fe*	*Cu*
1:100	0.05	5.00	85.1	101.0
			82.2	101.6
			84.2	99.1
1:10	0.50	5.00	102.0	98.8
			99.2	101.6
			96.8	100.8
1:1	5.00	5.00	99.1	99.6
			98.4	102.1
			97.8	98.0
10:1	5.00	0.50	100.4	95.0
			98.5	92.5
			101.5	106.5

In further experiments, the metal ratios at which iron(III) chloride can be separated from copper(II) or cobalt chlorides were established. These separations could be carried out similarly to the separation of iron from nickel. Experimental

TABLE II

SEPARATION OF IRON(III) AND COBALT CHLORIDES AT DIFFERENT METAL RATIOS BY FOAM CHROMATOGRAPHY IN THE HYDROCHLORIC ACID–TRIBUTYL PHOSPHATE SYSTEM

Fe : Co ratio	*Taken (mg)*		*Found (%)*	
	Fe	*Co*	*Fe*	*Co*
10^8 : 1	1.00	$1.00 \cdot 10^{-8}$	98.2	98.8
			97.8	100.4
			101.2	97.6
10^4 : 1	1.00	$1.00 \cdot 10^{-4}$	97.8	100.0
			101.2	98.4
			100.0	104.2
10^2 : 1	1.00	$1.00 \cdot 10^{-2}$	100.0	98.4
			98.2	97.0
			101.2	98.4
10 : 1	1.00	$1.00 \cdot 10^{-1}$	99.5	102.7
			97.8	99.5
			97.8	97.2
1 : 1	1.00	1.00	100.0	104.0
			100.0	102.2
			101.6	96.5
1 : 10	0.50	5.00	97.4	100.0
			96.1	98.8
			99.5	101.2
1 : 20	0.10	2.00	82.0	99.5
			85.0	99.5
			86.8	98.5

results are summarized in Tables I and II. Each determination consisted of three parallel measurements carried out on three different columns. The data indicate that no quantitative limitations can be established for the unbound component.

In view of the results obtained, the following procedure is suggested for the separation of iron. The sample containing at least 0.5 mg of iron and having a volume of 1–2 ml is fed to the suitably prepared column. The column is then washed with 5 *M* hydrochloric acid at a flow rate of 1 ml min^{-1} until 25 ml of eluate is collected. The eluate contains the inert component. Subsequently elution is continued with 0.01 *M* hydrochloric acid. The first 3 ml of the eluate are discarded and 25 ml of the eluate are collected, containing the iron recovered from the column.

The separation of iron and cobalt was studied in more detail, this problem being of some practical importance. The γ-peaks of ^{59}Fe and ^{58}Co isotopes are so close to each other that they cannot be resolved with a scintillation crystal. It is therefore important to separate the carrier-free ^{59}Fe isotope from the cobalt target material used in its preparation. ^{59}Fe and ^{58}Co isotopes were separated on the chromatographic column prepared in the described manner. The purity of the separated isotopes was checked by means of their γ-spectra taken with a Ge/Li detector. The

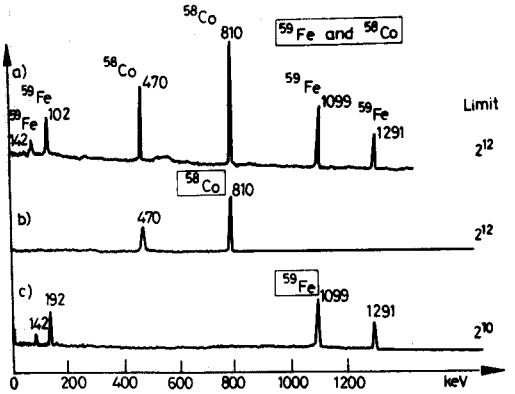

Fig. 9. γ-Spectra of a mixture of ^{59}Fe and ^{58}Co and of the fractions obtained by separation on a TBP (polyurethane foam) chromatographic column. (a) Before separation; (b) and (c) fractions obtained after separation.

spectra of the initial solution and the solutions containing the separated isotopes are presented in Fig. 9. Quantitative yields of cobalt were obtained in the separation, while iron recoveries close to 100% were only possible in the case of larger amounts of iron. Therefore the iron isotope must either be diluted by a carrier, or—if carrier-free iron isotope is required—one must be contented with a yield of about 80%.

SUMMARY

The separation of iron from cobalt, copper and nickel by reversed-phase foam chromatography was investigated. The distribution of Fe, Co and Cu in TBP–HCl and TBP (polyurethane foam)–HCl systems was measured. Iron can be separated from the three other metals on polyether-type polyurethane foam columns loaded with TBP. The break-through curve of iron on TBP (polyurethane foam) columns was measured. The column was found suitable for the separation of ^{58}Co and ^{59}Fe isotopes.

RÉSUMÉ

Une étude est effectuée sur la séparation du fer d'avec cobalt, cuivre et nickel par chromatographie sur mousse. On mesure la distribution de Fe, Co et Cu dans des systèmes TBP–HCl et TBP/mousse de polyuréthane/HCl. Le fer peut être séparé d'avec les trois autres métaux sur colonnes de mousse de polyuréthane de type polyéther, chargées de TBP. Ce type de colonne convient pour la séparation des isotopes ^{58}Co et ^{59}Fe.

ZUSAMMENFASSUNG

Die Trennung von Eisen von Kobalt, Kupfer und Nickel durch Schaum-Chromatographie mit umgekehrten Phasen wurde untersucht. Die Verteilung von Fe, Co und Cu in den Systemen TBP–HCl und TBP (Polyurethanschaum)–HCl

wurde ermittelt. Eisen kann von den drei anderen Metallen mittels Säulen abgetrennt werden, die mit TBP beladenen Polyurethanschaum vom Polyäthertyp enthalten. Die Durchbruch-Kurve von Eisen an TBP (Polyurethanschaum)-Säulen wurde gemessen. Die Säule eignete sich für die Trennung der Isotope ^{58}Co und ^{59}Fe.

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AN AUTOMATED SYSTEM FOR PHOTOMETRIC TITRATION BY STEPWISE ADDITION OF EQUAL VOLUMES OF TITRANT

LENNART PEHRSSON and AXEL JOHANSSON

Department of Analytical Chemistry, Royal Institute of Technology, Stockholm 70 (Sweden)

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Johansson[1] has described a new method of photometric titrations. The titrant is added stepwise in equal volumes to the sample solution with measurement of absorbance after each addition, and the equivalence volume is then calculated from the measured absorbances. The choice of indicator is governed by somewhat different principles than those usual in photometric titrations with visual monitoring of the end-point.

Titrations based on this method are well adapted for automation and the aim of this paper is to show how a fully automated instrumental system for these titrations can be built up from commercially available components. The system delivers measured volumes of sample, indicator solution and buffer solution to the titration vessel, titrates, and finally washes the titration vessel before reuse. It can carry out *ca.* 30 titrations per hour and has a loading capacity of 200 samples. The system has been tested by titrating calcium with EGTA in the presence of calmagite as indicator.

THEORETICAL

The basic theory applied to complexiметric titrations can be summarized as follows[1].

If V_0 ml of a metal ion solution is titrated by adding V ml of a C_y molar solution of a complexing agent Y, the following equation is valid before the equivalence point

$$V_e - V = \frac{V_0 + V}{C_y} \cdot [M] \tag{1}$$

where V_e is the equivalence volume and [M] is the free metal ion concentration.

[M] can be calculated from photometric titration data by using the following equation

$$[M] = \frac{A_I - A}{A - A_{MI}} \cdot \frac{1}{K'_{MI}} = \frac{A_I - A}{A - k \cdot A_I} \cdot \frac{1}{K'_{MI}} \tag{2}$$

where A is the absorbance measured after addition of V ml, A_I the absorbance of the uncomplexed indicator, A_{MI} the absorbance when the indicator is fully complexed by the metal M, K'_{MI} the conditional stability constant of the metal

indicator complex and $k = a_{MI}/a_I$, where a_{MI} and a_I are the absorptivities of the metal indicator complex and the free indicator, respectively.

Combining eqns. (1) and (2) gives:

$$V_e - V = \frac{1}{K'_{MI} \cdot C_y} \cdot (V_0 + V) \cdot \frac{A_I - A}{A - k \cdot A_I} \quad (3)$$

A more accurate equation is obtained if a correction is applied for the amount of metal ion bound by the indicator

$$V_e - V = \frac{1}{K'_{MI} \cdot C_y} \left[(V_0 + V) \cdot \frac{A_I - A}{A - k \cdot A_I} + V_0 \cdot C_I \cdot K'_{MI} \cdot \frac{A_I - A}{A_I - k \cdot A_I} \right] \quad (4)$$

where C_I is the total concentration of the indicator. This correction is usually small, and it is only necessary to use approximate values of C_I and K'_{MI}. If the square-bracketed term is plotted against V, a straight-line plot, intersecting the V-axis at V_e, is obtained.

Optimal precision is obtained if half the indicator is bound to the metal and half is free at the half-neutralization point[1]. Thus log K'_{MI} should equal ($pC_M + 0.3$), where C_M is the total concentration of metal.

Samples containing 0.025–0.075 *M* calcium were automatically titrated, with EGTA as complexing agent and calmagite as indicator. After dilution with indicator and buffer solutions, the calcium concentration was lowered by a factor of about 1/7. (pCa + 0.3) thus varied from 2.2 to 3.0, and log K'_{CaI} should have a value of about 2.6. If a 1:1 ammonia:ammonia buffer is used, log K'_{CaI} can be held constant at *ca.* 2.7[1].

EXPERIMENTAL

Instrumental system components

The system layout is shown in Fig. 1, and Fig. 2 shows schematically the system design. It comprises units for solution handling, absorbance measurement and system control.

The solution handling unit consists of six automatic pipettes, two fraction collectors and three pneumatic lifts. The automatic pipettes (AGA AB, Lidingö, Sweden)[2] are driven by compressed air and controlled by magnetically operated valves. An Ultro Rac fraction collector (Model 7000, LKB Produkter AB, Bromma, Sweden) with capacity for 200 samples is used as a sample feeder. A conventional circular fraction collector is used as a titration vessel holder. The titration vessels consist of polypropene centrifuge tubes (17 mm diam. and 110 mm length).

Necessary vertical and horizontal movements of the inlet and outlet tubes of the pipettes and the photometer (see Fig. 1) are carried out by pistons driven by compressed air.

The absorbance measurement unit consists of an automatic photometer (AGA AB, Lidingö, Sweden), a digital voltmeter and a tape punch. Figure 3 shows the photometer without the cover. It is a double-beam instrument having a cylindrical cuvette, and a glass rod, used as a reference sample. The detection system consists of two interference filters and two cadmium sulphide photocells. Signals from these

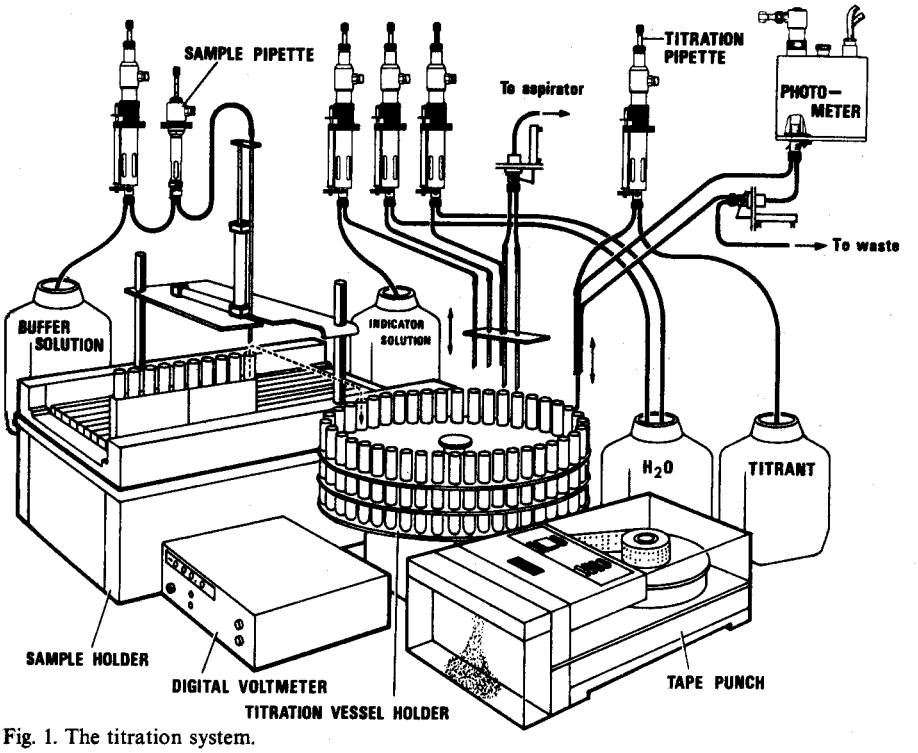

Fig. 1. The titration system.

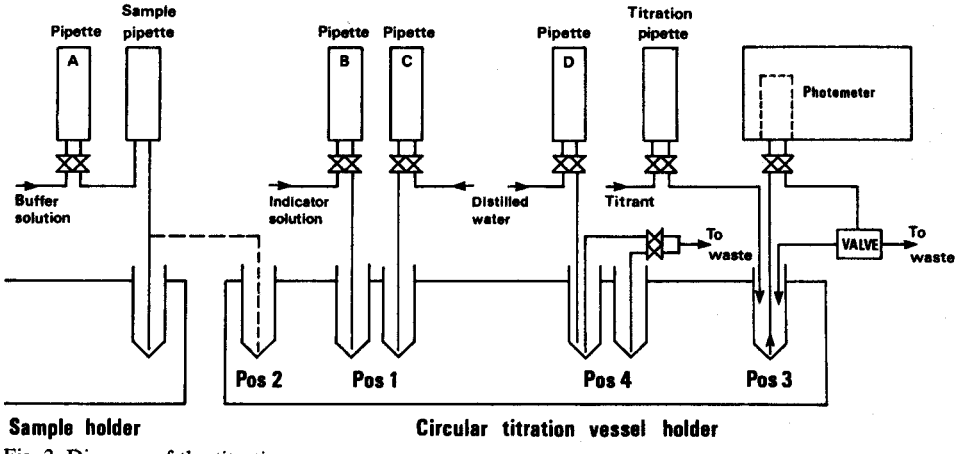

Fig. 2. Diagram of the titration system.

photocells are amplified and converted to a log ratio. The cuvette is fitted with a compressed-air driven plunger and a two-way valve, so that solution can be sucked up to the cuvette through one tube and pumped out through another.

The control unit consists of a digital comparator and two motor-driven switching units, used as programmers.

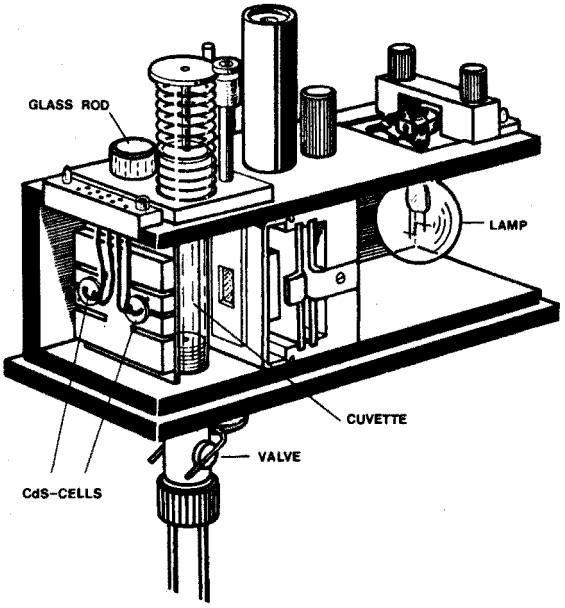

Fig. 3. The photometer.

System operation

The system carries out the following operations (see Fig. 2).

Transfer of measured volumes of sample, addition of indicator and buffer solutions. Measured volumes of a sample, indicator and buffer are added to every second titration vessel. The remaining vessels are filled with rinse water.

At *position 1* the outlet tubes of pipettes B and C are lowered into two neighbouring titration vessels. By pipette B 1 ml of indicator solution is added to one of the vessels; the other vessel is filled with 10 ml of distilled water by pipette C. After the system has completed one cycle the outlet tubes are raised, the titration vessel holder is rotated two steps counter-clockwise, the tubes are lowered into the next two vessels, etc. When the titration vessels leave position 1, every second vessel thus contains indicator solution and the other vessels contain distilled water.

At *position 2* sample and buffer solution are added to a titration vessel containing indicator solution. The tube of the sample pipette is lowered into a vessel in the sample feeder, and 0.7 ml of the sample is sucked up by the sample pipette. The tube is then raised, moved across and briefly dipped into a vessel containing distilled water (to a depth of about 3 mm) to remove excess of sample on the outside of the tube, and then the sample is introduced into the following titration vessel (containing indicator solution). A 2.5-ml aliquot of buffer solution is then pipetted by reagent pipette A through the sample pipette, with the plunger in its lowest position, into the titration vessel. This rinses the sample delivery system.

Titration. The samples, diluted with indicator and buffer solutions, are titrated at *position 3.* The outlet tube of the titration pipette and the inlet and outlet tubes of the photometer are lowered into the titration vessel (only the inlet tube of the

photometer is allowed to dip into the titration mixture). Titrant is added in portions by means of the titration pipette, and the absorbance of the titration mixture is measured after each addition. (To obtain complete mixing, the titration mixture is pumped through the cuvette twice before each absorbance measurement.) When the indicator has been converted to its free form, two or three further titrant additions are made, and then the titration is stopped. Measured absorbances are recorded with the sample identification number on data tape for subsequent data processing.

Rinsing. Cuvette and tubing are rinsed with distilled water from the following titration vessel before the next sample is titrated. Two aliquots of distilled water are pumped through the cuvette to waste. A third aliquot is pumped through the cuvette back to the titration vessel, by means of a pneumatically operated two-way valve which switches between the titration vessel and waste.

Titration vessels are rinsed at *position 4*. Two tubes are lowered into two neighbouring vessels to suck off the titrated mixture and the rinsing water, respectively. The vessel that contained the titrated mixture is then rinsed with 10 ml of distilled water from pipette D.

Sample change-over

In order to determine A_I values (see eqn. 4), one or more titrant portions must be added and the corresponding absorbance measurements carried out after the equivalence point has been reached. The indicator is completely converted to its free form slightly after the equivalence point. Further titrant additions will lower the absorbance of the titration mixture by dilution. When an absorbance reading is less than the preceding value, the comparator (see Fig. 4) closes a gate, which, after one more titrant addition and absorbance measurement, allows sample change-over.

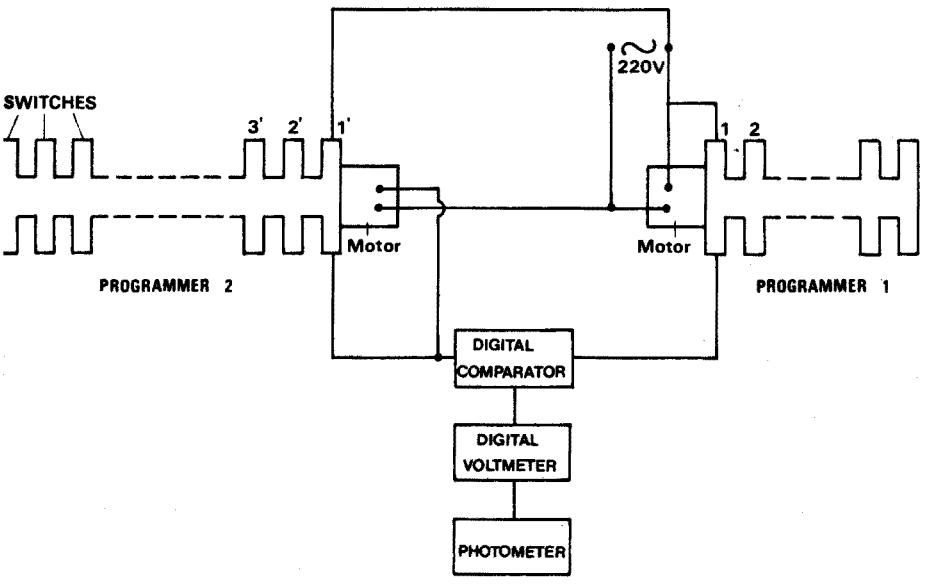

Fig. 4. Diagram of the control unit.

The comparator and the two programmers operate as follows. Programmer 1 has a cycle time of 20 s; it operates continuously and controls the titration pipette, the photometer and the digital voltmeter. Programmer 2 has a cycle time of 40 s and is used to control the remaining system functions. It operates intermittently and is started by programmer 1 and the comparator. Switch 1, in programmer 1, closes for *ca.* 5 s during each cycle, allowing, if the comparator gate is open, mains current to flow to the programmer 2 motor. This programmer starts, controls all sample change-over procedures, restores the comparator and is then stopped by switch 1', in programmer 2. Programmer 1 begins the next titration while these procedures are being carried out. The comparator is also equipped with a shut-off unit to close the gate, when a pre-set maximum number of titrant additions have been made.

Titration of calcium(II)

The value of the conditional stability constant of the metal–indicator complex, K'_{MI}, must not change during the titration. pH and ionic strength affect K'_{MI} and should therefore be constant. The volumes of the diluted sample solution and the titrant added are similar, and particularly the ionic strength of the titration mixture may change appreciably during the titration if there is a large difference in their ionic strengths.

To keep pH and the ionic strength constant, the diluted sample solution and the titrant are given the same, relatively high, concentration of the buffer. If the buffer concentration in the titrant is m, the buffer solution delivered by pipette A should have a concentration of $m \cdot V_0/V_A$, where V_A is the volume delivered by pipette A and V_0 is the sum of the pipetted volumes of sample, indicator and buffer solutions, and the volume of distilled water remaining in the photometer tubing after rinsing.

Reagents for titration of calcium. Indicator solution: $5 \cdot 10^{-4}$ *M* calmagite. Buffer solution: 0.5 *M* ammonia solution–0.5 *M* ammonium chloride. Titrant: 0.015 *M* Na_4-EGTA in 0.25 *M* ammonia solution–0.25 *M* ammonium chloride.

Evaluation of titration data

The data tape is fed to a computer, which calculates the equivalence volume for each titration by means of eqn. (4) and linear regression. The exact values of k; V_0 and the volume delivered by the titration pipette, and approximate values of C_I and K'_{MI} must be known and stored in the computer. (k and K'_{MI} are easily calculated from the absorbances recorded when a standard is titrated, if the sample pipette volume and the titrant concentration are known[1].) The last two absorbance values from each titration are used to determine A_I. The third last absorbance value may represent a point before or after the equivalence point and this is tested by the computer before the equivalence volume is calculated.

RESULTS

Samples containing 0.025–0.075 *M* calcium(II) were titrated. Results are shown in Table I.

TABLE I

TITRATION OF CALCIUM(II)

Calcium concentration (M)	0.02500	0.04000	0.05000	0.06000	0.07500
Number of samples titrated	10	10	20	10	10
Titration time (s)	80	100	120	140	160
Number of titrant additions before the equivalence point	2	3	4	5	6
Mean value of the found calcium concentration (M)	0.02505	0.04006	Used for calibration	0.05998	0.07503
Standard deviation (M)	0.00008	0.00008	0.00010	0.00009	0.00013
Coefficient of variation (%)	0.32	0.20	0.19	0.16	0.18

Determination of carry-over errors

In this system carry-over may arise from the following sources.

(a) Incomplete rinsing of sample pipette inlet tube. This type of carry-over was measured as described by Johansson and Pehrsson[2]. The sample inlet tube is made of Teflon with a length of 0.8 m and a diameter of 1.2–1.8 mm. With a sample pipette volume of about 0.7 ml, no sample will enter the pipette. Rinsing with 2.5 ml of buffer solution gives a carry-over of less than 0.1%.

(b) Incomplete rinsing of the cuvette and the inlet and outlet tubes to the cuvette with distilled water between successive samples. This was measured by filling every second titration vessel with distilled water. The remaining titration vessels were sequentially filled with two 6.5-ml samples of copper sulphate solution and two 6.5-ml samples of distilled water. The photometer unit and the titration vessel holder were set in operation as described above. For each sample the absorbance at 700 nm, being a measure of the copper sulphate concentration in the sample, was printed out. Carry-over for each cycle was then calculated[2], giving a mean carry-over for 20 such cycles of 0.2%.

(c) Incomplete rinsing of the titration vessels. The carry-over from this source was measured as described by Johansson and Pehrsson[2]. The mean carry-over for 30 determinations was less than 0.01%.

DISCUSSION

Equation (4) is not valid if the samples are coloured, *i.e.* absorb radiation at the wavelength of measurement. In this case the indicator has to be added at position 3, after the absorbance of the diluted sample (A_0) has been measured. A_0 is then subtracted from the absorbances measured during the following titration. The only disadvantage of this system modification is that the time of analysis is increased by 20 s.

Some advantages of the titration system described may be summarized in the following points.

1. High analysis rate. The time required for a complete determination, *i.e.* sample pipetting, addition of reagents and titration (plus rinsing of the cuvette and the titration vessel) is about 2 min.

2. The precision is sufficient for most routine analysis. The coefficient of variation is about 0.2%, which includes both sample pipetting error and titration error.

3. Low carry-over.

4. Low reagent consumption.

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SUMMARY

A completely automatic system for photometric titrations is described. The system delivers measured volumes of sample, indicator solution and buffer solution, titrates and finally rinses the titration vessels. Titrations are performed by adding titrant stepwise in equal volumes to the sample, with measurement of absorbance after each addition. These results are used to calculate equivalence volumes. The system performs about 30 titrations per hour and has a loading capacity of 200 samples. It was tested by titrating calcium with EGTA in presence of calmagite as indicator.

RÉSUMÉ

On décrit un appareil totalement automatique pour des titrages photométriques. Il assure la distribution de volumes mesurés d'échantillon, de solution d'indicateur et de solution tampon, le titrage, et finalement le rinçage des récipients de titration. Le dosage s'effectue par additions régulières de titrant, en volumes égaux à l'échantillon, avec mesure de l'absorbance après chaque addition. Les résultats des mesures permettent de calculer les volumes équivalents. On peut ainsi effectuer environ 30 titrages par heure, avec une capacité de charge de 200 échantillons. Ce système a été essayé avec un titrage de calcium, au moyen d'EGTA, en présence de calmagite comme indicateur.

ZUSAMMENFASSUNG

Ein vollständig automatisiertes System für photometrische Titrationen wird beschrieben. Das System liefert abgemessene Volumina von Proben, Indikatorlösung und Pufferlösung, titriert und spült schliesslich die Titrationsgefasse. Die Titrationen werden ausgeführt, indem der Titrant stufenweise in gleichen Volumenanteilen zu der Probe gegeben wird, wobei die Extinktion nach jeder Zugabe gemessen wird. Diese Werte werden benutzt, um die Äquivalenzvolumina zu berechnen. Das System führt pro Stunde etwa 30 Titrationen aus und hat eine Kapazität von 200 Proben. Es wurde getestet, indem Calcium mit EGTA in Gegenwart von Calmagit als Indikator titriert wurde.

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Analytica Chimica Acta, 66 (1973) 75–84

THERMOMETRIC TITRATION OF SOME MOLYBDATES, MOLYBDIC ACID, AND MOLYBDENUM TRIOXIDE

NOBUTOSHI KIBA and TSUGIO TAKEUCHI

(Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya Japan)

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Molybdates, molybdic acid, and molybdenum trioxide of reagent grade are usually assayed gravimetrically as the oxinate complex, $MoO_2(C_9H_6ON)_2$[1–4]. Orthomolybdate (MoO_4^{2-}) is often determined by titrating its neutral solution with standard lead(II) solution[5,6] or by back-titrating the excess of an added complexone[7,8]. Redox titrations can also be applied for the determination of molybdenum(VI) after its reduction[9].

Burns *et al.*[10] developed a method of assaying ammonium paramolybdate $[(NH_4)_6Mo_7O_{24}]$, in which a sample solution was titrated with a standard sodium hydroxide solution, the change of pH on depolymerization of polymolybdate being followed. However, no method for assaying orthomolybdate based on its polymerization to paramolybdate on titration with a mineral acid, seems to have been reported. This is probably because, in all cases of pH titration[11,12], conductometric titration[11] and thermometric titration[12,13], the equivalence point (molar ratio of acid added to molybdenum) varied with the concentration of molybdate initially taken; the molar ratio varied from 1.143 to 1.500 at the first inflection of the titration curve. Cannon[11], investigating the reaction between alkali molybdate and a mineral acid, suggested the possibility of a conductometric titration of molybdate at concentrations of 0.07–0.007 *M* with an accuracy of 0.3%.

The present authors have investigated the same reaction with the aid of thermometric titrations[12,13]; it was found that when a neutral salt such as alkali chloride was added to the test solution, the molar ratio at the inflection point no longer varied with the concentration of molybdate, but was constant at 1/7 = 1.143. The reaction thus proceeded quantitatively as molybdate was titrated with acid:

$$8\ H^+ + 7\ MoO_4^{2-} = Mo_7O_{24}^{6-} + 4\ H_2O$$

and this was applied for the thermometric determination of molybdates.

In the work described here, the depolymerization of ammonium paramolybdate with sodium hydroxide solution was also applied for the thermometric determination of polymolybdate. As is well known, molybdic acid ($MoO_3 \cdot H_2O$) and molybdenum trioxide are only slightly soluble in water; therefore, they were first dissolved in a definite volume of standard sodium hydroxide solution, the excess of which was then back-titrated with standard hydrochloric acid solution. This was recommended by Burns *et al.*[10] for the pH titration of molybdic acid. However, the

thermometric titration is preferable, because the suspension of molybdic acid and molybdenum trioxide does not interfere and the molybdic acid and molybdenum trioxide can be determined directly with sodium hydroxide standard solution.

With regard to the thermometric titration, Jordan[14], Tyrrell and Beezer[15], and Bark and Bark[16] have described the theory and the instrumentation. The thermal change is usually detected by a single thermistor or two thermistors in a bridge, and the end-point of the titration is determined as the point of intersection after extrapolation of the titration curve before and after the end-point; however, the reproducibility is invariably poor when the inflection of the curve is not sharp. Accordingly, the present authors employed a differential thermistor probe[17–19] in order to obtain more precise data.

EXPERIMENTAL

Reagents

Orthomolybdates. In order to prepare solutions of various molybdates, a specially prepared molybdic acid solution[13] which was 0.1 *M* in molybdenum, was treated with lithium hydroxide, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide or tetraethylammonium hydroxide in double the molar quantity of molybdic acid; magnesium hydroxide in an equal molar quantity to the molybdic acid was added to prepare magnesium molybdate. These solutions were evaporated to dryness, and the powdered molybdates obtained were dried *in vacuo* at 40°. The molybdenum content of the molybdic acid and molybdate solutions was determined gravimetrically with oxine[4].

Samples. Sodium molybdate, potassium molybdate, ammonium paramolybdate, molybdic acid (molybdenum trioxide monohydrate), and molybdenum trioxide (guaranteed reagents, Wako Chemicals Co.) were used without purification. Other molybdates were prepared as above. Molybdic acid and molybdenum trioxide were dissolved in sodium hydroxide solution, and molybdenum was determined gravimetrically[4].

Hydrochloric acid solutions. Suitably diluted reagent-grade hydrochloric acid was standardized against sodium carbonate in the usual way.

Sodium hydroxide solutions. These were prepared from solid reagent and standardized against standard hydrochloric acid.

Potassium permanganate solutions. Reagent-grade potassium permanganate was dissolved in water; standardization against sodium oxalate was used.

Other reagents were of reagent grade, and were used without purification.

Apparatus

Thermometric titrator. A thermometric titrator with an electronic recorder (TOA Electronics Co.) was employed. The differential thermistor probe consisted of two thermistors of identical temperature characteristics (B-constant 2800 ± 10°K, $R_{25} = 20$ kΩ $\pm 10\%$, time constant 0.3 s), connected to a bridge circuit. The two thermistors were placed in a glass probe, as shown in Fig. 1, so as to give a time-lag between the responses of the two thermistors. The difference in the responses of the two thermistors was detected, for exothermic or endothermic reactions, throughout the titration; the output of the probe was connected to the

recorder. The end-point of the titration was obtained from the inflection point of the recorded curve of thermal difference against titrant volume.

For reference, titration curves obtained with the normal response thermistor, the delayed-response thermistor, and the differential thermistor couple are shown in Fig. 2; the difference between the two curves obtained with single thermistors curve C) is amplified when both are used (curve D). In order to check this curve, the titration curves obtained with two injection syringe-type automatic burettes[1,2] were obtained at the same time as previously described.

Potentiometric titrator. A Metrohm Potentiograph E 336 and glass electrode were used.

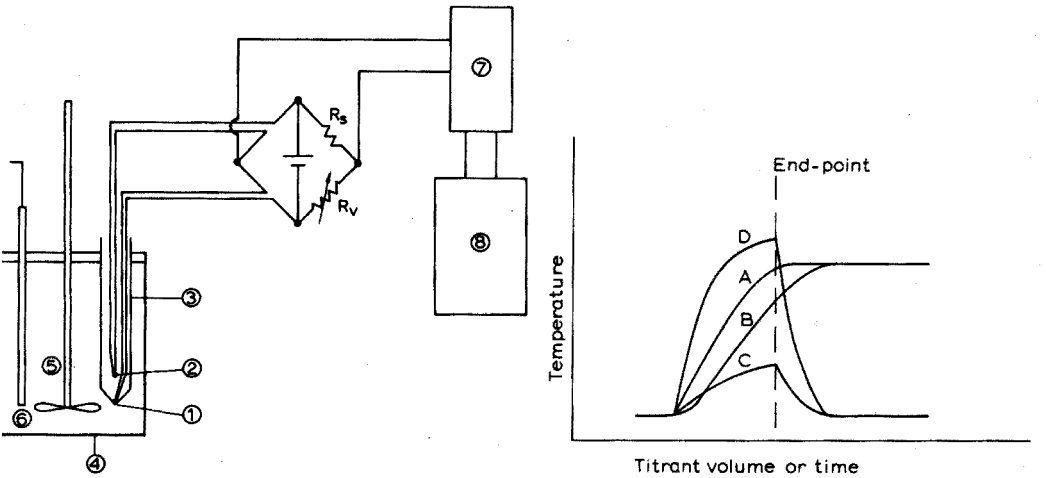

Fig. 1. Thermometric titration apparatus equipped with differential thermistor. (1) Normal response thermistor; (2) delayed-response thermistor; (3) glass probe, o.d. 5 mm; (4) titration cell, 50-ml Daiflon; (5) stirrer; (6) capillary nozzle; (7) amplifier; (8) recorder; $R_s = 20$ kΩ, R_v = variable resistor.

Fig. 2. Thermometric titration curves. (A) By normal-response thermistor, (B) by delayed-response thermistor alone, (C) by difference in temperature change between (A) and (B), (D) by differential thermistor (amplified C).

Procedure

In the case of molybdates, samples were taken in the following weights so as to give 0.5–0.005 *M* solutions in 200-ml measuring flasks: sodium molybdate, 24.2–0.242 g; potassium molybdate, 32.8–0.328 g; magnesium molybdate, 20.2–0.202 g; tetramethylammonium molybdate, 32.6–0.326 g; tetraethylammonium molybdate, 43.8–0.438 g; ammonium paramolybdate, 17.3–0.173 g. The weighed sample was dissolved in water together with 7.5 g of potassium chloride, and the solution was transferred to a 200-ml measuring flask and diluted with water to the mark. A 20-ml aliquot of this solution was pipetted into a 50-ml titration cell made of Daiflon (a trifluorochloroethylene polymer) and titrated with a standard solution of hydrochloric acid. In the case of ammonium paramolybdate, potassium chloride was added, and the solution was titrated with a sodium hydroxide solution.

In the case of molybdenum trioxide or molybdic acid, the weights were

selected to give a 0.5–0.01 *M* solution in a 50-ml titration cell: molybdic acid, 1.6–0.033 g; molybdenum trioxide, 1.4–0.029 g. Water (20 ml) was added and the solution was titrated with a standard sodium hydroxide solution.

The concentration of the titrant was chosen so that the volume required at the end-point would not exceed 10% of the titrand volume. The titrant was injected at a rate of 2 ml per 5 min from an automatic syringe burette with a capillary nozzle. The titration curve was recorded at a constant chart speed of 12 cm min^{-1}.

RESULTS AND DISCUSSION

Titration curves

Titration curves for 0.4 *M* lithium molybdate with hydrochloric acid (Fig. 3), 0.01 *M* ammonium paramolybdate with sodium hydroxide solution (Fig. 4), and 0.1 *M* molybdenum trioxide with sodium hydroxide solution (Fig. 5) are given to illustrate the results obtainable; curves obtained by a reference method are also shown. It can be seen that the titration curves by the differential method give much sharper inflections than those by the reference method, so that end-points can be detected more readily.

Titration of orthomolybdate

In the titration of orthomolybdate with an acid, the *Z*-value of the first

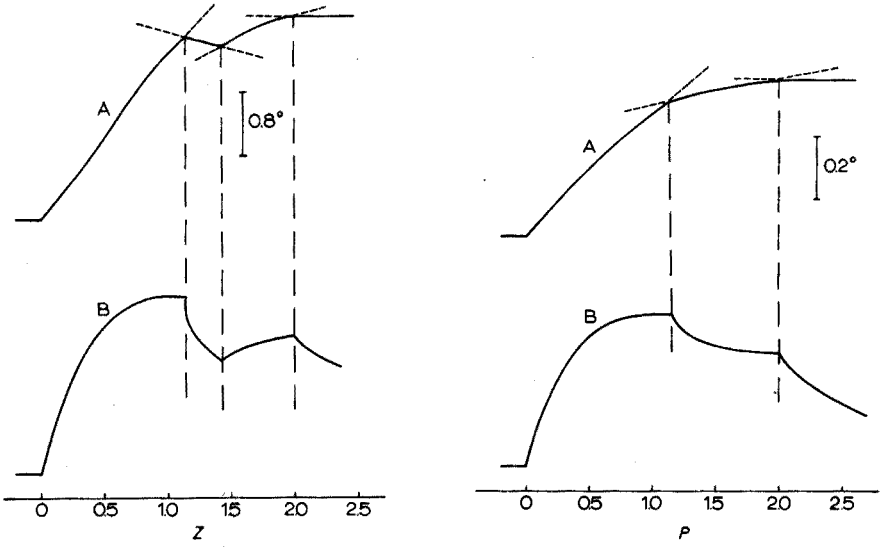

Fig. 3. Thermometric titration of 0.4100 *M* lithium molybdate with hydrochloric acid. The ordinate is the relative heat change during the titration; *Z* is the number of moles of acid added per mole of molybdate. (A) By reference method, and (B) by differential method.

Fig. 4. Thermometric titration of 0.01132 *M* ammonium paramolybdate with sodium hydroxide. *P* is the number of moles of base added per mole of molybdenum. (A) By reference method, and (B) by differential method.

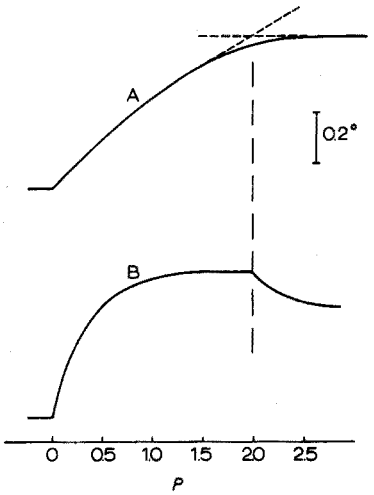

Fig. 5. Thermometric titration of 0.002013 mole of MoO_3 in 20 ml of water with sodium hydroxide. P is the number of moles of base added per mole of molybdenum trioxide. (A) By reference method, and (B) by differential method.

inflection of the curve varies from 1.143 (the normal value) when the concentration of molybdate is less than 0.09 M; the Z-value becomes 1.500 when the concentration is as low as 0.005 M. However, when a neutral salt such as potassium chloride is added, the Z-value is fixed at 1.143 in every case. This salt effect of chlorides has been shown[20] to decrease in the following order: $Cs > Rb > K > NH_4 > Na > Mg > Li$. Potassium chloride was preferred for its effectiveness and cost.

The amount of salt required to keep the Z-value of the first inflection at 1.143 was determined by titrating 0.09–0.005 M lithium molybdate in the presence of different amounts of potassium chloride. The results (Table I) were obtained by

TABLE I

AMOUNT OF POTASSIUM CHLORIDE REQUIRED TO KEEP THE Z-VALUE AT 1.143

Li_2MoO_4 (mole l^{-1})	KCl (mole l^{-1})	Z-value	Li_2MoO_4 (mole l^{-1})	KCl (mole l^{-1})	Z-value
0.09225	0.30	1.155	0.01025	0.040	1.163
	0.40	1.146		0.055	1.143
	0.50	1.143		0.55	1.143
	1.00	1.143	0.008200	0.031	1.202
0.06150	0.28	1.148		0.041	1.143
	0.35	1.143		0.41	1.143
	0.38	1.143	0.005125	0.020	1.233
	1.00	1.143		0.027	1.143
0.03045	0.10	1.150		0.40	1.143
	0.15	1.144			
	0.18	1.143			
	0.98	1.143			

the differential method. The salt effect was apparent when the salt concentration was more than five-fold that of molybdate; even 50-fold amounts showed no interference.

Interfering ions. Cations such as lead, calcium, and silver, which precipitate molybdates, caused positive errors, because the polymerization reaction proceeded between solid and liquid, so that the reaction rate was seriously retarded and the inflection point was delayed. Hydroxide ions did not affect the detection of the end-point, because the equilibrium constant of the neutralization process is far larger than that of the polymerization process, and the heat evolved is also larger. In the course of the titration, the large inflection based on neutralization appeared first and then the inflection caused by polymerization followed. Thus, a differential determination of hydroxide and molybdate can be achieved. Anions such as WO_4^{2-}, VO_4^{3-}, VO_3^-, and CrO_4^{2-}, which are also polymerized on addition of a mineral acid, affected the titration curves for molybdate, giving positive errors.

Assay method. Commercial sodium molybdate and potassium molybdate, and other molybdates prepared by the authors, were assayed by the proposed method.

TABLE II

COMPARISON OF RESULTS FOR DETERMINATION OF MOLYBDATES

Compound	*Sample taken (mole/200 ml)*	*Molybdenum (%)*			s_r (%)	*Accura (%)*
		Jones method	*Reference method*	*Differential method*[a]		
$Na_2MoO_4 \cdot 2H_2O$	0.10110	39.5_4	39.6_1	39.6_1	0.1_1	−0.07
	0.01011	39.3_9	39.6_0	39.6_1	0.3_3	−0.07
	0.00101	38.8	39.6	39.6	0.5	−0.09
$K_2MoO_4 \cdot 5H_2O$	0.10052	29.0_5	29.2_1	29.2_1	0.1_5	−0.03
	0.01005	28.8_7	29.2_1	29.2_1	0.3_0	−0.03
	0.00105	28.0	28.9	29.1	0.4	−0.4
$MgMoO_4 \cdot 2H_2O$	0.10204	47.7_0	47.7_4	47.7_4	0.1_4	−0.01
	0.01020	47.0_6	47.6_7	47.7_0	0.1_8	−0.09
	0.00102	44.6	47.1	47.4	0.8	−0.7
$((CH_3)_4N)_2MoO_4 \cdot 2H_2O$	0.09989	29.4_2	29.4_2	29.4_2	0.2_0	−0.01
	0.00999	29.0_6	29.3_3	29.4_0	0.3_1	−0.08
	0.00100	25.5	29.2	29.3	0.6	−0.4
$((C_2H_5)_4N)_2MoO_4 \cdot 2H_2O$	0.10152	21.8_7	21.9_0	21.9_0	0.1_8	−0.05
	0.01015	21.6_5	21.8_4	21.8_7	0.2_6	−0.09
	0.00102	20.5	21.0	21.5	1.0	−1.8

[a] Mean of seven determinations.

Table II shows the results obtained by the differential method and the reference thermal method. For comparison, results obtained by permanganate titration, after treatment in a Jones reductor[21] are also given. The assay of molybdate showed an accuracy, as well as precision, of 1.8% for 0.5–0.005 *M* molybdate solutions.

Assay of ammonium paramolybdate

Two inflections were observed on the titration curve, based on the following reactions:

'ABLE III

'OMPARISON OF RESULTS FOR DETERMINATION OF AMMONIUM PARAMOLYBDATE

'ample aken mole/200 ml)	*Molybdenum (%)*				
	Burns et al.[10] *method*	*Differential method*[a]			
		1st inflection	s_r (%)	*Accuracy* (%)	*2nd inflection*
'.01388	54.3_1	54.3_1	0.08	−0.01	54.3_2
'.01057	54.3_1	54.3_1	0.1_1	−0.01	54.3_2
'.00763	54.5	54.3	0.2	−0.03	54.3
'.00472	55.0	54.2	0.2	−0.2	54.3
'.00139	56.1	54.1	0.3	−0.4	54.3
'.00106	58.7	54.1	0.3	−0.4	54.4
'.00076	—	54	0.4	−0.6	55
'.00047	—	54	0.6	−0.6	57
'.00014	—	53	1.5	−2.4	60

[a] Mean of seven determinations.

$$(NH_4)_6Mo_7O_{24} + 8\ NaOH = 3(NH_4)_2MoO_4 + 4\ Na_2MoO_4 + 4H_2O$$
(1st inflection)

$$(NH_4)_2MoO_4 + 2\ NaOH = Na_2MoO_4 + 2\ NH_4OH \text{ (2nd inflection)}$$

The values given in Table III were calculated by means of the above equations from the amount of sodium hydroxide consumed. The precision and accuracy of the determinations based on the first inflection were maintained invariably even when the concentration of the molybdate was low, but results based on the second inflection depended on the molybdate concentration, because of the ambiguous end-point at low concentrations (Fig. 4). Ammonium paramolybdate in concentrations between 0.07 and 0.0007 *M* could be determined with an accuracy and precision usually better than 2.4%. The pH titrations suggested by Burns *et al.*[10] were also tested; the results (Table III) showed that molybdate could be determined in the 0.07–0.005 *M* range, but with lower concentration, no inflection was observed.

Assay of molybdic acid and molybdenum trioxide

Molybdic acid and molybdenum trioxide react with sodium hydroxide as follows:

$$2\ NaOH + MoO_3 = Na_2MoO_4 + H_2O$$
$$2\ NaOH + MoO_3 \cdot H_2O = Na_2MoO_4 + 2\ H_2O$$

The values given in Table IV were calculated according to the above equations. Molybdic acid was found to have a lower content of molybdenum than the theoretical value (59.92%), and the sample seemed to be contaminated with ammonia; this low content was confirmed by the pH titration of Burns *et al.*[10] and by the gravimetric method.

The assay of molybdic acid and molybdenum trioxide could be achieved by thermometric titration with a precision of 1.0% or better.

TABLE IV

COMPARISON OF RESULTS FOR DETERMINATION OF MOLYBDENUM TRIOXIDE AND MOLYBDIC ACID

Compound	*Sample taken (mole/20 ml)*	*Molybdenum (%)*			s_r (%)	*Accuracy (%)*
		Jones method	*Gravimetric method*[4]	*Differential method*[a]		
MoO_3	0.01023					
	0.01011					
	0.01033					
	0.00989	66.6_0	66.6_1	66.6_1	0.2_7	−0.02
	0.01024					
	0.00978					
	0.00973					
	0.00115					
	0.00136					
	0.00103					
	0.00125	65.1	66.3	66.4	0.4	−0.4
	0.00104					
	0.00111					
	0.00217					
	0.00026					
	0.00028					
	0.00023					
	0.00035	60	58	66	0.9	−0.9
	0.00027					
	0.00030					
	0.00031					
$MoO_3 \cdot H_2O$	0.01132					
	0.01133					
	0.01006					
	0.01089	54.2_5	54.3_2	54.1_7	0.3_8	−9.6
	0.00958					
	0.00972					
	0.00894					
	0.00036					
	0.00035					
	0.00048					
	0.00039	42	37	54	1.0	−9.9
	0.00027					
	0.00029					
	0.00030					

[a] Mean of seven determinations.

Conclusion

Thermometric titration with a new differential thermistor titrator could be applied for the assay of orthomolybdates with a standard solution of hydrochloric acid, and ammonium paramolybdate, molybdic acid and molybdenum trioxide with a standard solution of sodium hydroxide. The recommended method is very rapid and simple, and the accuracy and precision of the method are good.

SUMMARY

A thermometric titrator equipped with differential thermistor is used for the titration of molybdenum in sodium molybdate, potassium molybdate, magnesium molybdate, tetramethylammonium molybdate, and tetraethylammonium molybdate, based on their reactions with hydrochloric acid, and in ammonium paramolybdate, molybdic acid, and molybdenum trioxide, based on their reactions with sodium hydroxide. Orthomolybdates and ammonium paramolybdate were determined in the 0.5–0.005 *M* range; sufficient solid molybdic acid or molybdenum trioxide was taken to give a final 0.01–0.5 *M* solution in 20 ml of water. The method is simple and very quick. The standard deviation varies from 0.5 to 1.5% depending on the amount of sample taken.

RÉSUMÉ

Un titrage thermométrique est proposé pour le dosage du molybdène dans molybdate de sodium, molybdate de potassium, molybdate de magnésium, molybdate de tétraméthylammonium et molybdate de tétraéthylammonium, basé sur leur réaction avec l'acide chlorhydrique et pour le dosage du molybdène dans paramolybdate d'ammonium, acide molybdique et trioxyde de molybdène, basé sur leur réaction avec hydroxyde de sodium. La méthode est simple et très rapide; la déviation standard varie de 0.5 à 1.5%, en fonction de la quantité d'échantillon.

ZUSAMMENFASSUNG

Ein mit einem Differentialthermistor versehener thermometrischer Titrator wird für die Titration von Molybdän in Natriummolybdat, Kaliummolybdat, Magnesiummolybdat, Tetramethylammoniummolybdat und Tetraäthylammoniummolybdat verwendet, wobei die Titration auf der Reaktion mit Salzsäure beruht. Molybdän in Ammoniumparamolybdat, Molybdänsäure und Molybdäntrioxid wird auf Grund der Reaktion mit Natriumhydroxid titriert. Orthomolybdate und Ammoniumparamolybdat wurden im Bereich 0.5–0.005 *M* bestimmt. Es wurde so viel Molybdänsäure oder Molybdäntrioxid in festem Zustand eingesetzt, dass sich zum Schluss eine 0.01–0.5 *M* Lösung in 20 ml Wasser ergab. Die Methode ist einfach und sehr schnell. Die Standardabweichung variiert je nach der verwendeten Probenmenge zwischen 0.5 und 1.5%.

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PREPARATION OF SULPHAMIC ACID SINGLE CRYSTALS AND THEIR ASSAY BY PRECISE COULOMETRIC TITRATION

TAKAYOSHI YOSHIMORI and TATSUHIKO TANAKA

Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo (Japan)

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Many investigations have recommended sulphamic acid as a primary standard for titrimetric analysis. Hofmann and Bielsalski[1] first studied the use of this acid for acidimetry, and many subsequent papers[2–6] confirmed their results. Although the acid possesses a somewhat lower equivalent weight than benzoic acid, the advantages of its use have been summarized as follows: it is moderately soluble in water and is a strong acid; it is stable at room temperature; and the stability of the solid in normal atmosphere is satisfactory. Owing to these advantages, JIS (Japanese Industrial Standard)[7] has established this reagent as a standard substance, and the British Analytical Methods Committee[8] as well as IUPAC[9] have recently also recommended the acid. In the method of preparation of the standard sulphamic acid, the reagent is exclusively purified by repeated recrystallizations from aqueous solution; the temperature of the aqueous solution must be lower than 80°, otherwise the acid decomposes rapidly by producing ammonium hydrogensulphate, and its yield becomes fairly low. The product almost always contains some mother liquor which is difficult to remove. Moreover, the acid decomposes by reaction with the occluded water or with moisture when it is heated at 100°. Therefore, the reagent is generally dried *in vacuo* over some powerful desiccant, *e.g.* by storage *in vacuo* over concentrated sulphuric acid for 48 h[10]. It has, however, been pointed out that the pure dried reagent is nonhygroscopic. Only about 0.002% of water could be found on the recrystallized sulphamic acid which had been dried *in vacuo* for 4 h and then stored in the atmosphere[8,9]. Although this amount is negligible, there is always some doubt about complete elimination of water.

In earlier work, single crystals of sodium chloride[11] and potassium dichromate purified by zone melting[12] were found to be satisfactory as primary standards without any special dehydration procedure. Accordingly, an attempt was made to prepare and use single crystals of sulphamic acid. The single crystals of this acid were grown by vapourization from saturated solutions[13,14]. The adsorbed water was determined, and the purities were established by precise coulometric titration. All results indicated that the single crystals can be recommended as a primary standard for titrimetric analysis.

EXPERIMENTAL

Apparatus and reagents

The single crystals were prepared from saturated aqueous solutions of

sulphamic acid by evaporation of water at constant temperature. The temperature of the solution was maintained at $30° \pm 0.5°$ with a thermostat.

The instruments for the coulometric titration of the acid were similar to those described previously[11]. The precautions in weighing of the sample and in the measurement of the electricity were also the same as previously reported[11]. The end-point of the titration was located potentiometrically with an "Expandomatic" pH meter (Beckman Instruments, Inc.).

A tall-form beaker (about 300 ml) made from borosilicate glass was used as the electrolytic cell. An anodic compartment was made of polyethylene tube and the bottom of it was sealed with an agar–agar gel. The generator cathode was a platinum foil of about 113 cm^2 in area, and the anode was a platinum spiral.

All reagents were of analytical grade, and were used without further purification.

Preparation of single crystals

About 26.5 g of sulphamic acid (analytical grade) was dissolved with about 100 ml of water in a 300-ml tall-form beaker below 60°. The bottom area of the beaker was about 29 cm^2. Because the solubility of the acid is 26.09 g per 100 g water at 30°[2], this solution is in slight supersaturation at 30°. After complete dissolution, a seed crystal of sulphamic acid (10–20 mg in weight) was introduced into the solution, and the beaker was then placed in the thermostat at 30°; the seed crystal was simply placed on the bottom of the beaker. After several weeks, it grew to about 7 g.

The water occluded in the large and clear single crystal was removed by breaking it into pieces of 0.2–0.4 g, under observation with a microscope (120× originally). The large crystal could be broken by pressing with the blade of a knife

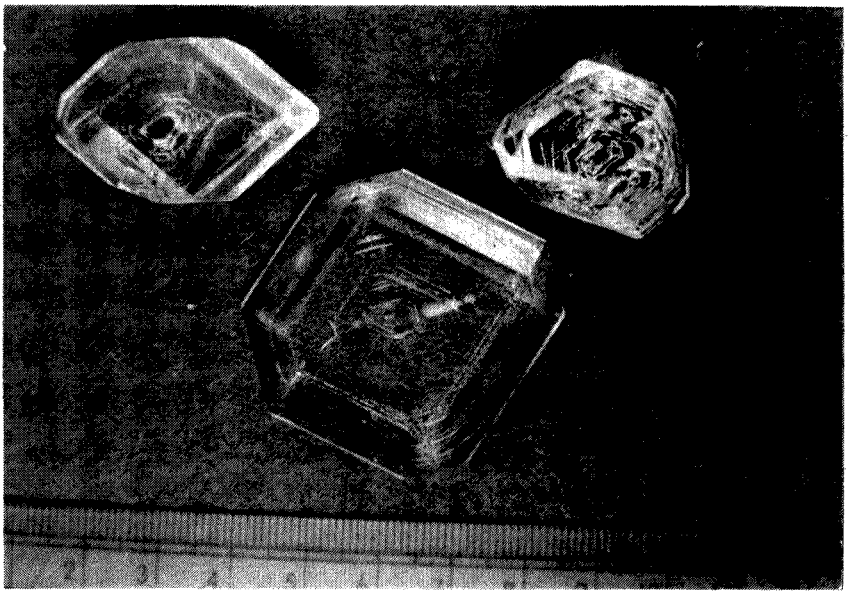

Fig. 1. Single crystals of sulphamic acid.

and tapping the back of the blade with a hammer. The surfaces of the fragments were polished with fine emery paper and rinsed with distilled water to free them from adhering powder and to round their edges and corners. After being washed with ethanol (99.5% v/v), the pieces were wiped with chamois, and then stored in a dish.

Coulometric titration

This procedure was nearly the same as described previously[15]. About 200 ml of 1 *M* potassium chloride solution was used as the catholyte. The same solution and about 500 mg of barium carbonate were added to the anode compartment. Nitrogen was passed through the catholyte for about 1 h to remove carbon dioxide.

As a pretitration, a few drops of dilute hydrochloric acid solution were added to the cell, and then the acid was titrated electrolytically to the inflection point of the titration curve. The weighed portion of sulphamic acid was then introduced into the cell and dissolved completely. The acid was titrated with the electrolytically generated base. A constant current of *ca.* 143 mA was used for the electrolysis. Near the end-point of the titration, the titrant was generated in as small increments as possible, and the pH was measured after the deflection of the pH meter became stable. The end-point of the titration was located from the differential titration curve.

RESULTS AND DISCUSSION

Single crystals of sulphamic acid

As shown in Fig. 1, colourless transparent single crystals more than 10 g in weight were readily prepared by the above technique. The rate of growth of the crystals was about 7 mg h^{-1}.

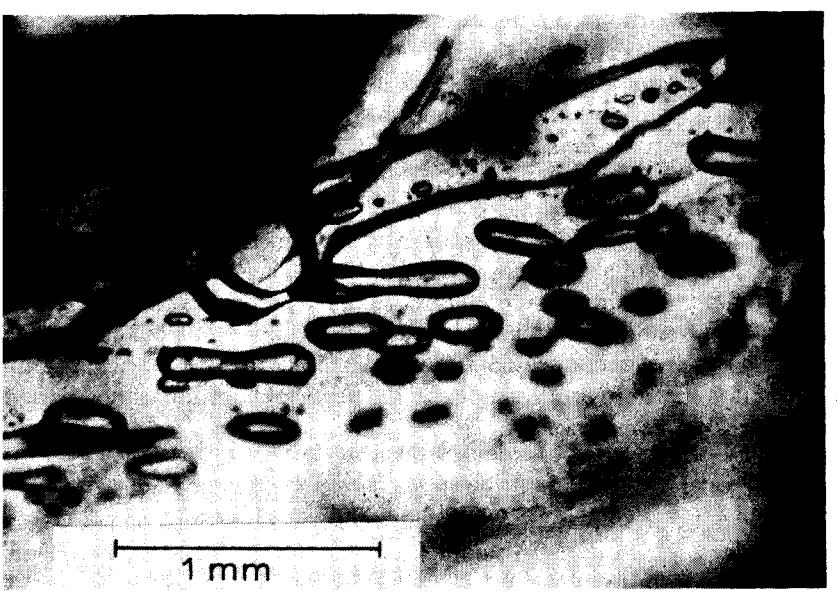

Fig. 2. Microscopic view of the many pinholes in a single crystal.

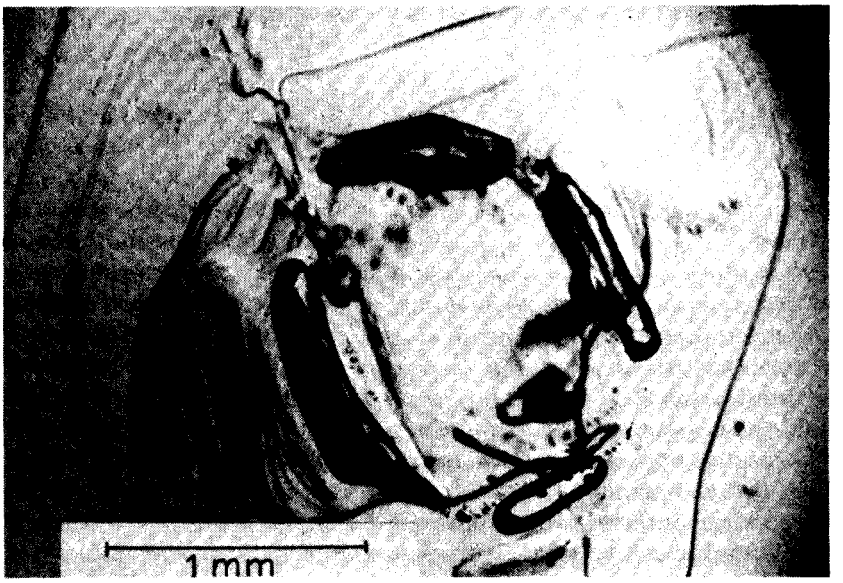

Fig. 3. Microscopic view of several pinholes surrounding the seed crystal.

Figures 2 and 3 are microscopic views of the crystals. Figure 2 shows that a crystal can contain many pinholes. These pinholes exist locally along the direction of crystal growth and were found as a layer. The pinholes occurred more frequently when the rate of growth was rapid. Furthermore, as shown in Fig. 3, they were often observed surrounding the seed crystal. This phenomenon was prominent when the crystal was grown from a more supersaturated solution. Therefore, the seed crystal was introduced into the solution at a temperature somewhat higher than 30°, and the solution was then gradually cooled in the thermostat.

The large crystals were broken, so as to exclude the portion containing the pinholes, and crystals in which pinholes could not be observed under the microscope were used as the samples for assays.

Water on the surfaces of single crystals

The weight loss of the single crystals was first measured under various drying conditions; the results are shown in Table I. The losses in weight of crystals dried by different methods were almost negligible, which indicates that the crystal can be used without a preliminary dehydration. The weights of the crystals increased slightly when they were heated at about 60° for 4 h; this was caused by the formation of ammonium hydrogensulphate[16]. The weights of the crystals dried at 140° for 1 h increased appreciably.

Assays of single crystals

The analytical-grade sulphamic acid used to prepare the single crystals was dried *in vacuo* over concentrated sulphuric acid for 48 h. The purity of the reagent was then assayed by the coulometric method. The mean value of 7 determinations was 99.808%, with a standard deviation of 0.042%.

TABLE I

LOSS IN WEIGHTS OF FOUR CRYSTALS DRIED SUCCESSIVELY BY VARIOUS METHODS

(Weight in mg)

Method of drying	*1*	*2*	*3*	*4*	*Average of weight loss (%)*
In atmosphere	840.038	790.043	551.045	882.492	—
Stored in conc. H_2SO_4 desiccator	840.037	790.041	551.045	882.491	0.000_1
In vacuo over conc. H_2SO_4 — 2 h	840.036	790.038	551.044	882.489	0.000_4
In vacuo over conc. H_2SO_4 — 48 h[a]	840.034	790.038	551.044	882.490	0.000_4
Heated at 60° for 4 h	840.038	790.041			0
Heated at 140° for 1 h	840.088	790.057	551.046	882.493	

[a] JIS method.

TABLE II

PURITIES OF SINGLE CRYSTALS

Sample	*Method of drying*	*Weight before breaking (g)*	*No. of detns.*	*Average purity (%)*	*s (%)*
Small crystal 200–400 mg	A[a]		6	99.882_3	0.090_2
	B[b]		5	99.899_1	0.097_7
Medium crystal 1–2 g	A		12	99.927_1	0.047_0
	B		5	99.896_3	0.056_3
Large crystal 4.5 g	A	7.0	4	99.979_1	0.004_1
		5.5	7	99.967_0	0.016_3
		4.8	6	99.972_8	0.013_8
	B	6.1	6	99.984_7	0.016_8
		8.5	6	99.984_5	0.019_9
		5.4	5	99.951_7	0.009_3
		7.9[c]	11	99.978_4	0.017_6
		7.0[d]	8	99.977_2	0.013_5

[a] *In vacuo* over concentrated sulphuric acid for 48 h.
[b] In the atmosphere.
[c] Crystal prepared from an unguaranteed reagent.
[d] Crystal grown at room temperature.

The crystals prepared were classified into three parts, the weights of which are shown in Table II. The small crystals were merely washed with ethanol and wiped with chamois. The medium and the large crystals were divided and washed as described above.

The purities of the small and medium crystals were about 99.9%, and the standard deviations of these results were fairly large. As shown in Figs. 2 and 3, the

lower results are due to the existence of many pinholes in the sample crystals.

The purities of the large crystals were satisfactory. They are equal to or somewhat better than the purity of the primary standard substance obtained from the Industrial Inspection Institute of Japan. The results also show that the starting material is purified by this method; the purities of crystals prepared from an unguaranteed reagent (assay value: *ca.* 99.7%) and grown at normal room temperature, were much the same as those obtained from analytical-grade reagent.

The purities of crystals dried *in vacuo* were approximately the same as those of non-dried crystals. This is consistent with the conclusions drawn from Table I. Raschig[13] early pointed out that a crystal of sulphamic acid is difficult to break, and the present authors also had the same experience; this problem, however, is one of technique, and seemed to be soluble. The other advantage of the proposed method is the yield of the reagent, when it is compared with the method of the Analytical Methods Committee[8,9].

The large single crystals of sulphamic acid prepared by the present method are of sufficient purity for use as a primary standard without drying.

SUMMARY

Single crystals of sulphamic acid were grown from aqueous solution. The occluded and adsorbed water of the crystals prepared was measured, and the purities of the single crystals were determined by precise coulometric titration. Large single crystals more than 10 g in weight were readily prepared. The adsorbed water on the surface amounted to *ca.* 0.0004%. The purities of the small and the medium crystals were not satisfactory for primary standard use. However, the purity of the pieces obtained by dividing a large crystal and polishing the surfaces, was about 99.98%, with a standard deviation of about 0.015%. These large single crystals of sulphamic acid are recommended as a primary standard.

RÉSUMÉ

Des cristaux simples d'acide sulfamique ont été formés en solution aqueuse. L'eau occluse et adsorbée des cristaux préparés a été mesurée. La pureté de ces cristaux a été déterminée par titrage coulométrique précis. De grands cristaux, pesant plus de 10 g, sont facilement obtenus. La quantité d'eau adsorbée sur la surface est d'environ 0.0004%. La pureté des cristaux petits et moyens n'est pas suffisante pour un étalon. Cependant la pureté des particules obtenues, en divisant un grand cristal et en polissant les surfaces, est d'environ 99.98%, avec une déviation standard de 0.015%. Un tel acide sulfamique peut servir d'étalon en analyse titrimétrique.

ZUSAMMENFASSUNG

Es wurden Einkristalle von Sulfaminsäure aus wässriger Lösung gezüchtet. Das okkludierte und adsorbierte Wasser wurde bestimmt; die Reinheit der Einkristalle wurde durch genaue coulometrische Titration ermittelt. Grosse Einkristalle mit einem Gewicht von mehr als 10 g wurden leicht erhalten. Das adsorbierte

Wasser an der Oberfläche betrug *ca.* 0.0004%. Die Reinheit der kleinen und mittleren Kristalle reichte für die Verwendung als Urtitersubstanz nicht aus. Jedoch hatten die Stücke, die durch Teilen eines grossen Kristalls und Polieren der Oberflächen erhalten worden waren, eine Reinheit von etwa 99.98% bei einer Standardabweichung von etwa 0.015%. Diese grossen Einkristalle von Sulfaminsäure werden als Urtitersubstanz empfohlen.

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RESPONSE-TIME PROPERTIES OF SOME HYDROGEN ION-SELECTIVE GLASS ELECTRODES IN NON-AQUEOUS SOLUTIONS

BO KARLBERG

Department of Analytical Chemistry, University of Umeå, S-901 87 Umeå (Sweden)

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Various observations and conclusions regarding the proper use of glass electrodes in non-aqueous solutions have appeared in the literature. The conclusions are often contradictory as is evident from reviews on the use of electrodes as end-point detecting devices[1–5]. The storage, equilibration, reconditioning and possible additions of water or salt to the solutions have been discussed without access to more systematic data. In the present paper, some measurements relevant to these problems, as well as to the development of a detailed picture of the processes in electrode surface layers, are reported.

It is a common belief that some water must be present on the surface of the electrode to ensure its function in non-aqueous media[6]. Dehydration of the glass electrode surface is assumed to cause a slow response, and is expected to occur during long-term usage in organic solvents. Immersion of the electrodes in water has been found to restore the rapid response behaviour[7–9]. In addition, the dehydration process itself might be the source of a drifting e.m.f. in non-aqueous solutions.

In the basic range in non-aqueous solutions, the glass electrode exhibits an alkaline error[10], so that the e.m.f. jumps may be diminished or even fail to appear during a titration[11]. Allen and Geddes[12] found that the glass electrode did not respond at all to changes in acidity in ethylenediamine solutions containing sodium ions. Harlow[13] obtained complex tiration curves in pyridine when the titrant contained potassium ions. He also observed differences in response behaviour between glass electrode made of the same kind of glass.

The glass electrode response was shown to be slow in isopropanol when the solutions were changed from basic to acidic and *vice versa*[14]. The e.m.f. change was correlated with ion-exchange processes in the gel-layer. In the basic regions, hydrogen ions in the gel-layer were replaced by alkali metal ions. The reverse exchange occurred on making a basic solution containing alkali metal ion more acidic, as would happen during a titration of a base with an acid. Despite the small total amount of exchanged ions—about 10^{-8} moles per cm^2 of glass area for most hydrogen ion glass electrodes, the exchange process is slow and results in an e.m.f. which varies with time.

There seems to be insufficient information concerning the response-time properties of glass electrodes in non-aqueous solvents. The present paper reports response-time characteristics of some commercial glass electrodes in isopropanol solutions. The detailed characteristics in other organic solvents may deviate from

those found in isopropanol, but the general behaviour should be similar. Isopropanol was chosen because this solvent is frequently used[2–5].

EXPERIMENTAL

Electrodes

Different glass electrodes were investigated. The general-purpose electrodes were Ingold 201, Beckman E-2 and Metrohm UX, the low-temperature electrode was Ingold LoT and the high-temperature electrode Ingold HA. A Metrohm electrode made of Corning 015 glass was also studied.

The glass electrodes were stored in dilute hydrochloric acid when not in use. Etching was performed by immersion in an aqueous 2% hydrofluoric acid solution for 2 min. The hydration was done in dilute hydrochloric acid and an electrode was considered to be fully hydrated after two weeks. The drying procedure entailed placing the bulbs of the glass electrodes in a warm air-stream (60–70°) from a hair-drier for 1–2 h; the electrode rods were turned so that the glass surfaces were as uniformly exposed as possible. Only glass electrodes with fully developed gel-layers were dried in this way and these are termed "dried" electrodes in the following.

An Ag/AgCl reference electrode was used; it was placed in a PVC tube sealed with a dialysis film and filled with supporting electrolyte containing chloride ions.

Solutions

The bases used were di-isopropylamine and N,N′-diphenylguanidine; picric and perchloric acids, both of which are strong acids in isopropanol[15], were used. Basic and acidic solutions were freshly prepared; aged solutions were found to behave non-ideally. Sodium and lithium perchlorate salts were dried at 130° before use. The water content of the isopropanol (Merck p.a.) was 0.06–0.07% as determined by Karl Fischer titration.

Ion-exchange capacity measurements

The glass bulb of the electrode was immersed in a solution comprising 0.01 *M* di-isopropylamine in isopropanol and 0.01 *M* sodium perchlorate. Hydrogen ions in the gel-layer are exchanged with sodium ions by this treatment[14]. An immersion time of 45 min was chosen; after this time the ion-exchange process was complete. The electrode was then removed and rinsed with pure isopropanol for exactly 10 s, wiped with a soft tissue paper, rinsed for a further 10 s and wiped. This procedure was repeated three times. To re-exchange the sodium ions after the rinsing, the bulb was placed in a small polythene vessel containing 4 ml of 0.01 *M* perchloric acid in isopropanol. The treatment described prevents any carry-over of sodium ions from the immersion solution to the leakage solution and also any "washing out" of the exchanged sodium ions in the gel-layer[14]. The sodium content was determined by flame emission spectrometry at 589.0 nm.

Titrations

Portions (15 ml) of acid or base solutions in isopropanol were titrated in a thermostatted vessel (25.0°). The titrant was continuously added from a syringe with a motor-driven piston. The e.m.f. signal from the glass–Ag/AgCl electrode

combination was recorded on a Mosley 680 recorder with an operational amplifier as follower (Analog Devices Model 301).

RESULTS

Response times within the "ideal" response range

Figure 1(a) shows the response of an Ingold 201 electrode. The starting solution, 20 ml of a 10^{-4} *M* picric acid solution containing 5 m*M* sodium perchlorate, was vigorously stirred by a motor-driven glass propeller in a thermostatted titration vessel; 2 ml of a 10^{-2} *M* picric acid solution (also 5 m*M* in $NaClO_4$) were rapidly added from a syringe. The test was performed for the hydrated, dried and etched electrodes. The dried electrode responded more slowly, and the etched electrode more quickly than the hydrated electrode.

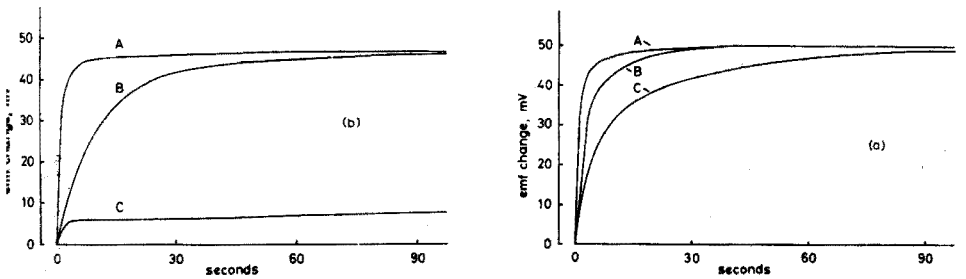

Fig. 1. Response to changes in hydrogen ion activity for an Ingold 201 electrode (a) and an Ingold HA electrode (b). The picric acid was rapidly increased from 10^{-4} *M* to about 10^{-3} *M*. Supporting electrolyte was 5 m*M* $NaClO_4$. The different curves denote the response for the freshly etched (A), the fully hydrated (B) and the dries states (C). Solvent: 2-propanol.

Figure 1(b) shows the results of the same tests for an Ingold HA electrode. The dried electrode almost ceased to respond to the change in hydrogen ion activity (curve C). An interesting and common finding for the two electrodes tested is that response-time characteristics identical with those observed for the hydrated states can be achieved for the dried electrodes if these are immersed in water for only 1 min.

Response to changes to and from the two-ion responsive range

It has previously been shown that the behaviour of the electrodes in regions where the response is Nernstian differs from that in regions where the electrode is subject to an alkaline error[9]. The results in Fig. 1 comprised changes within the acidic region where the response is ideal, *i.e.* Nernstian. If the electrodes are transferred to and from a basic solution, there will be an alkali error in the basic solution, *i.e.* the electrode will respond to both hydrogen and alkali metal ions.

Figure 2 shows the e.m.f. changes with time for two glass electrodes, Ingold HA and Ingold 201, in different states when transferred from a basic to an acidic solution and *vice versa*. As can be seen, steady e.m.f. values are achieved more slowly in going from the basic to the acidic solution, than in the reverse transfer for both electrodes, if each state is considered separately. In all situations the drying treatment caused delayed response behaviour. Etching obviously improves the response time.

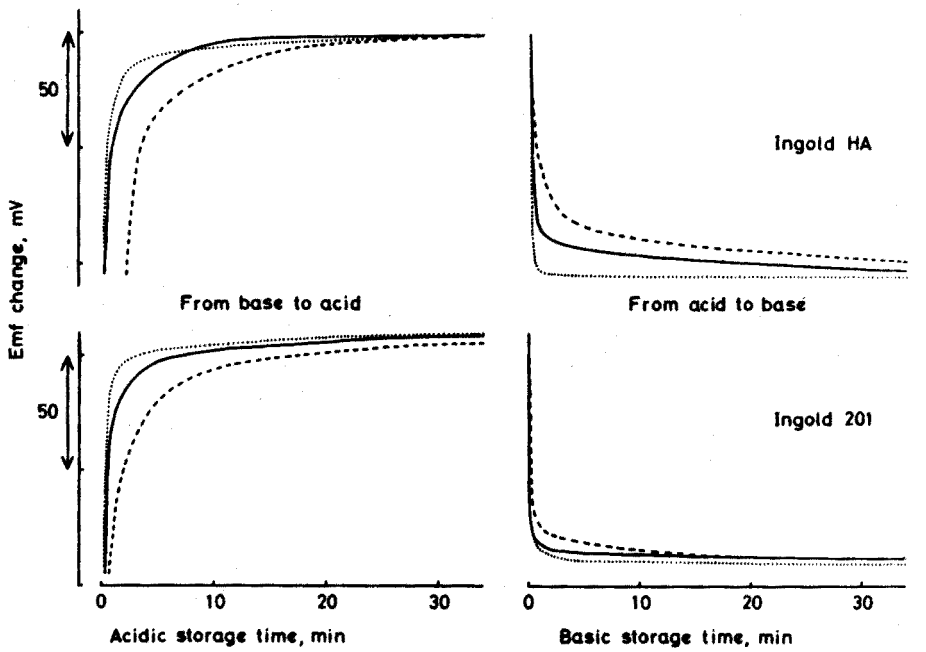

Fig. 2. E.m.f. change as a function of time for Ingold HA and Ingold 201 electrodes. Basic solution: 0.01 *M* di-isopropylamine + 0.01 *M* $LiClO_4$. Acidic solution: 0.01 *M* $HClO_4$ + 0.01 *M* $LiClO_4$. Electrode state: Fully hydrated (——), dried (– – – –) and etched (· · · ·). Solvent: 2-propanol.

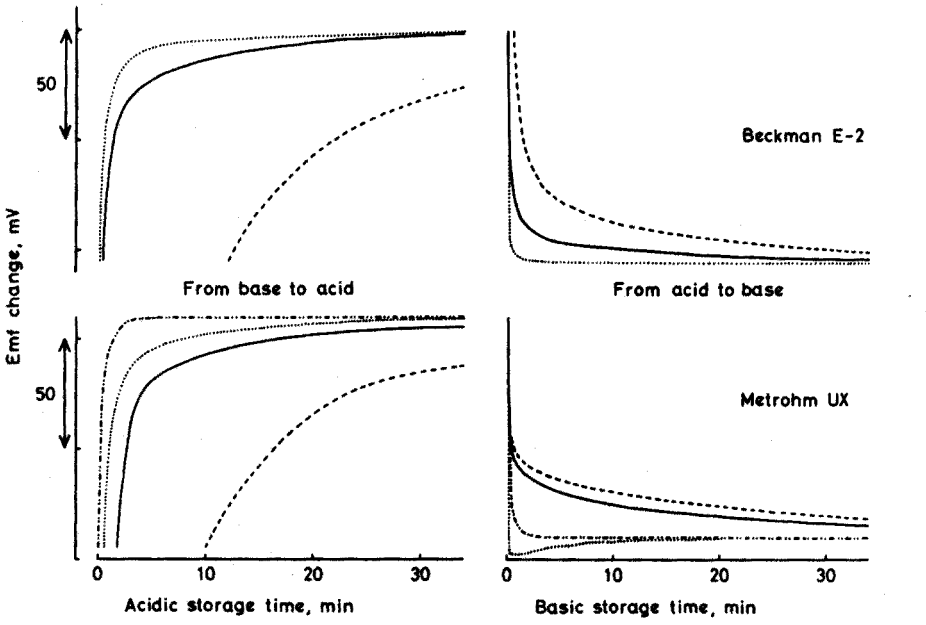

Fig. 3. E.m.f. change as a function of time for Beckman E-2 and Metrohm UX electrodes. Basic solution: 0.01 *M* di-isopropylamine + 0.01 *M* $LiClO_4$. Acidic solution: 0.01 *M* $HClO_4$ + 0.01 *M* $LiClO_4$. Electrode states: Fully hydrated (——), dried (– – – –) and etched (· · · · ·); for the Metrohm UX electrode, the lines (– · – ·) indicate the state "etched and then hydrated for 1 h". Solvent: 2-propanol.

The e.m.f. changes obtained in a similar manner for Metrohm UX and Beckman E-2 general-purpose electrodes were also studied (Fig. 3). For the Metrohm UX electrode, the behaviour obtained after a hydration period of 1 h was also studied. Both electrodes are sensitive to drying treatments, a strongly retarded response being observed, especially when the electrodes are transferred from base to acid. A small e.m.f. disparity appears for the etched Metrohm UX electrode in basic solution; when this etched electrode was hydrated for 1 h, response times were greatly improved.

In Fig. 4, further results of this type are given for the electrodes Ingold LoT and Metrohm Corning 015. The general trend is not broken and the conclusions drawn above also apply to these electrodes. However, poor reproducibility was obtained with the Metrohm Corning 015 electrode and slight transient phenomena always occurred in basic solutions.

Many other glass electrode types, as well as several specimens of the same type, were investigated in the same way. Individual differences exist between glass electrodes made from the same type of glass, and even between glass electrodes made by the same glassblower in sequence in the manufacturing process. The same general picture is valid for all electrodes tested; in all cases dried electrodes showed a slower response and etched electrodes a faster response than the response of fully hydrated electrodes.

Ion-exchange capacity measurements

In Fig. 5, the ion-exchange capacity is given as a function of the hydration

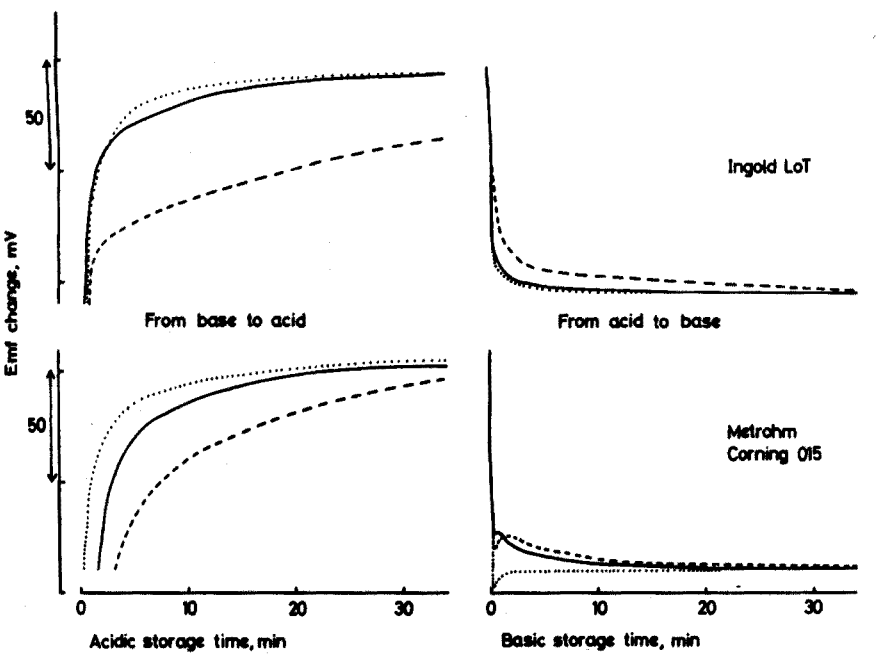

Fig. 4. E.m.f. change as a function of time for Ingold LoT and Metrohm Corning 015 electrodes. Conditions and indication of curves as in Fig. 3.

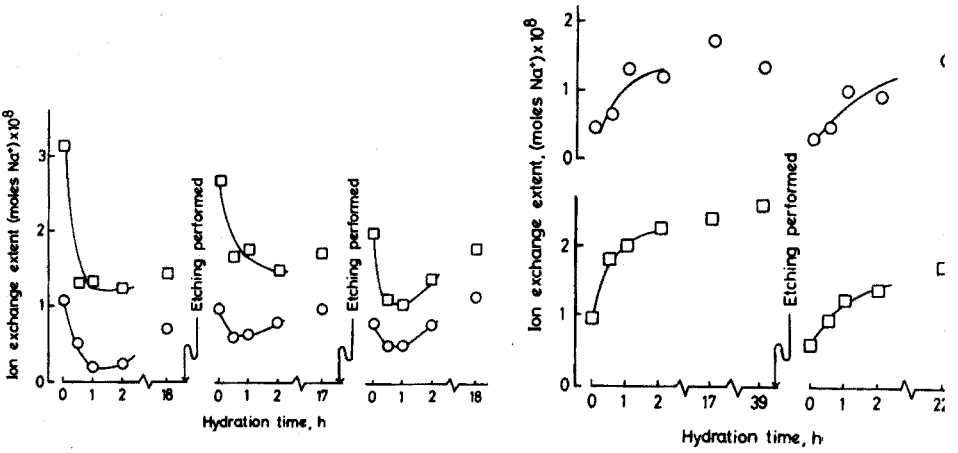

Fig. 5. Ion exchange as a function of hydration time for the Metrohm UX electrode (□) and th Ingold 201 electrode (○). Basic immersion solution: 0.01 *M* di-isopropylamine+0.01 *M* $NaClO_4$ i 2-propanol. Acidic leakage solution: 0.01 *M* $HClO_4$ in 2-propanol.

Fig. 6. Ion exchange as a function of the hydration time for two specimens of the Ingold LoT electrod type. Conditions as for Fig. 5.

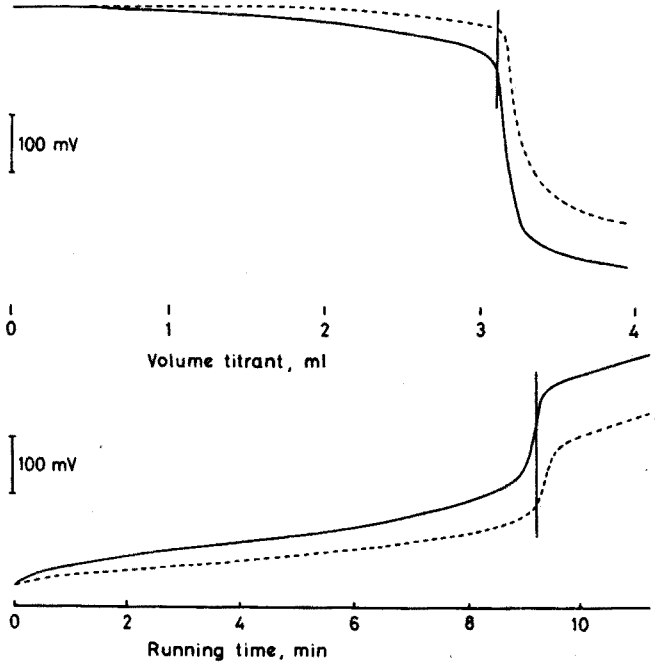

Fig. 7. Titration of 15 ml of 0.011 *M* picric acid with 0.053 *M* diphenylguanidine (upper curves) an titration of 15 ml of 0.010 *M* diphenylguanidine with 0.045 *M* picric acid (lower curves). Supportin electrolyte: 0.01 *M* $LiClO_4$. Titration rate: 0.364 ml min^{-1}. Theoretical equivalence points are denote by vertical lines. Indicator electrode was a Metrohm UX electrode, fully hydrated (——) and slightl dried in a warm air-stream for 30 min (----). Solvent: 2-propanol.

time for two of the electrodes. The bulb area is 3.0 cm^2 for the Ingold 201 and 4.4 cm^2 for the Metrohm UX electrode. Both curves show minima at about 1–2 h of hydration.

Figure 6 illustrates the same function for two Ingold LoT electrodes. The extent of ion exchange increases monotonically with the hydration time for this electrode type.

Titrations

Titration curves obtained with a hydrated Metrohm UX electrode and with the same electrode in a slightly dried condition are shown in Fig. 7. A common feature for both types of titration (acid with base and base with acid) is that the slightly dried electrode yields erroneous equivalence points owing to the slow response, despite the restrained titration rate. A fair evaluation can be made when the hydrated electrode is used. The e.m.f. jumps obtained are larger when acid is titrated with base than in the reverse titration. This behaviour is to be expected on the basis of the results for the Metrohm UX electrode presented in Fig. 3. Further drying of the electrode converted it into a completely unusable device for end-point detection.

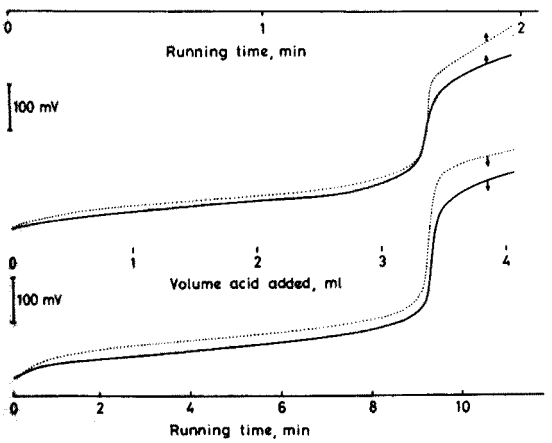

Fig. 8. Titration of 0.010 *M* diphenylguanidine with picric acid. Titration rate: 2.07 ml min^{-1} (upper curves) and 0.364 ml min^{-1} (lower curves). Indicator electrode was an Ingold 201 electrode, fully hydrated (——) and etched (· · · · · ·). Supporting electrolyte: 0.01 *M* $LiClO_4$. Solvent: 2-propanol.

Figure 8 shows the result of optimization of the conditions for the titration of diphenylguanidine with picric acid in isopropanol with reference to analysis time and precision. From the results shown in Figs. 2–4, the Ingold 201 is expected to be the most appropriate end-point detector; the etched state is preferable. Lithium perchlorate (0.01 *M*) served as supporting electrolyte. Barium perchlorate has been suggested as a supporting electrolyte in this connection[10], and its use might further enhance the e.m.f. jumps. As can be seen in Fig. 8, no displacement of the equivalence point in time occurs when the titration speed is increased. The largest e.m.f. jumps are obtained when the etched electrode is used. A titration of this kind can be performed without loss in precision within 2 min.

DISCUSSION

The "ideal" response range of the glass electrode

The response to small changes in hydrogen ion activity within the range of Nernstian behaviour is extremely fast in aqueous solutions[16–18], and also in non-aqueous solutions if the buffer capacity is sufficiently high[9,15]. However, factors other than the buffer capacity can influence the response time (Fig. 1).

There is evidence which indicates that the fully developed gel-layer of a glass electrode consists of two regions[14,19,20]. The outer region is assumed to have a loose structure; penetration of alkali metal ions[14] and halide ions[19] occurs in the alkaline error and acid error ranges, respectively. The other region, closest to the bulk glass, is assumed to be more rigid, and contains less water than the outer loose region[20]. The rigid part of the gel-layer thus seems to be of secondary importance when the response properties of the electrode are discussed.

If the outer gel-layer is defined as a separate phase, despite its infinitesimal dimensions, the establishment of two-phase boundary potentials arising at each side of this region must be considered. During the non-equilibrium conditions when hydrogen ions undergo redistribution in the layer, *i.e.* when the total potential is changing, a temporary potential drop over this layer may contribute to the observed potential[9]. However, the response time is still a function of the redistribution velocity, no matter where the potential contributions arise. Variations in the response time must therefore be ascribed to differences in the rates at which steady hydrogen ion concentration profiles in the loose part of the gel-layer are established. The rate of movement of hydrogen ions should depend partly on the water content of this layer and partly on the distance of movement.

During the etching treatment, the thickness of the outer loose layer is presumably reduced; this might explain the fast response observed for an etched electrode. The drying treatment removes water from the outer layer, so that the probability of a proton transfer via a water molecule is decreased; the less effective transfer in the proper direction results in a slow attainment of the steady hydrogen ion concentration profile. The fact that the rapid response is restored when a dried electrode is immersed in water for just one minute supports the view that only a very shallow region of the gel-layer is of importance for the response behaviour. Penetration of water molecules into the deeper regions would require more time.

The two-ion response range of the glass electrode

When two ions contribute to the total potential of the glass electrode, the ion-exchange process in the gel-layer must be considered when the response to concentration changes is interpreted. Transient phenomena may appear when sudden concentration changes are made within the two-ion responsive range[9]. In the present study, the changes were made from the one-ion response range to the two-ion response range and *vice versa*. The kinetics of the ion exchange must be considered. The theory of Helfferich[21] has been shown to constitute a basis for qualitative interpretation[9,14] and the results obtained in the present work (Figs. 2–4) further support this view. The ion-exchange process occurs more rapidly when the faster of

he two ions, in this case the hydrogen ion, leaves the exchanger, compared with he process when the faster ion replaces the slower ion in the exchanger. This is onsistent with the results shown in Figs. 2–4; for all the electrodes tested, the e.m.f. alues become steady more quickly in going from acidic to basic solutions than or the reverse movement. In basic solution, the hydrogen ions in the outer gel-ayer are replaced by lithium ions.

The rate of interdiffusion is determined by the mobilities of the individual ons within the ion exchanger, *i.e.* the loose gel-layer, and by the distance involved. he drying treatment reduces the water content in the exchanger, so that the obilities of the ions are lowered; the interdiffusion equilibrium and a steady .m.f. are then more slowly achieved. The etching treatment is assumed to shorten he interdiffusion distance, causing a fast response.

The ion-exchange capacity may be taken as a measure of the interdiffusion istance; the lower the capacity the shorter the distance. For the Metrohm UX nd Ingold 201 electrodes, minima in the ion-exchange capacities appear after about h of hydration (Fig. 5); this might explain the rapid response times obtained for the pecially treated UX electrode in Fig. 3. The Ingold 201 electrode was similarly ested, some improvement in the response being found in the acidic solution. No esponse improvement was observed for the Ingold LoT electrodes when the ydration time was increased from zero, the state of a freshly etched electrode; his is in accordance with the results shown in Fig. 6. In general, the electrode with he smallest ion-exchange capacity seems to have the fastest response, other param-ters being equal.

It seems that a thick response region in the electrode glass can be connected ith poor time characteristics. In aqueous solutions, the electrode glass is hydrated ontinuously, simultaneously with dissolution of the outer glass layers. When the ydration and dissolution rates are equal, the gel-layer will have a constant thickness. f these processes differ in rate, a drifting e.m.f. is caused by changes in the thickness of he gel-layer. For a freshly etched electrode, the hydration rate exceeds the dis-olution rate in a neutral or acidic aqueous solution and the thickness of the gel-ayer increases. The situation is reversed when a glass electrode with a fully developed el-layer is used in a basic aqueous solution. The absence of water in non-aqueous olvents permits the use of freshly etched glass electrodes without running the risk f obtaining an e.m.f. drift by hydration.

ONCLUSIONS

The above experiments and the results of earlier investigations can be sum-arized in a few recommendations for the user of glass electrodes in non-aqueous olutions.

1. An electrode type with a small ion-exchange capacity should be selected. general-purpose electrode should be preferred to a low-temperature electrode.

2. Etching of the electrode in 2% hydrofluoric acid in water for 2 min at room emperature, and hydration in dilute hydrochloric acid for about 1 h will improve ie electrode response in non-aqueous solutions. This partially hydrated electrode not suitable for use in aqueous solutions because further hydration will cause drift.

3. A supporting electrolyte should be present and it should contain ions which

produce a negligible alkaline error. Salts of magnesium, calcium, barium or organic cations are preferred to salts of the alkali metal ions.

4. If the direction of a titration can be selected, titrating an acid with a base is more favourable than the reverse titration.

5. In making measurements other than titrations, the electrode should be equilibrated in a solution similar to the sample solution.

6. If an etched electrode is used, it can be stored in the organic solvent in question; no further hydration will then occur. Immersion in water for a few minutes before use is recommended. If an electrode with a fully developed gel-layer is used, it should be stored in water.

7. Dehydrating conditions during the measurements may cause the electrode performance to deteriorate. It may be possible to restore it by removing the electrode and immersing in water.

8. Since the impedance in the region between the gel-layer and the unhydrated (bulk) glass increases in non-aqueous solutions[19,22], a pH-meter with a high input impedance should be selected.

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SUMMARY

The response times of some commercial glass electrodes have been studied in isopropanol solutions. The response to changes in hydrogen ion concentration made within the ideal response range was found to be of the order of seconds while changes to and from the two-ion response range caused e.m.f. variations during several tens of minutes. Dehydration of the glass surface caused very slow response to changes in concentration, while etching generally shortened the response time. Optimal response was obtained when the ion-exchange capacity of the gel-layer attained its minimal value, which for some general-purpose glass electrodes appeared after about 1 h of hydration. By using etched glass electrodes the time required to perform an acid–base titration in isopropanol could be reduced to less than 2 min without loss in precision.

RÉSUMÉ

Une étude est effectuée sur les temps de réponse, en milieu isopropanol, de quelques électrodes de verre du commerce. La déshydratation de la surface du verre est la cause d'une réponse très lente aux changements de concentration. La réponse optimale est obtenue lorsque la capacité d'échange ionique de la couche-gel atteint sa valeur minimale, qui généralement se produit après 1 h d'hydratation environ. On peut réduire à moins de 2 min la durée d'un titrage acide–base dans l'isopropanol en utilisant des électrodes de verre attaqué sans diminuer la précision.

ZUSAMMENFASSUNG

Die Ansprechzeiten einiger handelsüblicher Glaselektroden in Isopropanollösungen wurden untersucht. Die Elektroden sprachen auf Änderungen der Wasserstoffionenkonzentration im idealen Ansprechbereich innerhalb von Sekunden an. Dagegen änderte sich die E.M.K. während einiger zehn Minuten, wenn die Konzentrationsänderung in den Zwei-Ionen-Ansprechbereich hinein oder aus ihm heraus erfolgte. Nach Dehydratation der Glasoberfläche sprachen die Elektroden auf Konzentrationsänderungen sehr langsam an, während Anätzen die Ansprechzeit im allgemeinen verkürzte. Ein optimales Ansprechverhalten wurde erreicht, wenn die Ionenaustausch-Kapazität der Gelschicht den Minimalwert annahm, was bei einigen Glaselektroden nach etwa einstündiger Hydratation der Fall war. Durch Verwendung angeätzter Glaselektroden konnte die für eine Säure–Base-Titration in Isopropanol erforderliche Zeit auf weniger als 2 min bei gleichbleibender Reproduzierbarkeit vermindert werden.

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THE ELECTROCHEMICAL REACTION OF LITHIUM ON MERCURY IN THE PRESENCE OF WATER IN N,N-DIMETHYLACETAMIDE

RUSSELL R. BESSETTE and DAVID F. HARWOOD

Department of Chemistry, Southeastern Massachusetts University, North Dartmouth, Mass. 02747 (U.S.A.)

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Electrolysis in aqueous media is limited by the electrochemical activity of water, the low overpotential for hydrogen evolution, and the great solvating power of water. Numerous nonaqueous solvents have been investigated in attempts to overcome these difficulties[1–5].

The interpretation of electrochemical data often leads to questions involving solute–solvent interactions and phenomena occurring at the electrode–solution interface. Several investigators[5–7] have discussed electron-transfer mechanisms where large solvation spheres act as electron bridges between the electrode surface and the electroactive species.

While N,N-dimethylacetamide has not been used extensively as a solvent for electrochemical purposes, the polarographic behavior of thallium, lead, cadmium, and zinc ions in this medium has been investigated[8]. The polarography of the alkali metal ions in dimethylacetamide has been described by Gutmann *et al.*[9]. This paper deals with a more detailed study of the electrochemical behavior of lithium in dimethylacetamide in the presence of varying concentrations of water. Polarographic, cyclic voltammetric and chronopotentiometric measurements were employed.

EXPERIMENTAL

Instrumentation

An Indiana Instruments Model ORNL 1988A controlled potential and derivative voltammeter and a Sargent Model SRG strip chart recorder were used to record d.c. polarograms.

All applied potentials were measured with a Fluke Model 8100A digital multimeter. Potential measurements in all cases were accurate to within 1%.

Instrumentation for stationary electrode polarography consisted of an Exact Electronics Model 500B waveform generator, a Wenking Model 68 FR 0.5 potentiostat, and a Moseley 135 M x–y recorder.

The polarographic cell, Brinkmann Instruments Model EA 876-20, was a water-jacketed three-electrode cell maintained at $25 \pm 0.2°$ with a Lo-Temptrol Model 154 water bath.

The dropping mercury electrode (D.M.E.) supplied by Sargent-Welch Inc. had a 3.00-s drop time and a mass flow rate of mercury equal to 2.57 mg s^{-1} at a column height of 101 cm and a potential of 0.000 V *versus* S.C.E.

The hanging mercury drop electrode had a mercury microfeeder (Brinkmann Instruments Model E 410).

The reference electrode was similar to the type used by Musha *et al.*[8]. In the present studies, a normal calomel electrode and 0.1 *M* tetraethylammonium perchlorate in a methylcellulose–dimethylacetamide salt bridge were used.

The current source for the chronopotentiometric measurements was a Monroe Electronics Model 226 precision source. The potential was monitored with a Hewlett Packard Model 419A d.c. null voltmeter, the signal of which was fed to a Moseley 135 M x–y recorder for recording the potential–time function.

A 1-min controlled potential reduction of the lithium and lead ions at an applied potential of −2.5 V (from the Wenking potentiostat) preceded an instantaneous conversion to the application of a constant anodic current of 0.140 μA and the recording of the potential–time function.

Reagents

Tetraethylammonium perchlorate (TEAP), 0.1 *M*, prepared as described by Kolthoff and Coetzee[3], was used as supporting electrolyte.

Anhydrous lithium and sodium perchlorate stock solutions were prepared as described elsewhere[10].

The lead nitrate was analytical-reagent grade (Mallinckrodt).

N,N-Dimethylacetamide was purified by triple distillation at a pressure of 3–5 mm of mercury. The first distillation was from calcium hydride over a standard Vigreux column 45 cm in height. The second and third distillations were performed in the absence of calcium hydride over a 100-cm column packed with glass helices. Solvent purity was confirmed by running a polarographic scan of solvent and supporting electrolyte only and noting the absence of faradaic current.

Polyvinyl chloride (PVC; Monsanto Chemical Co.) was used as a maximum suppressor[8].

The mercury was high-purity Vacumetal (Merck Chemical Division).

Airco prepurified nitrogen was used for deaeration.

Solvent dryness was verified by the addition of lithium perchlorate to the dimethylacetamide–TEAP solution and noting the absence of faradaic current.

RESULTS AND DISCUSSION

Polarography

The effect of varying the concentration of water on the reduction of lithium ion in dimethylacetamide is summarized in Table I. Throughout the concentration range investigated, graphs of limiting current *versus* the square root of the mercury column height corrected for back pressure were linear. These results indicate diffusion-controlled conditions and exclude any possibility of chemical kinetic or catalytic effects. No adsorption effects or polarographic maxima were observed. In the presence of 4% by volume of water, the diffusion current varied linearly with lithium ion concentration in the 0.44–2.2 m*M* range and the $E_{\frac{1}{4}}$ remained constant at −2.37 V. This lack of concentration-dependence of $E_{\frac{1}{4}}$ suggests that ion-pair formation is not a controlling factor. The polarographic waves became more reversible, I_d increased, and $E_{\frac{1}{4}}$ became more positive as the volume concentration of water was increased to 3% and they remained constant at higher concentrations of water. These results are consistent with those obtained by Gutmann *et al.*[9] (Table I).

TABLE I

POLAROGRAPHIC REDUCTION OF LITHIUM PERCHLORATE IN N,N-DIMETHYLACETAMIDE[a]

Vol. conc. H_2O (%)	*$E_{\frac{1}{2}}$ (V)*	*Slope (mV)*	*I_d[b]*	*$D \cdot 10^6$ ($cm^2\ s^{-1}$)*
0.50	−2.50	177	0.477	0.457
0.76	−2.46	139	0.687	0.947
1.00	−2.45	127	0.916	1.68
1.50	−2.41	88	0.943	1.78
2.00	−2.40	77	1.05	2.21
3.00	−2.37; −2.38[c]	64; 66[c]	1.14; 0.95[c]	2.61; 2.44[c]
5.00	−2.39	68	1.10	2.43
7.00	−2.38	65	1.25	3.14
12.00	−2.37	65	1.26	3.19

[a] Lithium ion concentration = 0.39 m*M*.
[b] $I_d = i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ where i_d is expressed in μA, C in mmole l^{-1}, m in mg s^{-1}, t in s. Values of t were calculated from the individual polarograms.
[c] Ref. 9.

The increase in the diffusion current constant with increasing water concentration could be due to viscosity changes in the solution. Since the viscosity of water (0.90 centipoise[11]) is quite similar to that of dimethylacetamide (0.92 centipoise[8]) at 25°, the variation in I_d suggests that the diffusion coefficient of the solvated lithium species is increasing and the size of the solvation sphere is decreasing with addition of water. One can then expect a transition from a predominantly dimethylacetamide complex at low concentrations of water to an aquo complex, as the concentration of water is increased similar to the equilibrium suggested by Elving *et al.*[12] for lithium in a pyridine–water mixture:

$$Li(DMA)_m^+ \rightleftarrows Li(DMA)_{m-1}(H_2O)^+ \ldots \rightleftarrows Li(H_2O)_{n-1}(DMA)^+ \rightleftarrows Li(H_2O)_n^+$$

The anodic shift in $E_{\frac{1}{2}}$ on addition of water indicated an increased ease of reduction of the lithium ion. The magnitude of the change in $E_{\frac{1}{2}}$ was greater than would be expected for a change in the liquid junction potential and was in the opposite direction to what would be expected for a change in dielectric constant of the solution on addition of water[12]. This result can be interpreted as indicating an electron-transfer mechanism where the water molecules act as electron bridges in the manner described by Taube[13].

Cyclic voltammetry

The trends in reversibility, peak potential and peak current for the cyclic voltammetric reduction wave (Table II) agree with the polarographic data presented earlier. Although only one reduction wave was present, a series of oxidation waves appeared on the reverse scan as shown in Fig. 1. The same effect was observed on running multiple scans at various concentrations of water and scan rates. The use of PVC as a maximum suppressor[8] did not affect the series of oxidation waves.

The cyclic voltammetric curve of lead nitrate in dimethylacetamide showed a single reduction wave ($E_p = -0.523$ V) and a single oxidation wave ($E_p = -0.435$

TABLE II

CYCLIC VOLTAMMETRIC DATA FOR THE LITHIUM ION REDUCTION WAVE

$\%\ H_2O$	$E_p\ (V)$	$E_p - E_{p/2}\ (mV)$
1	−2.50	109 ± 19.4
4	−2.48	80 ± 11
8	−2.43	73 ± 11

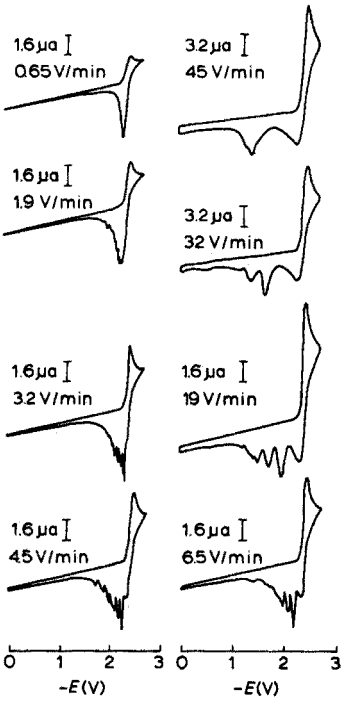

Fig. 1. Voltammograms of lithium in N,N-dimethylacetamide containing 4% water.

V). The ΔE_p of 88 mV indicates some irreversibility in agreement with the results obtained by Musha *et al.*[8]. These results indicate that the series of oxidation waves obtained with lithium were not due to instrumental instability.

The peak potential of the first oxidation wave (Table III) was constant at various scan rates under reversible conditions (high water concentrations), indicating that the reactant for oxidation is the same in all cases, namely lithium amalgam. The peak potential of this wave varied with scan rate in the irreversible case at 1% water by volume as predicted[14].

The constancy of elapsed time between the successive oxidation waves indicates that a periodicity may be attached to the waves (Table IV). Indira and Rangarajan[15] have summarized the wide variety of systems in which periodic phenomena in deactivating systems have been observed. Oscillations have been attributed to film formation and to gas evolution at the electrode solution interface[15].

ABLE III

EAK POTENTIALS FOR THE FIRST THREE LITHIUM OXIDATION WAVES[a]

Vol. conc. H_2O / can ite ($V\ min^{-1}$)	1%			4%			8%		
	$E_P(V)$ I	$E_P(V)$ II	$E_P(V)$ III	$E_P(V)$ I	$E_P(V)$ II	$E_P(V)$ III	$E_P(V)$ I	$E_P(V)$ II	$E_P(V)$ III
9.2	2.03	1.24	—	2.30	1.88	1.64	2.23	1.20	—
5.38	2.16	1.75	1.45	2.30	2.15	2.06	2.26	2.06	1.75
4.47	2.24	1.98	1.76	2.32	2.24	2.17	2.28	2.18	2.00
3.19	2.26	2.09	1.95	2.33	2.30	2.26	2.31	2.24	2.16
1.92	—	2.16	2.07	—	2.35	2.33	—	2.26	2.22
	One wave			One wave			One wave		
0.64	2.27			2.30			2.28		

All potentials are negative of the reference electrode used.

TABLE IV

ELAPSED TIMES BETWEEN THE FIRST AND SECOND, AND FIRST AND THIRD OXIDATION WAVES IN 4 VOL.-% WATER

Scan speed ($V\ min^{-1}$)	t_{I-II} *(s)*	t_{I-III} *(s)*
19.2	1.3	2.1
6.38	1.4	2.3
4.47	1.1	2.0
Ave.	1.3 ± 0.2	2.1 ± 0.2

In the present study, the series of oxidation waves could be due to formation of a lithium hydroxide film and the evolution of hydrogen gas at the electrode surface resulting from the following reaction:

$$2\ \mathrm{Li(Hg)}_x + 2\ \mathrm{H_2O} \rightarrow 2\ LiOH + \mathrm{H_2}\uparrow + 2x\ \mathrm{Hg}$$

The product of the reduction of lithium ion on mercury in N,N-dimethylacetamide has been shown to be lithium amalgam[9]. At the water concentrations used and at applied potentials slightly positive of the standard reduction potential, it is reasonable to assume that the above reaction would take place. The lithium hydroxide and hydrogen gas were not detected because of the small concentrations of materials present.

Chronopotentiometry

Indira and Rangarajan[15] have attributed oscillations in potential obtained under chromopotentiometric conditions for nickel in sulfuric acid to electrode deactivation. The chronopotentiometric oxidation of lithium amalgam is depicted in Fig. 2. The curves for the solvent-supporting electrolyte background and for the oxidation of lead amalgam in dimethylacetamide follow theoretical predictions. The curve for the oxidation of lithium amalgam shows a potential oscillation of

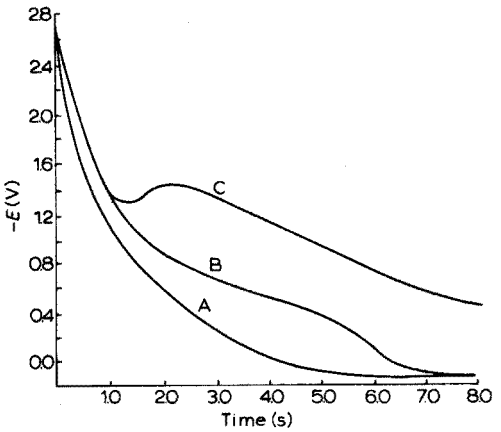

Fig. 2. Chronopotentiometric curves for tetraethylammoniumperchlorate, lead and lithium in N,N-dimethylacetamide. (A) Solvent background, DMA–0.1 *M* TEAP; (B) oxidation of lead amalgam in DMA–0.1 *M* TEAP; (C) oxidation of lithium amalgam in DMA–0.1 *M* TEAP. $Li^+ = 1.16$ m*M*; $Pb^{2+} = 1.70$ m*M*; anodic current density = 0.104 μA mm^{-2}.

90 mV from peak to peak. These data, in light of earlier discussion[15], may be interpreted as the result of electrode deactivation caused by formation of the lithium hydroxide film mentioned previously.

SUMMARY

The displacement of N,N-dimethylacetamide molecules by water molecules in the lithium ion solvation sphere as the concentration of water in dimethylacetamide is increased, is confirmed. An electron-transfer mechanism where the water molecules act as electron bridges is suggested. Cyclic voltammetric experiments yield a single lithium ion reduction wave and a number of oxidation waves which vary with scan rate or water concentration. The constancy of elapsed time between the successive oxidation waves indicates a periodicity, which is attributed to electrode deactivation as a result of lithium hydroxide film formation. Chronopotentiometric data are presented to substantiate electrode deactivation.

RÉSUMÉ

Une étude est effectuée sur la réaction électrochimique du lithium sur le mercure, en présence d'eau dans la N,N-diméthylacétamide. Un mécanisme de transfert électronique où les molécules d'eau se comportent comme des ponts d'électrons est proposé. Les essais voltammétriques cycliques produisent une vague de réduction de l'ion lithium simple et un certain nombre de vagues d'oxydation variant avec la vitesse ou avec la concentration en eau. Des valeurs chronopotentiométriques sont données pour établir la déactivation de l'électrode.

ZUSAMMENFASSUNG

Die Verdrängung von N,N-Dimethylacetamid-Molekülen durch Wasser-

noleküle in der Solvatationssphäre von Lithiumionen bei Erhöhung der Konzentration von Wasser in Dimethylacetamid wird bestätigt. Es wird ein Elektronenübertragungs-Mechanismus vorgeschlagen, bei dem die Wassermoleküle als Elektronenbrücken wirken. Bei der cyclischen Voltammetrie werden eine einzige Lithiumionen-Reduktionsstufe und eine Anzahl von Oxidationsstufen erhalten, die mit der Abtastgeschwindigkeit und der Wasserkonzentration variieren. Die Konstanz der Zeit, die zwischen den aufeinanderfolgenden Oxidationsstufen verstreicht, weist auf eine Periodizität hin, die einer Elektroden-Desaktivierung als Folge der Bildung eines Lithiumhydroxidfilms zugeschrieben wird. Es werden chronopotentiometrische Ergebnisse vorgelegt, die die Elektroden-Desaktivierung bestätigen.

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ÉTUDE DES CHÉLATES MIXTES DES IONS FERRIQUES AVEC LES ACIDES NITRILOTRIACÉTIQUE, SULFO-5-SALICYLIQUE ET PYROCATECHOLDISULFONIQUE-3,5

M. MORIN et J. P. SCHARFF

Laboratoire de Chimie Minérale I, Université Claude Bernard, Lyon I, 69621-Villeurbanne (France)

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Nous présentons les résultats obtenus au cours de l'étude des interactions, en solution aqueuse, entre les ions ferriques, un coordinat tétradenté A (anion de l'acide nitrilotriacétique), et un coordinat bidenté B (anion de l'acide sulfo-5-salicylique ou de l'acide pyrocatécholdisulfonique-3,5).

Les premiers travaux de notre Laboratoire sur la chélation mixte mettant en jeu des coordinats polydentés furent publiés par Martin et Pâris[1,2]. Ils furent suivis par de nombreux autres dont font état des publications d'ensemble plus récentes[3–5] en ce qui concerne les équilibres en solution, tandis que la structure et la géométrie des complexes mixtes faisaient l'objet d'articles particuliers[6,7]. Cependant il faut noter que les données relatives à de tels systèmes mixtes des ions ferriques sont extrêmement rares et on constate que dans des revues rassemblant plusieurs centaines de données numériques[4,5] on ne trouve que trois exemples de ce type.

Une méthode protométrique nous a permis de détecter les différentes espèces $M_pH_qA_rB_s$ susceptibles de se former au sein de telles solutions et d'affiner, par une méthode des moindres carrés, leurs constantes globales de stabilité ionique β_{pqrs}.

D'autre part l'application d'une méthode spectrophotométrique trichrome permet de vérifier les résultats obtenus notamment en ce qui concerne les différentes zones d'existence des espèces chélatées.

TECHNIQUES EXPÉRIMENTALES

Leur principe en a été décrit précédemment[8,9]. Toutes les mesures furent effectuées à la température de 25° ± 0.1°, en milieu de force ionique 0.5 *M* maintenue constante par du nitrate de sodium.

Traitement des données expérimentales

Au cours de titrages protométriques par un acide fort ou une base forte, à température et pression constante, l'état d'un système chimique contenant les quatre constituants M, H, A et B est entièrement défini par les équations suivantes écrites dans le cas le plus général:

$$C_M = m + \Sigma p \cdot \beta_{pqrs} \cdot m^p h^q a^r b^s \quad (1)$$

$$C_A = a + \Sigma r \cdot \beta_{pqrs} \cdot m^p h^q a^r b^s \quad (2)$$

$$C_B = b + \Sigma s \cdot \beta_{pqrs} \cdot m^p h^q a^r b^s \quad (3)$$

$$C_H = h - oh + \Sigma q \cdot \beta_{pqrs} \cdot m^p h^q a^r b^s \quad (4)$$

Dans ces relations les différents symboles ont la signification suivante: C_M, C_A, C_B = concentrations totales des constituants M, A, B, C_H = concentration totale des protons neutralisables, m, a, b, h, oh = concentration des constituants libres et des ions H^+ et OH^-. β_{pqrs} = constante de stabilité de l'espèce $M_pH_qA_rB_s$; $\beta_{pqrs} = [M_pH_qA_rB_s]/m^p h^q a^r b^s$ où p, r, s $\geqslant 0$ et où par convention q peut être négatif (cas de la fixation de groupements OH^-).

Les données expérimentales brutes: quantités des réactifs, potentiels d'électrodes, peuvent être transformées en courbes normalisées $\bar{q}_{exp} = f(-\log h)$ où $\bar{q}$ représente le nombre moyen de protons fixé par coordinat: $\bar{q} = (c_H - h + oh)/(c_A + c_B)$.

Le principe de l'affinement déjà décrit en détail[10-12] consiste à rendre minimum la somme $U = \Sigma(\bar{q}_{exp} - \bar{q}_{calc})^2$ par la méthode du "pit-mapping".

Pour cela des valeurs initiales approchées des constantes β_{pqrs} peuvent être estimées par divers moyens (calcul approché, considérations statistiques, etc.). A l'aide de ces valeurs grossières le système des quatre équations (1)–(4) permet le calcul de m, a, b et $\bar{q}_{calc}$* que l'on compare à $\bar{q}_{exp}$. L'opération est alors répétée pour différentes valeurs de β_{pqrs} déduites des valeurs initiales par des variations systématiques fixées par un "pas" choisi au préalable. Il reste alors à extrapoler les valeurs des constantes β_{pqrs} vers des valeurs voisines de celles rendant minimum l'expression de U.

La méthode est extrêmement féconde car au cours de l'affinement il est possible d'introduire de nouvelles constantes correspondant à la présence d'espèces hypothétiques. On peut alors conclure à l'existence ou à l'absence de ces espèces suivant que la valeur de U diminue ou augmente du fait de cette introduction.

LES SYSTÈMES SIMPLES

Le système fer–acide nitrilotriacétique

Avant d'aborder l'étude de la chélation mixte, il était nécessaire de repréciser, pour nos conditions expérimentales, les constantes de stabilité relatives au système simple fer(III)–acide nitrilotriacétique. En effet, bien que cette étude ait déjà été abordée par de nombreux auteurs aussi bien en solution aqueuse, que plus récemment à l'état solide[13,14] les conclusions ne sont pas unanimes quant au nombre et à la stabilité des espèces formées. Ceci est dû à la diversité des conditions expérimentales et des méthodes utilisées (protométrique[15,16], protométrique et redox[17-19], polarographique[20,21], partage liquide–liquide[22]).

Les constantes d'ionisation de l'acide nitrilotriacétique ont été déterminées potentiométriquement. Les courbes de titrage par l'hydroxyde de sodium ou par l'acide nitrique de solutions 0.5 M en nitrate de sodium et 10^{-2} M en sel disodique de l'acide nitrilotriacétique permettent de tracer la courbe $\bar{q} = f(-\log h)$ directement exploitable. Cependant afin d'utiliser un nombre maximum de données, nous avons

* Tous les calculs de ce travail ont été effectués par le centre Interdisciplines régionale de calcu électronique d'Orsay grâce au programme ACREF-3A établi par R. P. Martin.

alculé la constante K_1^H pour divers points de la courbe de titrage. Nous avons insi obtenu: $pK_1^H = 8.95 \pm 0.02$ (moyenne de 37 valeurs). En milieu acide, compte enu des valeurs respectives de pK_2^H et pK_3^H, le calcul algébrique n'est plus utilisable. Nous avons alors fait appel à la méthode des approximations successives pour affiner es valeurs. Le convergence est rapide et conduit après quatre itérations successives ux valeurs: $pK_1^H = 8.95$; $pK_2^H = 2.28$; $pK_3^H = 1.70$.

En ce qui concerne les complexes ferriques nous avons neutralisé par l'hydroxyde de sodium des solutions acides contenant l'ion métallique et le coordinat à différents rapports $R = c_A/c_M = 2.5$; 5; 10. Après avoir constaté que la méthode de Bjerrum était inutilisable (courbes de formation non confondues pour ces différents rapports), nous avons transformé les données expérimentales en courbes normalisées $\bar{q} = f(-\log h)$.

A l'aide du programme ACREF-3A nous avons pu résoudre les équations 1)–(4) en introduisant comme valeurs approchées des constantes β_{pqrs}, les valeurs de Schwarzenbach et Heller[18]:

$$\beta_{1010} = 7.413 \cdot 10^{15} \qquad \beta_{1020} = 2.089 \cdot 10^{24}$$
$$\beta_{1-110} = 6.166 \cdot 10^{11} \qquad \beta_{1-210} = 1.047 \cdot 10^{4}$$

Pour tous les rapports envisagés, nous avons affiné chaque constante dans le domaine de pH approprié. C'est ainsi que nous avons obtenu: $\beta_{1010} = 2.137 \cdot 10^{16}$ pour le complexe FeA dans une zone de pH 2.12–2.80, et $\beta_{1-110} = 2.260 \cdot 10^{12}$ pour le complexe FeAOH dans une zone de pH 2.80–4.40. A titre d'exemple indiquons que pour 148 couples de données choisies parmi toutes les courbes de neutralisation nous avons obtenu $U = 5.56 \cdot 10^{-3}$. L'introduction de la constante β_{1020} faisant augmenter très fortement la valeur de U, nous en avons déduit que l'espèce MA_2 n'existait pas pour les pH envisagés ci-dessus. Nous verrons d'ailleurs lors de l'étude des systèmes mixtes, que les espèces FeA_2 et $FeA(OH)_2$ ont une influence négligeable, étant donné qu'elles doivent exister dans un domaine de pH élevé où se forment préférentiellement les complexes mixtes d'une part et les espèces simples très stables.

En conclusion, nous avons détecté, dans les conditions expérimentales utilisées tout au long de cette étude, les seuls complexes du type FeA et FeA(OH): $\log \beta_{1010} = 16.33$ et $\log \beta_{1-110} = 12.35$.

Nous insistons particulièrement sur le fait que pour des conditions différentes il est probable que d'autres espèces interviennent et en particulier dans le cas où $R = 1$ on a formation de dérivés hydroxydés polynucléaires comme l'ont montré Gustafson et Martell[16] ainsi que Gilmour *et al.*[23].

Les systèmes fer–acide sulfo-5-salicylique et fer–acide pyrocatécholdisulfonique-3,5

Le Tableau I rassemble les valeurs des constantes de stabilité relatives aux systèmes fer(III)–acide sulfo-5-salicylique et fer(III)–acide pyrocatécholdisulfonique-3,5, déterminées au cours de précédents travaux[8,9].

LES SYSTÈMES MIXTES $M_pH_qA_rB_s$

Dans le cas du système fer(III)–acide nitrilotriacétique–acide pyrocatécholdisulfonique-3,5, Schwarzenbach et Willi[24] avaient déjà montré, par spectrophoto-

TABLEAU I

STABILITÉ IONIQUE DES ESPÈCES $M_pH_qB_s$

Espèces	*B = acide sulfosalicylique*	*B = acide pyrocatéchol-disulfonique-3,5*
MHB		$\log \beta_{1101} = 20.86$
MB	$\log \beta_{1001} = 12.08$	$\log \beta_{1001} = 18.74$
MB_2	$\log \beta_{1002} = 23.22$	$\log \beta_{1002} = 32.97$
MB_3	$\log \beta_{1003} = 30.24$	$\log \beta_{1003} = 43.25$

TABLEAU II

CONDITIONS D'ÉTUDE DU SYSTÈME FeAB (B = ACIDE PYROCATÉCHOLDISULFONIQUE-3,5 OU ACIDE SULFO-5-SALICYLIQUE)

($c_M = 1.025 \cdot 10^{-3}$ *M*; $[HNO_3]_T = 1.034 \cdot 10^{-2}$ *M*)

Rapports Fe–A–B	c_A	c_B
Acide pyrocatécholdisulfonique-3,5		
1–10–10	$1.000 \cdot 10^{-2}$ *M*	$1.000 \cdot 10^{-2}$ *M*
1– 5–10	$5.000 \cdot 10^{-3}$ *M*	$1.000 \cdot 10^{-2}$ *M*
1–10– 5	$1.000 \cdot 10^{-2}$ *M*	$5.000 \cdot 10^{-3}$ *M*
Acide sulfo-5-salicylique		
1– 3– 6	$3.000 \cdot 10^{-3}$ *M*	$6.000 \cdot 10^{-3}$ *M*
1– 5–10	$5.000 \cdot 10^{-3}$ *M*	$1.000 \cdot 10^{-2}$ *M*
1–10–10	$1.000 \cdot 10^{-2}$ *M*	$1.000 \cdot 10^{-2}$ *M*
1–10–20	$1.000 \cdot 10^{-2}$ *M*	$2.000 \cdot 10^{-2}$ *M*

métrie, l'existence d'un complexe mixte de formule FeAB pour lequel ils calculaien une constante "d'association" valable à pH 5.4: $K = [FeAB]/[H_2B][FeA(OH)] = 1.22 \cdot 10^4$. Il était donc logique de penser qu'il y aurait formation d'une espèc ternaire semblable dans le système fer(III)–acide nitrilotriacétique–acide sulfo-5 salicylique, en raison de son analogie avec le système précédent.

Etude potentiométrique

Nous avons titré par l'hydroxyde de sodium, des solutions contenant l'io métallique et les deux coordinats dans les différents rapports (Tableau II). Le calculs ont été conduits d'une manière tout à fait analogue à celle décrite pour l système simple FeA. En supposant dans un premier temps, qu'il n'existe aucu complexe mixte dans le système fer(III)–acide nitrilotriacétique–acide pyrocatéchol disulfonique-3,5 ($\beta_{1011} = 0$), *U* prend la valeur $1.57 \cdot 10^{-1}$ pour 74 couples de donnée expérimentales. L'introduction de la valeur $\beta_{1011} = 1.50 \cdot 10^{30}$ (constante approché de l'espèce mixte déduite de celle de Schwarzenbach et Willi[24] à l'aide de nos valeur de constantes relatives aux espèces H_2B et FeA(OH)) fait décroître très nettemen la différence $(\bar{q}_{calc} - \bar{q}_{exp})$ pour chaque point expérimental. En fin d'affinement nou obtenons: $\beta_{1011} = 6.33 \cdot 10^{30}$ et *U* prend alors la valeur $2.67 \cdot 10^{-3}$ relative aux 7 couples de données. La concordance de $\bar{q}_{exp}$ et de $\bar{q}_{calc}$ se révèle être très satisfaisant dans une zone de pH allant de 2.70 à 5.40. Nous pouvons en conclure que dans no

conditions expérimentales, il se forme la seule espèce mixte FeAB pour laquelle $\log \beta_{1011} = 30.80$.

En ce qui concerne le système fer(III)–acide nitrilotriacétique–acide sulfo-5-salicylique, la condition "U minimum" a été remplie en admettant l'existence d'une espèce mixte unique FeAB de constante de stabilité ionique $\log \beta_{1011} = 26.60$. Pour les quatre rapports étudiés nous observons une bonne concordance de $\bar{q}_{exp}$ et $\bar{q}_{calc}$ dans un vaste domaine de pH allant de 2.30 à 8.70.

Méthode trichrome

Le principe de la méthode trichrome et son application à l'étude des complexes métalliques en solution[25] a déjà été exposé dans plusieurs publications de notre Laboratoire[8,9,26,27].

Dans le cas du système fer(III)–acide nitrilotriacétique–acide pyrocatéchol-disulfonique-3,5 nous avons tracé les spectres d'absorption en fonction du pH dans la région 410–710 nm de solutions contenant l'ion métallique et les deux coordinats dans les rapports suivants:

Fe–A–B:1–5–10:

$$c_M = 1.281 \cdot 10^{-4}\, M;\ c_A = 6.250 \cdot 10^{-4}\, M;\ c_B = 1.250 \cdot 10^{-3}\, M$$

Fe–A–B:1–10–5:

$$c_M = 1.281 \cdot 10^{-4}\, M;\ c_A = 1.250 \cdot 10^{-3}\, M;\ c_B = 6.250 \cdot 10^{-4}\, M$$

Fe–A–B:1–10–10:

$$c_M = 1.281 \cdot 10^{-4}\, M;\ c_A = 1.250 \cdot 10^{-3}\, M;\ c_B = 1.250 \cdot 10^{-3}\, M$$

La détermination des coordonnées trichromatiques complèmentaires u, v, w a été faite dans les trois intervalles spectrophotométriques: 410–510 nm, 510–610 nm, et 610–710 nm.

Nous avons représenté sur la Fig. 1, les courbes $u, v, w = f(pH)$ pour le rapport 1–10–10, ainsi que les courbes de répartition en fonction du pH de toutes les

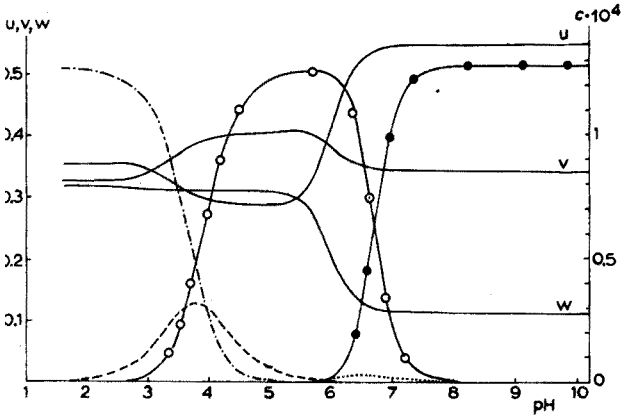

Fig. 1. Méthode trichrome (traits pleins) et courbes de répartition (traits discontinus) pour le système fer(III)–acide nitrilotriacétique–acide pyrocatécholdisulfonique-3,5. (–·–·–·–) FeA; (– – – –) FeA(OH); ○) FeAB; (------) FeB_2; (●) FeB_3.

espèces présentes simultanément en solution, calculées à partir des valeurs de la constante de stabilité du complexe mixte et de celles des complexes simples déterminées précédemment pour les conditions de concentrations indiquées ci-dessus.

Nous observons ainsi des droites parallèles à l'axe des pH pour des pH < 2.60. Ceci est dû au fait que dans ce domaine d'acidité coexistent les deux espèces FeA (jaune clair) et FeA(OH)(incolore). L'absorption est donc extrêmement faible. A partir de pH 2.60 apparaît l'espèce mixte FeAB (bleu-violet). Le palier correspondant à cette espèce n'est jamais net car ce complexe est toujours en équilibre soit avec FeA qui subsiste jusqu'à pH 5, soit FeB_2(bleu-violet) pour des pH compris entre 5.80 et 7.80 et enfin avec FeB_3 (rouge) qui se forme à partir de pH 5.80. L'apparition du troisième palier à pH 7.40 caractérise l'existence de FeB_3 en accord avec les courbes de répartition qui montrent qu'à partir de cette valeur FeAB et FeB_2 sont en proportions négligeables et que seule FeB_3 subsiste au sein de la solution.

Un point important à remarquer est la formation préférentielle de l'espèce mixte FeAB pour des pH 3–7 au détriment de l'espèce simple FeB_2 de stabilité ionique voisine, puis la prépondérance de l'espèce FeB_3 pour des pH > 8.

En ce qui concerne le système fer(III)–acide nitrilotriacétique–acide sulfo-5-salicylique des essais ont été effectués pour les rapports Fe–A–B = 1–3–6 et 1–10–10. Les spectres d'absorption enregistrés en fonction du pH dans le domaine 385–560 nm montrent l'existence d'un seul complexe coloré dont le maximum d'absorption est situé à 455 nm. Ce maximum ne pouvant correspondre aux complexes simples FeA ou FeB_3 est donc caractéristique de l'espèce mixte FeAB. Les coordonnées trichromatiques complémentaires u, v, w déterminées en fonction du pH dans les trois intervalles 385–435, 435–485 et 485–535 nm sont représentées sur la Fig. 2 pour le rapport 1–10–10. Pour des pH acides, nous observons des portions de courbes non parallèles à l'axe des pH. Ce fait est expliqué par l'examen des courbes de répartition des espèces (Fig. 3) qui montrent que dans ce domaine d'acidité l'espèce simple FeA (jaune clair) est en équilibre avec l'espèce mixte FeAB (orangée). A partir de pH 4.50 et jusqu'à pH 9.50, nous notons l'existence d'un palier unique correspondant au complexe mixte. Il faut remarquer que dans cette zone, le complexe FeA(OH) existe en quantité notable, mais étant incolore, il n'influe pas sur les coordonnées trichromatiques. D'autre part la proportion relative de FeA(OH) diminue très nettement quand la concentration de B augmente. Elle passe de

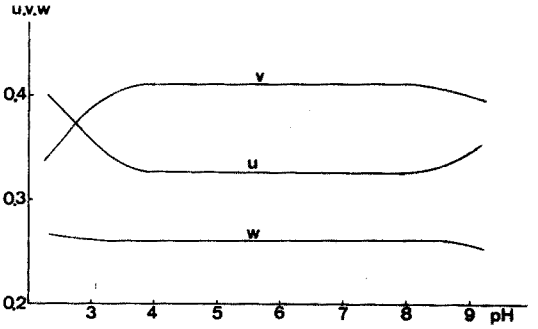

Fig. 2. Méthode trichrome pour le système fer(III)–acide nitrilotriacétique–acide sulfo-5-salicylique.

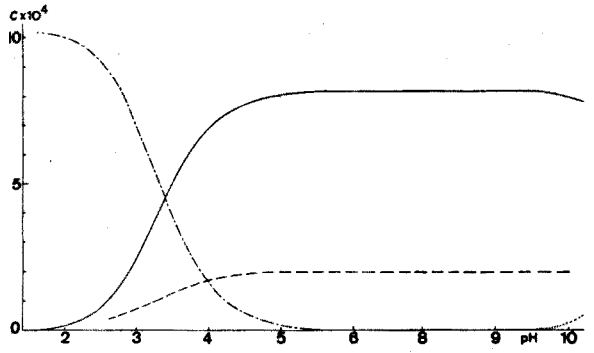

Fig. 3. Courbes de répartition pour le système fer(III)–acide nitrilotriacétique–acide sulfo-5-salicylique. (-·-·-) FeA; (----) FeA(OH); (——) FeAB; (------) FeB_3.

FeA(OH)/FeAB = 39% pour Fe–A–B = 1–3–6 à 12% pour Fe–A–B = 1–10–20. Enfin vers pH 9, apparait l'espèce FeB_3 (rouge) ce qui explique que le palier soit limité du coté des pH alcalins.

La méthode trichrome confirmée par les courbes de répartition des espèces vient donc corroborer nos résultats potentiométriques qui avaient mis en évidence la formation d'une seule espèce mixte FeAB dans le cas des deux systèmes ternaires examinés.

CONCLUSION

En employant, de façon générale, de fortes proportions de coordinat et en utilisant largement les méthodes de calcul mises au point depuis plusieurs années dans notre Laboratoire, nous avons pu mettre en évidence dans les deux systèmes ternaires envisagés des espèces mixtes du type FeAB dont les constantes de stabilité ionique ont été affinées.

Dans le but d'obtenir une confirmation toujours souhaitable de nos conclusions, nous avons confronté nos résultats numériques, concrétisés par les courbes de répartition des espèces avec les données de la méthode trichromatique complémentaire.

Du point de vue quantitatif, la stabilité des espèces mixtes peut être comparée par la méthode proposée par Sigel[28] qui envisage les deux réactions:

$$MA + B \rightleftarrows MAB$$

$$M + B \rightleftarrows MB$$

pour lesquelles le rapport des constantes d'équilibre est un paramètre sans dimension K_Δ caractérisant la stabilisation du complexe mixte. K_Δ est aussi la valeur de la constante d'équilibre pour la réaction:

$$MA + MB \rightleftarrows MAB + M$$

et l'on a $\log K_\Delta = \log \beta_{1011} - (\log \beta_{1010} + \log \beta_{1001})$. Pour les complexes ferriques étudiés dans ce travail, on trouve: système Fe(III)–A–acide sulfo-5-salicylique: $\log K_\Delta = -1.82$; système Fe(III)–A–acide pyrocatécholdisulfonique-3,5: $\log K_\Delta = -4.27$. On peut en déduire que le complexe mixte avec l'acide sulfo-5-salicylique

est relativement plus stable que celui formé avec l'acide pyrocatécholdisulfonique-3,5. Ceci peut d'ailleurs être remarqué sur les courbes de répartition où l'on constate que l'espèce FeAB existe en quantité prépondérante par rapport aux autres espèces dans un plus large domaine de pH lorsque B représente l'anion de l'acide sulfo-5-salicylique, que lorsque B représente l'anion de l'acide pyrocatécholdisulfonique-3,5.

Nous remercions très vivement le Professeur R. A. Pâris pour l'aide et les conseils qu'il a pu nous apporter dans la réalisation de ce travail.

RÉSUMÉ

Après avoir reprécisé les données relatives aux complexes simples, notamment dans le système Fe(III)–acide nitrilotriacétique (H_3NTA), les auteurs montrent l'existence en solution d'espèces mixtes du type FeAB dans les systèmes Fe(III)–NTA–acide sulfo-5-salicylique et Fe(III)–NTA–acide pyrocatécholdisulfonique-3,5. Les compositions et les constantes de stabilité de toutes les espèces formées ainsi que les résultats de la méthode spectrophotométrique trichrome sont donnés.

SUMMARY

A detailed examination of mixed chelate formation in systems containing iron(III), nitrilotriacetic acid, and 5-sulphosalicylic acid or pyrocatechol-3,5-disulphonic acid, has been made. Precise stability constants for the iron(III)–nitrilotriacetic acid system were established. Potentiometric methods and tristimulus colorimetry were used to establish mixed chelate formation. The compositions and stability constants of all the species formed are given.

ZUSAMMENFASSUNG

Die Bildung gemischter Chelate in Systemen, die Eisen(III), Nitrilotriessigsäure und 5-Sulfosalicylsäure oder Brenzcatechin-3,5-disulfonsäure enthalten, wurde eingehend untersucht. Für das System Eisen(III)-Nitrilotriessigsäure wurden genaue Stabilitätskonstanten ermittelt. Für die Untersuchung der Chelatbildung wurden potentiometrische Methoden sowie die Methode der Spektralphotometrie in drei Wellenlängenbereichen angewendet. Die Zusammensetzungen und die Stabilitätskonstanten der gebildeten Spezies werden angegeben.

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Analytica Chimica Acta, 66 (1973) 123–129

THE REACTION OF GOLD AND DITHIZONE

J. J. COX and D. M. SERVANT
Department of Chemistry, The Polytechnic, Wolverhampton WV1 1LY (England)
(Received 7th December 1972)

There has been a number of investigations into the reaction between aqueous solutions of gold(III) and organic solutions of the dithizone (1,5-diphenyl-3-thiolformazan, H_2Dz) and various recommendations have been made for its use in the determination of gold. Several stoicheiometries Au : HDz have been reported for the product: 2 : 1[1,2], 1 : 1[1–6], 2 : 3[7,8], 1 : 2[4,8], and 1 : 3[7,9], and most of them have been assigned to both a red form and a yellow or brown form (Table I). Most metals form

TABLE I

STOICHEIOMETRIES ASSIGNED TO Au : HDz COMPLEXES

Stoicheiometry	λ_{max}	*Solvent*	*Reference*
2 : 1	Red		1, 2
2 : 1	Yellow		3
1 : 1	Yellow		1, 2
1 : 1	Golden-brown	$CHCl_3$	4
1 : 1	450 nm (ε 2.6 · 10^4)	C_6H_6	5
$Au(HDz)(OH)_2$	460, 605 nm	$CHCl_3$	6
$Au(HDz)Cl_2$	540, 570 nm	$CHCl_3$	6
1 : 1	Red-brown		3
2 : 3	Red		7
2 : 3	Lemon-yellow		8
1 : 3	Yellow, *ca.* 400 nm, sh. 520 nm	CCl_4	9
1 : 3	Yellow, 450 nm	CCl_4	7
Not given	Yellow, 460 nm	CCl_4	10
Not given	Red, 550 and 570 nm	$CHCl_3$	10
Not given	Violet		10
Not given	438 and 570 nm	$CHCl_3$	11

only one or two complexes with dithizone; copper, for example, is notable in forming both a primary and a secondary dithizonate (*i.e.* with HDz^- and with Dz^{2-}) in both its common valences. The behaviour of gold then, in appearing to form some ten complexes, is strikingly different from that of other metals which react with dithizone. Since the reports of earlier work do not always specify the conditions very closely, a careful re-investigation of this reaction under a wide range of experimental conditions has been carried out. The results are reported below.

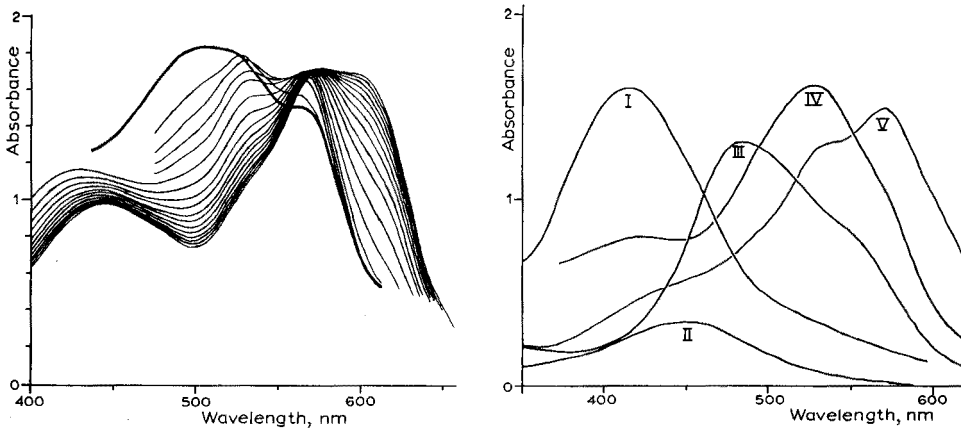


Fig. 1. Spectrum *vs.* time for the organic extract from gold(III) ($5 \cdot 10^{-3}$ *M*) in 3 *M* hydrochloric acid with dithizone in chloroform ($2 \cdot 10^{-4}$ *M*). The heavy line was the initial spectrum; the remainder were recorded at 5 × 1 min, and then at 2-min intervals.

Fig. 2. Spectra of the individual peaks. (I) Gold(III), $6 \cdot 10^{-3}$ *M*; chloride, 0.775 *M*; dithizone in chloroform, $8.4 \cdot 10^{-5}$ *M*. (II) Gold(III), $2 \cdot 10^{-5}$ *M*; sodium chloride, 0.5 *M*; dithizone in chloroform, $5 \cdot 10^{-5}$ *M* (with dithizone in chloroform as reference solution). (III) Gold(III), $1.24 \cdot 10^{-4}$ *M*; sulphuric acid, 11 *M* dithizone in chloroform, $3.6 \cdot 10^{-5}$ *M*. (IV) Gold(III), $6 \cdot 10^{-3}$ *M*; hydrochloric acid, 6 *M*; dithizone in chloroform, $6.5 \cdot 10^{-5}$ *M*. (V) Gold(I) iodide, solid; dithizone in chloroform, $4.4 \cdot 10^{-4}$ *M*.

RESULTS

When gold(III) in 3 *M* hydrochloric acid was extracted with dithizone in chloroform, the spectrum of the organic phase changed with time and exhibited peaks at 420, 450, 490, 520 and 570 nm (Fig. 1); thus peaks were found at or about all the wavelengths previously reported for "gold dithizonate" (*cf.* Table I), with the addition of 490 nm. Similarly, under most conditions several of these peaks were obtained together. However, the species responsible for each band could be made the principal component of the system by adjusting the conditions appropriately (Table II and Fig. 2).

TABLE II

CONDITIONS FOR GENERATING INDIVIDUAL PEAKS

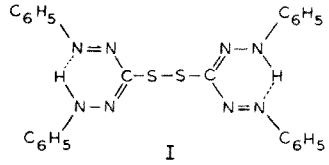
Wavelength (nm)	*Acid concentration (M)*	*Gold concentration (M)*
420	0–1	$>10^{-4}$
450	0–1	$<5 \cdot 10^{-5}$
490	1–15	$<10^{-4}$
520	1–15	$>10^{-3}$
570	1–15	AuI, solid

DISCUSSION

Since all the peaks previously assigned to "gold dithizonate", and an additional

one, could be obtained in a single system, the reaction was clearly more complex than the simple formation of a dithizonate. In view of the ready oxidation of dithizone and the complexity of the products[12], the formation of at least some of these oxidation products had to be considered.

Known oxidizing agents for dithizone are iron(III)[13,14], iodine[12], thallium III)[15], and selenium(IV)[16], although the last has been contested[17]. The redox potentials in these systems are: iron(III)/iron(II), 737 mV in 2 *M* perchloric acid; iodine/iodide, 628 mV in 0.5 *M* sulphuric acid; thallium(III)/thallium(I), 770 mV in 0.5–1.0 *M* hydrochloric acid; and selenium(IV)/selenium(0), 740 mV in acidic medium extrapolated to zero ionic strength[18]. The redox potentials for the various possible systems involving gold are: tetrachloroaurate(III)/dichloroaurate(I), 926 mV; tetrabromoaurate(III)/dibromoaurate(I), 805 mV; dichloroaurate(I)/gold(0), 1154 mV; and dibromoaurate(I)/gold(0), 963 mV (all corrected to zero ionic strength)[18]. Thermodynamically then, gold(III) or gold(I) should oxidize dithizone, and more readily in the presence of chloride than of bromide, though kinetically the process may be very slow.



I

The characteristics reported for bis-3,3′-(1,5-diphenylformazan)disulphide (I)[12] closely resembled those for the band at 420 nm, and Table III shows a comparison between this species, our own product from the oxidation of dithizone with aqueous iodine (*cf.* Irving *et al.*[12]) and the data given by Irving *et al.*[12] (see also Fig. 3). The excellent agreement with data from authentic samples and the highly characteristic spontaneous regeneration of dithizone, up to 50% of the original, showed that the compound generated under these conditions was the disulphide.

The species absorbing at 450 nm seemed to be that assigned the stoicheiometry $Au(HDz)_3$ by Iwantscheff[7]. Since all the dithizone was not consumed at a ratio of gold to dithizone of 1:2.5 (Experimental and Fig. 2), the stoicheiometry 1:3 was unlikely unless the dithizonate had a low formation constant which seemed very improbable. The alternative, a gold(I) dithizonate Au(HDz) was also unlikely because

TABLE III

THE OXIDATION OF DITHIZONE TO BIS-3,3′-(1,5-DIPHENYLFORMAZAN)DISULPHIDE

	Gold(III)	*Aq. iodine*	*Irving et al.*[12]
$\lambda_{max}(CHCl_3)$ (nm)	415–420	410–415	420
$\varepsilon_{max}(CHCl_3)$ (l mol^{-1} cm^{-1})	$4.4 \cdot 10^4$	$4.6 \cdot 10^4$	$4.2 \cdot 10^4$
Spontaneous regeneration of dithizone	Up to 50%	Over 43%	50% (Theory)
Regeneration of dithizone by reducing agents	Over 90%	—	Up to 100%

then the molar absorptivity (based on gold) was *ca.* 16.7×10^3 l mol^{-1} cm^{-1}, *i.e* lower than any dithizonate reported and by a factor of two in most instances (*e.g* ref. 7). The peak at 490 nm has not been reported previously and may be due to a gold dithizonate; if so gold dithizonate is a very ephemeral species under most o the conditions examined here.

The variation in relative intensity of the peaks at 520 and at 570 nm mad it most unlikely that both were due to the same species as has been reported[6,10] particularly since that at 570 nm could be made the predominant species in th reaction of dithizone with gold(I). Similar peaks have been obtained by the oxidatio of dithizone solutions with strongly acidic iron(III) chloride solutions (Fig. 3 an Experimental), and by oxidation with selenium(IV) in 10 *M* hydrochloric acid[16] Accordingly, it seems likely that these two peaks are due to oxidation products.

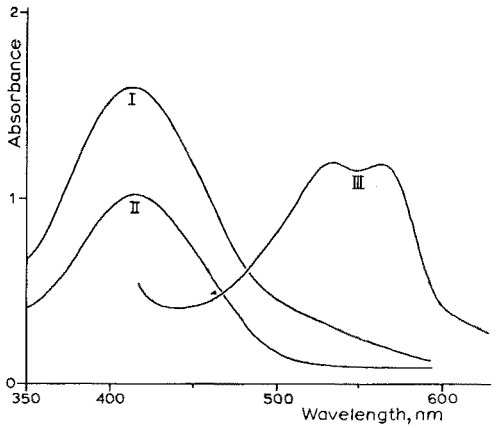


Fig. 3. Oxidation products. (I) Gold(III), $6 \cdot 10^{-3}$ *M*; sodium chloride, 0.775 *M*; dithizone in chloro form, $8.4 \cdot 10^{-5}$ *M*. (II) Aqueous iodine, $5 \cdot 10^{-5}$ *M*; dithizone in chloroform, $9 \cdot 10^{-5}$ *M*. (III) Dithizone i chloroform, $3.6 \cdot 10^{-5}$ *M*, shaken with 10 *M* sulphuric acid and solid iron(III) chloride added.

Gold dithizonate does not appear to be formed as a stable entity unde any of the conditions examined in this work, and the confusion in the literature ove "gold dithizonate" arises from the fact that the main product from gold(III) an dithizone is a mixture of oxidation products, the composition depending critically on extraction conditions. The complexity of the system is increased by one com ponent, bis-3,3′-(1,5-diphenylformazan)disulphide spontaneously regenerating *ca* 50% of its dithizone content. Accordingly, analytical methods for gold based on it reaction with dithizone should be treated with extreme caution, and the process b recognised as an oxidative one.

EXPERIMENTAL

The concentrations[5] of purified solutions of dithizone in chloroform wer determined spectrophotometrically from the absorbance at 605 nm[19], and that o gold solutions as tetrabromoaurate(III)[20]. Ammonia and hydrochloric acid solu tions were prepared by isopiestic distillation[21].

Extractions were carried out as follows unless otherwise stated. Equal volume

(4–10 cm^3) of aqueous gold(III) and purified dithizone in chloroform were shaken manually as vigorously as possible in a separating funnel (50 cm^3). When the first colour change was complete (typically 10 s), the organic phase was immediately removed and its spectrum recorded a number of times to follow the changes with time. The reagent concentrations unless stated are given in the text (Table II).

Reaction in the presence of 3 M hydrochloric acid

After separation the changing spectrum of the organic phase exhibited peaks at 420, 450, 490, 520, 570 and 605 nm (Fig. 1). The peaks at 420, 490, and 520 nm decayed: that at 490 nm within seconds, and the other two over some minutes. The peaks at 450, 570, and 605 nm grew: that at 570 nm over some minutes, and the other two over *ca.* 1 h, showing the regeneration of dithizone. However, the final ratio of absorbances A_{605}/A_{450} was lower than that for pure dithizone and showed the presence of another species absorbing at 450 nm.

The peak at 420 nm

Extrapolation to zero time of the plot of absorbance *vs.* time gave a molar absorptivity of $\varepsilon_{420}=4.4\cdot10^4$ l mol^{-1} cm^{-1}, assuming two dithizone residues per molecule (*cf.* Table III). The presence of halide ions ($I^- > Br^- > Cl^-$) lowered the rate of decay of the absorbance. In these extracts the decay of the peak at 420 nm had a linear relationship with the growth of peaks at 450 and 605 nm, *i.e.* the regeneration of dithizone. This regeneration, as measured by the absorbance at 605 nm was 49% and 47% in two experiments. Treatment of the extract with aqueous sodium thiosulphate (10%) immediately after separation gave almost quantitative regeneration (over 90%).

The peak at 450 nm

The aqueous phase was gold(III) ($2\cdot10^{-5}$ *M*) in 0.5 *M* sodium chloride solution with the minimal concentration of acid. The spectrum of unreacted dithizone was compensated by using a dithizone solution of appropriate concentration as a blank; less satisfactory was to "strip" the excess of dithizone with ammonia. A similar spectrum was obtained by extracting gold(III) ($5.6\cdot10^{-6}$ *M*) and dithizone (*ca.* 10^{-6} *M*) in 100 cm^3 of aqueous $4\cdot10^{-2}$ *M* ammonia with chloroform.

The peak at 490 nm

The extraction of gold(III) ($1.24\cdot10^{-4}$ *M*) in aqueous 11 *M* sulphuric acid with dithizone in chloroform ($3.6\cdot10^{-5}$ *M*) gave an organic phase with a peak at 490 nm, usually with satellites at 520 and/or 570 nm. The peak at 490 nm decayed within seconds.

The peak at 520 nm

Organic phases extracted from 12 *M* sulphuric acid exhibited this peak which decayed slowly; the satellites usually found at 490 and 570 nm were reduced by shorter, more gentle shaking. Extrapolation to zero time of the plot of absorbance *vs.* time gave a molecular absorptivity $\varepsilon_{520}=ca.\ 4\cdot10^4$ l mol^{-1} cm^{-1}. Almost the whole (over 90%) could be regenerated as dithizone by shaking with aqueous sodium thiosulphate (10%) immediately after extraction. Concentrations of sulphuric

acid greater than *ca.* 15 *M* rapidly transferred dithizone to the organic phase as a pink material.

The peak at 570 nm

Attempts to reduce gold(III) to gold(I) with ascorbic acid were hampered by reduction to the metal; partially reduced systems reacted with dithizone to give an increased absorbance at 570 nm. On shaking solid gold(I) iodide with dithizone in chloroform ($4.4 \cdot 10^{-4}$ *M*) the organic extract had a peak at 570 nm; shoulders at 530 and 440 nm had absorbances that varied with the preparation, but could not be entirely eliminated.

The action of a little solid iron(III) chloride in 10 *M* sulphuric acid on dithizone in chloroform gave the peak at 570 nm. Prior treatment of the dithizone with 10 *M* sulphuric acid gave absorbances of approximately equal intensity at 520 and 570 nm.

SUMMARY

On thermodynamic grounds gold(III) and gold(I) are likely to oxidize dithizone rather than to form complexes. Conditions are described to obtain all the spectra previously ascribed to "gold dithizonate" both in a single system and separately. Oxidation products are responsible for several of the peaks, and it is unlikely that any of the species obtained is a gold dithizonate except possibly that giving the transitory peak at 490 nm. Analytical processes based on the reaction of gold and dithizone should be recognised as involving oxidation and treated with extreme caution.

RÉSUMÉ

Thermodynamiquement, il apparait que la réaction entre or(III), or(I) et la dithizone correspond à une oxydation, plutôt qu'à une formation de complexes. On décrit les conditions permettant d'obtenir le spectre précédemment attribué au "dithizonate d'or". Les produits d'oxydation fournissent un certain nombre de pics, ne correspondant pas à un dithizonate d'or, à l'exception de celui obtenu à 490 nm. Comme les procédés analytiques basés sur la réaction entre l'or et la dithizone comprisent de l'oxydation il faut prendre de grandes précautions.

ZUSAMMENFASSUNG

Aus thermodynamischen Gründen werden Gold(III) und Gold(I) wahrscheinlich Dithizon eher oxydieren als hiermit Komplexe bilden. Es werden die Bedingungen beschrieben, unter denen die gesamten Spektren erhalten werden, die bisher dem "Golddithizonat" zugeschrieben worden sind, und zwar sowohl in einem einzigen System als auch getrennt. Verschiedene Peaks werden durch Oxydationsprodukte hervorgerufen, und es ist unwahrscheinlich, dass irgendeine der erhaltenen Spezies ein Golddithizonat ist, ausgenommen möglicherweise diejenige, die einen vorübergehenden Peak bei 490 nm ergibt. Analytische Verfahren, die auf der Reaktion von Gold und Dithizon beruhen, sollten als Oxydation betrachtet und mit äusserster Vorsicht angewendet werden.

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Analytica Chimica Acta, 66 (1973) 130–13

SHORT COMMUNICATION

The direct determination of mercury by atomic fluorescence spectrometry in a nitrogen-separated air–acetylene flame with excitation at 184.9 nm

G. F. KIRKBRIGHT, T. S. WEST and P. J. WILSON
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY (England
(Received 2nd January 1973)

The determination of mercury by flame atomic fluorescence spectrometry (a.f.s.) has been described by several workers. Winefordner *et al.*[1] obtained a detection limit of 0.1 p.p.m. with an air–hydrogen flame and a microwave-excited electrodeless discharge lamp source; West *et al.*[2] reported a similar figure for aqueous media. Higher sensitivity (detection limit 0.002 p.p.m.) was obtained by Vickers and Merrick[3] who nebulized mercury in an organic solvent medium into an oxy–hydrogen flame; Larkins[4] reported the detection of 0.07 p.p.m. mercury by atomic fluorescence spectrometry, using a non-dispersive system and a nitrogen-separated air–acetylene flame. In each case, the resonance atomic fluorescence line at 253.7 nm produced by excitation at this wavelength was measured; this line originates from the spin forbidden $^1S_0$–3^3P_1 transition. The gain in sensitivity for atomic absorption spectrometry of mercury which results from the use of the Hg 184.96 nm resonance line ($^1S_0$–$^1P_1$) has recently been demonstrated for both non-flame[5] and flame[6] cells. Similarly the determination of mercury by a.f.s. should provide greater sensitivity if excitation at 184.96 nm could be provided. This communication describes the use of radiation at this wavelength to excite mercury atomic fluorescence in a nitrogen-separated air–acetylene flame. Both resonance fluorescence at 184.96 nm and stepwise-line emission at 253.7 nm with excitation at 184.96 nm were observed, and the use of the stepwise-line fluorescence is proposed for analytical use. A significant improvement in detection limit was obtained by a simple modification to earlier experimental arrangements used for mercury a.f.s.: the optical path between source and flame was purged with nitrogen and a nitrogen-separated air–acetylene flame was used.

Apparatus

A Techtron model AA4 flame spectrophotometer equipped with a Servoscribe potentiometric chart recorder was employed. The mercury electrodeless discharge lamp was made from fused silica tubing (i.d. 8 mm, wall thickness 1 mm) and was *ca.* 240 mm long; it contained 5 mg of elemental mercury and an argon filler gas pressure of 3 Torr. The source was operated at 2450 MHz in a $\frac{3}{4}$-wave resonant cavity (Model 210L) from a microwave power generator (Microtron Mk11, Electromedical Supplies Ltd., Wantage, U.K.). The source output was modulated electro-

ically at 285 Hz in phase with the amplifier. A nitrogen-separated premixed air–acetylene flame was supported at a cylindrical burner head (Beckman, RIIC) containing 13 orifices each of 1.2 mm diameter arranged in a square of side 9 mm. The flame was supplied with aqueous sample solutions by the indirect nebulizer of the AA4 spectrophotometer. A glass tube 120 mm in length and 25 mm diameter fitted with a 25-mm diameter silica window at one end was cemented to the viewing part of the $\frac{1}{4}$-wave resonant cavity. This cavity and tube assembly was positioned at 90° to the flame–monochromator axis so that the silica window on the extension tube from the cavity just entered the stream of nitrogen used to separate the secondary reaction zone of the flame. The cavity and its extension arm were then purged with nitrogen to permit transmission to the flame of radiation at 184.96 nm. For study of resonance fluorescence at 184.96 nm, the monochromator housing was also purged with nitrogen, and a nitrogen-purged tube fitted with a silica window was placed between the flame and the monochromator entrance slit. A solar-blind photomultiplier tube (Hamamatsu Type R166) was used.

Results

The flame stoichiometry and height of observation of the mercury atomic fluorescence in the flame were optimized by measuring the resonance fluorescence signal at 253.7 nm with excitation at 253.7 nm (unpurged optics). The greatest sensitivity was attained when a slightly fuel-rich flame was employed and the mercury atomic population in the flame was irradiated and viewed between 5 and 10 mm above the burner head. The operating power for the lamp was optimized independently to provide for highest sensitivity (*a*) with irradiation at 253.7 nm for measurement of resonance fluorescence at 253.7 nm, and (*b*) with irradiation at 184.96 nm *via* the nitrogen-purged cavity assembly for measurement of resonance fluorescence at 184.9 nm (monochromator purged) or stepwise-line fluorescence at 253.7 nm (no monochromator purge); the optimal powers were 45 W and 25 W, respectively. The use of higher power for 184.96 nm irradiation led to signal attenuation, presumably owing to self-reversal of the line used. The maximal attainable spectral half-band pass of the monochromator (0.99 nm) was employed at both 184.96 nm and 253.7 nm.

Resonance fluorescence at 253.7 nm. The limit of detection for mercury observed for optimal operating conditions in the air–acetylene flame with irradiation and measurement at 253.7 nm depends on whether mercury(I) or mercury(II) solutions are nebulized[7]. The detection limits obtained were 0.20 and 0.25 p.p.m. for Hg(I) and Hg(II), respectively. These values are poorer by a factor of two than those obtained by West *et al.*[2] with a similar source and nebulizer unit but with an air–hydrogen flame and double-pass irradiation. The calibration curves under these conditions (Fig. 1) were linear to 100 p.p.m. for mercury(II) but only *ca.* 5 p.p.m. for mercury(I).

Resonance fluorescence at 184.96 nm. When the source cavity and its side-arm and the monochromator assembly were purged with nitrogen, the detection limits obtained for mercury resonance fluorescence at 184.9 nm were 0.03 and 0.04 p.p.m. for mercury(I) and mercury(II), respectively, in aqueous solution. The calibration curves obtained (Fig. 1) were linear to 25 p.p.m. for mercury(II) and 10 p.p.m. for mercury(I).

Stepwise-line fluorescence at 253.7 nm with excitation at 184.96 nm. Detection

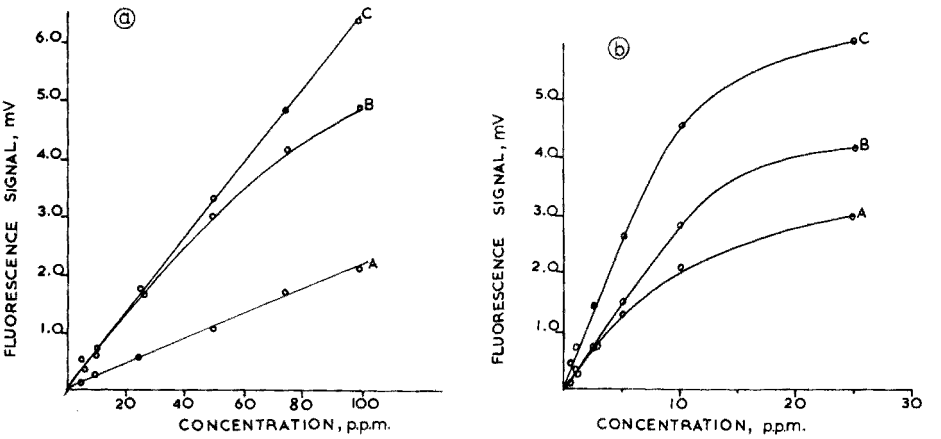

Fig. 1. Calibration curves for atomic fluorescence of mercury(II) solutions (a) and mercury(I) solutions (b). (A) Resonance fluorescence at 253.7 nm; (B) resonance fluorescence at 184.96 nm; (C) resonance and stepwise-line fluorescence at 253.7 nm (excitation at 184.96 and 253.7 nm).

limits of 0.02 and 0.025 p.p.m. were obtained for mercury(I) and mercury(II), respectively, when the source cavity and side-arm were purged with nitrogen and the monochromator was set to view at 253.7 nm without nitrogen purging. The fluorescence emission measured corresponded to the sum of the resonance fluorescence at 253.7 nm and the stepwise-line fluorescence at 253.7 nm stimulated by excitation at 184.96 nm. The proportion of the signal attributable to the latter process was established simply by measuring the fluorescence intensity with and without nitrogen purging of the excitation path length; it was found that 85% of the radiation received at 253.7 nm originated by stepwise-line emission after excitation at 184.96 nm. The calibration curves obtained for this mode (Fig. 1) were linear to 100 p.p.m. for mercury(II) and *ca.* 8 p.p.m. for mercury(I).

Interferences

The determination of mercury(I) by a.f.s. is subject to severe interference from both oxidizing and reducing species, and the additional sensitivity attained by use of mercury(I) rather than mercury(II) is difficult to exploit unless a preliminary separation of mercury from foreign ions is undertaken. For mercury(II), no significant interference on the fluorescence signal for 5 p.p.m. mercury in the air–acetylene flame was observed for any of the above three measurement arrangements in the presence of a 50-fold (weight) amount of Th, Fe(III), W, Sr, Co(II), Cu, V(V), chloride, iodide, nitrate or sulphate. In the presence of a 50-fold (weight) amount of Cr(VI), Mn(II), Ni, Al or Ba, however, interference (enhancement) was observed in each mode of measurement. This effect is attributable to scattering of the incident source radiation; it is severe for measurements at 184.96 nm but less pronounced for measurement of resonance fluorescence at 253.7 nm and only just detectable for measurement of the stepwise-line fluorescence at 253.7 nm.

Discussion

By the provision of a nitrogen-purged optical path and relatively transparent

nitrogen-separated air–acetylene flame, the determination of mercury by a.f.s. may be done by measuring the mercury resonance fluorescence at 184.96 nm. This provides *ca.* 6-times greater sensitivity with similar instrumentation than that attainable at 253.7 nm. The stepwise-line fluorescence signal observed at 253.7 nm results from excitation at 184.96 nm *via* the $^1S_0$–$^1P_1$ transition; the existence of appreciable spin–orbital coupling in mercury may then result in deactivation and crossing to the $^3P_1$ state from which emission at 253.7 nm ($^3P_1$–$^1S_0$) is observed. If a nitrogen-purged source cavity and excitation path length is combined with an unpurged monochromator measurement of this stepwise-line fluorescence and the resonance fluorescence at 253.7 nm, there is a 10-fold gain in sensitivity compared to that obtained for measurement at 253.7 nm with an unpurged excitation path length. This results from utilization of the strongest source emission (and mercury atomic absorption) line for excitation and measurement of the fluorescence emission at the wavelength transmitted and registered most sensitively by the monochromator and photomultiplier tube employed. Exploitation of the stepwise-line fluorescence emission also allows greater freedom from interference caused by the scattering of the source radiation and a greater linear range for working curves than those attainable by measurement of resonance fluorescence at 184.96 nm.

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SHORT COMMUNICATION

A new n.m.r. method for the analysis of fatty acid methyl ester mixtures with $Eu(DPM)_3$ in carbon disulfide

DOUGLAS B. WALTERS

Animal Products Laboratory, Russell Research Center, ARS, USDA, Athens, Ga. 30604 (U.S.A.)
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The use of carbon disulfide as a solvent for $Eu(DPM)_3$ has, for the first time, made possible the analysis of fatty acid methyl ester mixtures by n.m.r. spectroscopy. This paper describes further uses of carbon disulfide as a solvent for $Eu(DPM)_3$, beyond those stated in a previous paper[1]. The increased solubility of $Eu(DPM)_3$ in CS_2, as compared to CCl_4 or $CDCl_3$, permits addition of enough shift reagent to a solution of a mixture of aliphatic short-chain methyl esters to distinguish the individual components. Induced changes in the chemical shifts of the methoxy resonances allow the initially coalesced methoxy signals to be separated into their respective absorbances so that components of the mixture can be identified.

N.m.r. spectra of an homologous series of saturated short-chain fatty acid methyl esters were run before and after addition of $Eu(DPM)_3$. The maximum chain length for which the overlapping methylene resonances were separated completely after the addition of $Eu(DPM)_3$ was eight carbons. The use of n.m.r. spectroscopy by lipid chemists has been limited because the methylene protons in most long-chain compounds are often essentially magnetically equivalent, producing a broad signal of overlapping resonances which precludes their identification, integration, and coupling constant determination. Since the initial report[2] on the use of n.m.r. shift reagents several authors[3–5] have used these compounds in $CDCl_3$ and CCl_4 for n.m.r. studies of other methyl esters. However, for the above reasons, no work has been reported on the analysis of ester mixtures.

Experimental

Spectra were obtained with a Varian HA-100 n.m.r. spectrometer at an ambient probe temperature of 30°. Calibrations were made with a Hewlett-Packard Model 5244L electronic frequency counter, and chemical shifts were measured relative to tetramethylsilane (TMS). Line positions are estimated to be accurate to ± 0.5 Hz. The instrument was tuned for each sample to compensate for changes in the magnetic field due to the paramagnetic metal present.

Methyl esters (Polyscience Corporation) were certified as 99.5+% pure. Carbon disulfide (Matheson, Coleman and Bell) was spectroquality and all other reagents were analytical grade. $Eu(DPM)_3$ was obtained from Norell Chemical Company.

Spectra were obtained of *ca.* 0.4–1.1 *M* solutions of the substrates in carbon disulfide, to which increments of $Eu(DPM)_3$ were added.

Results and discussion

Figure 1A shows the proton n.m.r. spectrum of a solution of methyl butyrate, hexanoate and heptanoate before the addition of $Eu(DPM)_3$; individual components of this mixture cannot be determined from this spectrum. Figure 1B shows the same

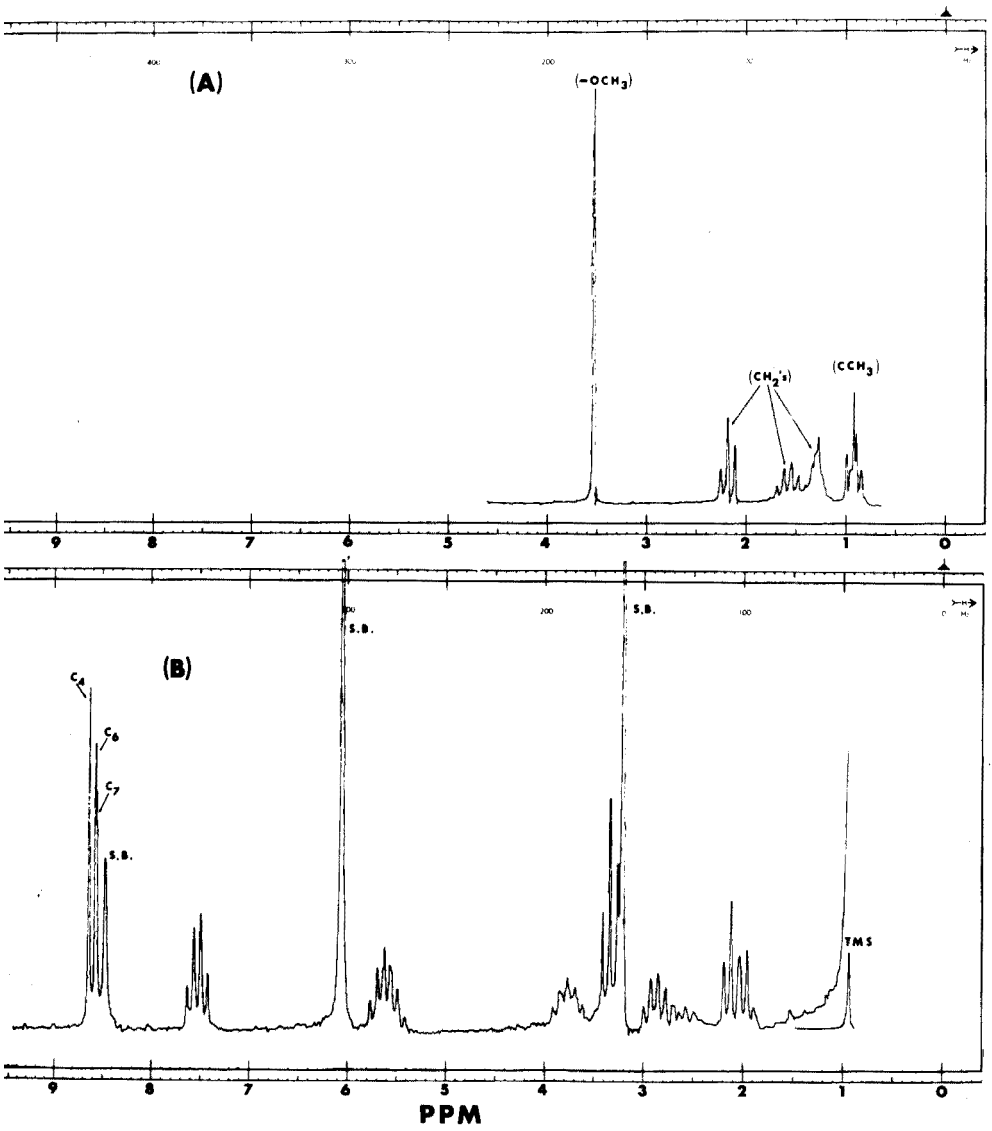


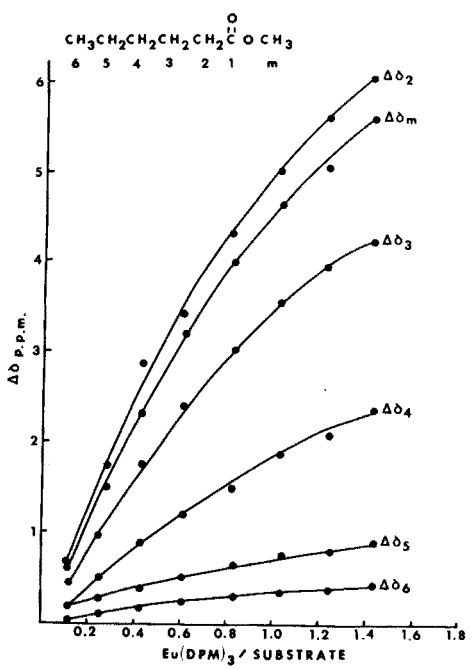
Fig. 1. 100 MHz ^1H n.m.r. spectrum of a mixture of methyl butyrate (0.288 mmole), methyl hexanoate (0.204 mmole) and methyl heptanoate (0.716 mmole). (A) Before addition of $Eu(DPM)_3$, (B) after addition of 0.3463 g $Eu(DPM)_3$.

mixture after the addition of 0.3463 g of $Eu(DPM)_3$. The three methyl esters are now distinguishable by their respective methoxy singlets. (This technique is described in an earlier paper[6].) The butyl, hexyl, and heptyl methoxy singlets absorb at 7.72, 7.66, 7.62 p.p.m. respectively whereas, initially all three signals coalesced at 3.53 p.p.m. Although the rest of the spectrum remains complex even after the addition of $Eu(DPM)_3$, the methylene region provides information by separating a unique absorbance for each of the individual constituents of the mixture. The spinning sidebands observed in Fig. 1B result from the *tert*-butyl group (−0.72 p.p.m.) of $Eu(DPM)_3$, as noted previously[1].

The example in Fig. 1 represents a severe test for the analysis of methyl ester mixtures, because the chain lengths are so close to one another. When the mixture is composed of esters differing by more than one carbon atom, it becomes progressively easier to distinguish the individual components of the mixture.

The above results prompted a study to determine the longest saturated unbranched methyl ester for which all the nearly equivalent methylene protons could be separated by addition of $Eu(DPM)_3$.

Table I lists an homologous series of methyl esters. The methylene regions of methyl acetate, propionate and butyrate were already resolved so addition of $Eu(DPM)_3$ was unnecessary. The methylene regions of methyl hexanoate, heptanoate, and octanoate were resolved after the addition of amounts of $Eu(DPM)_3$ shown in parentheses in column 3. It was not possible to resolve the methylene region of methyl nonanoate. These results are shown in Figs. 2–4 in which the



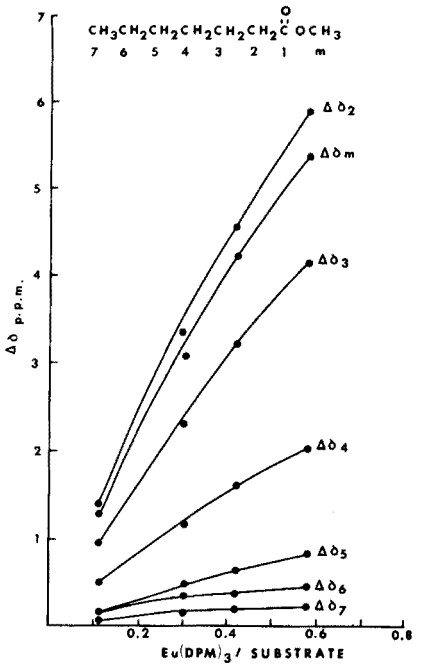


Fig. 2. Variation in the chemical shifts of the protons of methyl hexanoate (0.234 mmole) in CS_2.

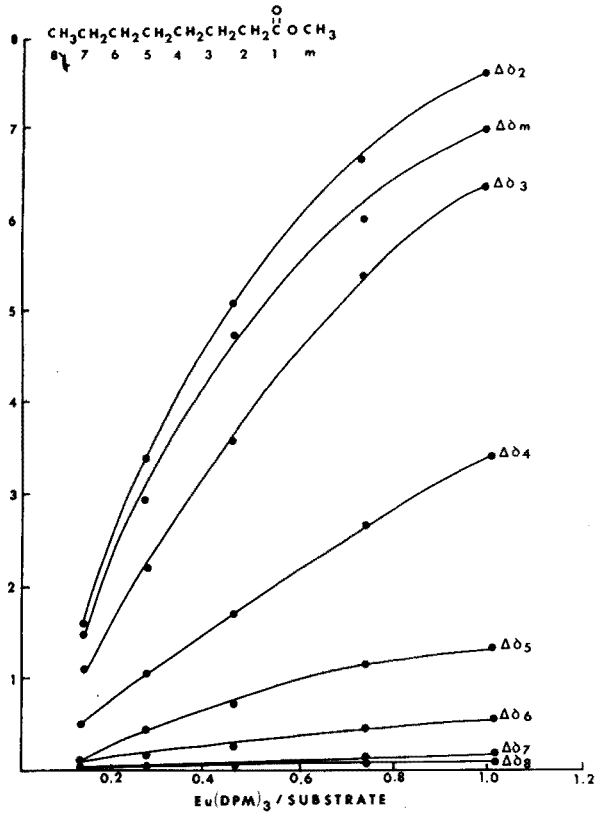
Fig. 3. Variation in the chemical shifts of the protons of methyl heptanoate (0.566 mmole) in CS_2.

BLE I

SOLUTION OF THE METHYLENE GROUPS OF VARIOUS METHYL ESTERS

thyl esters	*Methylene region before addition of Eu(DPM)$_3$*	*Methylene region after addition of Eu(DPM)$_3$*[a]
thyl acetate	Resolved	—
thyl propionate	Resolved	—
thyl butyrate	Resolved	—
thyl pentanoate	Not available	Not available
thyl hexanoate	Not resolved	Resolved (0.0705)
thyl heptanoate	Not resolved	Resolved (0.1738)
thyl octanoate	Not resolved	Resolved (0.3626)
thyl nonanoate	Not resolved	Not resolved

umbers in parentheses indicate amount of Eu(DPM)$_3$, in g, added to achieve resolution.



. 4. Variation in the chemical shifts of the protons of methyl octanoate (0.502 mmole) in CS_2.

ange in chemical shifts, $\Delta\delta$ (the difference in chemical shift before and after dition of Eu(DPM)$_3$), *versus* the mole ratio of shift reagent to substrate is plotted. r methyl hexanoate, resolution was obtained after addition of *ca.* 70 mg of Eu-PM)$_3$ (*ca.* 0.4 mole ratio). For methyl octanoate, resolution occurred only after ad-

dition of *ca.* 300 mg $Eu(DPM)_3$ (*ca.* 0.9 mole ratio). Values for methyl heptanoat accordingly fell between these two compounds. Since the solubility of Eu(DPM) is *ca.* 600 mg/0.5-ml in CS_2 and *ca.* 130 mg/0.5 ml in CCl_4 or $CDCl_3$[1], CS_2 was neces sarily the solvent of choice.

This study illustrates the advantages that $Eu(DPM)_3$ in carbon disulfide offe the analytical lipid chemist. It should be noted that when esters larger than C_8 ar examined, shift reagents are still of great value since the presence of other functiona groups, such as double bonds[6] or a unique absorbance like the methoxy group, enabl the analysis to be performed and provide valuable structural information whic cannot be obtained by other methods.

The author is indebted to Dr. L. H. Keith and the Southeast Wate Laboratory, E.P.A., for extending the use of the instrument for completion of thi work.

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HORT COMMUNICATION

he determination of organo-sulfur compounds by thin-layer chromatography via a gand-exchange process

OLAND W. FREI, BRIAN L. MACLELLAN and JAMES D. MACNEIL*

race Analysis Research Center, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia Canada)

Received 29th December 1972)

Several methods for the detection and determination of sulfur-containing rganophosphorus pesticides on thin-layer chromatograms have been reported in cent years[1–3]. Recently, a palladium chloride–calcein spray reagent has been sed for the detection and determination of a number of these compounds, and was also reported that this reagent may be used for the detection of other sulfur-ontaining compounds[4]. Palladium chloride has been used previously as a chro-atographic spray reagent for sulfur-containing pesticides, and palladium(II) is nown to quench the fluorescence of calcein. When a sulfur-containing pesticide eparated on a thin-layer chromatogram is sprayed with a palladium chloride–alcein reagent, a ligand-exchange process occurs during which palladium com-lexes with the sulfur in the chromatographed species, thus liberating free calcein. he fluorescence of the liberated calcein may then be used as a quantitative measure f the pesticide.

As some sulfur compounds, such as methylmercaptan, are known organic ollutants[5], the possible extension of this method to analyses for mercaptans and ther sulfur-containing organic compounds is of interest. The method had shown xcellent sensitivity when applied to the pesticides, and it was hoped that it would rove equally useful for the analysis of other sulfur-containing compounds in which ie sulfur was in a similar valence state.

xperimental

Reagents. A 10^{-3} *M* stock solution of calcein (G. Frederick Smith Chemical o., Columbus, Ohio) was prepared by dissolving the calcein in an equivalent mount of 0.1 *M* sodium hydroxide and diluting to volume; it was stored in a efrigerator. Palladium was used as a 0.005 *M* solution in 0.1 *M* hydrochloric acid, repared from 5% palladium chloride in hydrochloric acid (Fisher Scientific).

The following sulfur-containing compounds were used: 2-benzimidazolethiol, -mercaptobenzoic acid, 2-thiobarbituric acid, 5-benzol-2-thiohydantoin (Eastman

*Present address: Canada Dept. of Agriculture, Research Station, Summerland, British Columbia, anada.

Organic Chemicals, Rochester, N.Y.); 2-mercaptobenzothiazole, thiocarbanili (Matheson, Coleman & Bell, East Rutherford, N.J.); mercaptosuccinic acid, thi acetamide, thioglycollic acid (British Drug Houses Ltd., Poole, England); thiour (J. T. Baker Co., Phillipsburg, N.J.). Stock solutions of these compounds (10 p.p.m.) were prepared, with methylene chloride or acetone as solvent.

Apparatus. Fluorescence spectra were measured with an Aminco-Bowm spectrophotofluorimeter equipped with a thin-layer chromatogram scanning attac ment. Determinations were made on a Zeiss chromatogram spectrophotometer wi a mercury lamp as source; a N365 filter was used in the excitation beam, while monochromator was used on the emission side set at maximum fluorescence. Plat were scanned at 30 mm min^{-1} and the results were recorded at 1 in min^{-1} cha speed. Peak areas were measured with a Gelman planimeter.

Chromatography. Thin-layer plates (20 × 20 cm) were prepared by coati silica gel-N (Macherey, Nagel & Co.) on glass plates at a thickness of 0.25 m with a Desaga applicator. Samples were spotted on the plates with Drummo microliter pipets and developed a distance of 10 cm with hexane–acetone (2: solvent. After development, the plates were dried in air and then sprayed un translucent with the spray reagent.

Preparation of spray reagent. Equal volumes of the 10^{-3} *M* calcein soluti and the 0.005 *M* solution of palladium chloride were mixed together and 0.04 phosphate buffer was added to adjust the pH to 7.2. This solution was then dilut with water to produce a spray reagent stock solution containing $2.0 \cdot 10^{-4}$ *M* p ladium(II) and $1.6 \cdot 10^{-4}$ *M* calcein. This solution was equilibrated overnight. was used after dilution with an equal volume of acetone.

After spraying, the plates were dried in air at room temperature for 5 m and then placed in a closed chromatography tank containing a saturated soluti of calcium nitrate for 50 min while the fluorescence developed under conditions controlled humidity. The plates were then measured on the Zeiss instrument.

Results and discussion

Qualitative results. Detection limits and R_F values of the compounds studi in the hexane–acetone (2:1) solvent system are given in Table I. Detection lim reported are after elution. Fluorescence spectra were the same as those report previously[4].

The reaction between palladium chloride and sulfur-containing compoun was found to be quite slow for organothiophosphorus pesticides[4]. Palladium forr stable complexes with sulfur in certain oxidation states, thus releasing the calce with which it had been complexed. The sulfur-containing compound is thus detect by the fluorescence of the free calcein. The compounds studied here reacted ve quickly with the spray reagent and fluorescence was detectable as soon as t plate appeared dry. However, there was some instability immediately after sprayi which may be attributed to the presence of solvent from the spray reagent. Maximu fluorescence intensity was observed 15–60 min after spraying. There was then gradual loss in intensity over 15 h, but the spots remained quite fluorescent f several days when the plates were stored in the dark.

Quantitative analysis. The quantitative application of the method to the compounds was investigated for thioacetamide. A linear response was obtained f

ABLE I

ETECTION LIMITS AND CHROMATOGRAPHY OF SELECTED SULFUR-CONTAINING OMPOUNDS ON SILICA GEL-N THIN-LAYERS IN A HEXANE–ACETONE (2:1) SOLVENT YSTEM

ompound	R_F[a]	*Visual detection limit (ng)*
Benzimidazolethiol	0.29	25
Benzol-2-thiohydantoin	0.41	20
Mercaptobenzoic acid	0.03	30
Mercaptobenzothiazole	0.55	40
ercaptosuccinic acid	0.00	30
iioacetamide	0.37	10
Thiobarbituric acid	0.00	30
iiocarbanilide	0.44	100
iioglycollic acid	0.01	30
iiourea	0.06	20

Average of three determinations.

ABLE II

EPRODUCIBILITY OF DETERMINATION OF THIOACETAMIDE *in situ* ON SILICA GEL-I THIN-LAYER CHROMATOGRAMS

oncn. (ng)	*Average r.s.d. (%)*[a]	*Average peak area (in²)*	*R.s.d.*[b] *(%)*
00	5.9	0.92	8.3
50	9.6	0.60	10.5
10	10.0	0.25	33.4

Average for seven plates (7–9 spots per plate of individual relative standard deviations for each plate).
Relative standard deviation from plate to plate.

plot of peak area *vs.* concentration for the range 10–100 ng. A change in slope was bserved at concentrations above 120 ng per spot, but the plot was then again linear o 500 ng per spot. Reproducibilities were determined for concentrations of 10, 50 nd 100 ng per spot (Table II); the results showed that thioacetamide could be etermined semiquantitatively at the visual detection limit (10 ng per spot). Average eak areas were quite uniform at 50 and 100 ng per spot concentrations on different lates, but for 10 ng per spot, the variations from plate to plate were quite marked. 'his may be attributed to the poorer signal-to-noise ratio at this concentration and ie resulting sensitivity of the measurement to changes in the plate background. :esults at the higher concentrations indicated that if the method were used on a outine basis, it should not be necessary to run a complete series of 4–5 standards to btain a calibration plot for the plate. Instead, once a sufficient number of these ad been run to obtain an average or standard calibration plot, only one or two eference standards would need to be run on each plate; this could result in a onsiderable saving in time both in the number of samples run and in the data nalysis.

Conclusions

The palladium chloride–calcein spray reagent may be used for the detectio: of many sulfur-containing compounds after separation on thin-layer chromatogram: Quantitative analyses may be performed in the nanogram range with acceptabl accuracy and precision. The results indicate that the method has excellent possibilitie for development as a routine technique.

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HORT COMMUNICATION

n automated method for the determination of trace amounts of metal ions by n-exchange chromatography
etermination of zinc(II) in waters

ARUO MATSUI
vernment Industrial Research Institute, Nagoya, Kita-ku, Nagoya (Japan)
eceived 14th January 1973)

Several studies of automated methods, based on the Technicon Autoanalyzer r the determination of trace amounts of metal ions have been reported in recent ars[1–5]. Colorimetric determinations have usually been applied and the main oblem has been how to remove interfering diverse ions. From this point of view, combination of ion-exchange separation and automated colorimetric methods ems very convenient.

A simple automated method for the determination of trace amounts of zinc-I) by ion-exchange chromatography and colorimetry is described in this communi-tion; zinc is determined colorimetrically with zincon, 2-carboxy-2′-hydroxy-5′-lfoformazylbenzene. Sebborn[1] reported a method with dithizone for determination zinc, but the proposed method is simpler. In the proposed method, 2.0–15.0 μg zinc can be determined without interference and with a maximum error of 3%. applications of this method, the zinc content of several kinds of water was deter-ined.

xperimental

Apparatus. A Shimadzu MPS-50 L recording spectrophotometer was used for e measurement of absorbances with a 5-mm flow cell. A Fuji midget pump -071-120 was used to supply the sample solutions or eluant to the ion-exchange olumn; the flow rate of this pump could be changed from 1 to 280 ml min^{-1}, and l surfaces in contact with the solutions were made of teflon or ceramics. A Mitsumi eristaltic pump SJ-1200 was also used.

Resin and reagents. Cation-exchange resin, Amberlite CG-120 (type 3, 400–600 esh, hydrogen form) was loaded into a jacketed glass column, to give a resin bed × 160 mm. The standard solution of zinc was prepared from zinc chloride in distilled ater containing a little hydrochloric acid. Zincon (0.1 mg) was dissolved in 20 l of 1 *M* sodium hydroxide and diluted to 1 l with distilled water; this solution as prepared weekly. A Clark and Lubs acetate buffer solution was prepared; the % acetic acid solution was passed through a cation-exchange column to remove ace amounts of zinc before use. The use of 50 ml of concentrated acetic acid used no error, but zinc impurities in acetic acid must be considered when large olumes are required. All other reagents were of the highest purity available.

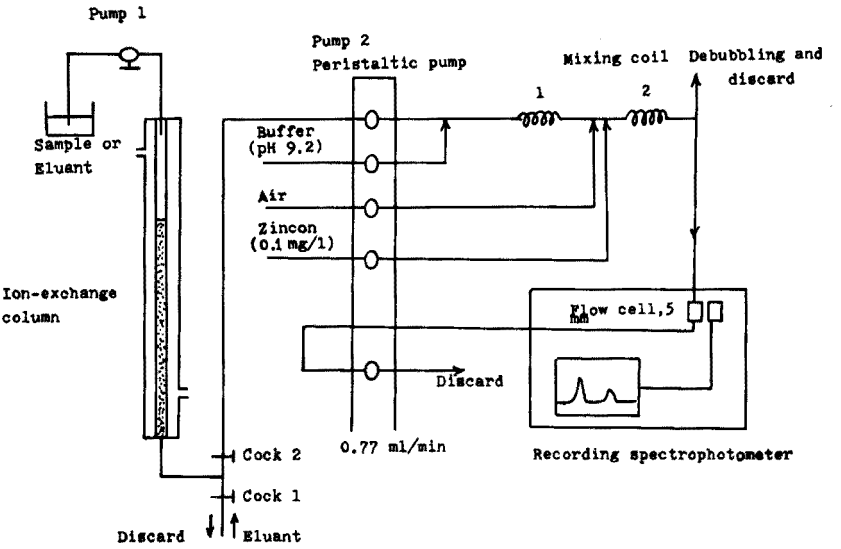

Fig. 1. Automated analysis for zinc in solutions. All systems are joined with teflon tubing (i.d. 0.8 mm). Mixing coils were made of teflon tube (i.d. 0.8 mm, length 1.5 m).

Procedure. Figure 1 shows the analysis system. Glacial acetic acid is added to the sample solution to give a 4% acetic acid solution. The ion-exchange column is heated at 60° to obtain sharp elution peaks. Stopcock 2 is closed and stopcock 1 opened, while the sample solution is passed through the column and discarded through cock 1, zinc being adsorbed quantitatively on the resin. Stopcock 1 is then closed and stopcock 2 opened, and zinc is eluted with 1.0 *M* ammonium chloride. During this process, the speed of pump 1 must be less than that of pump 2 and some eluant must be supplied through stopcock 1, to ensure that the whole eluate enters the analytical system. Eluted zinc is recorded as a peak on the recorder and the amount of zinc is calculated from a calibration curve based on peak area measurements.

Results and discussion

Adsorption of zinc and choice of eluant. The adsorption of zinc on ion-exchange resins has been studied for many kinds of solutions; the anion-exchange studies in hydrochloric acid solution by Kraus and Moore[6] are a typical example. In the proposed automated method, the vital point is to maintain the eluate near pH 9; concentrated acid or alkaline solutions are unsuitable as eluants, and neutral or weakly acidic or alkaline solutions are necessary in the adsorption and elution steps. The use of 4% acetic solution for the adsorption step with 1.0 *M* ammonium chloride for elution, was found to be most appropriate.

Calibration curve. There was a straight-line relationship between the peak areas and zinc concentrations in the range 2.0–15.0 μg. Above 15.0 μg, the calibration plot curved towards the peak area axis. The peak area for 2.0 μg of zinc was 1.1 cm^2. However, this method was easily applied for the separation of zinc in concentrations above 15 μg from other metal ions. The volume of sample in calibration

TABLE I

DETERMINATION OF 10 μg OF ZINC IN DIFFERENT VOLUMES OF SAMPLE

Sample volume (ml)	1	5	20	100	500	1000
Zn found (μg)	10.0	10.3	10.0	9.8	9.7	9.5

ests was 50 ml; Table I shows the effect of sample volume, and indicates that amples should not exceed 500 ml.

Behaviour of diverse ions. The metal ions which react with zincon are Al(III), Be(II), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Mo(VI), Ni(II), Ti(IV), and Zn(II)[7]. Molybdenum was not adsorbed on the resin, but the other ons were. However, in the elution step, only Co(II), Cu(II), Mn(II), Ni(II), Zn(II) vere eluted, giving measurable elution peaks for concentrations below 25 μg.

The volume distribution coefficients (D_v) of these eluted ions were measured rom the peak elution volume (V) by the equation:

$$D_v = V/X - \varepsilon$$

vhere ε is the relative interstitial volume (0.4) and X is the bed volume (8 ml). The D_v values found were: 5.4 for Zn(II), 9.9 for Cu(II), 12.8 for Mn(II), 13.0 for Ni(II) and 13.1 for Co(II). Zinc(II) was thus eluted clear of other metal ions, while Mn(II), Ni(II) and Co(II) could not be separated. Zinc(II) in amounts of 10.0 μg ould be determined with an error of less than ±3% in the presence of 100 μg Cu(II), 00 μg Co(II), Ni(II), Mn(II), Be(II), Cr(III), or Ti(IV), or 1,000 μg Fe(III), Al(III), Bi(III) or Cd(II) by the proposed method.

Determination of trace amounts of zinc in natural waters. The proposed method s suitable for determining trace amounts of zinc in almost neutral solutions, such as atural waters. In this Institute, natural underground water is used in the laboratories o prepare distilled water, owing to the high cost of municipal water; some water anks, pipes and taps are zinc-plated. The zinc contents in the water in different arts of the Institute were therefore determined: the results are given in Table II. The original water supply contained 0.05 p.p.m. of zinc, thus 0.02–2.28 p.p.m. of zinc vas leached from the plumbing. Municipal water contained no zinc, when analyzed y the same method.

TABLE II

ZINC CONTENT OF LABORATORY WATER

Place of sampling	*Date*	*Zinc content (p.p.m.)*	*Place of sampling*	*Date*	*Zinc content (p.p.m.)*
Building No. 1 1 fl.	Oct. 19	0.41	Building No. 3 1 fl.	Oct. 9	0.14
2 fl.	Oct. 2	0.07	2 fl.	Oct. 4	1.43
3 fl.	Oct. 20	1.70	3 fl.	Oct. 14	1.38
Building No. 2 1 fl.	Oct. 18	0.80	Building No. 4 1 fl.	Oct. 19	0.83
2 fl.	Oct. 19	0.68	2 fl.	Oct. 18	1.58
3 fl.	Oct. 16	2.33	3 fl.	Oct. 7	0.69

TABLE III

DETERMINATION OF ZINC IN RIVER AND SEA WATERS

Place of sampling	*Literature*[8]		*This work*	
	Date	*Zinc content (p.p.b.)*	*Date*	*Zinc content (p.p.b.)*
Shonai-gawa River (Nagoya)	Aug. 30, 1946	5.5	Nov. 14, 1972	180
Yada-gawa River (Nagoya)	Aug. 30, 1946	4	Nov. 13, 1972	340
Ise Bay (Off Toba)	Aug. 6, 1947	5	Dec. 10, 1972	2

River and sea waters were also analyzed. Morita[8] reported in 1955 the zinc contents of many river and sea waters of Japan. Results obtained for local Nagoya waters are compared with present results in Table III. It is known that the river waters are grossly polluted by drainage from ceramic industries in the upper reaches. The difference in the values for sea water is insignificant, probably because the site is near the Pacific Ocean.

The uptake of zinc from sea water by cation-exchange resins was studied by Kusaka and Ozaki[9]; calcium, magnesium and sodium ions interfered at pH 1.5 (hydrochloric acid). In the present work, zinc was adsorbed quantitatively from water containing the same amounts of these ions as sea water, acidified to 4% acetic acid; 2 p.p.b. of zinc is the limit of this method.

Separation of zinc and other metal ions. As described above, copper(II), manganese(II), nickel(II) and cobalt(II) could be eluted with 1.0 *M* ammonium chloride and the peaks recorded. Further study of the separation of zinc and these ions showed that clear separations were possible. When the column temperature was increased to 82° to obtain sharp elution peaks, zinc (10 μg) appeared in the 30–50 ml fraction, whereas nickel, manganese or cobalt (10–25 μg) appeared in the 110–135 ml fraction. Copper appeared in the 70–100 ml fraction, and the simultaneous determination of zinc and copper is under investigation.

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SHORT COMMUNICATION

The solvent extraction of platinum-group metals and gold with 2-mercaptobenzothiazole

A. DIAMANTATOS

J.C.I. Minerals Processing Research Laboratory, Knights, Transvaal (South Africa)

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The chemical literature shows that, in general, thio-organic compounds are very reactive with the platinum metals. In early work, Ubaltini[1] used 2-mercaptobenzothiazole for the sensitive precipitation of platinum, palladium and rhodium. This same reagent was also used to precipitate palladium and rhodium in potassium hydroxide solution, thus separating these metals from platinum[2]; unlike platinum, alkaline solutions of palladium and rhodium react instantly to form red precipitates. Although methods for the gravimetric determinations of platinum[1,2], palladium[3], rhodium[4], iridium[5] and gold[6] with 2-mercaptobenzothiazole, have been established, the application of this compound as an extractable chelating agent for the precious metals, has not been systematically investigated. Indeed, this reagent with its anionic -SH group and the uncharged basic =N– group, seems to be ideal for the formation of extractable chelates. In fact, Majumdar and Chakrabartty[3], by dissolving the red palladium–2-mercaptobenzothiazole precipitate in ethanol, developed a spectrophotometric method for palladium.

It is the purpose of this communication to extend the scope of application of 2-mercaptobenzothiazole to the solvent extraction of all the platinum-group metals and gold. The solvent used throughout this investigation was chloroform.

Apparatus and solutions

A Carl Zeiss spectrophotometer was used for absorbance measurements. For pH readings a Radiometer PHM 24e pH meter was used.

Standard palladium solution. 0.1006 g of "Specpure" palladium wire was dissolved in aqua regia and nitric acid was expelled by repeated evaporations with small additions of hydrochloric acid. The solution was finally diluted to 100 ml in 1 *M* hydrochloric acid.

Standard platinum solution. 0.0998 g of Johnson Matthey "Specpure" platinum wire was treated as described above for the palladium solution.

Standard rhodium solution. 0.3856 g of Johnson Matthey ammonium chlororhodite $[(NH_4)_3RhCl_6 \cdot 1.5\ H_2O]$ was dissolved in 100 ml of 1 *M* hydrochloric acid; it was standardized gravimetrically with thiobarbituric acid[7].

Standard iridium solution. 0.230 g of Johnson Matthey "Specpure" ammonium chloroiridate was dissolved in 0.1 *M* hydrochloric acid by heating, and the solution

was diluted to 100 ml. The solution was standardized gravimetrically by the hydrolytic precipitation method[8].

Standard ruthenium solution. 0.206 g of pure ruthenium chloride was dissolved in 0.1 *M* hydrochloric acid. The ruthenium content was determined gravimetrically by precipitation with thionalide, followed by gentle ignition in air and then reducing in hydrogen[9].

Standard osmium solution. 0.5 g of pure osmium tetroxide was dissolved in 200 ml of 0.1 *M* sodium hydroxide and then diluted to 500 ml with distilled water. The solution was standardized by the method of Klobbie[10].

Standard gold solution. 0.1013 g of "Specpure" gold wire was treated as described above for the palladium solution.

Reagent solution. A 0.5% (w/v) 2-mercaptobenzothiazole (Merck, recrystallized) solution in ethanol was used. Chloroform was distilled before use.

Extraction of palladium

Seven solutions, in separating funnels, each containing 0.5 mg of palladium in 100-ml volumes but at different hydrochloric acid concentrations (0.1, 0.2, 1, 2, 3, 4, 5 *M*), were treated individually with 10 ml of the reagent solution. The addition of the reagent resulted in red precipitates being formed almost instantaneously. After 5 min, 100 ml of chloroform was added and the funnels were shaken for 4–5 min. When the phases had equilibrated, the red complex had been extracted into the organic solvent, while the aqueous phase was water clear. However, in order to check for any unextracted palladium, the raffinate was evaporated to dryness and the organic residue was destroyed by fuming to dryness with nitric and perchloric acids; finally hydrochloric acid and a few drops of hydrogen peroxide were added and the solution was boiled for a few minutes. When the *p*-nitrosodimethylaniline method was applied, all the tests were negative; thus, according to the limit of detection, it seems that more than 99.5% of the palladium was extracted into the chloroform phase at all the acidities examined.

TABLE I

EXTRACTION OF PLATINUM

Acidity	pH 3	pH 2–0.1 *M*	0.2–2 *M*	3 *M*	4 *M*	5 *M*
Pt extd. (%)	1.8	2.0	2.5	3.0	4.1	5.5

Behaviour of other metals in the above extraction. Nine 100-ml hydrochloric acid solutions, each containing 1 mg of platinum, were treated as in the above test. This time there was no coloration of the platinum solution and only a white turbidity appeared, owing to the insolubility of the reagent in water. After shaking with chloroform, both phases were absolutely clear. The chloroform phase, after evaporation of the solvent, was tested for any extracted platinum by applying the tin(II) chloride photometric method. The experimental data are shown in Table I. The same test was applied to rhodium, iridium, ruthenium and osmium, but none of them was extracted.

Extraction of gold

Hydrochloric acid solutions of gold, each containing 0.5 mg of the metal, at acidities ranging from 0.1 to 6 *M*, were treated with 10 ml of the 2-mercaptobenzothiazole solution and shaken with chloroform. In all cases, not even traces of gold remained in the raffinate. This suggests an excellent method for the extraction of gold.

Extraction of palladium from alkaline solutions and its separation from platinum

The above experiments showed that by using 2-mercaptobenzothiazole as a chelating reagent, complete extraction of palladium from acidic medium, was achieved. However, although this extraction isolated palladium from rhodium, iridium, ruthenium and osmium, it did not provide a quantitative separation of palladium from platinum, a small percentage of the latter being co-extracted (Table I). The extractability of palladium and platinum from alkaline solutions was therefore investigated.

The extractive procedure used in the previous tests was repeated in alkaline solutions ranging from pH 10 to 1 *M* sodium hydroxide. The results obtained indicated a complete extraction of palladium from all the alkaline solutions, whereas platinum was not extracted at all.

Extraction of platinum after heating

As shown above, no extractable chelate was formed with platinum at room temperature. The reagent was therefore tested at elevated temperatures.

Ten platinum solutions, each containing 1 mg of platinum, at different acidities, were brought to the boil, 10 ml of the reagent solution was carefully added and boiling continued for 5–10 min. Yellow precipitates appeared. After cooling, the solutions with precipitates were transferred to separatory funnels and shaken with 100 ml of chloroform for 4–5 min. Both phases were absolutely clear for all the acidities and the chloroform phases were yellow, which indicated extraction of the platinum chelate. The raffinates were analysed for platinum as usual, in order to estimate the efficiency of the extraction.

For boiling times of 10 min, the percentage extraction of platinum increased from 34.2% for 0.5 *M* hydrochloric acid to 96.0% for 3 *M* hydrochloric acid. It was observed that at these acidities (0.5–3 *M*), some yellow skin remained in the interface. Indeed, the lower the acidity, the more the skin, which when analysed, showed retention of some platinum, thus explaining the incomplete extraction. However, separations at higher acidities (4–6 *M*) were excellent; the extraction of platinum was complete (>99.8%) even after boiling for only 5 min. An acidity of 5 *M* hydrochloric acid and a boiling time of 5–10 min are, therefore, recommended.

Extraction of platinum with 2-mercaptobenzothiazole and tin(II) chloride

The effect of tin(II) chloride solution on the extraction of the platinum–2-mercaptobenzothiazole complex was investigated at different acidities Platinum (1 mg) solution and 10 ml of reagent solution were mixed, and 20 drops of 20% tin(II) chloride solution in hydrochloric acid were added. This addition caused immediate formation of yellow precipitates. After 10 min, the chelate was extracted into 100 ml of chloroform by shaking for 5 min. A sharp separation of

the phases was then obtained, the organic phase being coloured yellow, and the aqueous one water clear. The aqueous phases were analysed as usual for any unextracted platinum, which was detected only for hydrochloric acid molarities of 5 *M* or more. Table II shows the results. It is clear that the yellow precipitate was formed more slowly as the acid concentration was increased. In strong acid solution, a slimy precipitate was formed and the extraction was incomplete.

TABLE II

EXTRACTION OF PLATINUM–2-MERCAPTOBENZOTHIAZOLE CHELATE AFTER ADDITION OF TIN(II)

M HCl	*Pt extracted (%)*	*Remarks*
0.25	>99.8	Fast precipitation
0.5	>99.8	Fast precipitation
1	>99.8	Coagulation after 5 min
2	>99.8	Coagulation after 5 min
5	85.5	Slimy precipitate

The results indicate that quantitative extraction of platinum can be accomplished from 0.25–2 *M* hydrochloric acid solutions if tin(II) is present.

Extraction of rhodium after heating

As shown above, 2-mercaptobenzothiazole does not form an extractable complex with rhodium at room temperature, and palladium and gold can be separated from rhodium. However, the reagent has been used for the gravimetric determination of rhodium, by precipitation from slightly acidic solution on boiling[4].

Tests on 0.5 mg of rhodium with 10 ml of reagent solution showed that heating for 7 min sufficed to form the rhodium complex in 4–6 *M* hydrochloric acid medium; quantitative (>99.8%) extraction with chloroform was then achieved. The percentage extraction was only 53.1% for 0.5 *M* hydrochloric acid, increasing to 97.7% for 3 *M*.

When this procedure was applied to 4–6 *M* hydrochloric acid solutions of iridium, and the extracts were analysed for iridium by the mixed acid photometric method, 6–10% of the metal was extracted.

Extraction of rhodium with 2-mercaptobenzothiazole and tin(II) chloride and its separation from iridium

These tests with tin(II) were carried out similarly to those described for platinum, red precipitates and orange extracts being obtained. As in the case of platinum, the lower the acidity, the faster the formation and coagulation of the precipitate. At 5 *M* hydrochloric acid, the precipitate was slimy, a thin red rhodium-containing skin appeared at the interface, and extraction was incomplete. However, quantitative (>99.7%) extraction was achieved in the range 0.25–2 *M* hydrochloric acid.

When iridium was tested in the same way, no colours appeared after the addition of the reagents, and no iridium could be detected in the extracts. It is

herefore concluded that a complete separation of rhodium from iridium can be ıchieved by extracting rhodium from 0.25–2 *M* hydrochloric acid solutions.

Extraction of ruthenium after heating and its separation from osmium

Ruthenium solutions which were 1–6 *M* in hydrochloric acid were boiled, 10 ml of the reagent solution was added and boiling was continued for 5 min. After cooling, the green to brown turbid solutions were extracted with chloroform, yielding coloured extracts. Tests showed that no ruthenium remained in the raffinates, thus confirming complete extraction of ruthenium.

When this procedure was applied to osmium solutions (1 mg Os), 0.8–1.4% osmium was extracted from 1–2 *M* hydrochloric acid, but very little ($< 0.4\%$) was extracted from 3–6 *M* solutions. A 6 *M* hydrochloric acid solution containing 1 mg each of ruthenium and osmium was treated as above. The analysis of the two phases confirmed the efficiency of the method for a quantitative separation of these two metals. It seems that the lower the acidity, the more osmium is extracted. In fact, in an extractive photometric method[11], the blue osmium–2-mercaptobenzothiazole precipitate formed at pH 4, is extracted completely with chloroform.

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SHORT COMMUNICATION

The potentiometric titration of potassium in sea water with a valinomycin electrod

TORBJÖRN ANFÄLT and DANIEL JAGNER
Department of Analytical Chemistry, University of Gothenburg, S-402 20 Göteborg 5 (Sweden)
(Received 12th January 1973)

The potassium concentration in sea water, which is *ca.* 0.01 *M* at 35°/ salinity, is normally determined either gravimetrically as the tetraphenylborate[1] by flame emission spectrometry[2]. The precision of these methods is not, in gener better than 1%. This is not sufficient to trace possible variations in the potassiu chlorinity ratio. It therefore seemed to be of interest to investigate whether or n the recently developed potassium-selective valinomycin electrode[3–9] could be us for highly precise determinations of potassium. In order to make optimal use of t electrode, such a determination ought preferably to be carried out as a titrati procedure in which all data collected are used to evaluate the potassium conce tration.

Theory

The valinomycin electrode is assumed to follow a modified Nernst equatio

$$E = E^0 + RT \ln 10 \log([K^+] + \Sigma\, k_i[M_i^{z_i}]^{1/z_i})/F \qquad (1$$

where k_i is the selectivity ratio for the interfering ion $M_i^{z_i}$ having a charge equal z_i. By taking the almost constant ratios of ion concentrations in sea water and t approximately known selectivity ratios for these ions into consideration, it can concluded that only sodium ions can contribute significantly to the membra potential. The order of magnitude of this contribution can be calculated at 25° be 0.3 mV, assuming a sodium concentration at 35°/$_{oo}$ salinity of 0.47 *M* and k_{Na^+} value of $2.6 \cdot 10^{-4}$. The relative contribution from sodium ions to the membra potential is almost independent of the salinity of the sea-water sample since t ratio $[Na^+]/[K^+]$ is almost constant in sea water.

A reagent which is sufficiently selective for the titration of potassium sea water is the tetraphenylborate ion. During a normal titration procedure t addition of titrant would, of course, decrease the potassium ion concentrati relative to the sodium ion concentration. Consequently, the contribution to t membrane potential from sodium ions would increase with increasing amount titrant added (*cf.* eqn. 1). Since, moreover, the selectivity ratio varies with varyi sodium and potassium concentrations, it would be difficult to evaluate the potassiu concentration from the titration data. It therefore seemed likely that a standard a dition titration technique would be more satisfactory, because in such a procedu

e $[K^+]/[Na^+]$ ratio would increase on addition of titrant, and the contribution ɔm sodium ions to the membrane potential would thus be negligible.

If v ml of t M potassium chloride are added to v_0 ml of sea water with a ɪtassium concentration of x M, then

$$(v_0+v)[K^+] \propto vt+v_0x \tag{2}$$

ovided that the amount of potassium ion-pairs is constant. Furthermore, if the ɔctrode is assumed to follow Nernst law, then

$$[K^+] \propto 10\exp(EF/RT \ln 10) \tag{3}$$

ıd, consequently, the function F,

$$F=(v_0+v)\ 10\exp(EF/RT \ln 10) \tag{4}$$

ll be linear when plotted against v ml of titrant added. Thus, if F is extrapolated zero it will intersect the v-axis at $v=v_{eq}$,

$$v_{eq} = -v_0x/t \tag{5}$$

cording to a procedure first outlined by Gran[10].

ɔperimental

Apparatus. The electrode couple consisted of a Philips IS 560 K potassium-ective membrane electrode and a Radiometer K 401 saturated calomel electrode, ɜ latter being bridged to the titration vessel through a 0.6 M sodium chloride ıction, in order to prevent the migration of potassium ions into the titration ssel. The titrations were carried out with a computer-processed titrator[11]. The ɔctrode couple was connected to the digital voltmeter of the titrator via a high-pedance operational amplifier coupled as a voltage follower.

Reagents. All reagents were of analytical grade. Standard potassium titrant lution was prepared by dissolving weighed amounts of potassium chloride in ply distilled water. This solution was used as a primary standard in the determina-ɪn of the potassium ion concentration. Standard Sea Water of chlorinity 19.380‰ ıs purchased from I.A.P.S.O. Service, Charlottenlund Slot, Denmark.

Titration procedure. Approximately 100 ml of the sea-water sample in the linity range 5–35‰ were accurately weighed into the titration vessel and rated with potassium chloride. The titrant concentration and the magnitude of ɜ titrant increment were chosen so that the potential difference between successive ɔrements was about 1–2 mV and about ten titration points were registered. In the mputer-processed titration procedure used, the criterion for a stable potential er each addition of titrant was that the average value of thirty potential readings ımpling time = 15 readings/s) did not differ from the average of the next thirty tential readings by more than 0.002 mV. This corresponds roughly to a time of s between successive titrant additions in a manual titration. The potassium ncentration was evaluated according to eqn. (4) by means of a straight line ɡression program, which formed part of the main program processing the complete ration procedure. In manual titrations the equivalence point could be evaluated ıphically.

Nernstian behaviour of the electrode. A Nernstian or pseudo-Nernstian

behaviour of the sensor electrode is of vital importance in all titration procedures the evaluation of which is based on Gran extrapolation. In order to study such behaviour for the valinomycin electrode, the electrode was stored in a sea-water solution of 12‰ salinity where $[Na^+] \approx 0.16$ *M* and $[Cl^-] \approx 0.19$ *M*. During storage the electrode couple was periodically taken out of the sea-water solution and calibrated in solutions containing known concentrations of potassium and sodium chloride, the Nernst factor being evaluated from the linear part of the calibration curve, *E* mV against pK^+. The results (Table I) prove that the Nernstian factor decreases on storage and, moreover, the electrode becomes less selective for potassium over sodium. This is probably partly due to an invasion of sodium and chloride ions into the membrane[1,2] by the Donnan effect. Denaturation of valinomycin also no doubt contributes to the unsatisfactory behaviour of the electrode. This difficulty might be overcome in future by a more suitable choice of membrane matrix.

TABLE I

NERNST FACTORS OBTAINED BY CALIBRATION WITH POTASSIUM CHLORIDE IN 0.05, 0.2, 0.4 AND 0.6 *M* SODIUM CHLORIDE AS A FUNCTION OF THE TIME OF STORAGE

Storage time (h)	*Nernst factor*			
	0.05 M	*0.2 M*	*0.4 M*	*0.6 M*
1	59.2	59.2	59.0	58.7
10	56.3	55.0	54.5	54.2
36	49.4	47.9	46.6	43.9
47	49.6	46.7	45.8	44.0
54	53.9	50.6	47.4	46.0
71	47.9	45.0	39.1	31.1
79	49.6	43.3	36.5	30.0
96	45.0	38.0	27.8	19.5

Results

Accuracy and precision. The change in Nernstian slope with time is, undoubtedly, the main limiting factor both for the precision and the accuracy of the standard addition titration of potassium. No doubt, even a small change in $RT \ln 10/F$ causes a considerable systematic error. Moreover, for a given value of $RT \ln 10/F$ the systematic error will, of course, increase with an increasing number of titration points included in the Gran plot. On the other hand, the precision of the titration increases as more titration points are included in the plot and, consequently, there must be an optimal number of points which are to be included[1,3]. For the titration conditions prevailing in the procedure given above, the optimal number of titration points was found to be about 10.

Potassium concentration in Standard Sea Water. The potassium concentration in Standard Sea Water was determined, from 97 titrations in which freshly prepared electrodes were used for approximately every tenth titration, to be 10.22 ± 0.03 mmole/100 g of sea water. This value corresponds to a potassium/chlorinity

atio of 0.02061 mg/$^{\circ}/_{\circ\circ}$ chlorinity, and is in good agreement with results obtained by ther methods[1]. The relative standard deviation for a single titration is not, owever, better than 0.026.

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SHORT COMMUNICATION

Internal electrolysis for the separation and determination of mercury and tin

A. K. MAJUMDAR and GOURI BHOWAL
Department of Chemistry, Jadavpur University, Calcutta-32 (India)
(Received 10th January 1973)

In previous communications[1–3] it was shown how by the use of different complexing agents and proper pH control, the need for diaphragms, collodion encasement and careful anode selection could be dispensed with in the internal electrogravimetric determination and separation of Cu, Cd, Pb, Bi, Ag, Sb, Co, Ni, Se, Te, Re and Mo ions. In this communication are reported: (*a*) the determination of mercury in presence of other ions and the separation of mercury, copper, cadmium, bismuth, antimony and lead from each other, and (*b*) the determination of tin and its separation from copper, cadmium, lead, antimony and arsenic.

Apparatus and solutions

A Cambridge pH indicator and the apparatus assembly consisting of a platinum gauze cathode and a zinc plate anode were the same as used earlier[1]. A copper plate, in place of zinc, was used only when mercury was to be separated from bismuth.

The chemicals used were of the highest purity available.

Standard tin solution. Dissolve tin(II) chloride (A.R.) in hydrochloric acid, and standardize by iodimetric and gravimetric methods[4].

Standard mercury solution. Dissolve mercury(II) chloride (reagent grade) in water containing a few ml of dilute hydrochloric acid, and standardize gravimetrically as the sulphide[4].

Standard solutions of bismuth, copper, cadmium, lead and antimony and of other cations and anions as well as 10% solutions of complexing agents such as EDTA (disodium salt), and potassium cyanide, were prepared as reported previously[1–3].

Determination of mercury

To the measured amount of mercury(II) chloride solution in a 400-ml beaker, add EDTA (disodium salt) or EDTA and potassium cyanide, each ten times the total quantity of the metal ion present. Dilute the solution to 250 ml and adjust the pH with dilute sulphuric acid or ammonia to 2.0–5.0 when only EDTA is used as the complexing agent, or to 5.0–9.0 when EDTA and cyanide are used. Electrolyze with the Pt–Cu or Pt–Zn electrode assembly for 4 h to deposit mercury completely on the platinum gauze cathode. Remove the electrode assembly, wash over the solution with a jet of water, and disconnect. Then wash the cathode with alcohol, dry by hot air and weigh.

For all subsequent separations, clean the platinum cathode by dipping into a olution of moderately strong nitric acid, wash well with water and ethanol, dry and eigh before use.

In studying the separation of mercury from mixtures of Be^{2+}, Zn^{2+}, Mn^{2+}, o^{2+}, Ni^{2+}, Sn^{4+}, Fe^{3+}, Al^{3+}, La^{3+}, Cr^{3+}, Ga^{3+}, In^{3+}, Tl^{+}, Zr^{4+}, Th^{4+}, Te^{4+}, a^{5+}, V^{5+}, Pb^{2+}, Cd^{2+}, alkali and alkaline earth metals, 10–20 mg of each of the reign ions were added, whereas in studying the influence of a particular metal n on the deposition of mercury, at least 100–200 mg of the ion were used. For ese separations the pH was kept at 9.0.

When 3–5 mg of mercury were determined by the above procedure, quantitative recoveries ($\pm 0.6\%$) were achieved in the presence of EDTA, or EDTA and yanide, in the specified pH ranges.

eparation of mercury and bismuth from each other

To the solution of mercury and bismuth, add EDTA in an amount ten mes the weight of the combined ions, dilute to 250 ml and adjust the pH 2.0–5.0. Deposit mercury, using a Pt–Cu electrode assembly, as in the above rocedure, and weigh. Treat the solution left after deposition of mercury with an cess of cyanide to mask copper, and deposit the bismuth present by electrolysis r 6 h at pH 9.0 with a Pt–Zn assembly.

When this procedure was applied to solutions containing 3–5 mg of mercury nd 1–3 mg of bismuth, quantitative recoveries ($\pm 1\%$) were achieved.

eparation and determination of mercury, bismuth, copper, lead, cadmium and antimony

Mercury and bismuth were first deposited over a period of 4 h from a olution containing EDTA, cyanide and iron(III). Iron(III) was added to prevent the eposition of antimony[2]. After being washed, the deposit was dissolved in nitric acid nd then mercury and bismuth were separately deposited as described above. he residual solution was electrolysed as reported earlier[2] to separate the rest of the ons. Typical results are shown in Table I.

etermination of tin and its separation from other ions

To a measured quantity of tin(II) chloride solution in a 400-ml beaker, add DTA in an amount ten times the quantity of the metal ion present. Dilute 250 ml, adjust the pH to 1.0–5.0 with dilute sulphuric acid or ammonia, and ectrolyze with a Pt–Zn assembly for 4 h. Wash the electrode assembly over the olution with water, and disconnect. Wash the cathode with ethanol, dry at 0–90° and weigh.

ABLE I. SEPARATION AND DETERMINATION OF Hg, Bi, Cu, Pb, Cd AND Sb

aken (mg)						*Found (mg)*						
lg	*Bi*	*Cu*	*Pb*	*Cd*	*Sb*	*Total deposit Hg + Bi*	*Hg*	*Bi*	*Cu*	*Pb*	*Cd*	*Sb*
.2	1.93	3.21	2.64	2.66	2.50	5.11	3.16	1.92	3.20	2.62	2.64	2.48
.8	0.96	3.21	2.64	1.33	3.75	5.77	4.75	0.95	3.21	2.61	1.32	3.72
.2	1.93	2.14	3.96	1.33	2.50	5.12	3.17	1.93	2.12	3.95	1.31	2.47

For the separation of tin from mixtures of foreign ions such as Be^{2+}, Zn^{2+} Mn^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, La^{3+}, Cr^{3+}, Zr^{4+}, Th^{4+}, alkali and alkaline earth metal 10–20 mg of each of the ions were taken. The influence of a particular ion wa studied by taking 100–200 mg of it. The solutions were treated with EDTA an adjusted to pH 2.0–4.0 before electrolysis as described above.

Tin in the range 2–4.5 mg could be recovered quantitatively ($\pm 1\%$).

Separation of tin from antimony

To a hydrochloric acid solution of tin and antimony, add iron(III) (a chloride) and EDTA (disodium salt) each in amounts ten times those of the ant mony and tin present. Adjust the pH to 0.5–1.0 after dilution to 250 ml, an electrolyze for 3 h to deposit antimony. Then evaporate the solution to abou 100 ml and treat with zinc dust or iron filings. When the reduction of tin(IV to tin(II) is complete, add more EDTA (1 g) and dilute the solution to 250 n for the deposition of tin at pH 3.0–4.0.

Separation of copper, cadmium, lead, antimony and tin from each other

Here iron(III) chloride solution and EDTA were added as for the separatio of tin and antimony. The volume of the solution was then adjusted to 250 ml an its pH to the values appropriate to the element to be deposited. Thus for coppe lead, cadmium and antimony, the pH values were maintained, respectively, at 9. 2.5, 4.0 and 1.0.

The solution resulting from the separation of copper, cadmium, lead an antimony was evaporated to 100 ml, acidified with hydrochloric acid and treate as described above for the deposition of tin at pH 3.0–4.0. The results a shown in Table II.

Arsenic in neither of its valence states interferes with the deposition tin or antimony from solutions at pH 2.0–5.0 containing EDTA.

TABLE II. SEPARATION AND DETERMINATION OF Cu, Cd, Pb, Sb AND Sn

Taken (mg)					*Found (mg)*				
Cu	*Cd*	*Pb*	*Sb*	*Sn*	*Cu*	*Cd*	*Pb*	*Sb*	*Sn*
2.14	2.66	2.64	3.75	3.30	2.11	2.63	2.63	3.72	3.26
3.21	2.66	2.64	3.75	2.20	3.19	2.62	2.61	3.71	2.18
2.14	1.33	3.96	2.50	3.30	2.12	1.31	3.93	2.48	3.25

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3 A. K. Majumdar and Gouri Bhowal, *Anal. Chim. Acta*, 38 (1967) 468; 48 (1969) 192; *Mikrochi Acta*, 6 (1967) 1086.
4 A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumen Analysis*, Longmans Green, London, 3rd Ed., 1962.

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Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

OOK REVIEWS

strumental Methods of Organic Functional Group Analysis, Edited by S. Siggia, iley–Interscience, New York, 1972, ix+428 pp., price £7.85.

Professor Siggia's earlier book, *Quantitative Organic Analysis via Functional oups*, requires no recommendation to organic analysts, having been an essential rt of their libraries since it first appeared in 1963. This new text has been signed as a sequel, concentrating on more "instrumental" techniques. Each chapter als with a particular group or type of group in the same pattern as the earlier xt. Because it is difficult to find specialists in groups rather than techniques, the rious authors have written on their own techniques, and the material has been organised by Professor Siggia. The editing has been skilfully done, and the result remarkably homogeneous.

The determination of each group is discussed under several headings: sorption spectrophotometry (i.r., u.v. and visible), gas chromatography, electro- alysis, n.m.r., radiochemistry. The final chapter is a very useful discussion of tomated wet chemical methods for the analysis of functional groups. An appendix ntains bibliographies for the techniques mentioned, and some brief general formation on gas chromatography and n.m.r.; the latter needs more detail to be any real value.

The line between wet chemical and instrumental methods is very tenuous and ther artificial. Most of the "instrumental" procedures require a wet chemical etreatment of some sort; and Siggia's earlier text was by no means limited to e balance and burette. The present book gives an excellent view of the manifold ssibilities in group analysis ten years on, and should prove as indispensable as predecessor to the practising analyst.

A. M. G. Macdonald (Birmingham)

echniques of Surface Chemistry and Physics, Vol. I, Edited by R. J. Good, R. R. romberg and R. C. Patrick, Marcel Dekker Inc., New York, 1972, ix+252 pp., ice $13.75.

The editors aim in this series to provide an easily accessible reference source r the major techniques of surface and colloid chemistry and physics. In this st volume five contributors describe the film balance and the evaluation of termolecular energies in monolayers, the measurement of monolayer permeability, trafiltration, bimolecular lipid membranes, and methods used in the visualization concentration gradients in solutions. Each article begins with an introduction the fundamentals of the subject matter before the details of the techniques are scussed. As a useful reference work on the practical details and background theory the techniques described, this first volume is acceptable. However, even at today's ices, one can question the costing of 250 pages of photo offset type at £8.85.

Charles M. Quinn (Birmingham)

The Analytical Chemistry of Sulphur and its Compounds. Part II, Edited b J. H. Karchmer, Wiley–Interscience, New York, 1972, xvi+835 pp., price £21.2

Parts I and III of this monograph have already appeared, Part I dealin with elemental sulphur, gases, inorganic sulphur compounds and thiols, and Part II with n.m.r. spectroscopy. Part II is entirely concerned with organic compounds c sulphur: sulphides (88 pp.), di- and polysulphides (344 pp.), thiophenes (58 pp. sulphur analogues of carbonyls, carboxylic acids and carbonic acids (255 pp.), an tetra- and hexavalent organosulphur compounds (57 pp.). The authors for eac chapter are mainly from the petroleum industry, and all describe their subject authoritatively.

Each variety of sulphur compound is discussed under the heading introduction (in which there is much useful information on the vexed topic c nomenclature), physical properties and analytical methods. All varieties of analysi are discussed, including chromatography, spectroscopy, electrochemical technique and chemical procedures. Naturally, the emphasis on a particular type of metho varies from compound to compound. The general weighting given to the differen aspects can hardly be faulted.

This is a very good book, comprehensive in its treatment, but authoritative i its selection of emphasis. It is a great pity that possible private buyers will b deterred by the price, for this book should be of great value to biochemists an petroleum chemists as well as the analytical chemists to whom it is primarily directe

A. M. G. Macdonald (Birmingham

J. D. Winefordner, S. G. Schulman and T. C. O'Haver, *Luminescence Spectrometr in Analytical Chemistry*, Vol. 38 in P. J. Elving and I. M. Kolthoff, *Chemic Analysis*, Wiley–Interscience, New York, 1972, xiii+354 pp., price £8.60.

This book describes the types of luminescence most commonly used fo analytical purposes—molecular fluorescence and phosphorescence in condense phases, and fluorescence of atoms in the gas phase. There are two main section In the first, the physicochemical bases of the luminescence processes are describe in a clear, detailed manner. The treatment of atomic fluorescence is particularl valuable, for such detailed information has not previously been assembled in a boo for analytical chemists. This section also describes the effect of numerous parameter on the luminescent output, and includes a description of atom production in flame and non-flame cells. The second part deals with instrumentation for atomic an molecular luminescence, including excitation sources, monochromators, photo detectors, amplifier-read-out systems, flames, noise, shapes of calibration curves, an methodology.

There is a short third section of the book which deals with the analytica uses of the techniques described. It is mainly a summary of the application and comparisons with other analytical techniques including (for atomic fluorescence other flame methods of analysis. The methods and applications are not discusse in detail, because these are to be included in another book, which may appear i 1973.

Many parts of this book are ideal for analytical chemists, students and others who wish to obtain a good fundamental grasp of atomic and molecular fluorescence. Some sections contain rather a lot of useful mathematics, but if desired, an appreciable amount of this can be ignored without detracting too much from the overall picture. The section on instrumentation gives clear descriptions of *modern* electronic and other devices, and appendices provide a bonus in the form of concise descriptions of Fourier Transform, Hadamard and other types of spectrometry, single photon-counting, non-photoemissive detectors and electronic signal processing instruments.

There is relatively little to criticize. The title is more comprehensive than the actual contents, so that the reader must not expect to find discussions of chemiluminescence (in the gas phase or in solution) nor candoluminescence. There is also no author index, nor a mention of separated flames. The appearance of lists of references at the end of the numerous sub-chapters makes them difficult to locate. A number of errors were discovered, such as chenium (p. 132), 10000^2 not 0,000° (p. 191), Hg instead of Hf (p. 279), and, of course, incorrect spelling of the reviewer's name. Luminol appears as an inorganic fluorimetric reagent, and the expressions AC and DC current glare out.

In general, however, this book is to be highly recommended.

A. Townshend (Birmingham)

D. Ambrose, *Gas Chromatography*, 2nd Ed., Butterworths, London, 1971, xi+321 p., price £4.00 (paperback £2.50).

The original literature on gas chromatography has expanded enormously during the ten years since the first edition of this book, and a large number of books on various aspects of the subject has appeared. The text has been extensively revised and expanded to take into account the major facets of the advances which have been made.

After a short general survey, the chapters cover columns and sample injection, detection systems, retention volumes, separations, practical techniques, special modifications, gas–solid chromatography, qualitative, quantitative and preparative methods, gas analysis, and teaching experiments. This short list cannot indicate the wealth of practical information provided, with sufficient theory to satisfy the needs of any general user.

This is an excellent book, very well written, deserving perusal even by experienced practitioners of the art, and superb as an introduction to gas chromatography.

A. M. G. Macdonald (Birmingham)

M. Hanocq, *Etude Analytique de Derivés Fluorés. Applications à l'Analyse Pharm ceutique*, Editions Arscia, Bruxelles–Librairie Maloine, Paris, 1972, 241 pp., p B.F. 490.0.

This survey and examination of analytical methods for fluorinated materi of pharmaceutical value will be of interest to specialists in this field. The text divided into six chapters which deal with introductory matter, spectrophotomet determination of fluoride, potentiometric determination of fluoride, microdiffusi analysis of organic compounds, and applications to pharmaceutical and toxicologi analysis. Experimental studies of the various methods are described in detail.

Actualités de Chimie Analytique, Publiées sous la direction de J.-A. Gaut P. Malangeau et F. Pellerin, 21ème Série, Masson et Cie, Paris, 1972, 186 p prix F 98.

The series of review articles organized by Professor Gautier and his colleag requires neither introduction nor recommendation to readers. The present volu contains surveys of the use of a.c. polarography in the study of metabolites, th layer chromatography of pharmaceuticals, the oxidizing action of vanadium(V) hydroxyl and carbonyl compounds, pesticide residues in foods, techniques of exa ination and determination of pesticide residues, selective chromatography molecular compounds by the formation of ionic complexes with the support material, and the application of n.m.r. to the analysis of fats and oils. All of th maintain the usual high standard of the series.

M. G. Brown, *Chemieliteratur kritisch gelesen*, Umschau Verlag, Frankfurt-am-Ma 1972, 92 pp., DM 9,80.

R. C. Whitfield, *Basis-Reaktionen in der organischen Chemie*, Umschau Verl Frankfurt-am-Main, 1972, 136 pp., DM 10,80.

These paperbacks form Band 16 and Band 18 of the series *Chemie Labor und Betrieb*. As with earlier volumes, they are translations of books in English language. The first appeared as *Critical Readings in Chemistry*, and conta extracts from published papers with questions to test comprehension. The seco appeared as *A Guide to Understanding Basic Reactions* which is a more explanat title than the German version; the various chapters deal with substitution, additi elimination and exchange reactions.

NEW JOURNAL

Marine Chemistry. An International Journal for Studies of all Chemical Aspe of the Marine Environment.

This new journal, the Editor-in-Chief of which is K. E. Chave, Departm of Oceanography, University of Hawaii, will appear at approximately quarte intervals, with one volume each year.

.B.S. Publications

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ritical Evaluation of Data in the Physical Sciences. A Status Report on the National andard Reference System — June 1972, Edited by S. A. Rossmassler, N.B.S. ech. Note 747, November 1972, 79 pp., price $1.25.

he Mechanisms of Pyrolysis, Oxidation and Burning of Organic Materials, Edited / L. A. Wall, N.B.S. Spec. Publ. 357, June 1972, 199 pp., price $3.25.

elected Tables of Atomic Spectra. Atomic Energy Levels and Multiplet Tables ,D,T, Edited by C. E. Moore, N.B.S. NSRDS-NBS 3, Section 6, September 1972,) pp., price 40 cents.

elected Specific Rates of Reactions of the Solvated Electron in Alcohols, Edited / E. Watson and S. Roy, N.B.S. NSRDS-NBS 42, August 1972, price 30 cents.

andard Reference Materials. The Characterization of Linear Polyethylene SRM 175, Edited by H. L. Wagner and P. H. Verdier, N.B.S. Spec. Publ. 260-42, eptember 1972, 39 pp., price 45 cents.

andard X-ray Diffraction Powder Patterns, Edited by H. E. Swanson, H. F. IcMurdie, M. C. Morris, E. H. Evans and B. Paretskin, N.B.S. Monograph 25, ection 10, November 1972, 161 pp., price $2.00.

n Evaluation of Cryogenic Turbine Flowmeters, Edited by J. A. Brennan, R. W. okes, D. B. Mann and C. H. Kneebone, N.B.S. Tech. Note 624, October 1972,) pp., price $1.00.

recision Measurement and Calibration: Colorimetry, Edited by I. Nimeroff, N.B.S.)ec. Publ. 300, Vol. 9, June 1972, 460 pp., price $5.50.

The above publications can be ordered prepaid (in U.S. currency) from the ıperintendent of Documents, U.S. Government Printing Office, Washington, D.C.)402. Foreign remittances must include 25% of the price to cover postage.

I.U.P.A.C. nomenclature recommendations

NOMENCLATURE, SYMBOLS, UNITS AND THEIR USAGE IN SPECTR CHEMICAL ANALYSIS. I. GENERAL ATOMIC EMISSION SPECTROSCOI

Pure and Applied Chemistry, 30 (1972) 653–679.

The purpose of this document is to propose a consistent nomenclature workers in spectrochemical analysis. Many of the terms have already been defin in several nomenclature documents, especially those developed by IUPAC, IUPA and ASTM. The fact that many of the symbols, units, nomenclature and definitic previously recommended are repeated in this document demonstrates that t nomenclature of a specific field, *i.e.*, spectrochemical analysis, is deeply rooted the general nomenclature of chemistry and physics. However, the adaptation o general system to a specialized field required a careful selection of general ter and the addition of new ones. The tentative version of Part I was published *Tentative Nomenclature Appendix* No. 1 (December 1969) to the *Information Bulle* After careful revision the Commission on Spectrochemical and other Opti Procedures for Analysis of the Analytical Chemistry Division has now produce definitive version for IUPAC.

Included in Part I are the following: General Recommendations a Practices; Terms and Symbols for Physical Quantities in General Use; Ter Symbols, and Units Related to Radiant Energy; Terms and Symbols for Descripti ofSpectrographic Instruments; Terms and Symbols Related to Analytical Procedur Terms and Symbols Related to Fundamental Processes Occurring in Light (Exci tion) Sources; Photographic Intensity Measurements (Photographic Photometr A statement by ASTM on General Principles of Nomenclature Standardization reprinted as an Appendix. A second Appendix deals with Application of Concept of Optical Conductance.

Available as a reprint from: IUPAC Secretariat, Bank Court Chambe 2–3 Pound Way, Cowley Centre, Oxford OX4 3YF, England. Price 40 p or $1. (Postage free if cash with order.)

ERRATUM

G. D'Ascenzo, U. B. Ceipidor, A. Marino and A. Magri, Thermal propert of some complexes of quinolinic acid with divalent metal ions, *Anal. Chim. Acta*, (1973) 105–113.

Page 112, 15th line down, step 2 should read: "2. $H_2O_{liq} \rightarrow H_2O_{vap}$"

tinued from page 4 of cover)

CONTENTS

(continued on inside page of cover)