ANALYTICA CHIMICA ACTA

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

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 53, No. 2, 225–480, February 1971
Published monthly
Completing Volume 53

Publication Schedule for 1971

In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1971. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

Vol. **53,** No. **1**	January 1971	
Vol. **53,** No. **2**	February 1971	**(completing Vol. 53)**
Vol. **54,** No. **1**	March 1971	
Vol. **54,** No. **2**	April 1971	
Vol. **54,** No. **3**	May 1971	**(completing Vol. 54)**
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Vol. **55,** No. **2**	July 1971	**(completing Vol. 55)**
Vol. **56,** No. **1**	August 1971	
Vol. **56,** No. **2**	September 1971	
Vol. **56,** No. **3**	October 1971	**(completing Vol. 56)**
Vol. **57,** No. **1**	November 1971	
Vol. **57,** No. **2**	December 1971	**(completing Vol. 57)**

Subscription price: $17.50 or Dfl. 63.— per volume plus postage. Total subscription price for 1971: $87.50 or Dfl. 315.— plus postage. Additional cost for copies by airmail available on request. For subscribers in the U.S.A. and Canada, 2nd class postage paid at New York, N.Y. For advertising rates apply to the publishers.

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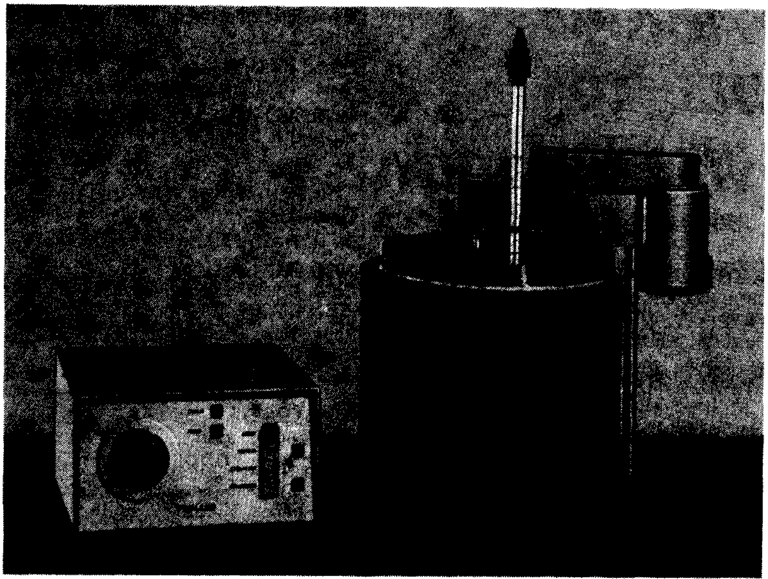

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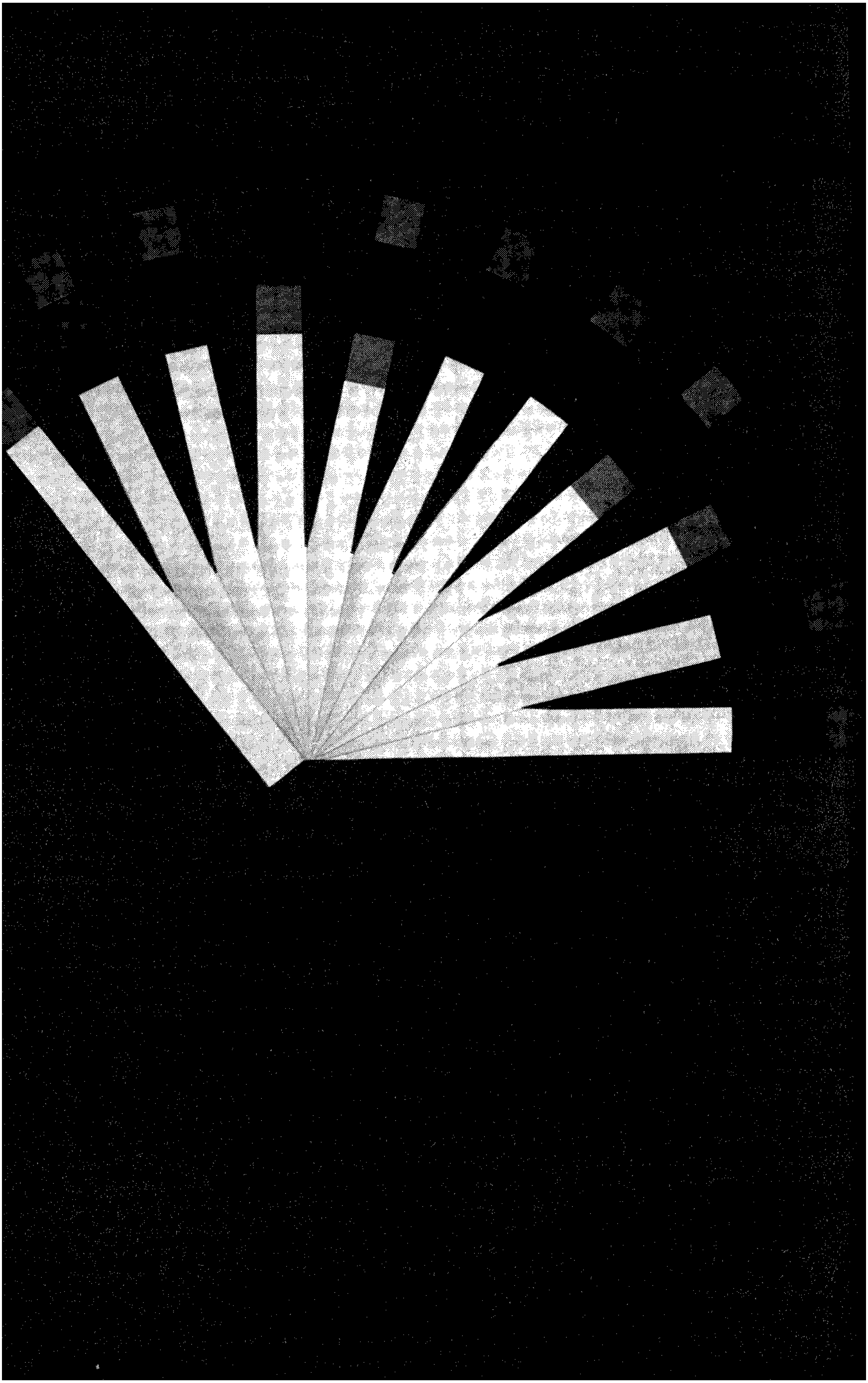

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE POTENTIOMETRIC TITRATION OF SILVER AND COPPER WITH DITHIOOXAMIDE

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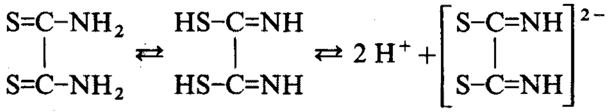
(Received 21st September 1970)

The determination of silver and copper in silver alloys and ores is of considerable interest. However, there are very few methods for determining silver and copper simultaneously in a sample. Furthermore, each of these methods suffers from certain disadvantages, ranging from elaborate and expensive equipment to lengthy and time-consuming physical operations[1-12]. The following is a description of a simple, inexpensive, direct and simultaneous potentiometric method for silver and copper in a sample.

Potentiometric titrations of copper with dithiooxamide and of silver with dithiooxamide have already been described[13,14]; in each case, an electrode system with silver metal as the indicating electrode was found to produce a high degree of precision and accuracy. During these investigations it was found that it was possible to titrate a mixture of silver and copper with dithiooxamide and to obtain two breaks in potential corresponding to the relative amounts of silver and copper present. In the present investigation, the method for silver and copper was thoroughly examined and its accuracy and precision evaluated.

Dithiooxamide was first used as a precipitation reagent by Ray and Ray[15]. It exists in solution in equilibrium with its tautomeric form[16]:



$$\begin{array}{c} S{=}C{-}NH_2 \\ | \\ S{=}C{-}NH_2 \end{array} \rightleftarrows \begin{array}{c} HS{-}C{=}NH \\ | \\ HS{-}C{=}NH \end{array} \rightleftarrows 2\,H^+ + \left[\begin{array}{c} S{-}C{=}NH \\ | \\ S{-}C{=}NH \end{array}\right]^{2-}$$

It reacts with metals such as zinc, copper, palladium, cobalt, and nickel to form 1:1 chelates which are stable at room temperature. The salts probably are polymeric compounds of dithiooxamide[17]. Iron(II), iron(III), ruthenium, silver, cadmium, and mercury ions form unstable compounds which rapidly decompose to yield sulfides[18]. By proper pH control and by complexation with fluoride and EDTA, the reagent can be made more selective.

EXPERIMENTAL

Standard solutions

Standard silver nitrate solution (0.200 *mg Ag ml*$^{-1}$). Weigh 315.0 mg of analytical-reagent silver nitrate (previously dried at 150° for 2 h), dissolve and dilute to 1 l with water.

Standard copper nitrate solution (0.1000 *mg Cu* ml^{-1}). Weigh 200.0 mg of electrolytic copper foil, dissolve in a minimum of concentrated nitric acid and dilute to 2 l with water.

Dithiooxamide solution. Heat 240.4 mg of dithiooxamide gently with 1400 ml of deionized, distilled water, with continuous stirring until dissolution is complete. Then cool and dilute to 2 l with water. The reagent appeared to be stable for at least one month.

Deionized distilled water was used throughout this work.

Instrument

A Corning Model 12 pH meter with a silver indicator electrode and glass reference electrode was employed in all titrations.

Procedure

To the sample solution in a 150-ml beaker, add 1.0 g of reagent-grade potassium hydrogen phthalate and 0.5 g of reagent-grade sodium fluoride; dilute to 100 ml with water. Titrate with the dithiooxamide solution, allowing the potential to come to equilibrium between additions; near the end-points, wait for 2–3 min before recording the potential. The potential jumps were sharp, and the equivalence point could be estimated to the nearest 0.01 ml.

After every titration the silver electrode was rubbed with a clean towel to remove any film that had formed; it was then immersed in a 0.05 *M* potassium cyanide solution for 1 min and rinsed with distilled water.

RESULTS AND DISCUSSION

The dithiooxamide solution was standardized independently against standard silver solution and against standard copper solution. (One mole of copper reacts with 1 mole of dithiooxamide. Since silver and dithiooxamide form an unstable compound which rapidly decomposes to form the sulfide, 4 moles of silver react with 1 mole of dithiooxamide.) The molarity of the dithiooxamide solution, measured against the silver standard, was determined to be 0.001027 and, against the copper standard, was found to be 0.001070. Apparently, the dithiooxamide solution, because of decomposition, contained a small amount of sulfide ion and this ion was responsible for the higher molarity against copper[13,14].

Solutions of silver and copper mixtures ranging from 1% silver to 99% silver were prepared by proper dilutions of the stock standard silver and standard copper solutions. On an absolute basis the silver content ranged from 0.05 p.p.m. to 50 p.p.m., while the copper content ranged from 0.5 p.p.m. to 10 p.p.m. Replicate determinations were made on each solution to establish the precision of the method. Typical titration curves are shown in Fig. 1. The first break in potential corresponds to the amount of silver present and the second to the amount of copper present. It was noted that the silver end-point (*i.e.* the point at which $\Delta E/\Delta$ml is maximum) occurs too early. This is characteristic of the titration of mixtures and the end-point error depends on the concentrations of the substances titrated and on the ratio of the instability constants and/or solubility products of the species involved[19]. Experimentally, it was found that in the range of mixtures investigated (1% to 99% silver) more accurate results were obtained if, on plotting the graph, the end-point for silver was taken as the three-fourths point on the longest straight line with the greatest slope that could be drawn through this break. Usually the mid-point of the longest straight line is taken as the end-point. These "three-fourths" values agreed well with the values that were obtained in titrations of solutions containing only silver ions where the mid-point was taken as the end-point. Table I, columns 3 and 4, indicates this as well as the average relative standard deviations, which ranged from 0.16 to 2.00% for silver and from 0.20 to 1.34% for copper.

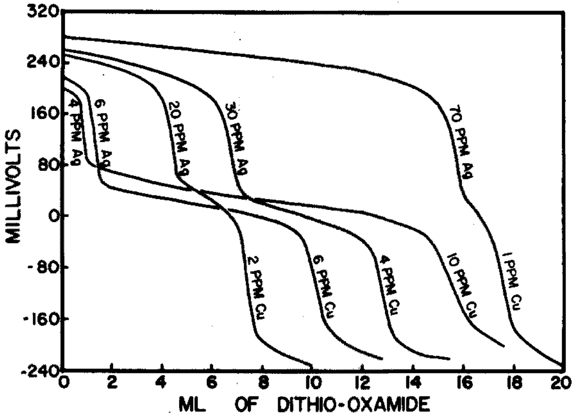


Fig. 1. Representative potentiometric titration curves for mixtures of silver and copper with dithiooxamide.

TABLE I

PRECISION OF DETERMINATION OF SILVER AND COPPER

Silver (p.p.m.)	*Copper (p.p.m.)*	*Dithiooxamide for silver (ml)*[a]	*Dithiooxamide for silver alone (ml)*	*Relative standard deviation (%)*	*Dithiooxamide for copper (ml)*[a]	*Relative standard deviation (%)*
50.0	0.50	11.31	11.35	0.16	0.82	1.34
30.0	1.00	6.72	6.75	0.33	1.45	1.28
20.0	2.00	4.50	4.50	0.28	2.95	0.66
10.00	3.00	2.27	2.26	0.20	4.40	0.36
10.00	5.00	2.28	2.26	0.48	7.26	0.23
6.00	6.00	1.37	1.37	0.45	8.74	0.20
4.00	10.00	0.92	0.93	1.28	14.63	0.20
1.20	5.00	0.30	0.29	2.00	7.25	0.65
0.60	6.00	0.143[b]	—	0.55	8.75	0.36
0.050	5.00	0.0110[c]	—	1.57	7.26	0.79

[a] Average of 6 determinations.

[b] For these titrations the dithiooxamide solution was diluted 10-fold; the figures shown have been corrected to account for this dilution.

[c] For these titrations the dithiooxamide solution was diluted 50-fold; the figures shown have been corrected to account for this dilution.

The last two samples indicated in Table I contained so little silver, in comparison to copper, that it was not possible to obtain two breaks in potential. In these cases two aliquots of silver and copper mixtures were prepared. To one aliquot, 0.10 g of EDTA was added. This aliquot was titrated with a more dilute dithiooxamide solution, indicating only the silver present, as the EDTA completely masks the copper. The second aliquot without EDTA was titrated in the usual manner and only one break was obtained which was due to the copper and silver present. The volume of dithiooxamide solution used in the titration of the first aliquot for silver was subtracted from the total volume used in the titration of the sum of copper and silver in the second aliquot. This difference gave the volume of dithiooxamide that reacted with the copper.

TABLE II

ANALYSIS OF SYNTHETIC UNKNOWNS

True composition		*Experimentally determined*		*Relative error (%)*	
Ag (p.p.m.)	*Cu (p.p.m.)*	*Ag (p.p.m.)*	*Cu (p.p.m.)*	*Ag*	*Cu*
30.0	1.00	29.83	1.00	−0.57	0.00
20.0	2.00	19.91	2.01	−0.45	+0.50
30.0	4.00	30.14	4.10	+0.47	+2.50
18.0	7.00	18.04	6.95	+0.22	−0.71
10.00	4.00	10.02	4.03	+0.20	+0.75
12.0	7.00	12.15	6.97	+1.25	−0.43
12.0	8.00	12.06	7.95	+0.50	−0.63
10.0	8.00	10.11	8.09	+1.10	+1.13
6.00	7.00	6.16	7.06	+2.67	+0.85
2.00	6.00	1.99	5.92	−0.50	−1.33
0.800	5.00	0.829[a]	4.97	+3.63	−0.60
0.100	5.00	0.097[b]	4.98	−3.00	−0.40

[a] For this titration the dithiooxamide solution was diluted 10-fold; the figure shown has been corrected to account for this dilution.

[b] For this titration the dithiooxamide solution was diluted 50-fold; the figure shown has been corrected to account for this dilution.

Unknown synthetic samples were prepared over the range investigated and were titrated with the standard dithiooxamide solution. The results are given in Table II. Over the range of mixtures (0.100–30.0 p.p.m. silver and 8.00–1.00 p.p.m. copper), an average accuracy of 1.21% was obtained for silver and an average accuracy of 0.82% for copper. Some of the error was due to the method of determining the first end-point (silver) as previously discussed. The "three-fourths" end-point selection represented a compromise and was satisfactory over the range investigated. However, this error could be substantially reduced by standardizing the dithiooxamide with mixtures of silver and copper whose compositions would be near the composition range of the unknowns, and from these curves determining a more appropriate end-point to be used with the unknowns.

Interferences

Previous work on the titration of copper(II) with dithiooxamide had shown that under the conditions employed, iron(III) up to 1000 p.p.m., cobalt(II) up to 400 p.p.m., and nickel(II) up to 400 p.p.m. did not interfere[13]. Previous work on the titration of silver with dithiooxamide also had shown that these ions did not interfere[14]. Therefore, it is to be expected that they would not interfere with the simultaneous titration of silver and copper. Rhodium, magnesium, aluminum, thallium, and bismuth ions do not react with dithiooxamide[18].

Zinc and cadmium would not be expected to react with the dithiooxamide in the acidic media used. However, since zinc is a common constituent of many silver alloys, especially silver solders, a series of silver–copper samples containing various amounts of zinc were prepared and analyzed to determine whether zinc interfered. The results (Table III) indicate that zinc at concentrations of 100 p.p.m. and below caused very little difficulty. Above this concentration, results for copper were slightly high. This effect could possibly have resulted from traces of copper in the zinc nitrate that was used to prepare the unknowns. Since the proportion of zinc in silver alloys is much less than the zinc concentrations employed in this study its presence would cause little or no difficulty in the simultaneous determination of silver and copper in such zinc containing alloys.

TABLE III

ZINC INTERFERENCE STUDIES

Sample	*True composition (p.p.m.)*	*Experimentally determined Ag (p.p.m.)*	*Experimentally determined Cu (p.p.m.)*
1	Ag 20.0; Cu 5.00; Zn 100	20.0	5.08
2	Ag 20.0; Cu 2.00; Zn 200	19.9	2.02
3	Ag 10.00; Cu 3.00; Zn 100	9.96	3.03
4	Ag 10.00; Cu 3.00; Zn 200	10.00	3.08
5	Ag 10.00; Cu 3.00; Zn 300	10.04	3.10
6	Ag 10.00; Cu 2.00; Zn 40	10.00	2.01
7	Ag 10.00; Cu 2.00; Zn 80	10.00	2.01
8	Ag 10.00; Cu 2.00; Zn 100	9.96	2.01
9	Ag 10.00; Cu 2.00; Pb 20	9.90	2.00

Small amounts of lead (20 p.p.m.) caused no error in the titration (Table III); apparently the lead ion reacts too slowly to cause difficulty. However, large amounts of lead interfere in this titration. It is possible to eliminate the lead interference completely by the addition of EDTA, but the EDTA also completely complexes the copper and eliminates the second potential break.

Mercury interferes, as mercury(II) and silver react simultaneously with the dithiooxamide. Gold and platinum are reduced to the metallic state by dithiooxamide[18]. It would be necessary to remove these metals before the silver and copper titration.

Comparison with other methods

There are very few simultaneous and direct methods for the determination of silver and copper in a sample. This determination is particularly important and suitable for the analysis of silver solders containing copper (15–30 %), silver (50–80 %), and zinc (0–15 %).

Perhaps the most common method of determining copper and silver in a sample is by electrodeposition. First the silver is plated from an alkaline cyanide solution, an ammoniacal solution, or a nitric acid–sodium nitrite medium[1-4]. The solution is usually acidified, then, the potential is raised, and the copper is plated out. The electrodeposition method requires a much longer time and a macro sample, and suffers from a number of interferences.

One of the earliest potentiometric methods involved the titration of silver with thiocyanate with a silver indicating electrode. The silver thiocyanate was then filtered off and the filtrate containing the copper was titrated with thiocyanate using a copper electrode[6]. This method suffers from many difficulties, ranging from the poor nature of copper as an indicating electrode to the inconvenience of separation by filtration.

Another potentiometric method to determine silver (20–100 p.p.m.) and copper (0.3–4.5 p.p.m.) involves precision null-point potentiometry[7]. This method requires not only special equipment, but two aliquots of the sample. The first aliquot is analyzed for silver by dilution of the unknown silver solution until the potential of the cell formed by a silver electrode in contact with the unknown solution and an identical silver electrode in contact with a standard silver solution becomes zero. The second aliquot is analyzed for copper by treatment with iodide ion to liberate iodine followed by potentiometric matching with a solution in which iodine is generated electrolytically. Since the ionic composition of the unknown solution is not exactly known, error arises in attempting to match the standard to the unknown. The presence of other unknown ions affects the potential of the unknown half-cell.

There are many colorimetric methods for determining silver alone and copper alone[8], but ordinarily, because of interferences, lengthy extractions and separation procedures are necessary. Even with the best procedures for each metal ion, there is the inconvenience of using two different methods with different color developing reagents. One method that uses a single reagent for both silver and copper is the dithizone method[8,9]. Silver can be determined in the presence of moderate quantities of copper, but copper cannot be determined in the presence of silver with dithizone; hence preliminary separations must still be performed.

A newer method of analysis appropriate for this type of determination is atomic absorption and it has been used separately for silver and for copper[10-12]. However, it requires rather expensive equipment which may not always be available.

The proposed potentiometric method possesses the following advantages over other methods: (*a*) only one aliquot, (*b*) very few interferences, (*c*) no preliminary separations, (*d*) rapidity, (*e*) high sensitivity, and (*f*) inexpensive common equipment.

SUMMARY

Potentiometric titration with dithiooxamide solution can be used to determine silver and copper in mixtures ranging from 1 to 99 % silver with a relative standard deviation ranging from 0.16 to 2.00 % for silver and from 0.20 to 1.34 % for copper. Analysis of twelve different unknown mixtures of silver (0.100–64.0 p.p.m.) and copper (8.00–1.00 p.p.m.) gave an average accuracy of 1.21 % for silver and 0.82 % for copper.

Interferences from a number of metals commonly associated with silver and copper are discussed. The advantages of the method over other methods for simultaneously determining silver and copper in a sample are outlined.

RÉSUMÉ

Un titrage potentiométrique au moyen de dithiooxamide peut être utilisé pour le dosage de l'argent et du cuivre dans des mélanges contenant 1 à 99 % d'argent, avec une déviation standard relative de 0.16 à 2.00 % pour l'argent et de 0.20 à 1.34 % pour le cuivre. L'analyse de douze mélanges differents inconnus d'argent (0.100–64.0 p.p.m.) et de cuivre (8.00–1.00 p.p.m.) ont donné une exactitude moyenne de 1.21 % pour l'argent et 0.82 % pour le cuivre. On examine l'influence de divers métaux, ainsi que les avantages de ce procédé.

ZUSAMMENFASSUNG

Durch potentiometrische Titration mit Dithiooxamid-Lösung können Silber und Kupfer in Gemischen mit 1 bis 99 % Silber mit einer relativen Standardabweichung von 0.16 bis 2.00 % bei Silber und 0.20 bis 1.34 % bei Kupfer bestimmt werden. Die Analyse von zwölf verschiedenen unbekannten Gemischen von Silber (0.100–64.0 p.p.m.) und Kupfer (8.00–1.00 p.p.m.) ergab eine durchschnittliche Genauigkeit von 1.21 % bei Silber und 0.82 % bei Kupfer. Störungen durch eine Reihe von Metallen, die häufig mit Silber und Kupfer zusammen vorliegen, werden diskutiert. Die Vorteile der Methode gegenüber anderen Methoden für die gleichzeitige Bestimmung von Silber und Kupfer in einer Probe werden dargelegt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BIAMPEROMETRIC TITRATION OF HEXACYANOFERRATE(III), IRON(III), COPPER(II), CERIUM(IV), AND IODINE WITH MERCURY(I) PERCHLORATE

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(Received 10th September 1970)

Amperometric titration with mercury(I) perchlorate at a rotating platinum electrode (R.P.E.) has been shown to permit the precise and accurate determination of submillinormal concentrations of iron(III)[1], copper(II)[2], iodine[3], hexacyanoferrate(III)[4], and cerium(IV)[5]. The simplicity of the equipment for biamperometric titration[6a] has prompted an examination of the utility of biamperometry in titrations with mercury(I) perchlorate.

EXPERIMENTAL

The *ca.* 0.1 *N* solution of mercury(I) perchlorate in 1 *M* perchloric acid was prepared and then standardized by the dichromate–iodide method, as described by Berka *et al.*[7]. The solution was stored in the dark over mercury. More dilute solutions were prepared as required by addition of 1 *M* perchloric acid. Other solutions were prepared as described earlier[1-5].

The biamperometric electrode system was that described by Stock[6b], with twin 24-gauge platinum wire electrodes. Each electrode had a surface area of 0.13 cm^2. The circuit arrangement was conventional[6c]. A black polyethylene shell enclosed the 150-ml beaker used as a titration vessel. Constant-speed magnetic stirring was used. Titrant was delivered from a 2-ml or 0.2-ml Gilmont microburet that was protected from the light.

Except where indicated, all titrations were performed in triplicate on 100-ml portions of solution, at room temperature (in the range 24°–28°). The medium used was that found satisfactory for R.P.E. amperometric titration of the particular titrand[1-5]. Readings were taken 1 min after each addition of titrant, except when approaching the end-point. The interval was then increased to 2–4 min. The electrodes were cleaned daily by immersion in concentrated nitric acid for 30 sec, followed by thorough rinsing. Before each set of titrations, a "conditioning titration" was run on a portion of the particular titrand.

RESULTS AND DISCUSSION

Except where noted, all titrations were performed with 0.1013 *N* mercury(I) perchlorate. The results are summarized in Tables I–V. These show that, by suitable choice of applied e.m.f. (*E*), the determination of any of the titrands in the concentra-

TABLE I

BIAMPEROMETRIC TITRATION OF HEXACYANOFERRATE(III) IN 0.5 *M* KSCN–0.01 *M* $HClO_4$[a]

E (mV)	*$K_3Fe(CN)_6$ concentration (μN)*		*Error (%)*
	Taken	*Found*	
50	100	101 ± 2.3[b]	+1
100	100	100 ± 0.8[b]	0
250	250	102 ± 2.5	+2
100	1000	1009 ± 9	+0.9
100	50	51.0 ± 0.5	+2
100	20	20.3 ± 0.3	+2
100	10	[c]	[c]

[a] Titrant normality, 0.098.

[b] Mean of 4 titrations.

[c] End-point not detectable.

TABLE II

BIAMPEROMETRIC TITRATION OF IRON(III) IN 0.1 *M* KSCN–0.1 *M* $HClO_4$

E (mV)	*Iron(III) concentration (μN)*		*Error (%)*
	Taken	*Found*	
50	100	105 ± 1.5	+5
100	100	99 ± 1.3[a]	−1
200	100	106 ± 3.5	+6
100	1000	1020 ± 5	+2.0
100	50[b]	49.1 ± 0.1	−2
100	10[b]	$9.7_5 \pm 0.07$	−3
100	5[b,c]	3.6_5	−27

[a] Mean of 5 titrations.

[b] Titrant diluted 10-fold.

[c] One titration only.

TABLE III

BIAMPEROMETRIC TITRATION OF IODINE IN 0.02 *M* KI–0.05 *M* H_2SO_4

E (mV)	*Iodine concentration (μN)*[a]		*Error (%)*
	Taken	*Found*	
50	100	99 ± 1.2	−1
100	100	100 ± 1.3	0
150	100	103 ± 0.9	+3
100	1000	990 ± 3	−1.0
100	50[b]	51.1 ± 1.7	+2
100	10[b]	11.9 ± 1.0	+19

[a] Introduced as KIO_3.

[b] Titrant diluted 10-fold.

TABLE IV

BIAMPEROMETRIC TITRATION OF COPPER(II) IN 0.3 M KSCN–0.02 M KI–0.02 M $HClO_4$

E (mV)	*Copper(II) concentration (μN)*		*Error (%)*
	Taken	*Found*	
50	100	102±2.2	+2
100	100	99±4.0[a]	−1
250	100	100±1.0	0
300	100	101±0.5	+1
250	1000	991±3	−0.9
250	50[a,b]	49.0±0.8	−2
250	10[b,c]	7.0	−30

[a] Mean of 5 titrations.
[b] Titrant diluted 10-fold.
[c] One titration only.

TABLE V

BIAMPEROMETRIC TITRATION OF CERIUM(IV) IN 0.01 M KI–0.2 M $HClO_4$[a]

E (mV)	*Cerium(IV) concentration (μN)*		*Error (%)*
	Taken	*Found*	
10	100	64±1	−36
50	100	99±0.7	−1
150	100	100±0.9[b]	0
300	100	98[c]	−2
150	1000	989±10	−1.1
150	50[d]	48.7±3.5	−3
150	10[d]	$10.7_5 \pm 2.1_0$	+8

[a] Cerium(IV) introduced after medium had been flushed with nitrogen.
[b] Mean of 4 titrations.
[c] One titration.
[d] Titrant diluted 10-fold.

tion range 50 to 1000 μN has an error that rarely exceeds 2%. In some cases, concentrations as low as 10 μN can be titrated, but the error is unacceptably large. With hexacyanoferrate(III), no end-point could be seen in 10 μN solutions, under conditions that were satisfactory for higher concentrations (Fig. 1). A re-examination of the titration of these highly dilute solutions by more refined biamperometric techniques is planned.

When hexacyanoferrate(III) in sodium hydroxide solution is progressively converted to hexacyanoferrate(II), the biamperometric curve has the hyperbolic form required by theory for a reversible titrand couple. The current, essentially zero at the beginning and at the completion of the conversion, reaches a peak at the half-titrated point[6d]. Figure 2 shows some of the titration curves of hexacyanoferrate(III) in acidic thiocyanate medium. Although peaked curves occur, the current is quite large at the beginning of the titration. This initial current is ascribed to partial depolarization of the anode, by a reaction such as

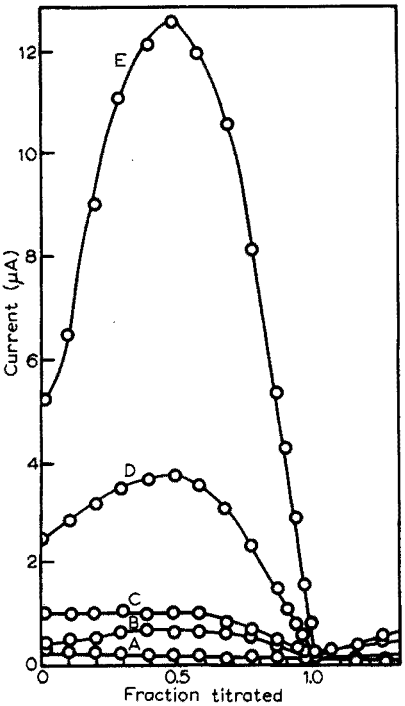
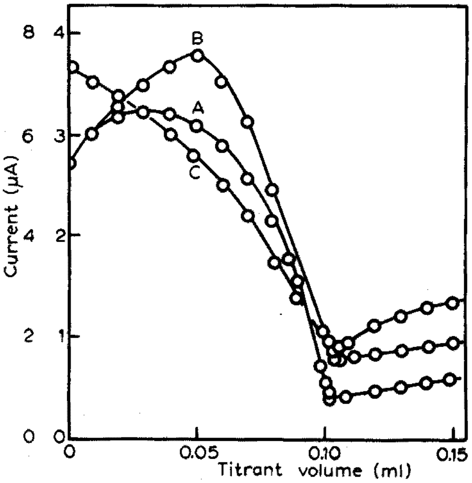


Fig. 1. Biamperometric titration curves of hexacyanoferrate(III) in 0.5 M KSCN–0.01 M $HClO_4$ with $Hg_2(ClO_4)_2$. $E = 100$ mV. $K_3Fe(CN)_6$ concentration (μN): (A) 10; (B) 20; (C) 50; (D) 100; (E) 1000.



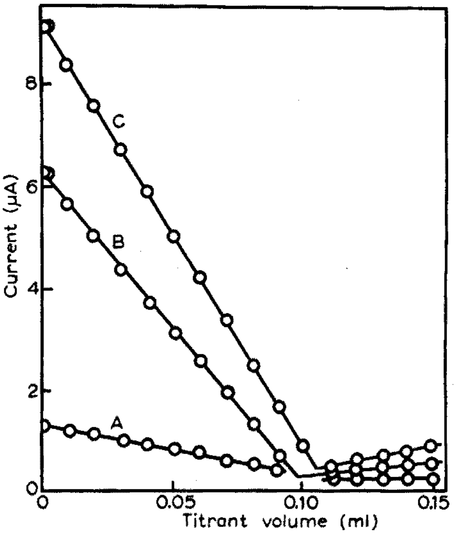


Fig. 2. Biamperometric titration curves of 100 ml of 100 μN hexacyanoferrate(III) in 0.5 M KSCN–0.01 M $HClO_4$ with 0.0982 N $Hg_2(ClO_4)_2$. (A) Inner ordinate, $E = 50$ mV; (B) inner ordinate, $E = 100$ mV; (C) outer ordinate, $E = 250$ mV.

Fig. 3. Biamperometric titration curves of 100 ml of 100 μN iron(III) perchlorate in 0.1 M KSCN–0.1 M $HClO_4$ with 0.1013 N $Hg_2(ClO_4)_2$. (A) $E = 10$ mV; (B) $E = 100$ mV; (C) $E = 200$ mV.

$$SCN^- + 4\,H_2O = CN^- + SO_4^{2-} + 8\,H^+ + 6\,e$$

Because of the poising effect of the hexacyanoferrate(III)–hexacyanoferrate (II) couple, the main effect of making E large is to increase the potential of the anode. This should cause the anode depolarizing effect to become more pronounced, so that the titration curve (curve C, Fig. 2) no longer has a peak. Even at the selected value of $E = 100$ mV, only the final 20–30% of the pre-equivalence branch of the titration curve exhibits the pseudolinearity necessary for simple graphical end-point location. This may account for the positive bias of the results in Table I.

Although iron(III) was also titrated in acidic thiocyanate medium, the curves were apparently linear and showed no peaks even when E was small (Fig. 3). In 0.1 M thiocyanate, the calculated formal potential of the iron(III)–iron(II) couple is *ca.* +0.6 V[1]. This is at least 100 mV more positive than the formal potential of the hexacyanoferrate(III)–hexacyanoferrate(II) couple at an acidity of 0.01 M[8]. At a given value of E, the depolarization of the anode by thiocyanate should, therefore, be more pronounced in the titration of iron(III) than in the titration of hexacyanoferrate(III).

Apparently linear curves were also obtained in the titration of iodine, copper-(II), and cerium(IV). These titrations, all performed in the presence of an excess of iodide ion, are presumably governed mainly by the biamperometric behavior of the largely-reversible iodine–iodide couple. The experimental conditions of quite high E, low titrand concentration (hence low current), and small total resistance in the cell circuit all favor an extended region of linearity of the titration curves[6e].

In the titration of high (1000 μN) concentrations of iron(III), iodine, copper(II), or cerium(IV), curves of shape qualitatively similar to that of C, Fig. 2, were obtained. The much larger currents involved at high titrand concentrations have two effects that can cause the curves to depart from linearity: (*i*) the value of E will be significantly smaller than that calculated from the ratio of the resistor values in the simple battery-operated voltage divider[6a], and (*ii*) the voltage drop caused by the total resistance in the cell circuit will be larger[6e]. The first effect can, of course, be eliminated by potentiostatic control of E.

COMPARISON OF AMPEROMETRIC AND BIAMPEROMETRIC TECHNIQUES IN REDOX TITRATIONS WITH MERCURY(I) PERCHLORATE

The basis for the comparison of amperometric and biamperometric techniques for redox titrations with mercury(I) perchlorate is day-to-day usage by an experienced operator, using solutions made from analytical-grade chemicals. The techniques are both quite rapid; the average time per titration is 15–20 min.

At concentrations down to 100 μN, both techniques yield results of approximately similar accuracy and precision. It is at lower concentrations that R.P.E. amperometric titration becomes preferable, especially if the end-point method A ("preaddition technique") described previously[1] is employed. The end-point is then located on the strictly linear portion of a current–concentration curve. Any of the titrands hexacyanoferrate(III), iron(III), copper(II), cerium(IV), or iodine can then be determined at a concentration level of 10 μN, with an error that does not exceed 5%. Useful results can sometimes be obtained at even lower concentrations[2]. No conditions have yet been found by which 10 μN concentrations of the titrands can be routinely determined by biamperometric titration with mercury(I) perchlorate.

Preliminary experiments have shown that the five titrands examined can also be titrated with mercury(I) perchlorate to a bipotentiometric end-point[6f].

This work was carried out with the partial support of the University of Connecticut Research Foundation.

SUMMARY

The biamperometric titration of hexacyanoferrate(III), iron(III), copper(II), cerium(IV), and iodine with mercury(I) perchlorate has been studied. In the concentration range 50 to 1000 μN, the error rarely exceeds 2 %. Although the biamperometric and R.P.E. amperometric techniques are of comparable utility at concentrations down to 100 μN, the amperometric technique is preferable for low-concentration titrations.

RÉSUMÉ

Une étude est effectuée sur le titrage biampérométrique de l'hexacyanoferrate(III), du fer(III), du cuivre(II), du cérium(IV), et de l'iode, au moyen de perchlorate de mercure(I). Pour des concentrations allant de 50 à 1000 μN, l'erreur excède rarement 2 %. Bien que les techniques biampérométriques et ampérométriques RPE sont comparables jusqu'à 100 μN, l'ampérométrie convient mieux pour les titrages de faible concentration.

ZUSAMMENFASSUNG

Die biamperometrische Titration von Hexacyanoferrat(III), Eisen(III), Kupfer(II), Cer(IV) und Jod mit Quecksilber(I)perchlorat wurde untersucht. Im Konzentrationsbereich 50–1000 μN ist der Fehler kaum grμsser als 2 %. Wenn auch biamperometrische und RPE–amperometrische Verfahren bei Konzentrationen bis zu 100 μN herab von gewissem Nutzen sind, ist das amperometrische Verfahren für Titrationen bei niedriger Konzentration vorzuziehen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE COULOMETRIC DETERMINATION OF MALTOSE WITH MALTASE*

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(Received 10th August 1970)

Various reagents have been employed in the determination of glucose, maltose, and other reducing sugars. Among the more common procedures are those which employ an alkaline copper reagent, picric acid, hexacyanoferrate(III), or other oxidizing agents. These have been widely described in the literature and a thorough review of the subject has been given by Henry[1].

Henry and others have reviewed the use of glucose oxidase for the determination of serum glucose. Simon *et al.*[2] employed glucose oxidase in the coulometric titration based on the amount of peroxide formed. The present procedure couples the enzyme maltase with glucose oxidase in a modification of their procedure.

Laidler[3] describes maltose as one of the most important members of the α-D-glucosides. Maltase acts upon maltose as well as other glucosides such as methyl, ethyl, or phenyl α-D-glucopyranosides. Larner and Gillespie[4] have studied the properties of intestinal maltase and reported an inhibition by glucose. Inhibition by some amines (TRIS buffer) and heavy metals, such as copper(II), mercury(II), zinc(II), and silver(I), was also reported.

EXPERIMENTAL

Apparatus

All coulometric titrations were made with a Microcoulometric Quantalyzer Model 6 (ChrisFeld Precision Instruments, Inc., Beltsville, Md.). The titration cell employed was similar to one previously described[5]. The biamperometric end-point detection method was used with a potential of 200 mV imposed a ross two identical platinum-foil electrodes. The potential across the indicating electrodes was supplied by a Sargent Model XV Polarograph. The excess of thiosulfate present in the titration cell was determined by titration with generated iodine. Beyond the equivalence point the excess of iodine causes a current to flow owing to the reversible nature of the iodine–iodide couple. The resultant titration curve has the familiar reverse L-shape. All titrations were made to the same indicator current level or excess of iodine. The same system has been described previously[2] in more detail.

Reagents

Acetate buffer, 0.6 *M*, *pH* 5.1. Dissolve 49.2 g of sodium acetate in about 800

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* Taken in part from the Ph.D. Dissertation of John R. Moody, University of Maryland, College Park, Md., 1970.

ml of distilled water. Add acetic acid to lower the pH to 5.10. Dilute to 1 l and check the pH.

Alkaline copper reagent (*Nelson–Somogyi*). Prepare before use by diluting 4 ml of copper solution B to 100 ml with copper solution A.

For solution A, dissolve 50 g of anhydrous sodium carbonate, 50 g of Rochelle salt, 40 g of sodium hydrogen carbonate, and 400 g of anhydrous sodium sulfate in 1600 ml of boiled, distilled water and then dilute to 2 l. For Solution B, dissolve 150 g of copper sulfate pentahydrate in 1 l of boiled, distilled water and add 0.5 ml of concentrated sulfuric acid.

Arsenomolybdate color reagent. Dissolve 50 g of ammonium molybdate in 900 ml of distilled water. Add 42 ml of concentrated sulfuric acid and mix. Dissolve 6 g of disodium *ortho*arsenate ($Na_2HAsO_4 \cdot 7\ H_2O$) in 50 ml of distilled water and add to the molybdate solution with stirring. Incubate at 37° for 24–48 h. The reagent is stable when protected from light.

Benzoate buffer, 0.02 *M*, *pH* 5.5. Add 2.44 g of benzoic acid to 800 ml of distilled water and heat to boiling. When cooled, add 1 *M* sodium hydroxide until the pH is 5.5, then dilute with water to 1 l. This reagent is a good preservative for use in preparing glucose and maltose standards.

Composite reagent. Dissolve 2.84 g of ammonium *para*molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), 4 ml of 0.1 *N* sodium thiosulfate, and 41.5 g of potassium iodide in 950 ml of boiled, distilled water. Adjust the pH to 7.00 with anhydrous sodium carbonate and then dilute to 1 l. The value of the titer may be adjusted with additional amounts of 0.1 *N* thiosulfate.

Deproteinizing reagents. Approximately 0.15 *N* barium hydroxide and 2.5% zinc sulfate are used. More important than the concentration of the reagents is that the reagents must exactly neutralize one another. The titers of the reagents should be determined by titration and adjusted until 10.00 ml of zinc sulfate is equivalent to 10.00 ± 0.05 ml of barium hydroxide. The barium hydroxide must be protected from carbon dioxide. Millipore filters can be used to produce reagents free of turbidity.

Glucose oxidase reagent. Triturate 500 mg of glucose oxidase (30 units mg^{-1}, Nutritional Biochemical Co.) reagent powder in a glass mortar with 0.6 *M* acetate buffer, pH 5.1. Dilute to 100 ml with buffer and store under refrigeration.

Glucose oxidase–maltase reagent. Triturate 500 mg of glucose oxidase and 63 mg of maltase (0.1 unit mg^{-1}, maltase grade II, crude, fungal, Sigma Chemical Co.) reagent powders in a glass mortar with 0.6 *M* acetate buffer, pH 5.1. Dilute to 100 ml with buffer and store under refrigeration. The reagent should be prepared daily and allowed to remain under refrigeration overnight before use.

Glucose standards. Any reagent-grade dextrose is weighed in amounts between 50 and 1500 mg as desired. The weighed samples are dissolved and made up to 100 ml in 0.02 *M* benzoate buffer, pH 5.5.

Maltose standards. A glucose-free maltose (Maltose Hydrate, Grade II, Sigma Chemical Co.) with an assay of less than 1% glucose is used to prepare maltose standards between 50 and 2000 mg%.

Sodium phosphate, 0.43 *M*. Dissolve 115 g of disodium hydrogen phosphate heptahydrate in distilled water and dilute to 1 l.

Versatol control sera. Both Versatol and Versatol-A (Warner-Chilcott, Morris Plains, N.J.) are prepared as directed and may be mixed to provide a set of control sera with different concentrations of glucose. For use in glucose analyses only, 0.5% sodium fluoride may be used to reconstitute the sera and provide stability for one week.

Procedures

The procedures for the determination of glucose have been described previously[2].

Procedure for the determination of maltose

Deproteinization step. Add 50 μl of serum or an aqueous maltose standard to 0.5 ml of barium hydroxide solution and mix. Add 0.5 ml of zinc sulfate reagent and shake to mix. Centrifuge for 5 min and remove a 0.5-ml aliquot by pipet for analysis. Transfer to a 30-ml beaker which is used as an incubation vessel and titration cell. When both glucose and maltose are present, a special procedure must be followed. For the determination of maltose alone, it is necessary to run a determination of maltose standards and the titer as well as the serum samples.

Incubation step. To the 0.5-ml aliquot from the deproteinization step, add 2 ml of composite reagent and 2 ml of the mixed glucose oxidase–maltase enzyme reagent and start timing the incubation period from this point. Cover the beaker with Parafilm and incubate for 1 h at 30° in a water bath.

Titration step. The electrodes are conditioned and the controls of the coulometer adjusted by two pre-titrations. To each of a pair of 30-ml beakers add 2 ml of composite reagent, 2 ml of enzyme reagent, 0.5 ml of distilled water, and 10 ml of sodium phosphate reagent. Rinse the electrodes with distilled water and fill the isolated compartment with sodium phosphate reagent.

Insert the electrode assembly into one of the beakers and titrate at a generation rate of 0.003 μeq sec^{-1}. Using a polarograph or other suitable means, impose a potential of 200 mV across the indicator electrodes and record the biamperometric current at a sensitivity of 0.006 μA mm^{-1}. The exact current used for the generation is not critical but a change in current will produce a corresponding inverse effect on the titration time. The titration is continued until the recorder pen rises 5 cm above the base line. The same fixed current rise is used for all titrations.

At the end of the 1-h incubation period, immediately remove the beaker from the water bath, add 10 ml of sodium phosphate solution, rinse the electrode assembly, and insert the electrodes into the beaker. Titrate all samples in the same manner as above. All samples should be titrated immediately after removal from the water bath. In addition to the titration of the samples and a standard, it is necessary to determine the titration time of the reagents alone; this is done by applying the entire procedure in the same manner as a blank.

The net titration time for each sample is the difference between the titration time of the tirer and the sample. Calculations are made with the following equation.

$$\begin{array}{l}\text{mg\% maltose}\\ \text{in sample}\end{array} = \frac{\text{net titration time of sample}}{\text{net titration time of standard}} \cdot \text{mg\% of standard maltose}$$

Other procedures

The Glucostat X4 Reagent kit from Worthington Biochemical Co. was used according to directions supplied by the manufacturer. Determinations of maltose were made with this reagent kit and the Sax and Trimble[6] modification of the Nelson–Somogyi[7] procedure for serum glucose.

RESULTS AND DISCUSSION

In order to determine the optimal amount of maltase required for a reasonable recovery of maltose, the following experiments were performed. A number of maltase and glucose oxidase solutions were prepared in pH 5.1 acetate buffer in concentrations such that when mixed, 2 ml of the resulting enzyme solution contained a fixed buffer concentration, a fixed activity of 300 units of glucose oxidase, and a variable number of units of maltase. Identical maltose solutions were determined with each of the resulting enzyme reagents in duplicate. Two units of maltase per sample resulted in a titer increase of 20% indicating the possible presence of an iodine-titratable substance in the maltase. A decrease in the amount of maltase used resulted in a decrease in this interference.

Table I summarizes the data obtained. The most desirable maltase concentration is the one which creates the smallest interferences, gives the best recovery of maltose as measured by titration times, and gives the most linear calibration curve for the various maltose standards used. A quantity of 0.125 units of maltase per sample proved optimal.

Subsequent work showed that the two enzymes could be triturated together with no detrimental effects. The procedure described in the *Experimental section* was

TABLE I

OPTIMAL CONCENTRATION OF MALTASE

(All samples and titers were determined in duplicate except * where 4 replicates were run. Average deviations given are the sum of the average deviations for the titer and the titration of the maltose sample. Conditions: 25 μl of maltose, 300 units of glucose oxidase, incubation at 30° for 1 h. The *m* value is the ratio of the net titration time to the concentration of maltose in the sample. The optimum value of maltase concentration is the one which produces the largest and most consistent *m* value for all the maltose samples)

Units of maltase	*Maltose concentrations*		
	51.4 *mg%*	96.0 *mg%*	148.8 *mg%*
	Net titration times and average deviations (sec)		
2.0	—	—	71.0±3.9 $m=0.477$
1.0	—	48.5±4.7 $m=0.505$	—
0.5	27.0±2.3* $m=0.526$	52.9±1.2 $m=0.530$	82.2±0.7 $m=0.552$
0.125	28.8±0.5* $m=0.561$	50.8±0.4 $m=0.530$	83.7±1.3 $m=0.563$
0.031	26.4±2.3 $m=0.514$	50.3±1.0 $m=0.524$	82.1±1.8 $m=0.552$

used for all other work. The mixed-enzyme reagent is stable for 2–3 days but daily preparation is recommended to avoid erratic results. The slope of the end-point current rise was investigated as a function of the presence of the enzymes and other reagents. The procedure described produces a negligible change in the end-point slope compared to the slope obtained in the generating electrolyte alone.

The optimal pH of the incubation mixture was investigated. Samples of 80 mg % maltose were analyzed in triplicate with mixed-enzyme reagents which differed only in the pH of the acetate buffer used to prepare the enzyme reagents. The pH values used were the actual measured values of the incubation mixture. A high incubation pH caused a slight increase in the pH of the final titration mixture. The optimum value for the mixed-enzyme reagent was a pH of 5.0 but there was little practical difference in using an incubation pH of 5.1. By selecting the latter pH, the same buffer solution might be employed to prepare both the glucose oxidase and the glucose oxidase–maltase enzyme reagents.

The recovery of 25-μl samples of 160 mg % maltose was next studied as a function of the length of the incubation period. The recovery of maltose increased with time and the shape of the curve was found to be similar to that which has previously been reported for glucose[2]. By using several different concentrations of maltose, a 1-h incubation period was selected to give the most linear calibration curve consistent with a high recovery of maltose.

A number of aqueous maltose standards were carried through the coulometric procedure. Table II summarizes data obtained on three consecutive days. The average

TABLE II

ANALYSIS OF MALTOSE STANDARDS BY THE COULOMETRIC PROCEDURE

(The net titration times are the averages for all results. The standard deviation (sec) is the value of the standard deviation of the titer plus the standard deviation of the maltose titrations. The *m* value is the ratio of the net titration time and the concentration of the sample. This value should be a constant)

Sample (mg %)	*Net titration times, m values, and standard deviations*		
	Day 1	*Day 2*	*Day 3*
50.0	30.0 $m=0.600$ S.D. = 1.0	26.2 $m=0.508$ S.D. = 1.4	26.0 $m=0.520$ S.D. = 1.2
99.8	55.0 $m=0.559$ S.D. = 1.7	52.2 $m=0.524$ S.D. = 1.3	52.5 $m=0.526$ S.D. = 1.6
149.9	80.3 $m=0.536$ S.D. = 2.8	77.2 $m=0.516$ S.D. = 1.6	78.1 $m=0.521$ S.D. = 1.1
200.4	107.4 $m=0.536$ S.D. = 2.0	104.8 $m=0.522$ S.D. = 1.8	103.9 $m=0.518$ S.D. = 2.0
Number of determinations	5	4	3

standard deviation of the net titration times was 1.6 sec. The generation current used for these particular titrations was slightly less than 0.5 mA. The recovery of maltose as calculated from the titrations averaged 42% of theory. Since the average recovery of glucose under these conditions is about 70%, the apparent conversion of maltose to glucose would appear to be about 60%. As may be seen from the data in Table II, the average recovery of maltose varies from day to day and this emphasizes the reason for including in the procedure an empirical standardization. The average deviation from the best straight line varied from 0.8 to 4% relative. These results may be compared with results obtained in the analysis of maltose standards by the modified Nelson–Somogyi procedure (Table III).

TABLE III

TYPICAL MALTOSE ANALYSES BY THE NELSON–SOMOGYI PROCEDURE

(25 μl of aqueous standard maltose were used but no deproteinization was performed)

Sample (mg %)	*Average absorbance*	*Replicates*	*σ (abs. units)*	*Net absorbance*	$Slope = \frac{A \cdot 1000}{mg\ \%\ maltose}$
Blank	0.041	2	0.003		
51.7	0.110	2	0.003	0.069	1.38
102.0	0.183	2	0.004	0.142	1.41
199.2	0.311	2	0.001	0.270	1.37
405.2	0.606	2	0.001	0.565	1.41
799.7	1.102[a]	2	0.009	1.061	1.32
1215	1.688[a]	2	0.002	1.647	1.36

[a] Final solution diluted to achieve a reasonable absorbance value. Correction factor applied to determine absorbance of the original solution.

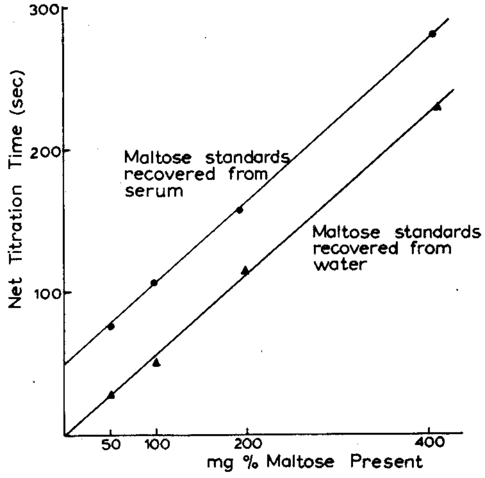

Fig. 1. Recovery of maltose from serum.

To evaluate the potential usefulness of the procedure for the determination of maltose in serum it was necessary to determine the recovery of maltose from serum. One set of maltose standards (50 μl of maltose plus 50 μl of water) was carried through the deproteinization step and the remainder of the procedure as above. Another set of maltose standards was added to Versatol control sera (50 μl of maltose plus 50 μl of Versatol) and treated in the same manner as the other samples. The results are shown graphically in Fig. 1. By comparing the slopes of the best straight lines for each set of data it was calculated that about 97% of the maltose could be recovered from Versatol. The two lines are displaced vertically by a distance corresponding to 92 mg% of glucose. This figure is just a few mg% higher than the known level of glucose in the Versatol control.

A study was undertaken to test the feasibility of using the two-enzyme reagent to determine both glucose and maltose in a mixture. The glucose oxidase reagent was found to give a significant response to maltose. A 1500-mg% maltose sample gave a response with glucose oxidase alone equivalent to a sample of 58.5 mg% glucose. While a small portion can be attributed to a glucose impurity in the maltose reagent, the majority of the response appeared to be due to some maltase activity in the glucose oxidase reagent.

TABLE IV

ANALYSIS OF GLUCOSE–MALTOSE MIXTURES

Sample	*Net titration time (sec)*	*σ (sec)*	$m = \frac{\text{Titration time}}{\text{Concentration}}$	*mg% found*
Titrations with glucose oxidase				
200 mg% glucose	180.6	1.3	0.903	—
1500 mg% maltose	105.8	3.5	0.074	—
Mixture of 100 mg% G and 200 mg% M	112.6	2.6	—	109 glucose 189 maltose
Mixture of 200 mg% G and 100 mg% M	187.8	2.6	—	200 glucose 105 maltose
Titrations with mixed-enzyme reagent				
200 mg% glucose	178.2	4.2	0.891	—
200 mg% maltose	177.4	3.6	0.887	—
Mixture of 100 mg% G and 200 mg% M	264.2	2.6	—	109 glucose 189 maltose
Mixture of 200 mg% G and 100 mg% M	270.0	3.8	—	200 glucose 105 maltose

Data from one set of analyses are shown in Table IV. Because of the maltose contribution to the titration times it was not possible to use any simple approach to the calculation of the maltose and glucose concentrations in admixture. Calculations were made by means of simultaneous linear equations,

$$0.903\ X + 0.074\ Y = \text{titration time in glucose oxidase}$$

$$0.891\ X + 0.887\ Y = \text{titration time in mixed-enzyme reagent}$$

where $X = \text{mg}\%$ of glucose and $Y = \text{mg}\%$ of maltose. Results were not as good as had been expected. It is suspected that the response of the glucose oxidase to maltose may be a function of the lot number of the glucose oxidase preparation as much better results were obtained with a different lot number of glucose oxidase.

The procedure has been designed to use 0.5-ml aliquots from the deproteinizing step; these aliquots contain between 10 and 100 μg of maltose or glucose. It is possible to use a different sample volume but the total volume of the sample, enzyme reagent, and composite reagent must be between 4.0 and 4.5 ml. A greater or lesser volume will result in curvature of the calibration curve. Thus a sample volume of 1 ml can be accommodated if the concentration of the enzyme reagents is doubled and the volume used is reduced to 1 ml.

The authors are indebted to the U.S. Army Medical Research & Development Command for partial support of this work under Contract No. DADA 17-67-C-7161.

SUMMARY

Maltose is commonly determined along with other reducing sugars in the classical saccharogenic procedures. In the proposed method maltase, an enzyme which hydrolyzes α-D-glucosides, is employed to hydrolyze maltose to glucose. The maltase is coupled with glucose oxidase which converts glucose to gluconic acid and hydrogen peroxide. The peroxide which is produced oxidizes iodide to iodine in the presence of molybdenum(VI). Iodine reacts with an excess of thiosulfate which is subsequently determined by titration with generated iodine.

Concentrations of maltose between 50 and 400 mg % may be determined in a sample size of 50 μl. Accuracy and precision are comparable to spectrophotometric procedures for maltose. A mixture of maltose and glucose may be determined using two enzyme preparations, but a considerably more complex procedure is required and results may be affected by the relative amount of glucose present.

RÉSUMÉ

On propose une méthode utilisant la maltase, enzyme permettant l'hydrolyse des α-D-glucosides, pour transformer le maltose en glucose. La maltose combinée à la glucose oxydase décompose le glucose en acide gluconique et peroxyde d'hydrogène. Ce dernier oxyde l'iodure en iode en présence de molybdène(VI). L'iode réagit avec le thiosulfate dont en titre l'excès par l'iode. On peut ainsi doser des concentrations en maltose de 50 à 400 mg % dans des échantillons de 50 μl. L'exactitude et la précision sont comparables à celles de la spectrophotométrie. Un mélange de maltose et de glucose peut être analysé, en utilisant deux préparations d'enzyme; mais la méthode est beaucoup plus compliquée et les résultats peuvent être affectés suivant la teneur en glucose.

ZUSAMMENFASSUNG

Maltose wird üblicherweise zusammen mit anderen reduzierenden Zuckern nach dem klassischen saccharogenen Verfahren bestimmt. Bei der vorgeschlagenen Methode wird ein Enzym verwendet, das α-D-Glucoside hydrolysiert, und zwar Maltase, die Maltose zu Glucose hydrolysiert. Die Maltase ist mit Glucoseoxidase gekoppelt, die Glucose in Gluconsäure und Wasserstoffperoxid umwandelt. Das gebildete Peroxid oxidiert Jodid zu Jod in Gegenwart von Molybdän(VI). Jod reagiert mit überschüssigem Thiosulfat, das darauf durch coulometrische Titration

mit Jod bestimmt wird. Maltosekonzentrationen zwischen 50 und 400 mg% können in einer Probengrösse von 50 μl bestimmt werden. Genauigkeit und Reproduzierbarkeit sind mit spektrophotometrischen Verfahren für Maltose wergleichbar. Ein Gemisch von Maltose und Glucose kann durch Verwendung zweier Enzympräparationen bestimmt werden; jedoch ist das Verfahren erheblich verwickelter, und die Ergebnisse können durch die relative Menge der vorliegenden Glucose beeinflusst werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

VOLTAMMETRY OF NEPTUNIUM(VI)–PROPIONATE COMPLEXES AT THE ROTATED GLASSY CARBON ELECTRODE*

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(Received 31st August 1970)

Many organic complexes of neptunium(VI) have been investigated in this laboratory[1–4] and elsewhere[5–8]. Propionic acid has not, however, been used as a complexing ligand for neptunium. In fact, the only investigation of the propionate complexes of the actinide elements has been limited to uranium[9]. This paper describes a voltammetric investigation of the neptunium(VI)–propionate complex at the rotating glassy carbon electrode.

EXPERIMENTAL

Apparatus

All voltammograms were obtained at 25° with a Sargent Model XXI recording polarograph. The applied potential was monitored by a Hewlett Packard Model DY-2401C integrating digital voltmeter. None of the measurements were damped. The electrolysis cell, the glassy carbon electrode (G.C.E.), the electrode mounting, and the cleaning of the electrode have been described[1,10].

The pH values of the solutions were measured using a Sargent Model DR pH meter and a glass electrode. The pH was adjusted with perchloric acid or sodium hydroxide.

The apparatus used for the conductometric and amperometric titrations have been described[3]. The viscosity values were obtained with a Gilmont falling-ball type viscosimeter (Cole-Parmer, U.S.A.).

Reagents

The preparation and standardization of the neptunium(VI) and the neptunium(V) stock solutions have already been described[4].

The sodium propionate stock solution was prepared by neutralizing propionic acid ('Baker Analyzed' Reagent) with an equivalent amount of sodium hydroxide.

All other chemicals were reagent grade and solutions were prepared in the usual manner. Purified nitrogen was used to deaerate the test solutions when necessary.

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* Work performed under U.S. Atomic Energy Commission Contract AT(29-1)-1106.

RESULTS AND DISCUSSION

Effect of pH

The effect of changes in acidity on the half-wave potential and on the limiting current of the neptunium(VI)–propionate complex was determined in solutions $5.89 \cdot 10^{-4}$ *M* in neptunium(VI), 1.00 *M* in sodium propionate, and 0.5 *M* in sodium perchlorate. The influence of the pH on the half-wave potential is clear from Fig. 1. The plot can be divided into three straight-line portions, corresponding to the pH ranges 0.1–1.7, 1.7–3.9, and 3.9–6.0. Above pH 6.0 the reduction wave become ill-defined.

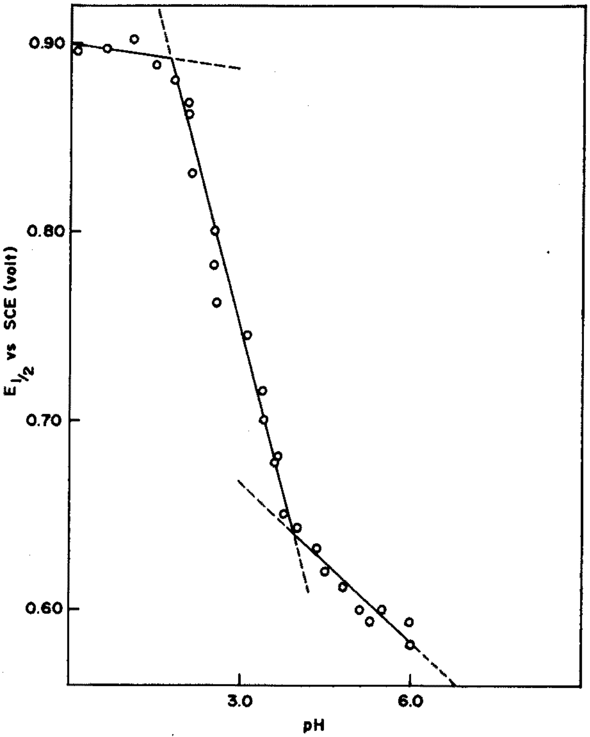

Fig. 1. Variation of the half-wave potential with pH: $5.89 \cdot 10^{-4}$ *M* neptunium(VI), 0.5 *M* $NaClO_4$, 1.00 *M* $NaC_3H_5O_2$.

In the pH range 0.1–1.7, the half-wave potential is essentially constant with the change of acid concentration, indicating that no hydrogen ions are involved in the reduction of neptunium(VI). The half-wave potential in this pH range averages 0.897 V *versus* the saturated calomel electrode (S.C.E.); this value is in good agreement with the potential reported for the reduction of the simple neptunium(VI) ion[10–12], which indicates that no complexation has taken place, or that the dissociation constant of neptunium(VI)–propionate is equal to the dissociation constant of neptunium(V)–propionate. Another indication that no complexation has taken place below pH 1.7 between the neptunium(VI) and the propionate ligand is that the pK_a of propionic acid is 4.87. Therefore, at pH 1.7 the concentration of the propionate ligand is less than 10^{-3} *M*, even when the formal concentration of sodium propionate is 1.0 *M*.

In the pH ranges 1.7–3.9 and 3.9–6.0, the half-wave potentials are a function of the pH. The respective slopes can be represented by the equations:

$$E_{\frac{1}{2}} = 1.085 - 0.114\ \text{pH} \tag{1}$$
$$E_{\frac{1}{2}} = 0.752 - 0.029\ \text{pH} \tag{2}$$

Equation (1) indicates that two hydrogen ions are involved in the reduction of one neptunium(VI) ion in the pH range 1.7–3.9. Equation (2) indicates that one hydrogen ion is involved in the reduction of two neptunium(VI) ions in the pH range 3.9–6.0.

Reversibility of the reduction of neptunium(V) in the pH range 0.1–6.0 was demonstrated by the value of the slopes for the plots of $E_{\text{R.G.C.}}$ *versus* log $i/(i_1 - i)$. The average value of these slopes was 0.0581 V which compares very well with the theoretical value of 0.0591 V for a one-electron reversible reduction. To confirm the reversibility of the electrode reaction, solutions were prepared which were $5.89 \cdot 10^{-4}$ *M* in neptunium(V), 0.5 *M* in sodium perchlorate, and 1.00 *M* in sodium propionate in the pH range 0.1–6.0. The neptunium(V) in these solutions was oxidized, and the half-wave potentials of the anodic and cathodic waves were compared (Table I). The values found were in good agreement, indicating that the electrode reduction of the neptunium(VI) in the pH range 0.1–6.0 at 1.00 *M* sodium propionate is reversible.

TABLE I

COMPARISON OF ANODIC HALF-WAVE POTENTIAL WITH CATHODIC HALF-WAVE POTENTIAL AT VARIOUS pH VALUES

($5.89 \cdot 10^{-4}$ *M* neptunium, 1.00 *M* $NaC_3H_5O_2$, 0.5 *M* $NaClO_4$)

pH	$(E_{\frac{1}{2}})_c$ *vs. S.C.E. (V)*	$(E_{\frac{1}{2}})_a$ *vs. S.C.E. (V)*
0.49	0.898	0.901
0.99	0.896	0.899
1.54	0.894	0.900
2.05	0.852	0.855
2.46	0.806	0.811
3.01	0.743	0.749
3.35	0.704	0.703
4.02	0.637	0.640
4.50	0.623	0.624
4.99	0.609	0.616
5.57	0.593	0.597
5.96	0.582	0.589

The effect of pH on the limiting current is shown in Fig. 2. The limiting current is independent of the pH in the pH range 0.1–3.9, which indicates that a complex species with a constant composition exists in this range. As the pH is increased above pH 3.9, the limiting current decreases, indicating competition between the hydroxyl ions and the propionate ions for the neptunium. Above pH 6.0 the reduction waves become ill-defined.

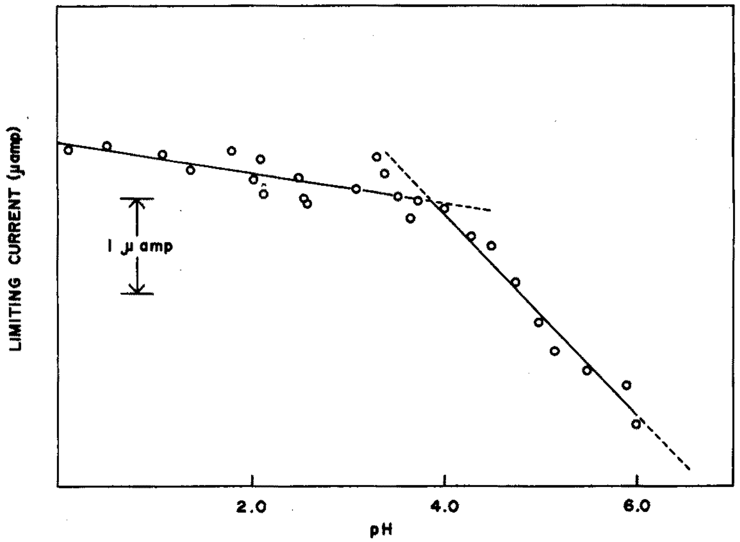

Fig. 2. Variation of the limiting current with pH: $5.89 \cdot 10^{-4}$ *M* neptunium(VI), 0.5 *M* $NaClO_4$, 1.00 *M* $NaC_3H_5O_2$.

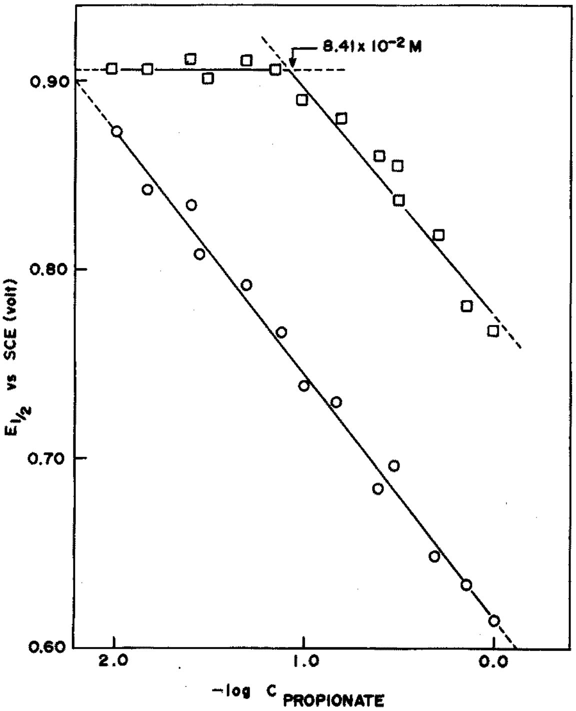

Fig. 3. Variation of half-wave potential with propionate concentration: $5.89 \cdot 10^{-4}$ *M* neptunium(VI), 0.5 *M* $NaClO_4$, (□) pH 2.80, (○) pH 4.80.

Effect of propionate concentration

The effect of changes in the sodium propionate concentration on the half-wave potential of the neptunium(VI)–propionate complex was determined in solutions $5.89 \cdot 10^{-4}$ *M* in neptunium(VI), 0.5 *M* in sodium perchlorate and at pH 2.80 and pH 4.80.

In the pH range 1.70–3.90 the half-wave potential is independent of the propionate concentration when the propionate concentration is less than $8.41 \cdot 10^{-2}$ *M* (Fig. 3). In the propionate concentration range $8.41 \cdot 10^{-2}$–1.00 *M*, the half-wave potential is a function of the propionate concentration.

When the concentration of the propionate is less than $8.41 \cdot 10^{-2}$ *M* at pH 2.80, the half-wave potential has an average value of 0.903 V *versus* S.C.E., which agrees very well with the potential reported for the reduction of uncomplexed neptunium(VI)[10–12]. This would indicate either that no complexation has taken place or that the dissociation constant of the neptunyl propionate complex is equal to the dissociation constant of the neptunium(V) propionate complex. It is more common for the dissociation constant of the oxidized complex to be less than that of the reduced complex. However, in this case, it appears likely at the lower ligand concentration that the dissociation constants of the oxidized complex and the reduced complex are nearly equal. This is borne out by the data below which indicated that the metal–ligand ratios at the lower ligand concentrations were 1 : 1 and 1 : 2. In the propionate concentration range $8.41 \cdot 10^{-2}$–1.00 *M* at pH 2.80, the slope of the plot is −0.122 V, which indicates that neptunium(VI) has twice the propionate ligands bound to it that neptunium(V) has.

Reversibility of the reduction of neptunium(VI) was demonstrated by the values of the slopes for the plots of log $i/(i_l - i)$ *versus* $E_{R.G.C.}$. The average value of these slopes in the propionate concentration range $1.0 \cdot 10^{-2}$–$8.41 \cdot 10^{-2}$ *M* was 0.0623 V, which is in reasonable agreement with the theoretical value for a one-electron

TABLE II

COMPARISON OF ANODIC HALF-WAVE POTENTIAL WITH CATHODIC HALF-WAVE POTENTIAL AT VARIOUS PROPIONATE CONCENTRATIONS AND AT pH 2.80 AND pH 4.80

($5.89 \cdot 10^{-4}$ *M* neptunium(VI), 0.5 *M* $NaClO_4$)

$NaC_3H_5O_2$ concn. (*moles* l^{-1})	*pH* 2.80		*pH* 4.80	
	$(E_{\frac{1}{2}})_c$	$(E_{\frac{1}{2}})_a$	$(E_{\frac{1}{2}})_c$	$(E_{\frac{1}{2}})_a$
	vs. S.C.E. (*V*)		*vs. S.C.E.* (*V*)	
$1.0 \cdot 10^{-2}$	0.904	0.904	0.875	0.875
$2.5 \cdot 10^{-2}$	0.907	0.900	0.835	0.824
$5.0 \cdot 10^{-2}$	0.905	0.902	0.793	0.785
$7.5 \cdot 10^{-2}$	0.902	0.902	0.767	0.762
0.10	0.891	0.897	0.739	0.747
0.25	0.859	0.848	0.686	0.695
0.50	0.816	0.812	0.651	0.656
0.75	0.781	0.789	0.634	0.633
1.00	0.766	0.775	0.614	0.617

reversible reduction. In the propionate concentration range $8.41 \cdot 10^{-2}$–1.00 M, the average value of the slopes was 0.0619, which is even closer to the theoretical value.

To confirm the reversibility of the electrode reaction, solutions were prepared which were $5.89 \cdot 10^{-4}$ M in neptunium(V) and 0.5 M in sodium perchlorate with various concentrations of propionate at pH 2.80. The neptunium(V) in these solutions was oxidized, and the half-wave potentials of the anodic and cathodic waves were found to be in good agreement (Table II). This indicates that the electrode reduction of the neptunium(VI) in the specified propionate concentration ranges is reversible.

At pH 4.80 the plot of the logarithm of the propionate concentration *versus* the half-wave potential (Fig. 3) showed that the half-wave potential is a function of the propionate concentration. In the propionate concentration range $1.00 \cdot 10^{-2}$–1.00 M, the slope of the plot is -0.129 V which would indicate that neptunium(VI) has two more ligands bound to it than does neptunium(V). Reversibility of the reduction of neptunium(VI) under these conditions was demonstrated by the value of the slopes for the plots of log $i/(i_l - i)$ *versus* $E_{R.G.C.}$. The average value of these slopes was 0.0643 V which is in fair agreement with the theoretical value. The reversibility of the electrode reaction was confirmed in the same way as at pH 2.80 (Table II).

Composition of the neptunyl–propionate complex

A conductimetric titration was used to determine the value of the metal–ligand ratio. The titrations were performed by diluting 5 ml of $14.73 \cdot 10^{-3}$ M neptunium(VI) solution to 340 ml with water and titrating the resultant solution with $29.46 \cdot 10^{-3}$ M sodium propionate solution. The titration curves (Fig. 4) show that when neptunium(VI) is in excess, the metal-to-ligand ratio of the complex formed is 1:1 and is 1:2 and 1:3 when the propionate is in excess.

To confirm the conductimetric results, amperometric titrations were per-

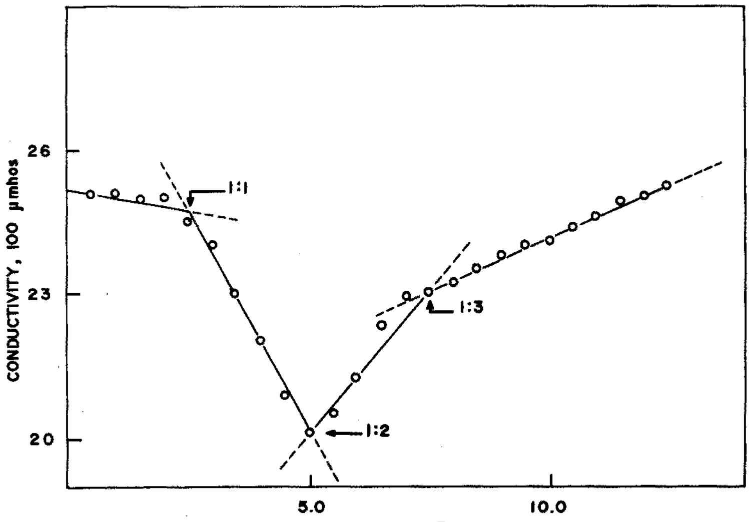

Fig. 4. Conductimetric titrations: 5 ml $14.73 \cdot 10^{-3}$ M-neptunium(VI), 335 ml water, $29.46 \cdot 10^{-3}$ M $NaC_3H_5O_2$.

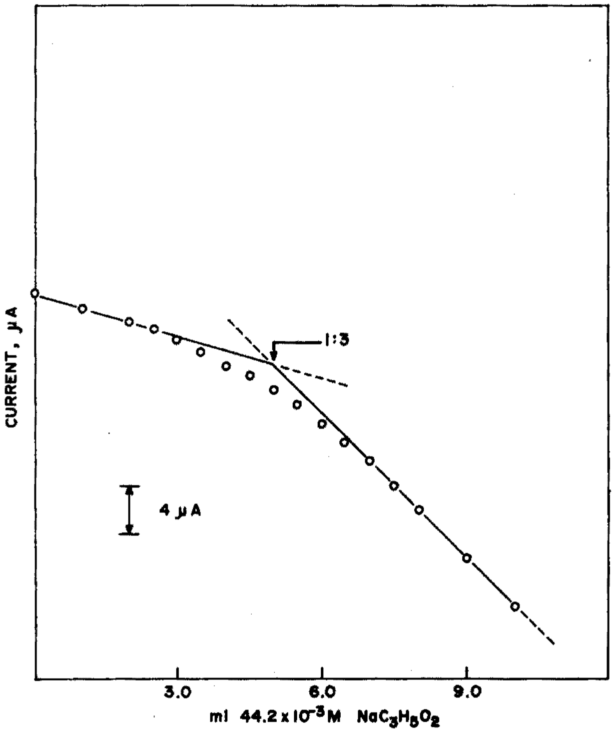

Fig. 5. Amperometric titrations: 5 ml $14.73 \cdot 10^{-3}$ M neptunium(VI), 10 ml 2.5 M $NaClO_4$, 10 ml water. $44.2 \cdot 10^{-3}$ M $NaC_3H_5O_2$ used as titrant.

formed. The solutions titrated contained 5 ml of $14.73 \cdot 10^{-3}$ M neptunium(VI) and 10 ml of 2.5 M sodium perchlorate and were diluted to 25 ml with water. The results of these titrations are shown in Fig. 5, and indicate only the maximum metal:ligand ratio which confirms the conductimetric results.

Electrode reactions

Based on the foregoing data and discussions, the electrode reactions are postulated as follows when the sodium propionate concentration is greater than $8.41 \cdot 10^{-2}$ M. The propionate ion is designated as A^-:

For $pH < 1.7$: $NpO_2^{2+} + e^- \rightarrow NpO_2^+$
For $pH > 1.7$ but < 3.9; $q = p - 2$: $NpO_2A_3^- + 2H^+ + e^- \rightarrow NpO_2A + 2HA$
For $pH > 3.9$ but < 6.0; $q = p - 2$:
$2NpO_2(OH)A_3^{2-} + H^+ + 2e^- \rightarrow 2NpO_2(OH)A^- + HA + 3A^-$

Diffusion coefficient

The diffusion coefficient of the neptunium(VI)–propionate complex was determined at 25° in solutions which were $5.89 \cdot 10^{-4}$ M ln neptunium(VI), 0.5 M in sodium perchlorate, 1.00 M in sodium propionate at pH 2.5 and 5.3, by means of equation[13]:

$$D^{\frac{1}{2}} = \frac{i_l v^{\frac{1}{2}}}{1.500 \cdot 10^5 n\, A C N^{\frac{1}{2}}}$$

where: i_l = limiting current (μA), v = kinematic viscosity, n = number of Faradays, A = electrode area (cm^2), C = concentration (mmoles l^{-1}), N = number of revolutions per sec.

The value for the diffusion coefficient was $0.56 \cdot 10^{-5}$ cm^2 sec^{-1} at pH 2.5, and $0.50 \cdot 10^{-5}$ cm^2 sec^{-1} at pH 5.5.

SUMMARY

The voltammetry of the neptunyl–propionate complex was investigated over varying conditions of ligand concentration and pH. A reversible one-electron wave was obtained in all propionate concentration ranges investigated over the pH range 0.0–6.0. The half-wave potential was independent of the pH in the range 0.0–1.7, but was a function of the pH in the ranges 1.7–3.9 and 3.9–6.0. The limiting current was independent of the pH in the range 0.0–3.9, but was a function of the pH above 3.9. The maximum metal : ligand ratio was found to be 1 : 3 by conductometric and amperometric titrations. The diffusion coefficient was $0.56 \cdot 10^{-5}$ cm^2 sec^{-1} at pH 2.5 and $0.50 \cdot 10^{-5}$ cm^2 sec^{-1} at pH 5.5.

RÉSUMÉ

Une étude est effectuée sur la voltammétrie du complexe neptunylpropionate, dans diverses conditions de concentration de "ligand" et de pH. On obtient une vague réversible à un électron pour toutes les concentrations de propionate examinées, entre les pH 0.0 à 6.0. Le potentiel de demi-vague est indépendant du pH de 0.0 à 1.7. Mais il varie entre les pH 1.7 à 3.9 et 3.9 à 6.0. Le courant limite est indépendant du pH de 0.0 à 3.9; mais il varie au-dessus du pH 3.9. Le rapport maximum métal : "ligand", trouvé par titrages conductométriques et ampérométriques, est de 1 : 3. Le coefficient de diffusion est de $0.56 \cdot 10^{-5}$ cm^2 sec^{-1}, au pH 2.5 et $0.50 \cdot 10^{-5}$ cm^2 sec^{-1}, au pH 5.5.

ZUSAMMENFASSUNG

Die Voltammetrie des Neptunyl–Propionat-Komplexes wurde bei verschiedenen Ligandkonzentrationen und pH-Werten untersucht. Bei allen Propionatkonzentrationen im pH-Bereich 0.0–6.0 wurde eine reversible Einelektronstufe erhalten. Das Halbstufenpotential war unabhängig vom pH-Wert im Bereich 0.0–1.7, es war jedoch eine Funktion des pH-Wertes in den Bereichen 1.7–3.9 und 3.9–6.0. Der Grenzstrom war unabhängig vom pH-Wert im Bereich 0.0–3.9, jedoch davon abhängig oberhalb 3.9. Durch konduktometrische und amperometrische Titration ergab sich ein maximales Metall : Ligand-Verhältnis von 1 : 3. Der Diffusionskoeffizient war $0.56 \cdot 10^{-5}$ cm^2 sec^{-1} bei pH 2.5 und $0.50 \cdot 10^{-5}$ cm^2 sec^{-1} bei pH 5.5.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ETUDE COMPAREE DES ULTRA-SONS ET DU SOXHLET DANS L'EXTRACTION DES HYDROCARBURES POLYCYCLIQUES ATMOSPHERIQUES

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(Reçu le 21 septembre 1970)

L'augmentation considérable, pendant ces dernières décennies, du nombre des appareils domestiques et industriels utilisant soit le charbon, soit, surtout actuellement, les dérivés du pétrole, a eu pour effet, l'augmentation corrélative de la pollution de l'atmosphère par les produits de combustion de ces sources d'énergie.

En particulier, le taux des hydrocarbures légers et lourds, de nature aliphatique ou polycyclique, en provenance essentiellement des essences et huiles lourdes s'est considérablement accru. Or, parmi ces hydrocarbures, il en existe qui appartiennent à la classe des hydrocarbures aromatiques polycycliques, susceptibles d'induire expérimentalement des cancers aux animaux de laboratoire.

Le taux de morbidité chez l'homme par cancer, et plus particulièrement par cancer broncho pulmonaire étant également en progression, on pouvait se demander si ce dernier n'était pas également induit par les hydrocarbures présents dans l'air environnant. C'est pourquoi de nombreux travaux ont été consacrés à l'analyse qualitative et quantitative de ces substances, dans le but essentiel de pouvoir estimer raisonnablement la toxicité d'un site donné (et ce, en particulier dans les grands centres urbains).

Une des étapes importantes de cette étude est donc l'extraction des substances organiques contenues dans le complexe organo-minéral que constituent les poussières atmosphériques.

D'une façon presque générale, l'extraction est réalisée actuellement à l'aide de solvants minéraux ou organiques spécifiques, au moyen d'un Soxhlet. Si le benzène est très souvent utilisé, d'autres solvants ont également été employés: l'acétone[1], le chloroforme[2], l'éther de pétrole[3], le mélange benzène–méthanol[4], le méthanol[5], la potasse alcoolique[6] ou l'acide acétique[7]. De plus pour Monkman[8], le chauffage des poussières atmosphériques en présence d'air, dégrade un certain nombre d'hydrocarbures polynucléaires. Cependant, après avoir essayé plusieurs solvants, cet auteur préconise l'utilisation du cyclohexane. L'*Organisation Mondiale de la Santé* devait d'ailleurs retenir ce mode d'extraction[9].

Cependant, lorsque l'échantillon initial est soluble dans un solvant organique, il est préférable d'utiliser un second solvant si l'on désire extraire les polynucléaires. Ainsi le couple *n*-heptane–diméthyl-sulfoxyde[10] donne de bons résultats; de même le mélange cyclohexane–méthanol à 90% additionné de 0.83% d'acide tétraméthylurique[11].

Ces méthodes d'extraction nécessitent cependant de trouver au préalable un solvant parfait de l'échantillon, ce qui est rarement possible. Leur emploi reste donc assez limité. Enfin, il a été mis en évidence[12] que les hydrocarbures adsorbés sur un support minéral sont particulièrement réactifs et sensibles à l'oxygène de l'air et à l'ozone qui se forme au cours des réactions photochimiques. L'extraction par des solvants portés à l'ébullition (surtout s'ils sont très polaires) risque donc d'introduire une modification et peut être un dégradation irréversible des hydrocarbures extraits.

Une méthode d'extraction à froid des hydrocarbures à partir des polluants atmosphériques paraissait donc souhaitable. C'est pourquoi nous avons fait appel aux *ultra-sons* dans le but de dissocier au maximum les poussières atmosphériques en leurs constituants organiques et minéraux. Les extractions ont été réalisées sur un lot de poussières homogènes. Elles ont été faites parallèlement à l'aide du Soxhlet, grâce aux ultra-sons, et par différents solvants. Un dosage du benzo(a)pyrène et des aromatiques totaux a été effectué dans tous les cas afin de pouvoir comparer la qualité des différentes méthodes.

PARTIE EXPÉRIMENTALE

Appareillage

Spectrophotomètre SP 800 B avec cuves de 1 cm; générateur d'ultra-sons: Sonic Oscillator Raythéon, Modèle DF-101 200 W, 10 Kc muni d'un dispositif de refroidissement; évaporateur rotatif Vapsilator; centrifugeuse Jouan, Modèle E.

Poussières atmosphériques

Elles proviennent d'un lot, prélevé dans la région Lyonnaise (France) à l'aide d'un nouveau collecteur à grand volume d'aspiration (1200 m^3 h^{-1}) mis au point par l'un de nous[13]. Le principe de cet appareillage repose sur le transfert, dans un très faible volume d'eau stérile et déminéralisée, des particules de 0.5 à 10 μm contenues dans un très grand volume d'air, environ $2 \cdot 10^7$ fois plus grand. L'eau est ensuite éliminée par lyophilisation.

Réactifs

Solvants. Ether éthylique, acétone, chloroforme, méthanol, benzène, cyclohexane (Prolabo), dichlorométhane (Merck).

Témoins. Fluoranthène, chrysène, benzo[*a*]pyrène, dibenz[*a,h*]anthracène (Eastman Organic Chemicals, Rochester 3, N.Y., U.S.A.), et benz[*a*]anthracène (Schuchardt, Münchenʳ Allemagne).

Réactifs pour le dosage. Pipéronal (héliotropine, méthylène-3,4-dioxybenzaldéhyde; Fluka, Buchs, Suisse), pentachlorure de phosphore (Prolabo), et acide trifluoroacétique (Schuchardt, München, Allemagne).

Constitution du réactif.* Le dosage du benzo[*a*]pyrène est réalisé grâce au test au pipéronal[14]. Le réactif utilisé est un mélange de 5 % de pipéronal (poids/volume) et de 6.8 % de pentachlorure de phosphore (poids/volume) dans du chloroforme. Il est

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* Il importe, lors de la constitution du réactif, de travailler sous hotte, le pentachlorure de phosphore étant très toxique. De plus, le mélange du pipéronal et du pentachlorure de phosphore donne lieu à une réaction exothermique favorisant le départ de vapeurs nocives.

utilisable immédiatement et sa durée de vie moyenne est de 4 h bien que nous ayons pu constater que son efficacité n'était que très légèrement diminuée au bout de 24 h.

Etalonnage du benzo[a]pyrène tèmoin

On prépare une solution de benzo[*a*]pyrène du commerce aux concentrations suivantes: 6 μg, 12 μg, 18 μg, 24 μg et 30 μg par ml de solvant. La coloration maximale est obtenue au cours du dosage, au bout de 5 min et la lecture au spectrophotomètre doit être faite dans la demi-heure qui suit.

Extraction des hydrocarbures polycycliques à partir des poussières atmosphériques

Par Soxhlet. Elle a toujours été faite sur 20 mg de poussières lyophilisées, dans 60 ml de solvant et pendant 8 h.

Par ultra-sons. 20 mg de poussières ont également été utilisées. En revanche, le volume de solvant, de même que la durée d'application des ultra-sons ont fait l'objet d'une étude particulière afin de déterminer les conditions optimales d'extraction à l'aide de ce procédé. Ainsi, des essais ont été réalisés avec 60 ml, puis avec 120 ml de solvant. Des extractions ont été effectuées après 15 min, 30 min, et 60 min d'ultra-sons.

Les conditions optimales ayant été ainsi définies, une étude systématique, comparative, entre Soxhlet et ultra-sons a été entreprise à l'aide de 7 solvants: ether éthylique (p.e. = 34°), dichlorométhane (p.e. = 40.1°), acétone (p.e. = 56.5°), chloroforme (p.e. = 61°), méthanol (p.e. = 64.7°), benzène (p.e. = 80°) et cyclohexane (p.e. = 81.4°).

Chaque extraction par ultra-sons a été suivie d'une centrifugation à 4000 r.p.m. pendant 15 min de façon à séparer les fractions minérale insoluble et organique soluble. Cette dernière a été ensuite évaporée à sec sous vide.

Dosage de l'échantillon

On prend 2 flacons de 10 ml. Dans le premier, on introduit 1 ml de chloroforme,

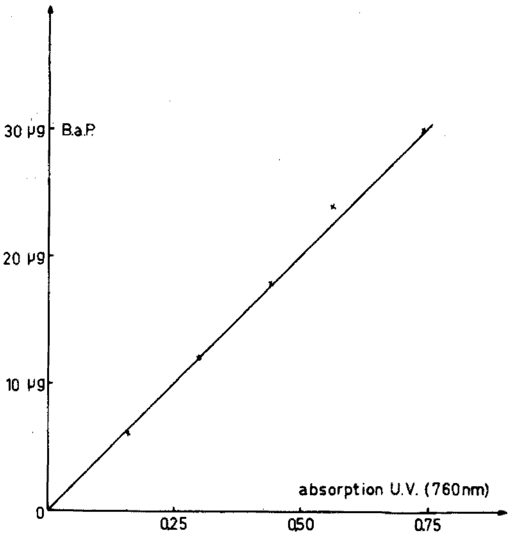

Fig. 1. Courbe d'étalonnage du benzo[*a*]pyrène.

contenant, en solution, le résidu d'extraction. Dans le second, on remplace la solution à analyser par 1 ml de chloroforme pur. Chaque flacon est alors complété à 10 ml en introduisant 1 ml de réactif et 8 ml d'acide trifluoroacétique. La lecture se fait au spectrophotomètre dans les mêmes conditions que celles données pour l'étalonnage. Le "blanc" est mis dans la cuve de référence et "l'échantillon" dans la cuve d'analyse.

RESULTATS ET DISCUSSION

Etalonnage du benzo[a]pyrène

La courbe représentative de ce dosage est une droite (Fig. 1).

Etude des conditions optimales d'extraction par ultra-sons

Elle est résumée dans le Tableau I. Il apparaît clairement que la meilleure extraction par ultra-sons est obtenue au bout de 30 min et dans un volume de solvant de 60 ml. Ce sont donc les conditions qui ont été retenues pour l'étude comparative Soxhlet–ultra-sons que nous allons envisager maintenant.

La prolongation de l'irradiation ultra-sonique au delà de 30 min n'apporte en effet aucune amélioration.

TABLEAU I

EFFET DE LA DURÉE DE L'IRRADIATION PAR ULTRA-SONS ET DU VOLUME DE SOLVANT UTILISÉ, SUR L'EXTRACTION DU BENZO[*a*]PYRÈNE ET DES AROMATIQUES TOTAUX

Extraction par ultra-sons	*Absorption*		*Poids de benzo[a]pyrène extrait (en µg) déduit de la courbe de référence (Fig. 1)*
	à 760 nm (benzo[a]pyrène)	*à 685 nm (aromatiques totaux)*	
15 min, 60 ml	0.56	1.24	22.6
30 min, 60 ml	0.64	1.46	26
60 min, 60 ml	0.64	1.34	26
15 min, 120 ml	0.54	1.18	22
30 min, 120 ml	0.53	1.18	21.6
60 min, 120 ml	0.54	1.22	22

TABLEAU II

ETUDE DE L'EXTRACTION DU BENZO(A)PYRENE ET DES AROMATIQUES TOTAUX PAR ULTRA-SONS DANS DIFFÉRENTS SOLVANTS

Solvants	*Absorption*		*Poids de benzo[a]pyrène extrait (en µg) déduit de la courbe de référence (Fig. 1)*
	à 760 nm (benzo[a]pyrène)	*à 685 nm (aromatiques totaux)*	
1. Ether éthylique	0.68	1.45	27.6
2. Dichlorométhane	0.64	1.50	26
3. Acétone	0.42	1.24	17
4. Chloroforme	0.70	1.45	28.4
5. Méthanol	0.42	1.06	17
6. Benzène	0.68	1.54	27.6
7. Cyclohexane	0.59	1.35	23.9

TABLEAU III

ETUDE DE L'EXTRACTION DU BENZO[*a*]PYRÈNE ET DES AROMATIQUES TOTAUX PAR SOXHLET DANS DIFFÉRENTS SOLVANTS

Solvants	*Absorption*		*Poids de benzo[a]pyrène extrait (en µg) déduit de la courbe de référence (Fig. 1)*
	à 760 nm (benzo[a]pyrène)	*à 685 nm (aromatiques totaux)*	
1. Ether éthylique	0.58	1.22	23.6
2. Dichlorométhane	0.64	1.34	26
3. Acétone	0.42	1.06	17
4. Chloroforme	0.57	1.18	23
5. Méthanol	0.52	1.20	21
6. Benzène	0.60	1.22	24.3
7. Cyclohexane	0.25	0.75	10

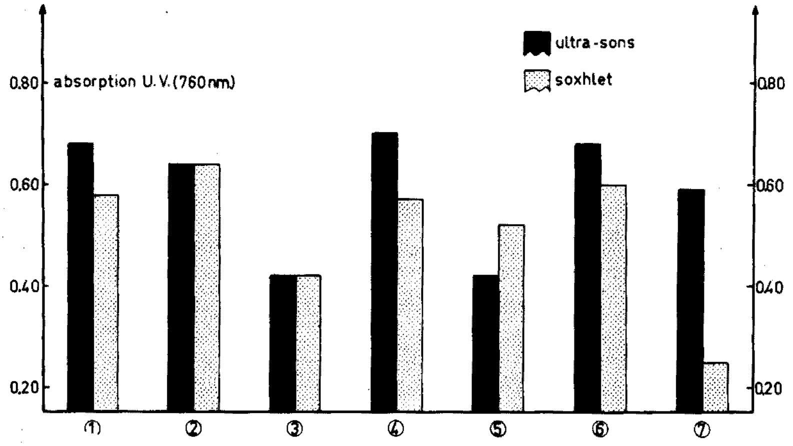

Fig. 2. Diagramme représentant les pics d'absorption à 760 nm du benzo[*a*]pyrène après extraction par ultra-sons ou Soxhlet, en fonction des différents solvants. (1) Ether éthylique, (2) dichlorométhane, (3) acétone, (4) chloroforme, (5) méthanol, (6) benzène, (7) cyclohexane.

Etude comparative de l'extraction par Soxhlet et par ultra-sons

Elle a été réalisée à l'aide de 7 solvants différents dont les points d'ébullition vont de 34° à 81.4°. Les résultats obtenus sont consignés dans les Tableaux II et III.

L'examen rapide des diagrammes correspondants (Figs. 2 et 3) montre qu'à part le méthanol, l'extraction par la méthode des ultra-sons est toujours la meilleure, aussi bien pour le benzo[*a*]pyrène (Fig. 2) que pour les aromatiques totaux (Fig. 3). Par ailleurs, 4 solvants semblent particulièrement efficaces, que l'extraction se fasse par Soxhlet ou par ultra-sons. Il s'agit, par points d'ébullition croissants, de l'éther, du dichlorométhane, du chloroforme et du benzène.

Plusieurs raisons nous font cependant préférer l'extraction par méthode physique:

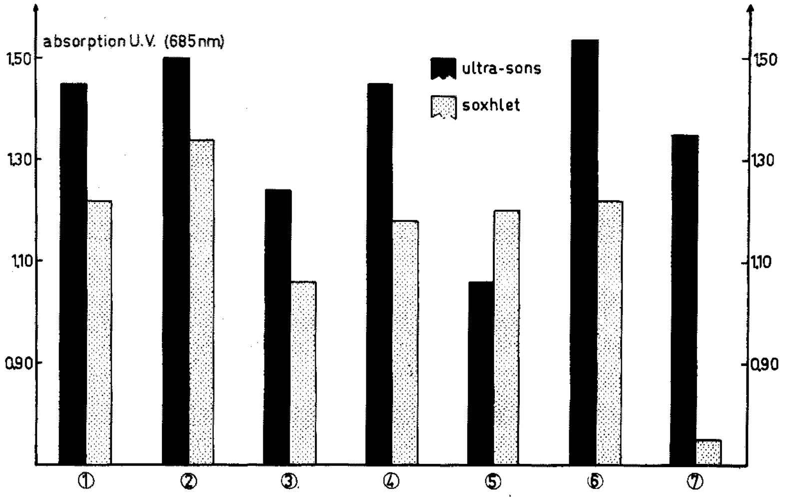

Fig. 3. Diagramme représentant les pics d'absorption à 685 nm des aromatiques totaux après extraction par ultra-sons ou Soxhlet, en fonction des différents solvants. Les chiffres ont la même signification que pour la Fig. 2.

la courte durée de l'opération. En effet, à l'aide du Soxhlet il est classique de poursuivre l'extraction pendant 8 h. Par ultra-sons, 30 min suffisent;

la faible température d'extraction (entre 0° et + 10°) alors qu'avec la technique du Soxhlet il est nécessaire de travailler à la température d'ébullition du solvant;

une extraction, dans la majorité des cas, meilleure grâce à ce procédé;

enfin la vérification, à l'aide d'hydrocarbures aromatiques témoins, qu'il ne se produit jamais de modification des spectres u.v. après traitement aux ultra-sons.

RÉSUMÉ

Une méthode d'extraction physique par ultra-sons des hydrocarbures atmosphériques est proposée et comparée à la méthode classique d'extraction par Soxhlet. Les résultats obtenus et les avantages du mode opératoire de l'extraction par ultra-sons nous font préférer cette technique.

SUMMARY

An ultrasonic method of extraction for atmospheric polycyclic hydrocarbons is described and compared with the classical Soxhlet extraction procedure. Extraction with ether, dichloromethane, chloroform or benzene is satisfactory; ultrasonic extraction is complete within 30 min compared to 8 h for Soxhlet extraction. Benz[*a*]pyrene and total aromatic hydrocarbons are determined.

ZUSAMMENFASSUNG

Es wird eine Ultraschallmethode zur Extraktion atmosphärischer polycyclischer Kohlenwasserstoffe beschrieben und mit dem klassischen Soxhlet-Extraktionsverfahren verglichen. Die Extraktion mit Äther, Dichlormethan, Chloroform oder Benzol ist zufriedenstellend. Die Ultraschallextraktion ist innerhalb 30 min vollständig, während die Soxhlet-Extraktion 8 h dauert. Es werden Benz[*a*]pyren und die gesamten aromatischen Kohlenwasserstoffe bestimmt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE EXTRACTION OF COMPLEX CYANIDES BY LIQUID ION EXCHANGERS

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(Received 17th September 1970)

Since the publication of the first review of the solvent extraction of inorganic complexes[1], much has been learnt concerning the many structural and physico-chemical factors involved. In particular, it has proved possible to formulate, and to justify experimentally, fairly comprehensive quantitative treatments of the liquid–liquid extraction of formally neutral metal chelates[2,3]. Even the synergic extraction of such neutral species can often be explained and handled quantitatively[4,5].

Problems posed by the extraction of acido-complexes are less amenable to any generalised treatment[6] in view of the more extensive interaction between the two phases both with each other and with the extractable species. However, much progress has been made in individual systems, notably those of special interest to the atomic energy industries. Whereas the extraction of ion-pairs can be handled quantitatively in particular instances[7], contemporary theory does not at present appear capable of predicting whether a given ion-pair will lend itself to extraction from water by a selected organic solvent, even when it may prove possible to predict which of a series of very closely related species would be most readily, and which least readily extractable. This hiatus in our knowledge can be illustrated by a specific example. It is generally accepted that the combination of a bulky cation with a bulky anion (of the same charge) to form a hydrophobic ion-pair is likely to favour partition equilibrium from water into a less hydrogen-bonded organic phase of suitable dielectric constant. The quantitative treatment turns on the lower energy required for 'hole-formation' in the organic solvent. Familiar examples are provided by the extraction of $(C_6H_5)_4As^+ReO_4^-$, $Fe(phenan)_3^{2+}\,(ClO_4^-)_2$, $N(C_6H_{13})_4^+\,Co(NH_3)_4\,(NO_2)_2^-$. There can, however, be surprises and disappointments. Isoelectronic with the stable sandwich compound ferrocene (bis-cyclopentadienyliron(II); $Fe(cpd)_2$) is the cobalticenium ion $Co(cpd)_2^+$ which, in view of its large bulk and high stability, might be considered a potentially useful cation for the extraction of bulky anions such as perchlorate, perrhenate or tetrachloroferrate(III). In practice, it was found that the cobalticenium salts of these anions were commonly more soluble in water than in chloroform[8]. Indeed, the perchlorate was so soluble in water that the saturated solution had the consistency of a thick syrup. The pronounced hydrophilic character found to be associated with such a large cation as $Co(cpd)_2^+$—which is considerably larger than, for example, caesium(I)—is certainly unexpected and it mitigates against its use in liquid–liquid extraction.

The use of long-chain quaternary ammonium ions (or salts of long-chain tertiary amines) is now well established in analytical chemistry where they have become familiar as liquid ion-exchangers. The large hydrophobic cations form ion-pairs which tend to be more soluble in organic solvents than in water and the following equilibrium is set up

$$n(\mathrm{NR_1R_2R_3R_4^+X^-})_{\mathrm{org}}+\mathrm{Y}^{n-} \rightleftharpoons ((\mathrm{NR_1R_2R_3R_4^+})_n\mathrm{Y}^{n-})_{\mathrm{org}}+n\mathrm{X}^- \qquad (1)$$

where $R_1R_2R_3$ are alkyl groups and R_4 is a hydrogen atom or an alkyl group: the subscript org is used to distinguish a species dissolved in the organic phase. What is not yet possible is to infer the position of equilibrium for a given pair of anions X^- and Y^{n-}. To phrase this more cogently, we are not yet in a position to say with certainty which of a series of anions will be capable of extraction by, *e.g.*, a solution of tetrahexylammonium chloride in dichloroethane and we cannot even hazard a guess at the magnitude of the extraction constant.

By using the 'hole-theory' as a guide, one would predict an increasing tendency to extract halide ions in the order of increasing size and decreasing hydrophobic character, *e.g.* $F^- < Cl^- < Br^- < I^-$. This is borne out by experiment. We have demonstrated elsewhere[8] the validity of the size sequence $Cl^- < ClO_3^- < ClO_4^-$ and have noted[9] the orders $ClO_4^- < IO_4^-$; $BF_4^- < PF_6^-$. The effect of changes in charge-type are even more striking as illustrated by $BeF_4^{2-} < BF_4^-$; $SiF_6^{2-} < PF_6^-$ and the difficulty of extracting sulphate, phosphate, hexacyanoferrate(II) and hexacyanoferrate(III)[9].

In the absence of any reliable theory, it was felt that there would be an advantage in collecting empirical data for a number of complex cyanides where a variety of charge-types and stereochemistry is possible, *e.g.* linear, singly charged $Ag(CN)_2^-$, tetrahedral doubly charged $Zn(CN)_4^{2-}$, square-planar, singly charged $Au(CN)_4^-$, square-planar doubly charged $Ni(CN)_4^{2-}$ and octahedral triply and quadruply charged $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$. In each case the structure is well known and the complex anions are so stable that complications arising from their dissociation in the aqueous phase can be neglected.

To compare the relative extractabilities the equilibrium constant, K_X, for the reaction

$$n(\mathrm{NR_4^+E^-})_{\mathrm{org}}+\mathrm{X}_n \rightleftharpoons ((\mathrm{NR_4^+})_{\mathrm{org}}+n\mathrm{E}^- \qquad (2)$$

was measured. Here R = *n*-hexyl and $E^- = Co(NH_3)_2(NO_2)_4^-$, the coloured anion of Erdmann's salt[10]. The position of equilibrium could be followed by taking a known amount of quaternary erdmannate dissolved in an organic solvent (usually hexone) and equilibrating this with an equal volume of an aqueous solution containing a soluble salt of the desired anion X^{n-} of known initial concentration. The equilibrium concentration of uncharged erdmannate in the organic phase $[NR_4^+E^-]_{org}$ and that of displaced erdmannate ions, $[E^-]$, in the aqueous phase were obtained spectrophotometrically.

That the above expression holds for the extraction of perchlorate ions ($X^{n-} = ClO_4^-$) by a solution of tetrahexylammonium erdmannate in a 20% hexone–80% xylene mixture has already been established[11]. The value $K_{ClO_4} = 1.7 \pm 0.2$ at 18° was derived for the equilibrium constant of the equation:

$$(\mathrm{NR_4^+E^-})_{\mathrm{org}}+\mathrm{ClO_4^-} \rightleftharpoons (\mathrm{NR_4^+ClO_4^-})_{\mathrm{org}}+\mathrm{E}^- \qquad (3)$$

These measurements have now been extended to solutions of the same quaternary ammonium salt in pure hexone at 18° where the initial concentration, $[NR_4^+E^-]_{tot}$ was varied from 0.0014 to 0.067 *M* and that of the perchlorate, $[ClO_4^-]_{tot}$ from 0.00165 to 0.1064 *M* (Table I). No attempt was made to control the ionic strength which will have varied in the range $I \sim 0.002$–0.11 *M*. A second series of measurements were carried out at 18°, 25° and 49° in which the ionic strength of the aqueous phase was maintained at 1.0 *M* by the addition of sodium sulphate which was shown, in independent measurements, not to displace the erdmannate ion (Table II).

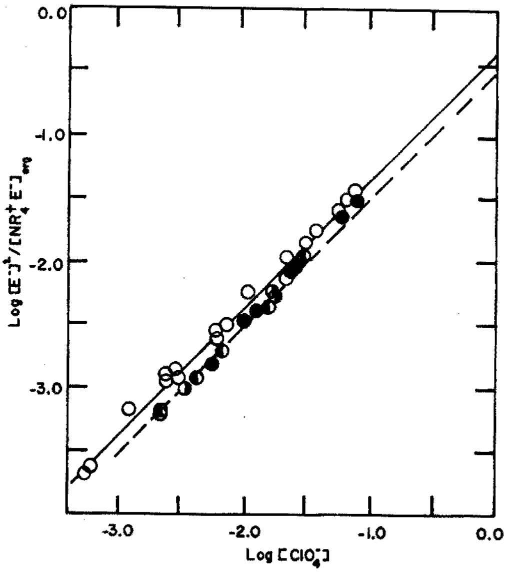
Since $[NR_4^+ClO_4^-]_{org} = [E^-]$ it follows that the equilibrium constant of eqn. (3) will be given by

$$K_{ClO_4^-} = [NR_4^+ClO_4^-]_{org}[E^-]/[NR_4^+E^-]_{org}[ClO_4^-]$$
$$= [E^-]^2/[NR_4^+E^-]_{org}([ClO_4^-]_{tot} - [E^-]) \quad (4)$$

whence

$$\log([E^-]^2/[NR_4^+E^-]_{org}) = \log K_{ClO_4} + \log([ClO_4^-]_{tot} - [E^-]) \quad (5)$$

The data of Tables I and II are shown plotted to conform with eqn. (5). In each case, the graph is linear and of the predicted unit slope, confirming the hypothesis that the partition equilibrium follows eqn. (3). The effect of increasing the ionic strength from the low variable range ($I \sim 0.002$–0.11 *M*) to the high value $I = 3.0$ *M* given by 1.0 *M* sodium sulphate has decreased the value of $\log K_{ClO_4^-}$ (the intercept at $\log [ClO_4^-] = 0$) from -0.33 to -0.47. If it is assumed that the activity coefficients of the ion-pairs $NR_4^+ClO_4^-$ and $NR_4^+E^-$ in the organic phase are very similar so that $\log (\gamma_{NR_4ClO_4}/\gamma_{NR_4E})_{org} \sim 0$, a full analysis of the situation shows that the difference of -0.14 between



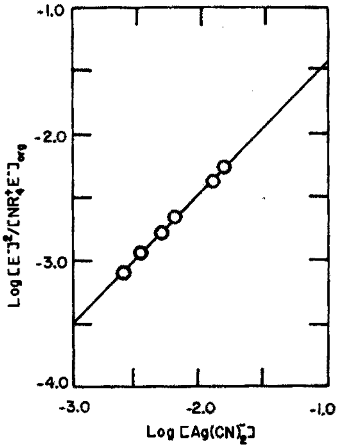


Fig. 1. The extraction of perchlorate ions by solutions of tetra-*n*-hexylammonium erdmannate in hexone. Open circles, variable ionic strength, equal phase volumes at 18°. Broken line, constant ionic strength $I = 3$ *M* (Na_2SO_4) with equal phase volumes at 18° (●), 25° (◑) and 49° (◐).

Fig. 2. The extraction of the anion $Ag(CN)_2^-$ by solutions of tetra-*n*-hexylammonium erdmannate in hexone at 25±1° and constant ionic strength $I = 3$ *M* (Na_2SO_4).

TABLE I

THE EXTRACTION OF PERCHLORATE IONS BY SOLUTIONS OF TETRA-*n*-HEXYLAMMONIUM ERDMANNATE IN HEXONE AT 18°

$10^4[NR_4^+E^-]_{org}$	$10^4[E^-]$	$10^4([ClO_4^-]_{tot}-[E^-])$	$K_{ClO_4^-}$
268.7	319.2	744.8	0.509
388.9	207.2	217.6	0.506
516.3	82.01	24.39	0.534
187.4	104.1	108.3	0.534
219.2	68.78	37.62	0.574
249.3	40.56	12.64	0.522
73.55	45.85	60.55	0.472
84.87	30.86	22.34	0.502
360.8	255.7	382.7	0.474
321.8	315.2	642.4	0.481
339.4	295.3	555.9	0.462
304.2	326.2	737.8	0.474
34.02	32.62	73.78	0.424
42.44	24.24	28.96	0.478
12.74	5.03	5.62	0.353
9.55	4.76	6.31	0.376
45.97	23.36	32.00	0.371
			Average 0.47 ±0.06

TABLE II

THE EXTRACTION OF PERCHLORATE IONS FROM AN AQUEOUS SOLUTION OF CONSTANT IONIC STRENGTH $I = 1$ *M* (Na_2SO_4) BY SOLUTIONS OF TETRA-*n*-HEXYLAMMONIUM ERDMANNATE IN HEXONE AT VARIOUS TEMPERATURES

Temp.	$10^3[NR_4^+E^-]_{org}$	$10^3[E^-]$	$10^2([ClO_4]^-_{tot}-[E^-])$	$K_{ClO_4^-}$
18°	33.24	32.05	7.44	0.415
	44.21	18.51	2.40	0.323
	30.77	29.97	7.64	0.382
	42.44	18.74	2.38	0.348
	33.38	27.33	5.78	0.387
	13.61	6.722	1.03	0.322
	16.97	8.266	1.30	0.310
	4.244	2.601	0.59	0.270
	2.193	1.147	0.23	0.269
				Average 0.34 ±0.05
25°	44.55	16.75	1.51	0.426
	41.02	14.82	1.76	0.306
	15.39	10.58	2.14	0.340
	4.668	6.436	2.55	0.348
	4.703	2.115	0.34	0.280
				Average 0.34 ±0.07
49°	8.206	4.078	6.56	0.309
	6.507	5.862	1.54	0.343
	4.951	6.877	2.50	0.382
	8.482	2.953	0.34	0.300
				Average 0.33 ±0.04

the two values of log $K_{ClO_4^-}$ can be explained by small differences in the two activity coefficients $\gamma_{ClO_4^-}$ and γ_{E^-} in the aqueous phase, owing to the latter ion having the larger radius. The value $K_{ClO_4^-} = 0.34 \pm 0.05$ is regarded as more reliable than the preliminary value[10] of 0.16 obtained with a mixture of 0.1 *M* sodium perchlorate and 0.9 *M* sodium sulphate. The absence of any marked temperature effect on the value of log $K_{ClO_4^-}$ implies an insignificant value for the entropy change, ΔS; this in turn is consistent with the absence of any change in the total number of the species in each phase upon equilibration (*cf.* eqn. (3)) and points to similar degrees of solvation in the species E^- and ClO_4^- (and $NR_4^+E^-$ and $NR_4^+ClO_4^-$) or to fortuitous compensatory changes. In this connection it is worth noting that the extraction of uranium(VI) by tri-*n*-octylammonium sulphate:

$$2((NR_3H^+)_2SO_4^{2-})_{org} + UO_2^{2+} + SO_4^{2-} \rightleftharpoons ((NR_3H^+)_4UO_2(SO_4)_3^{4-})_{org}$$

decreases by as much as 20–30% for every 10° rise in temperature. This is attributed to the net decrease in the number of species and a decrease in entropy during the extraction.

That the extraction of the uninegative dicyanoargentate(I), $Ag(CN)_2^-$, conforms to the equation

$$(NR_4^+E^-)_{org} + Ag(CN)_2^- \rightleftharpoons (NR_4^+Ag(CN)_2^-)_{org} + E^- \qquad (6)$$

is shown by the experimental results (Table III) which are shown in the form of a graph of log $([E^-]^2/[NR_4^+E^-]_{org})$ against log $([Ag(CN)_2^-]_{tot} - [E^-])$ in Fig. 2. The graph is linear and of the predicted unit slope. From the intercept, $K_{Ag(CN)_2^-} = 0.36 \pm 0.03$, which shows that this anion is extracted as readily as the perchlorate ion for which $K_{ClO_4^-} = 0.34 \pm 0.05$ under comparable conditions. Independent experiments showed that the cyanide ion does not displace erdmannate ions.

TABLE III

THE EXTRACTION OF DICYANOARGENTATE FROM 1 *M* SODIUM SULPHATE BY A SOLUTION OF TETRA-*n*-HEXYLAMMONIUM ERDMANNATE IN HEXONE AT 25±1°

$10^4[NR_4^+E^-]_{org}$	$10^4[E^-]$	$10^2[Ag(CN)_2^-]_{tot}$	$K_{Ag(CN)_2}$
49.50	52.36	2.08	0.356
164.4	82.67	2.08	0.332
76.38	41.00	1.04	0.349
65.07	33.06	0.83	0.336
32.54	15.94	0.42	0.420
6.08	8.47	0.42	0.352
			Average 0.36±0.03

A survey of the extraction of a number of complex cyanides was carried out, with the results shown in Table IV. For those species for which the net charge is −2 the equilibrium constant for the extraction equation

$$M(CN)_4^{2-} + 2(NR_4^+E^-)_{org} \rightleftharpoons ((NR_4^+)_2M(CN)_4^{2-})_{org} + 2E^- \qquad (7)$$

was calculated from the expression

$$K_{\mathrm{M(CN)^{2-}}} = [\mathrm{E}^-]^3/2[\mathrm{NR}_4^+\mathrm{E}^-]^2_{\mathrm{org}}[\mathrm{M(CN)}_4^{2-}] \tag{8}$$

It will be shown in a later paper[12] that with mercury the extraction of the (solvated) ion $\mathrm{Hg(CN)}_3^-$ plays an important role with $K_{\mathrm{Hg(CN)}_3^-} = 0.41$ as compared to $K_{\mathrm{Hg(CN)}_4^{2-}} = 0.008$.

TABLE IV

EXTRACTION CONSTANTS FOR COMPLEX CYANIDES FROM AQUEOUS SOLUTION AT 25 ± 1° BY AN EQUAL VOLUME OF TETRAHEXYLAMMONIUM ERDMANNATE IN HEXONE

Metal	*Anion, X^-*	*Extraction constant K_{X^-}*
Ag(I)	$\mathrm{Ag(CN)}_2^-$	$K_{\mathrm{Ag(CN)}_2^-} = 0.38$
Au(I)	$\mathrm{Au(CN)}_2^-$	$K_{\mathrm{Au(CN)}_2^-} = 15.8$
Au(III)	$\mathrm{Au(CN)}_4^-$	$K_{\mathrm{Au(CN)}_4^-} = 165 \pm 20^a$
Hg(II)	$\mathrm{Hg(CN)}_3^-$	$K_{\mathrm{Hg(CN)}_3^-} = 0.41$
Zn(II)	$\mathrm{Zn(CN)}_4^{2-}$	$K_{\mathrm{Zn(CN)}_4^{2-}} = 4.5 \cdot 10^{-4}$
Cd(II)	$\mathrm{Cd(CN)}_4^{2-}$	$K_{\mathrm{Cd(CN)}_4^{2-}} = 7.8 \cdot 10^{-4}$
Hg(II)	$\mathrm{Hg(CN)}_4^{2-}$	$K_{\mathrm{Hg(CN)}_4^{2-}} = 8.0 \cdot 10^{-4}$
Ni(II)	$\mathrm{Ni(CN)}_4^{2-}$	$K_{\mathrm{Ni(CN)}_4^{2-}} = 0.11 \cdot 10^{-4}$
Pd(II)	$\mathrm{Pd(CN)}_4^{2-}$	$K_{\mathrm{Pd(CN)}_4^{2-}} = 1.22 \cdot 10^{-4}$
Pt(II)	$\mathrm{Pt(CN)}_4^{2-}$	$K_{\mathrm{Pt(CN)}_4^{2-}} = 3.56 \cdot 10^{-4}$

[a] High extraction constants can only be measured with lower precision. The extraction of the species $\mathrm{Cu(CN)}_4^{3-}$, $\mathrm{Fe(CN)}_6^{3-}$ and $\mathrm{Fe(CN)}_6^{4-}$ and that of indium(III) from 1 *M* KCN was too small to be measured.

Copper(II) does not exist in anionic cyanide complexes since it is readily reduced. However, no copper(I) was extractable from a solution of copper(I) cyanide in excess potassium cyanide. This must be due to the triple negative charge on the species $\mathrm{Cu(CN)}_4^{3-}$, for it will be clear from Table III that the extraction of singly negatively charged ions is favoured over that of doubly negatively charged anions; the continuance of this trend is supported by the failure to extract any $\mathrm{Fe(CN)}_6^{3-}$ or $\mathrm{Fe(CN)}_6^{4-}$.

The adverse effect of an increase in anionic charge is very noticeable for the two square-planar species $\mathrm{Au(CN)}_4^{4-}$ and $\mathrm{Pt(CN)}_4^{2-}$ where the respective extraction constants decrease from 165 to $3.56 \cdot 10^{-4}$.

For ions of the same geometry and charge-type, there is a progressive increase in extractability with atomic number (and thus overall anionic volume). For example,

(i) linear ions $\mathrm{Ag(CN)}_2^- \ll \mathrm{Au(CN)}_2^-$;
(ii) tetrahedral ions $\mathrm{Zn(CN)}_4^{2-} < \mathrm{Cd(CN)}_4^{2-} \ll \mathrm{Hg(CN)}_4^{2-}$;
(iii) square-planar ions $\mathrm{Ni(CN)}_4^{2-} \ll \mathrm{Pd(CN)}_4^{2-} < \mathrm{Pt(CN)}_4^{2-}$.

The sequences can be justified by the 'hole-theory'. That tetrahedral ions are more readily extracted than comparable square-planar anions (*e.g.* $\mathrm{Zn(CN)}_4^{2-} > \mathrm{Ni(CN)}_4^{2-}$; $\mathrm{Cd(CN)}_4^{2-} > \mathrm{Pd(CN)}_4^{2-}$; $\mathrm{Hg(CN)}_4^{2-} > \mathrm{Pt(CN)}_4^{2-}$) again reflects the greater energy gain in transporting the more voluminous anion from water into the organic phase.

The much more favourable extraction of dicyanoaurate(I) as compared to dicyanoargentate(I) is unexpected in view of difference in anionic volume alone. Even though copper(I), silver(I) and gold(I) are similar to the extent of forming complexes of the type $\mathrm{M(CN)}_2^-$, both copper(I) and silver(I) are known to form three- and four-coordinate complexes whereas those of gold(I) are formed only with chelating agents such as diteriary arsines. This difference is ascribed by Nyholm[13] to the large *s–p* separation energy for gold(I) which tends to favour lower coordination numbers. If the dicyanoaurate(I) anion does not interact strongly with water for this reason, its ease of extraction can be rationalised.

Gold(III) presents an interesting case, for it only gives 4-coordinate, square-planar complexes such as $AuCl_4^-$. Iron(III) also gives 4-coordinate tetrahedral anions with halogens, *e.g.* $FeCl_4^-$, but with cyanide ions only the octahedral species $Fe(CN)_6^{3-}$ is formed, for the excess negative charge on the metal can here be removed by d_π–p_π bonding. Both gold(III) and iron(III) can be extracted by long chain amines from chloride media but only the former is extractable from aqueous cyanide.

Many cases are known where an unstable complex can be solvent-extracted, provided that it has favourable charge and size characteristics. The anion, tetraiodoindate(III), provides an excellent example[14]. Since indium(III) is very electropositive, its cyanide complexes are likely to be very unstable in aqueous solution and none have been reported. That the possible species $In(CN)_4^-$ does not exist, or at least has a negligible extraction coefficient, was shown by our failure to extract indium(III) labelled with the radionuclide 114-indium from a 1 *M* solution of potassium cyanide by a solution of tetrahexylammonium erdmannate in 1,2-dichloroethane.

From Table IV it can be shown that the extraction of 10^{-3} *M* metal by a 0.1 *M* solution of quaternary erdmannate would exceed 97% for silver and mercury and exceed 99.9% for gold(I) or (III). On the other hand the extraction of Zn, Cd, Hg, Ni, Pd, Pt and of Fe(II), Fe(III) and In(III) will be quite small and a number of valuable analytical separations become possible.

EXPERIMENTAL

The preparation of Erdmann's salt and of a solution of the quaternary ammonium erdmannate in hexone has already been described[11]. Pure salts of the desired complex cyanides were prepared by literature methods and their compositions were checked by analysis. $KAg(CN)_2$ formed shining white platelets (found Ag, 53.15; calc. 53.22%).

$KAu(CN)_4 \cdot H_2O$ was prepared from pure gold (found Au, 64.37; calc. 63.89%).

$K_2Zn(CN)_4 \cdot H_2O$ (found Zn, 24.61; calc. 24.77%).

$K_2Cd(CN)_4 \cdot H_2O$ (found Cd, 35.87; calc. 36.1%).

$K_2Hg(CN)_4$ (found Hg, 52.4; calc. 52.43%).

$K_2Pt(CN)_4 \cdot 12H_2O$ was prepared from K_2PtCl_6 after first reducing this to K_2PtCl_4 with sulphur dioxide (found Pt, 31.5; calc. 32.9%).

$K_2Ni(CN)_4 \cdot H_2O$ (found Ni, 22.64; calc. 22.68%).

$K_2Pd(CN)_4 \cdot H_2O$ (found Pd, 34.85; calc. 34.85%).

Solutions of the above complex cyanides were prepared by weighing out the required amount and dissolving in water or 1 *M* sodium sulphate. A solution containing $Cu(CN)_4^{3-}$ was obtained by dissolving a known weight of pure CuCN in a calculated small excess of potassium cyanide solutions. The procedure for equilibration and for measuring the concentration of erdmannate ion, $[E^-]$, in the aqueous phase and of unreacted quaternary erdmannate $[NR_4^+E^-]_{org}$ absorptiometrically is described elsewhere[12].

SUMMARY

The extraction of a number of complex cyanides from aqueous solution by solutions of tetrahexylammonium erdmannate in hexone is reported. High extractability is found for uninegative complexes of silver, gold(I), gold(III) and mercury(II): *viz.* $Ag(CN)_2^-$ (0.38), $Au(CN)_2^-$ (15.8), $Au(CN)_4^-$ (165 ± 20), $Hg(CN)_3^-$ (0.41), extraction constants being given in parentheses. Di-negatively charged species, such as $Zn(CN)_4^{2-}$ ($4.5 \cdot 10^{-4}$), $Cd(CN)_4^{2-}$ ($7.8 \cdot 10^{-4}$), $Hg(CN)_4^{2-}$ ($8 \cdot 10^{-4}$), $Ni(CN)_4^{2-}$ ($1.1 \cdot 10^{-5}$), $Pd(CN)_4^{2-}$ ($1.22 \cdot 10^{-4}$) and $Pt(CN)_4^{2-}$ ($3.56 \cdot 10^{-4}$) are poorly extracted and $Cu(CN)_4^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ and indium(III) could not be extracted at all from aqueous cyanides. These results are discussed in terms of the size and stereochemistry of the complex anions. The extraction of perchlorate ions and of the cyanoargentate(I) ion is shown to follow the theoretical equations with extraction constants $K_{ClO_4^-} = 0.34 \pm 0.05$ and $K_{Ag(CN)_2^-} = 0.36 \pm 0.03$ at $25 \pm 1°$ and $I = 3\ M$ (Na_2SO_4).

RÉSUMÉ

On examine l'extraction de cyanures complexes, en solution aqueuse, par des amines quaternaires à longue chaîne, dans l'hexone. Les constantes d'extraction sont données; $Cu(CN)_4^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ et indium ne peuvent pas être extraits dans ces conditions. L'extraction des perchlorates et du cyanoargentate(I) suit les équations théoriques avec des constantes d'extraction de $K_{ClO_4^-} = 0.34 \pm 0.05$; $K_{Ag(CN)_2^-} = 0.36 \pm 0.03$ à $25 \pm 1°$ et $I = 3$ M(Na_2SO_4).

ZUSAMMENFASSUNG

Es wird über die Extraktion einiger komplexer Cyanide aus wässriger Lösung durch Lösungen von Tetrahexylammoniumerdmannat in Hexon berichtet. Hohe Extrahierbarkeit wird für folgende einfach negative Komplexe von Silber, Gold(I), Gold(III) und Quecksilber(II) gefunden: $Ag(CN)_2^-$ (0.38), $Au(CN)_2^-$ (15.8), $Au(CN)_4^-$ (165 ± 20), $Hg(CN)_3^-$ (0.41); die Werte in Klammern sind die Extraktionskonstanten. Zweifach negativ geladene Spezies wie $Zn(CN)_4^{2-}$ ($4.5 \cdot 10^{-4}$), $Cd(CN)_4^{2-}$ ($7.8 \cdot 10^{-4}$), $Hg(CN)_4^{2-}$ ($8 \cdot 10^{-4}$), $Ni(CN)_4^{2-}$ ($1.1 \cdot 10^{-5}$), $Pd(CN)_4^{2-}$ ($1.22 \cdot 10^{-4}$) und $Pt(CN)_4^{2-}$ ($3.56 \cdot 10^{-4}$) werden schlecht extrahiert, und $Cu(CN)_4^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ und Indium(III) konnten aus wässrigen Cyanidlösungen überhaupt nicht extrahiert werden. Diese Ergebnisse werden in Zusammenhang mit Grösse und Stereochemie der Komplexanionen diskutiert. Die Extraktion von Perchlorat und Cyanoargentat(I) folgt den theoretischen Gleichungen mit den Extraktionskonstanten $K_{ClO_4^-} = 0.34 \pm 0.05$ und $K_{Ag(CN)_2^-} = 0.36 \pm 0.03$ bei $25 \pm 1°$ und $I = 3\ M$ (Na_2SO_4).

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE EXTRACTION OF MERCURY(II) AS CYANIDE COMPLEXES BY SOLUTIONS OF LONG-CHAIN QUATERNARY AMINES

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(Received 11th September 1970)

In the previous paper[1] it was noted that the tendency to extract tetracyano complexes of zinc, cadmium and mercury(II) by solutions of a tetrahexylammonium salt in hexone (methyl isobutyl ketone) increased in the order $Zn(CN)_4^{2-} < Cd(CN)_4^{2-} \ll Hg(CN)_4^{2-}$. Although one might have expected an increase in extractability with increasing atomic number (and hence volume of the complex anion) down elements of the same periodic group, the variation in the equilibrium constants for the reaction

$$M(CN)_4^{2-} + 2(NR_4^+E^-)_{org} \rightleftharpoons ((NR_4^+)_2M(CN)_4^{2-})_{org} + 2E^- \qquad (1)$$

(where M = Zn, Cd, Hg; R = *n*-hexyl; and $E^- = Co(NH_3)_2(NO_2)_4^-$) with $K_{Zn(CN)_4} = 4.5 \cdot 10^{-4}$, $K_{Cd(CN)_4} = 7.8 \cdot 10^{-4}$ and $K_{Hg(CN)_4} = 1.2 \cdot 10^{-2}$ invited further study.

The equilibrium constant for eqn. (1) (M = Hg) which will be designated as $\bar{K}_2$ was measured by equilibrating an aqueous solution of the salt $K_2Hg(CN)_4$ with an equal volume of a solution of tetrahexylammonium erdmannate in hexone and measuring absorptiometrically the concentration, $[E^-]$, of the brown erdmannate ion displaced into the aqueous phase and that of the extractant, $[NR_4^+E^-]_{org}$, remaining in the organic phase. Writing Q^+ for NR_4^+, the mass balances are as follows:
Total mercury

$$[Hg]_{tot} = [Hg(CN)_4^{2-}] + [Q_2^+Hg(CN)_4^{2-}]_{org}$$

Total erdmannate

$$[E]_{tot} = [Q^+E^-]_{org} + [E^-] \qquad (3)$$

Total quaternary ammonium ion

$$[Q]_{tot} = [Q^+E^-]_{org} + 2[Q_2^+Hg(CN)_4^{2-}]_{org} \qquad (4)$$

Since $[E]_{tot} = [Q]_{tot}$ we arrive at

$$\bar{K}_2 = [Q_2^+Hg(CN)_4^{2-}]_{org}[E^-]^2/[Hg(CN)_4^{2-}][Q^+E^-]_{org}^2$$
$$= [E^-]^3/(2[Hg]_{tot} - [E^-])[Q^+E^-]_{org}^2 \qquad (5)$$

Table I(a) shows experimental results for a series of measurements in which the total concentration of mercury remained the same while that of the extractant was varied systematically. The ionic strength was maintained at 1.0 *M* with sodium sulphate, preliminary experiments having shown that the sulphate ion did not displace

TABLE I

THE EXTRACTION OF MERCURY AS CYANIDE COMPLEXES FROM AQUEOUS SOLUTION ($I = 1.0$ M Na_2SO_4) AT 25 ± 1° BY AN EQUAL VOLUME OF TETRAHEXYLAMMONIUM ERDMANNATE IN HEXONE

(a) $[Hg]_{tot} = 0.01062$ *M and* $[Q]_{tot}$ *varied*

$10^4[E^-]$	$10^4[Q^+E^-]_{org}$	$10^3\bar{K}_2$	$\bar{K}_1$
20.72	60.82	12.6	0.43
13.22	17.68	37.2	0.46
12.34	13.97	48.2	0.48
9.92	10.75	41.8	0.39
9.59	8.63	58.5	0.45
9.17	7.07	76.1	0.50
8.20	5.80	80.4	0.48
8.16	5.94	76.6	0.47
8.04	6.08	68.9	0.44
5.38	2.40	130.8	0.47
5.00	2.40	104.8	0.44

(b) Both $[Hg]_{tot}$ *and* $[Q]_{tot}$ *varied*

10^4Hg_{tot}	$10^4[E^-]$	$10^4[Q^+E^-]_{org}$	$10^3\bar{K}_2$	$\bar{K}_1$
94.93	63.93	94.77	6.3	1.72
95.28	45.19	282.9	7.9	0.88
95.28	28.65	91.9	17.2	0.67
95.28	27.33	83.5	17.9	0.68
97.12	30.42	127.4	10.6	0.56
106.2	32.85	107.5	17.1	0.74
106.2	23.81	55.88	23.0	0.61
106.2	22.93	53.75	22.1	0.57
265.0	111.3	512.8	12.5	2.0
485.6	65.00	155.6	12.5	0.70
485.6	66.14	191.0	8.8	0.60
529.9	138.9	450.9	14.3	1.81
1214	63.93	94.77	12.3	0.55
1214	103.7	240.5	8.3	0.68
1214	154.3	441.1	8.3	1.05
1319	68.32	73.55	22.9	0.78
1324	189.5	486.3	11.7	0.67

erdmannate ions under the conditions used. The calculated values of $\bar{K}_2$ are not constant and show a marked tendency to increase as the ratio $[E^-]/[Q^+E^-]$ increases and as the amount of extractant is decreased. The inconstancy of $\bar{K}_2$ is confirmed by results shown in Table I(b) where the concentration of total mercury and total extractant were both varied over a wide range.

Clearly the extraction cannot be proceeding according to eqn. (1). Now, one peculiarity of complexes of mercury(II) with halides and pseudohalides such as cyanide is the sudden drop in the magnitude of the step-stability constants after the coordination of the second ligand. Thus for the system Hg^{2+}–CN^- we have[2] $\log K_1 = 18.0$, $\log K_2 = 16.7$, $\log K_3 = 3.83$ and $\log K_4 = 2.98$. This means that the dissociation of the complex anion when the potassium tetracyanomercurate(II) is dissolved in water, will give rise to negligible amounts of Hg^{2+}, $Hg(CN)_2^+$ and $Hg(CN)_2$, but there will be some uni-negatively charged tricyanide, $Hg(CN)_3^-$, formed in accordance with eqn. (6)

$$Hg(CN)_4^{2-} \rightleftharpoons Hg(CN)_3^- + CN^- \tag{6}$$

with an equilibrium constant of $10^{-2.98}$. Explicitly, the composition of a solution with $[Hg]_{tot} = 0.01062\ M$ will be $[Hg(CN)_4^{2-}] = 7.768 \cdot 10^{-3}$, $[Hg(CN)_3^-] = [CN^-] = 2.852 \cdot 10^{-3}$, pointing to extensive dissociation. Experience has shown that, *ceteris paribus*, uninegative ions are more strongly extracted than those with higher charges[1] and it might well be that the extraction of mercury is influenced or even dominated by the reaction

$$Hg(CN)_3^- + (Q^+E^-)_{org} \rightleftharpoons (Q^+Hg(CN)_3^-)_{org} + E^- \tag{7}$$

to which is ascribed an equilibrium constant $\bar{K}_1$. Equations (2) and (4) must therefore be extended as follows:

$$[Hg]_{tot} = [Hg(CN)_4^{2-}] + [Hg(CN)_3^-] + [Q_2^+Hg(CN)_4^{2-}]_{org} + [Q^+Hg(CN)_3^-]_{org} \tag{2a}$$

$$[Q]_{tot} = [Q^+E^-]_{org} + 2[Q_2^+Hg(CN)_4^{2-}]_{org} + [Q^+Hg(CN)_3^-]_{org} \tag{4a}$$

and a fourth condition, *viz.*, total cyanide

$$\begin{aligned}[CN]_{tot} = {} & [CN^-] + 4[Hg(CN)_4^{2-}] + 3[Hg(CN)_3^-] \\ & + 4[Q_2^+Hg(CN)_4^{2-}]_{org} + 3[Q^+Hg(CN)_3^-]_{org}\end{aligned} \tag{8}$$

must be added to eqn. (3). If it is postulated that $\bar{K}_2 = 0$, *i.e.* that the species $Hg(CN)_4^{2-}$ does not extract at all, the term $[Q_2^+Hg(CN)_3^{2-}]_{org}$ can be deleted from eqns. (2a), (4a) and (8). We then have from eqns. (3) and (4a)

$$[Q^+Hg(CN)_3^-]_{org} = [E^-] \tag{9}$$

and since $[CN]_{tot} = 4[Hg]_{tot}$, from eqns. (2a) and (8)

$$\begin{aligned}[CN^-] &= [Hg(CN)_3^-] + [Q^+Hg(CN)_3^-]'_{org} \\ &= [Hg(CN)_3^-] + [E^-]\end{aligned} \tag{10}$$

Substituting for $[CN^-]$ in eqn. (8) and remembering that

$$K_4 = [Hg(CN)_4^{2-}]/[Hg(CN)_3^-][CN^-], \tag{11}$$

we obtain

$$K_4[Hg(CN)_3^-]^2 + (1 + K_4[E^-])[Hg(CN)_3^-] - ([Hg]_{tot} - [E^-]) = 0 \tag{12}$$

a quadratic from which $[Hg(CN)_3^-]$ can be calculated.

$$\begin{aligned}\text{Hence } \bar{K}_1 &= [Q^+Hg(CN)_3^-]_{org}[E^-]/[Hg(CN)_3^-][Q^+E^-]_{org} \\ &= [E^-]^2/[Hg(CN)_3^-][Q^+E^-]_{org}\end{aligned} \tag{13}$$

can readily be computed. The results of such calculations are shown in Table I(a) and lead to $\bar{K}_1 = 0.46 \pm 0.03$. The data in Table I(b) point to a higher value of *ca.* 0.8 and it becomes obvious that the experimental data as a whole can only be interpreted if it is assumed that both the uninegative species $Hg(CN)_3^-$ and (to a lesser degree) the doubly charged anion $Hg(CN)_4^{2-}$ participate in the partition equilibria.

From eqns. (2a), (3), (4a), (8) and (11) in their extended form, it can be shown that

$$2K_4[CN^-]^2+(2+\bar{K}_1R)[CN^-]-(2[Hg]_{tot}-[E^-])(1+\bar{K}_1R)=0 \qquad (14)$$

$$\text{and } \bar{K}_2=\left\{\frac{([Hg]_{tot}-[CN^-])(1+\bar{K}_1R)}{K_4[CN^-]^2}-1\right\}/\ R^2 \qquad (15)$$

where $R=[Q^+E^-]_{org}/[E^-]$. By adopting the value $K_4=10^3$ for the stepwise formation of the species $Hg(CN)_4^{2-}$, values of $[CN^-]$ were calculated for each set of experimental results ($[Hg]_{tot}$, $[E^-]$ and R) by solving the quadratic eqn. (14) for an arbitrarily chosen value of $\bar{K}_1$. These values of $[CN^-]$ were then used to calculate the corresponding individual values of $\bar{K}_2$ from eqn. (15). The average value of $\bar{K}_2$ and its standard deviation for this arbitrary value of $\bar{K}_1$ was calculated for the combined data of Table I(a) and (b). The process was then repeated for different values of $\bar{K}_1$ with the results shown in Table II. The relative standard deviation, $\sigma/\bar{K}_2$, decreases sharply when $\bar{K}_1=0.30$ but there is no clearly defined minimum since there is no effective change when $\bar{K}_1$ is increased from 0.42 to 0.47. On the other hand, when arbitrary values of $\bar{K}_1>0.40$ are assigned, some calculated values of $\bar{K}_2$ are negative, which is physically meaningless. Clearly $\bar{K}_1$ is close to 0.4 and we adopt the values $\bar{K}_1=0.41$ and $\bar{K}_2=0.008$, results which confirm the greater tendency of the uninegative anion, $Hg(CN)_3^-$, to extract as compared to the doubly charged anion $Hg(CN)_4^{2-}$.

The fact that $Hg(CN)_3^-$ plays an important role in the extraction process can be demonstrated indirectly. Figure 1 displays the amount of mercury(II) extracted from mixtures of mercury(II) nitrate and potassium cyanide as measured by the amount

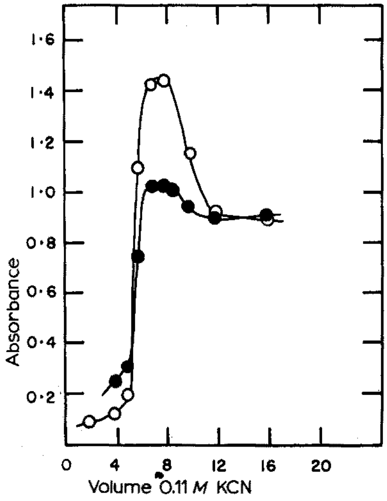


Fig. 1. The extraction of mercury(II) from aqueous potassium cyanide by solutions of tetra-*n*-hexylammonium erdmannate in (a) hexone (open circles) and (b) 1,2-dichloroethane (filled circles).

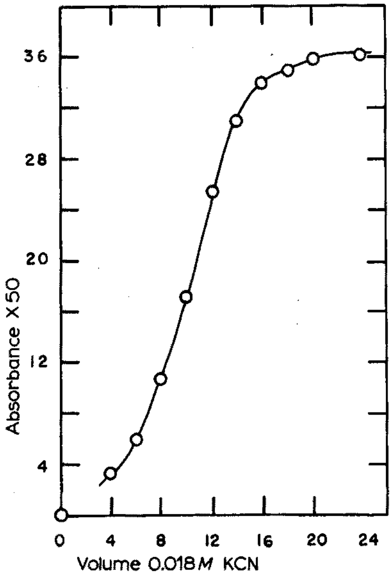


Fig. 2. The extraction of $2.08\cdot10^{-3}$ *M* cadmium(II) from aqueous potassium cyanide by an equal volume of tetrahexylammonium erdmannate in hexone.

TABLE II

CALCULATION OF THE VALUES OF K_1 AND K_2

Value assumed for K_1	*Calc. mean value for* $10^3 K_2$	*Standard deviation* $10^3\sigma$	σ/K_2	*Number of positive values*[a]
0.	37.2	35.6	0.96	28
0.10	34.7	34.8	1.00	28
0.20	25.0	24.6	0.98	28
0.30	16.3	14.4	0.88	28
0.40	8.1	5.8	0.72	28
0.41	8.2	5.4	0.66	26
0.42	7.8	4.4	0.56	25
0.43	7.1	3.9	0.55	25
0.44	6.3	3.4	0.54	25
0.45	5.7	3.1	0.54	25
0.46	5.2	2.7	0.52	24
0.47	4.8	2.5	0.52	23

[a] When K_1 was set at a value >0.4, the calculated value of K_2 became negative in 2 cases; the number of such negative values increased rapidly for K_1 >0.46.

of erdmannate ion displaced into the aqueous phase from a known constant excess of extractant, Q^+E^-, in the organic phase. The extraction increases rapidly as the ratio $[Hg^{2+}]:[CN^-]$ reaches 1:3, reaches a maximum at 1:4, then decreases and reaches a plateau when the ratio exceeds 1:6. These results are consistent with the successive formation of the species $HgCN^+$ and $Hg(CN)_2$ (no extraction) followed by $Hg(CN)_3^-$ (high extraction) and $Hg(CN)^{2-}$ (much lower extraction) when excess of cyanide is present. The behaviour should be compared with that of the system Cd^{2+}–CN^- (Fig. 2) where the concentration of displaced erdmannate increases monotonically with the ratio $[CN^-]/[Cd^{2+}]$.

Mercury(II) shows a strong tendency to retain a tetrahedral configuration in its complexes, and salts of the anion HgX_3^- often crystallize with one molecule of solvent. Thus $KHgCl_3$ forms a monohydrate and a monoalcoholate[3] and the main complex ion in a solution containing equimolar amounts of mercury(II) iodide and potassium iodide has been shown[4] to be $HgI_3(H_2O)^-$. It is not improbable, therefore, that the tricyanide should be formulated as $Hg(CN)_3(H_2O)^-$ and the presence of coordinated water should make this anion more hydrophilic and less readily extractable.

The above assumption is supported by results obtained by extracting mercury from an aqueous cyanide medium with solutions of tetrahexylammonium erdmannate in hexone or in dichloroethane (Fig. 1). Here the hexone, an oxygen donor solvent, can displace coordinated water to give a bulkier and less hydrophilic anion, $Hg(CN)_3$(hexone)$^-$, which should be more extractable than $Hg(CN)_3(H_2O)^-$. As shown in Fig. 1 the ratio of peak maximum to plateau, which can be regarded as a measure of the relative tendency to extract $Hg(CN)_3$(solvent)$^-$ and $Hg(CN)_4^{2-}$, is higher for hexone than for the non-coordinating chloroparaffin.

The preferential extraction of $Q^+(Hg(CN)_3\text{solvent})^-$ rather than $Q_2^+Hg(CN)_4^{2-}$ can also be regarded as demonstrating the greater stability of the former species in the organic phase, *i.e.* as demonstrating the tendency of the equilibrium

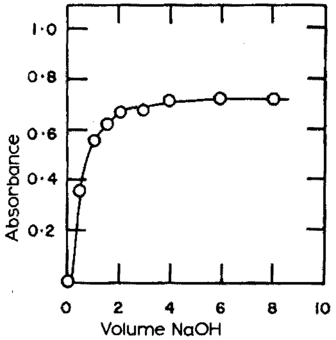
$$(Q_2^+Hg(CN)_4^{2-})_{org} \rightleftharpoons (Q^+Hg(CN)_3^-)_{org} + (Q^+CN^-)_{org}$$

to lie well to the right. It has certainly been shown by spectrophotometric and conductivity studies that in 10^{-3}–10^{-6} M solutions of $(NEt_4^+)_2\ HgI_4^{2-}$ in acetone, the mercury exists entirely as the anion HgI_3^- which is probably solvated[5].

Mercury(II) cyanide is soluble in water to the extent of *ca.* 11% but the solubility is increased by the presence of alkali halides and hydroxides. This has been attributed to the formation of anionic complexes $Hg(CN)_2X^-$ ($X=Cl$, Br, I, OH) whose existence is confirmed by infrared spectroscopy[6]. The possibility of extracting the uninegatively charged species $Hg(CN)_2(OH)^-$ according to the equation

$$(NR_4^+E^-)_{org} + Hg(CN)_2(OH)^- \rightleftharpoons (NR_4^+Hg(CN)_2(OH)^-)_{org} + E^- \qquad (16)$$

was examined experimentally with the results shown in Fig. 3. Unlike the results shown in Fig. 1, the amount of extraction (as measured by the concentration of erdmannate ions displaced into the aqueous phase) increases rapidly as one equivalent of alkali is added but there is no subsequent decrease in the presence of excess alkali, indicating the absence of such species as $Hg(CN)_2(OH)_2^{2-}$. This confirms infrared studies[6] which establish the existence of $Hg(CN)_2(OH)^-$ as the unique complex in solutions of mercury(II) cyanide in sodium hydroxide. Independent studies[1] have shown that hydroxyl ions do not displace erdmannate ions under these experimental conditions.



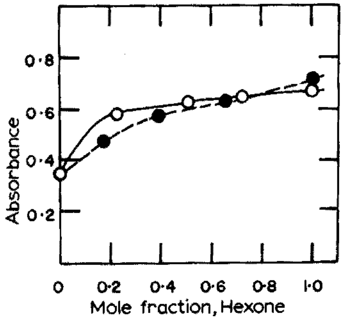


Fig. 3. The extraction of mercury(II) cyanide from aqueous solutions of sodium hydroxide by a solution of tetrahexylammonium erdmannate in hexone.

Fig. 4. The extraction of mercury(II) cyanide from 0.08 M sodium hydroxide by 0.01 M solutions of tetra-*n*-hexylammonium erdmannate in (a) mixtures of hexone and benzonitrile (open circles), and (b) hexone and dichloroethane (filled circles, broken line).

It is to be expected that the species $Hg(CN)_2(OH)^-$ would complete a tetrahedral structure by coordinating one molecule of a unidentate donor molecule. If so a synergic effect would be expected when the water in $Hg(CN)_2(H_2O)(OH)^-$ is replaced by a less hydrophilic donor. Such an effect is demonstrated by studies of the extraction of the species $Hg(CN)_2(OH)^-$ into mixtures of the donor solvent hexone with inert solvents such as dichloroethane or benzonitrile shown graphically in Fig. 4.

EXPERIMENTAL

The preparation of Erdmann's salt and of a solution of quaternary *n*-hexylammonium erdmannate in an organic solvent has already been described[7]. Hexone (methyl isobutyl ketone), dichloroethane and benzonitrile used in the present work were fractionated before use.

Preparation of $K_2Hg(CN)_4$

The solution obtained by concentrating a mixture of mercury(II) chloride with a slight excess of potassium cyanide deposited white platelets of the desired complex which were recrystallized from water (found Hg, 52.4; calc. for $K_2Hg(CN)_4$ 52.4%).

Procedure for equilibration

A stock solution of 0.1062 *M* $K_2Hg(CN)_4$ was prepared by weighing out the dried salt into a 1 *M* solution of sodium sulphate to give a final constant ionic strength of 3 *M*. This solution (2 ml) was equilibrated with 2 ml of quaternary erdmannate by shaking for 15 min in a thermostat at 25.0±0.1°. After centrifugation the absorbance of the erdmannate ion was measured in each phase (after appropriate dilution) at 353 nm. The blank for the organic phase was pure organic solvent; for the aqueous phase the blank was obtained by equilibrating the organic solution of the quaternary erdmannate with an equal volume of 1 *M* sodium sulphate solution. The concentrations of erdmannate in each phase, $[E^-]$ and $[Q^+E^-]_{org}$ were calculated by using the appropriate molecular absorptivities[7]. Results are given in Table I.

Extraction of mercury(II) nitrate from aqueous cyanide

Portions (2 ml) of 0.11 *M* mercury(II) nitrate were mixed with *x* ml of 0.11 *M* potassium cyanide and the volume made up to 25 ml before equilibration at 25±1° with an equal volume of tetrahexylammonium erdmannate in hexone. Absorbances (*A*) were measured after 25-fold dilution.

x(ml)	2	4	5	6	7	8	12	16	20
A	0.09	0.12	0.20	1.10	1.42	1.44	0.92	0.88	0.80

Corresponding measurements with a solution of the quaternary erdmannate in 1,2-dichloroethane gave the following results:

x(ml)	2	4	5	6	7	8	10	12	16	20
A	0.24	0.24	0.30	0.74	1.02	1.02	0.94	0.90	0.90	0.90

The extraction of cyanohydroxy complexes of mercury(II)

Portions (2 ml) of 0.1099 *M* mercury(II) cyanide and *x* ml of 0.1191 *M* sodium hydroxide were made up to a total of 10 ml and equilibrated at 25±1° with an equal volume of 0.01 *M* quaternary ammonium erdmannate. The aqueous phase was diluted 50-fold before measuring its absorbance, *A*, at 353 nm.

x(ml)	0.5	1.0	1.5	2.0	3.0	4.0	6.0	8.0
A	0.36	0.56	0.63	0.68	0.68	0.72	0.72	0.71

Similar extractions were carried out with mixtures of hexone and dichloroethane or benzonitrile.

(*a*) *Hexone and dichloroethane*

Mole fraction, hexone	0.00	0.17	0.39	0.65	1.00
A (353 nm)	0.33	0.43	0.56	0.63	0.71

(*b*) *Hexone and benzonitrile*

% hexone (v/v)	0	25	50	75	100
A (353 nm)	0.34	0.58	0.63	0.65	0.68

We are indebted to Dr. P. Gans for his invaluable assistance with computing problems. One of us (A.D.D.) thanks the Colombo Plan Authorities and the Atomic Energy Establishment, Trombay, India, for financial assistance.

SUMMARY

The equilibration of an aqueous solution of the salt $K_2Hg(CN)_4$ with one of tetra-*n*-hexylammonium erdmannate in hexone is shown to lead to the extraction of mercury(II) as the anion $Hg(CN)_4^{2-}$ and to a still greater extent as the uninegative species $Hg(CN)_3^-$. The respective equilibrium constants are $\bar{K}_2 = 0.008$ and $\bar{K}_1 = 0.41$. The species $Hg(CN)_3^-$ is probably solvated and its extraction is greater from the donor solvent hexone than from 1,2-dichloroethane; the extraction of $Hg(CN)_4^{2-}$ is not significantly altered by this change in solvent. The mixed anion $Hg(CN)_2(OH)(\text{solvent})^-$ is shown to be extracted from solutions of mercury(II) cyanide in sodium hydroxide. Hexone synergically enhances the extractability by solutions of tetrahexylammonium erdmannate in benzonitrile or dichloroethane.

RÉSUMÉ

On examine l'extraction du mercure(II) sous forme de $K_2Hg(CN)_4$, au moyen d'amines quaternaires à longue chaîne, dans l'hexone. Le mercure est extrait comme $Hg(CN)_4^{2-}$ et $Hg(CN)_3^-$ avec les constantes d'équilibre respectives de $K_2 = 0.008$ et $K_1 = 0.41$. L'anion mixte $Hg(CN)_2(OH)(\text{solvant})^-$ est extrait de solutions de cyanure de mercure(II) dans l'hydroxyde de sodium.

ZUSAMMENFASSUNG

Aus einer wässrigen Lösung des Salzes $K_2Hg(CN)_4$ wird durch eine Lösung von Tetra-*n*-hexylammoniumerdmannat in Hexon Quecksilber(II) als Anion $Hg(CN)_4^{2-}$ und in noch grösserem Masse als einfach negatives Anion $Hg(CN)_3^-$ extrahiert. Die zugehörigen Gleichgewichtskonstanten sind $\bar{K}_2 = 0.008$ und $\bar{K}_1 = 0.41$. Das Anion $Hg(CN)_3^-$ ist wahrscheinlich solvatisiert; es wird durch das Donor-Lösungsmittel Hexon besser extrahiert als durch 1,2-Dichloräthan; die Extraktion von $Hg(CN)_4^{2-}$ wird durch diesen Wechsel des Lösungsmittels wenig beeinflusst. Das gemischte Anion $Hg(CN)_2(OH)(\text{solvient})^-$ wird aus Lösungen von Quecksilber(II)-cyanid in Natriumhydroxid extrahiert. Hexon erhöht synergetisch die Extrahierbarkeit duch Lösungen von Tetrahexylammoniumerdmannat in Benzonitril oder Dichloräthan.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

UNTERSUCHUNGEN ÜBER DIE EXTRAKTION VON THORIUM, BLEI UND EISEN(III) ALS VERBINDUNGEN DER CAPRONSÄURE

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(Eingegangen den 10. September 1970)

In einer Übersichtsarbeit wurde über die Möglichkeit der Extraktion von verschiedenen Metallionen mit Vertretern der homologen Reihe der Carbonsäuren von C_3 bis C_{10} unter Verwendung von Chloroform als Extraktionsmittel berichtet[1]. Dabei konnte gezeigt werden, dass sowohl der Kreis der mit den einzelnen Carbonsäuren extrahierbaren Metallionen, wie auch das Ausmass der Extrahierbarkeit im Allgemeinen, mit der Länge der Kohlenstoffkette zunimmt. Ein ähnliches Verhalten wurde bereits früher in der Reihe aliphatischer Arsinsäuren aufgefunden[2]. Bei den Carbonsäuren hat Buttersäure bereits in Verbindung mit Chloroform als Extraktionsmittel eine quantitative Extraktion des Thoriums ermöglicht[3]. Nunmehr sollte zu Vergleichszwecken die Thoriumextrahierbarkeit mit Capronsäure ermittelt, und auch die Extrahierbarkeit von weiteren gut extrahierbaren Metallionen anderer Wertigkeit bearbeitet werden.

EXPERIMENTELLER TEIL

Das Reagens Capronsäure kam stets in Form seiner Chloroformlösung zur Anwendung. Die Reagenslösung wurde durch Lösen von 3.75 g reiner Capronsäure mit p.A. Chloroform zu 250 ml hergestellt.

Allgemeine Arbeitsweise

Sowohl bei Thorium wie auch bei Blei und Eisen(III) wurde im wesentlichen die gleiche Arbeitsweise eingehalten, die bei den einzelnen Metallen nur den jeweils vorliegenden speziellen Extraktionsbedingungen angepasst wurde. Im Folgenden wird darauf noch im Einzelnen eingegangen werden.

In einen Schütteltrichter von 200 ml Inhalt mit Schliffstopfen wurden die wässerigen, sauren, Metalllösungen eingebracht und auf ein Volumen von 80 ml verdünnt. Hierauf erfolgte der Zusatz von 20 ml Reagenslösung mit nachfolgendem kräftigen Schütteln zur Gleichgewichtseinstellung der Capronsäure. Nach Lüften des Schliffstopfens, unter entsprechendem Abspülen mit reinem Chloroform, konnte der pH der wässerigen Lösung mit verdünntem Ammoniak auf den jeweils günstigsten Wert eingestellt werden. Hierauf erfolgte neuerliches kräftiges Schütteln mit nachfolgendem Lüften und Abspülen des Stopfens. Nach Trennen der Schichten wurde die untere metallhaltige Chloroformschicht in einen Titrierkolben abgelassen und Hahnbohrung sowie Rohransatz des Schütteltrichters mehrmals portionsweise mit reinem Chloroform nachgespült.

Bei den quantitativen Extraktionen erfolgte noch eine zweimalige Nachextraktion mit je 10 ml Reagenslösung, wobei in der gleichen Weise, wie zuvor geschildert, verfahren wurde. Ein Nachstellen des pH-Wertes der wässerigen Lösung bei den Nachextraktionen war in den meisten Fällen notwendig.

Nunmehr erfolgte unter Beigabe einiger Glaskugeln zur Vermeidung von Siedeverzügen das Abdestillieren des Chloroforms der vereinigten Extrakte aus den Titrierkolben in einer geeigneten einfachen Apparatur. Das Erhitzen wurde dabei so lange fortgesetzt bis auch die zum Schluss zurückbleibende geringe Menge Capronsäure fast vertrieben war.

Das Lösen der Abdampfrückstände geschah hierauf mit verdünnten Säuren, Thorium und Blei mit Salpetersäure und Eisen mit Salzsäure, in der Hitze. Nach Verdünnen mit Wasser konnte die Bestimmung der extrahierten Metalle mit einer Masslösung von Äthylendiamintetraazetat nach den üblichen Vorschriften erfolgen. Bei Blei und Eisen traten durch die noch vorhandenen geringen Mengen Capronsäure keinerlei Schwierigkeiten ein, lediglich bei Thorium musste nach dem Verdünnen mit Wasser so lange gekocht werden, bis kein Geruch von Capronsäure mehr festzustellen war.

pH-Abhängigkeit der Extraktionen

Bereits in der eingangs zitierten Arbeit[1] wurde in groben Zügen ein Überblick über die Beziehungen zwischen Extraktionsausmass und pH-Wert gegeben. Die Feststellung der genauen Lage der besten pH-Werte erfolgte unter Verwendung von 20 ml Reagenslösung mittels einmaliger Extraktion aus wässeriger Lösung. Die Tabelle I gibt die erhaltenen Werte sowie das Extraktionsausmass an.

TABELLE I

OPTIMALER EXTRAKTIONS-pH-WERT UND RELATIVES EXTRAKTIONSAUSMASS

Metallion	*Bester pH-Wert*	*Extraktionsausmass* (%)
Th^{4+}	6.5	88
Pb^{2+}	7.6	98
Fe^{3+}	5.5	85–95

In allen Fällen tritt bei dieser Arbeitsweise eine mehr oder weniger starke Bildung von Niederschlagsteilen auf, die sich bei der Extraktion an der Phasengrenzfläche sammeln und auch bei den Nachextraktionen hartnäckig bestehen bleiben. Dies kann jedoch, unter gleichzeitiger Erhöhung des Extraktionsausmasses, vermieden werden, wenn man in die wässerigen Metallsalzlösungen Zusätze von Natriumnitrat bzw. Methanol gibt. Bei Thorium war bei Zusatz von 5 g festem Natriumnitrat zu den angegebenen 80 ml wässerigen Volumens bereits bei der Erstextraktion mit 20 ml Reagenslösung eine praktisch vollständige Extraktion zu erreichen. Bei Blei und Eisen bleibt ein Zusatz von Natriumnitrat wirkungslos, doch kann die Extraktionsausbeute, im Zusammenhang mit der Verringerung der Niederschlagsbildung, wesentlich verbessert werden, wenn der wässerigen Lösung Methanol zugesetzt wird. Praktisch vollkommen ist die Extraktion, wenn sich in 80 ml wässerigen Volumen 40 ml Methanol befinden. Aus dieser 50%ig methanolischen Lösung ist auch bei Blei und Eisen bereits die Erstextraktion quantitativ, was man besonders im Falle des Eisens bereits visuell gut erkennen kann.

Unter Einbeziehung dieser Arbeitsvariationen ergeben sich die folgenden besten Extraktionsmethoden der untersuchten Metallionen.

Thoriumextraktion

Die salpetersaure Thoriumlösung wird unter Zusatz von 5 g Natriumnitrat auf 80 ml verdünnt. Nach Zusatz von 20 ml Reagenslösung erfolgt gegen Spezialindikatorpapier Merck die Einstellung des pH auf den Wert von 6.5. Nach Durchführung der Erstextraktion wird aus Sicherheitsgründen noch zweimal mit je 10 ml Reagenslösung nachextrahiert.

Blei- und Eisenextraktion

Die salpeter- bzw. salzsaure Metallionenlösung wird unter Zusatz von 40 ml p.A. Methanol auf 80 ml verdünnt. Nach Zugabe von 20 ml Reagenslösung wird der pH mit verdünntem Ammoniak gegen Spezialindikatorpapier Merck auf 7.5 bzw. 5.5 eingestellt. Auch in diesen Fällen extrahiert man aus Sicherheitsgründen noch zweimal mit je 10 ml Reagenslösung nach.

Beispiele für Einzelextraktionen nach den angegebenen Arbeitsvorschriften sind in der Tabelle II zusammengestellt.

TABELLE II

EXTRAKTIONSBEISPIELE AUS REINLÖSUNGEN DER METALLSALZE

Metallion	*Gegeben(mg)*	*Gefunden(mg)*
Th^{4+}	22.6	22.5
		22.7
	45.2	45.4
		45.4
	116.0	116.2
		115.9
	232.0	232.0
		232.0
Pb^{2+}	10.7	10.7
		10.6
	42.8	42.8
		42.9
	85.8	85.8
		85.8
	413.8	414.0
		413.8
Fe^{3+}	9.9	9.9
		10.0
	29.8	29.8
		29.9
	49.8	49.7
		49.6
	99.5	99.3
		99.4

Wie man aus den Ergebnissen ersehen kann, verläuft die Extraktion durchaus zufriedenstellend. Die auftretenden Fehler sind nicht so sehr auf die Extraktion als auf die bei den massanalytischen Bestimmungsmethoden auftretenden Tropfenfehler zurückzuführen.

Trennungsmöglichkeiten

Nach der bereits eingangs zitierten Arbeit[1] sollte die Abtrennung der Metallionen Th^{4+}, Pb^{2+} und Fe^{3+} von einer ganzen Reihe begleitender Metallionen möglich sein. Dies trifft im Falle des Thoriums, wo der wässerigen Lösung lediglich Natriumnitrat zugesetzt wurde, auch weitgehend zu. Bei Blei und Eisen hingegen werden

TABELLE III

BEISPIELE FÜR EXTRAKTIVE ABTRENNUNG

Metall-ion	*Geg. (mg)*	*Gef. (mg)*	*Begleit-metall*	*Geg. (mg)*	*Gef. (mg)*
Th^{4+}	113.2	113.2	Ca	34.7	34.8
		113.3			34.9
	113.2	113.2	Ca	1200	—
		113.3			
	113.2	113.1	Mg	20.1	20.1
		113.2			20.0
	113.2	113.2	Mg	1600	—
		113.2			
	113.2	113.2	Sr	49.8	50.0
		113.1			50.1
	113.2	113.1	Sr	1600	—
		113.3			
	113.2	113.2	Ba	70.0	70.0
		113.1			70.1
	113.2	113.3	Ba	1200	-
		113.3			
	113.2	113.2	Cd	60.5	60.5
		113.3			60.4
	113.2	113.3	Cd	1000	—
		113.3			
Pb^{2+}	107.0	107.0	Ba	100.0	99.8
		106.8			—
	107.0	106.9	Sr	99.7	99.9
		106.8			—
	107.0	107.0	Sr	1600	—
		107.3			
Fe^{3+}	29.9	29.9	Ba	70.0	70.0
		29.9			—
	29.9	29.8	Ba	600	—
		29.8			—
	29.9	29.8	Sr	49.9	49.6
		29.9			49.7
	29.9	29.9	Sr	800	—
		29.9			—

die Trennungsmöglichkeiten durch den Zusatz des Methanols, der zur Erreichung einer quantitativen Extraktion von Blei und Eisen erforderlich ist, stark verringert. Im selben Umfang wie durch den Methanolzusatz die Extraktion von Blei und Eisen zunimmt, nimmt auch die Extrahierbarkeit einer ganzen Reihe von anderen Ionen zu, die aus rein wässeriger Lösung nicht extrahiert werden können. So kann Thorium ausser von den Erdalkalien auch von Magnesium und Cadmium und, wenn keine sehr hohe Trenngenauigkeit erforderlich ist, auch von Nickel, Kobalt und Zink abgetrennt werden. Blei und Eisen(III) hingegen lassen sich nur von Strontium und Barium abtrennen, allerdings bis zu einem sehr hohen Verhältnis. Einen Überblick gibt die Tabelle III.

UNTERSUCHUNGEN ZUR KENNTNIS DER ZUSAMMENSETZUNG DER MIT CHLOROFORM EXTRAHIERBAREN METALLVERBINDUNGEN

Um Verbindungen zu erhalten, die hinsichtlich ihrer Löslichkeit in Chloroform, wie auch ihrer Zusammensetzung, untersucht werden können, wurden Fällungspräparate hergestellt. Dazu wurden die Metallionen in saurer Lösung mit einem berechneten ausreichenden Überschuss an Capronsäure versetzt und durch Alkalisieren gefällt. Um die benötigte Menge Capronsäure in Lösung zu halten, war es notwendig, dem Fällungsvolumen Alkohol zuzusetzen. Auf diese Weise ähnelte die Fällungslösung stark den Extraktionslösungen. Die erhaltenen Niederschläge wurden abgesaugt und sehr gründlich ausgewaschen. Nachdem sie bei Zimmertemperatur zur Konstanz getrocknet waren, erfolgten die einzelnen Untersuchungen.

Neben den Analyse auf Metallgehalt, Kohlenstoff und Wasserstoff, wurde noch das Molekulargewicht, die Löslichkeit in Chloroform und die thermogravimetrische Zersetzungskurve aufgenommen. Die erhaltenen Ergebnisse konnten mit theoretisch berechneten Werten für die mögliche Zusammensetzung verglichen werden. Die Tabelle IV gibt die Analysenergebnisse sowie die erhaltenen Molekulargewichte an.

Alle drei hergestellten Präparate waren in Chloroform sehr gut löslich. Die Thorium- und Bleiverbindung lösten sich ohne Rückstand, während bei der Eisenverbindung ein geringer Teil ungelöst blieb. Von der Eisenverbindung wurde daher nur die in Chloroform leicht lösliche Substanz der Analyse unterzogen, während die Thorium- und Bleiverbindung unmittelbar der Analyse zugeführt wurden.

Die bei einer Temperaturzunahme von 4° pro Min in Luft aufgenommenen

TABELLE IV

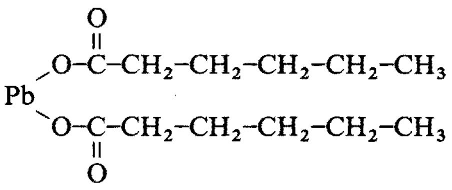
ZUSAMMENSETZUNG UND MOLEKULARGEWICHT DER CAPRONATE DER METALLE

Metall	*Metallgehalt* (%)	*Kohlenst.* (%)	*Wasserstoff* (%)	*Molekulargewicht*
Th	49.2	27.4	4.49	8640
	49.1	27.3	4.56	
Pb	47.7	33.2	5.02	150
	47.6	33.4	5.03	
Fe	34.5	31.6	5.22	3180
	34.6	31.5	5.28	

thermogravimetrischen Gewichtsverlustkurven zeigen bei der Thorium- und Bleiverbindung ein sehr ähnliches Verhalten. Die Thoriumverbindung bleibt gewichtsstabil bis 200°, nimmt dann an Gewicht rasch ab, und wird ab etwa 300° zum Oxyd, welches bei weiterer Temperatursteigerung wieder leicht an Gewicht zunimmt. Die Bleiverbindung ist gewichtsstabil bis 275°, verliert dann rasch an Gewicht und erreicht ab 370° das konstant bleibende Gewicht des Bleioxydes. Von der präparativ hergestellten Eisenverbindung der Capronsäure wurde sowohl das Grundpräparat wie auch die aus dem Chloroformextrakt gewonnene, in Chloroform rückstandsfrei lösliche, Verbindung untersucht. Das Grundpräparat verliert bereits ab 60° langsam an Gewicht und erreicht erst ab etwa 500° das konstant bleibende Gewicht des entsprechenden Eisenoxydes. Die in Chloroform leicht lösliche Verbindung bleibt gewichtsstabil bis 150°, verliert dann an Gewicht und erreicht ab 300° das endgültige Gewicht des entsprechenden Eisenoxydes. Es ist aus diesem Befund, sowie aus dem gesamten Verhalten bei der Extraktion, zu schliessen, dass es sich bei der Thorium- und Bleiverbindung der Capronsäure um wasserfreie Verbindungen handelt, während im Falle des Eisens mehr oder weniger basisches Eisencapronat vorliegt.

In Verbindung mit der Analyse, der Molekulargewichtsbestimmung und dem gesamten Verhalten bei der Extraktion werden daher für die Metallverbindungen der Capronsäure die folgenden Formeln vorgeschlagen.

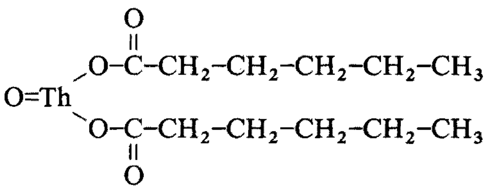
Bleiverbindung



$$\mathrm{Pb}\begin{cases}\mathrm{O{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}\\ \mathrm{O{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}\end{cases}$$

Es dürfte sich um eine einfach zusammengesetzte Verbindung handeln. Auffallend ist nur das geringe erhaltene Molekulargewicht, das möglicherweise auf eine Dissoziation hinweist. Mit Sicherheit ist jedoch eine Assoziation oder das Vorliegen eines polymeren Moleküls auszuschliessen.

Thoriumverbindung

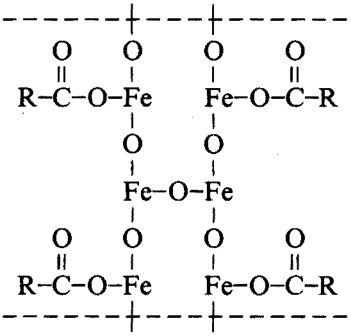


$$\mathrm{O{=}Th}\begin{cases}\mathrm{O{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}\\ \mathrm{O{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}\end{cases}$$

Die vorgeschlagene Formel kommt dem Analysenergebnis am nächsten. Die Molekulargewichtsbestimmung zeigt jedoch, dass die Formel nur den Grundbestandteil wiedergibt, und es sich bei der Verbindung um ein wesentlich grösseres Molekül handelt, das aus rund 18 solchen Einheiten zusammengesetzt ist. Ob es sich dabei um ein echtes Makromolekül handelt, oder um ein Assoziat, mag dahingestellt bleiben.

Eisenverbindung

Im Falle der Eisenverbindung lässt sich eine Formel der Verbindung nur mit Vorbehalt vorschlagen. Wie die Analyse zeigt, handelt es sich um eine Verbindung mit so hohem Eisen- und so geringem Kohlenstoff und Wasserstoffgehalt, dass nicht einmal auf jedes Eisenatom ein Molekül Capronsäure kommt. Unter Berücksichtigung der thermogravimetrischen Befunde, ist es daher wahrscheinlich, dass es sich um ein basisches Eisencapronat handelt. Die Molekulargewichtsbestimmung zeigt aber auch, dass es sich um ein sehr grosses Molekül handeln muss. Die vorgeschlagene Formel trägt diesen Tatsachen Rechnung.



$R = CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$

Die Analysenergebnisse entsprechen nur dem Grundbaustein des aus etwa drei solchen Teilen bestehenden Gesamtmoleküles, das in diesem Falle wohl eher ein polymeres Molekül, als ein Assoziat sein dürfte.

RÉSUMÉ

On décrit une méthode d'extraction du thorium, du plomb et du fer(III) sous forme de caproates dans le chloroforme. Les conditions expérimentales sont données en détail, ainsi que des examples d'extraction simple et de méthodes de séparation. Le composition des composés métalliques dans la couche chloroforme a pu être établie.

ZUSAMMENFASSUNG

Es wird über die Möglichkeit der Extraktion von Thorium, Blei und Eisen(III) als Capronsäureverbindungen mit Hilfe von Chloroform als Extraktionsmittel berichtet. Die Arbeitsbedingungen werden im Detail beschrieben und Beispiele für Einzelextraktionen und Trennungsmöglichkeiten angegeben. Formeln für die in Chloroform löslichen Metallverbindungen werden in Vorschlag gebracht.

SUMMARY

The possibility of extracting thorium, lead and iron(III) with caproic (*n*-hexanoic) acid as their caproates into chloroform is described. Experimental conditions are detailed and examples of single extraction and separation methods are

given. The composition of the metal compounds in the chloroform layer has been established.

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Anal. Chim. Acta, 53 (1971) 287–294

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

STABILITY CONSTANTS OF THE MOLYBDENUM(VI) COMPLEXES OF DTPA AND TTHA

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(Received 21st September 1970)

It is well known that hexavalent molybdenum forms binuclear, as well as mononuclear complexes with polyaminopolycarboxylic acids. However, there exist little quantitative data on the stability of these complexes. The molybdenum(VI) complexes formed with ethylenediaminetetraacetic acid (EDTA) have received most attention recently, being discussed by Kula[1,2], Schultz and Sawyer[3], and Podlahova *et al.*[4]. Kula has also studied the complexes formed with iminodiacetic acid[5] and N-methyliminodiacetic acid[6].

The present paper describes the complex formation of molybdenum(VI) with diethylenetriaminepentaacetic acid (DTPA), as well as with triethylenetetraminehexaacetic acid (TTHA). The stability constants of the various complexes were determined from potentiometric pH titration data. As the number of amino and carboxylic acid groups increase, the number of protonated bi- and mononuclear complexes in equilibrium increase also. Consequently, the calculation of the stability constants becomes rather involved. However, by means of a least-squares method utilizing a high-speed digital computer[7], it was possible to calculate all the constants in question.

EXPERIMENTAL

Materials

Stock solutions of triethylenetetraminehexaacetic acid (TTHA; Geigy Chemical Co., Basel, Switzerland) and diethylenetriaminepentaacetic acid (DTPA; Geigy Chemical Co., New York, U.S.A.) were prepared as described previously[7,8]. A 0.01 *M* stock solution of disodium molybdate was prepared by titrating molybdenum trioxide (Baker Analyzed Reagent) with sodium hydroxide. A molybdate solution was also prepared from disodium molybdate dihydrate (Riedel-de Haen A. G., p.a.). The carbon dioxide-free sodium hydroxide solution was standardized by potentiometric titration against potassium hydrogeniodate.

Apparatus

The potentiometric pH titrations were performed in a double-walled glass cell, the temperature of the solution being kept at 25.0°. The pH was measured with a Beckman Research pH meter and glass and calomel electrodes. The meter was standardized with 0.05 *M* potassium hydrogenphthalate and 0.01 *M* borax buffers. The pH values were converted to hydrogen ion concentrations by assuming the activity coefficient f_H of the hydrogen ion to be 0.80[9,10]. The hydroxyl ion concentration was calculated by means of the equation

$$[H^+][OH^-] = K_w(f_H f_{OH}/a_{H_2O})^{-1}$$

$[H^+][OH^-]$ was calculated to be $1.61 \cdot 10^{-14}$ in 0.1 *M* potassium chloride at 25°[7,11].

The ionic strength of all the solutions to be titrated was 0.1 *M* in potassium nitrate. The total concentration of ligand (DTPA or TTHA) was *ca.* $5 \cdot 10^{-4}$ *M*.

RESULTS

DTPA complexes

The titration curves of DTPA and of 1:1, 2:1 and 3:1 mixtures of molybdate and DTPA are shown in Fig. 1. The pH of the solution is here drawn as a function of *a*, the number of mole of alkali added per mole of the acid. The solution becomes less acidic on addition of molybdate to DTPA, implying that hydrogen ions are consumed during the reaction. Above $a = 3$, however, the four curves almost coincide. By analogy with the EDTA complexes, the formation of the various possible molybdate–DTPA complexes can be described by the following equations:

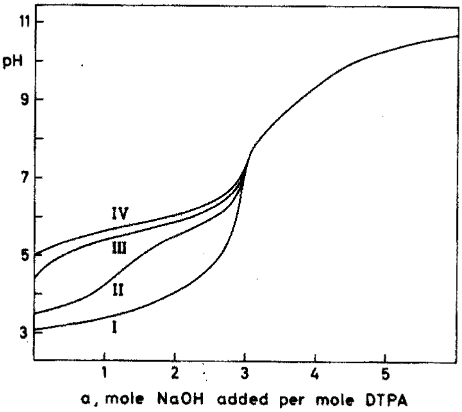

Fig. 1. Titration curves of $5 \cdot 10^{-4}$ *M* DTPA (I), and of 1:1 (II), 2:1 (III) and 3:1 (IV) mixtures of molybdate and DTPA.

$$2\,MoO_4^{2-} + H_5A = (MoO_3)_2HA^{4-} + 2\,H_2O \qquad (1)$$

$$2\,MoO_4^{2-} + H_4A^- = (MoO_3)_2A^{5-} + 2\,H_2O \qquad (2)$$

$$MoO_4^{2-} + H_5A = MoO_3H_3A^{2-} + H_2O \qquad (3)$$

$$MoO_4^{2-} + H_4A^- = MoO_3H_2A^{3-} + H_2O \qquad (4)$$

$$MoO_4^{2-} + H_3A^{2-} = MoO_3HA^{4-} + H_2O \qquad (5)$$

$$MoO_4^{2-} + H_2A^{3-} = MoO_3A^{5-} + H_2O \qquad (6)$$

where H_5A represents the DTPA. The stability constants K_{1-6} of the six possible complexes $(MoO_3)_2HA^{4-}$, $(MoO_3)_2A^{5-}$, $MoO_3H_3A^{2-}$, $MoO_3H_2A^{3-}$, MoO_3HA^{4-} and MoO_3A^{5-} are defined by eqns. (1)–(6), respectively.

The relationship between a and pH (Fig. 1) is defined implicitly through the equations:

$$C_M = G_1[M]+S_1[A^{5-}][M]+2\,S_2[A^{5-}][M]^2 \tag{7}$$

$$C_A = Q[A^{5-}]+S_1[A^{5-}][M]+S_2[A^{5-}][M]^2 \tag{8}$$

$$5C_A-aC_A+[OH^-] = [H^+]+P[A^{5-}]+G_2[M]+S_3[A^{5-}][M] + S_4[A^{5-}][M]^2 \tag{9}$$

where M represents the molybdate ion, C_M and C_A are the total concentrations of molybdate and DTPA, respectively, and the constants P, Q, G and S are defined by the equations:

$$P_n = \frac{[H^+]^n}{k_5 k_4 \ldots k_{(6-n)}} \qquad n = 1\text{–}5$$

$$P = \sum_1^5 nP_n \quad \text{and} \quad Q = 1+\sum_1^5 P_n$$

$$G_1 = 1+g_1[H^+]+7\,g_2[H^+]^8[M]^6(1+g_3[H^+]+g_3g_4[H^+]^2)$$

$$G_2 = g_1[H^+]+g_2[H^+]^8[M]^6(8+9\,g_3[H^+]+10\,g_3g_4[H^+]^2)$$

$$S_1 = P_5K_3+P_4K_4+P_3K_5+P_2K_6$$

$$S_2 = P_5K_1+P_4K_2$$

$$S_3 = 5P_5K_3+4P_4K_4+3P_3K_5+2P_2K_6$$

$$S_4 = 5P_5K_1+4P_4K_2$$

The k_{1-5} values represent the dissociation constants of the DTPA, and the g_{1-4} symbols represent the formation constants of the various protonation and polymerization products of the molybdate ion. The dissociation constants given by Moeller and Thomson[12], and the molybdate constants given by Sillen *et al.*[13] were used for the calculations.

The calculation of the stability constants K_{1-6} proceeds as follows. By introducing approximate values for the stability constants, an approximate value for a (a_{calc}) can be calculated by means of eqns. (7)–(9), for each value of $[H^+]$. The calculation of a_{calc} was carried out by first eliminating $[A^{5-}]$ from eqn. (7) by means of eqn. (8), then solving eqn. (7) numerically with respect to [M], and finally calculating a from eqn. (9). The stability constants were then determined by applying the method of least squares to the difference $d = a_{exp} - a_{calc}$, where a_{exp} is the experimental a value. The derivatives of a were calculated numerically. The constants were calculated one at a time, and the whole sequence of calculations was repeated several times, till no changes in the resulting constants were observed. Details of the calculation procedure are given in a previous paper[7].

The constants previously reported for the Mo(VI)–EDTA complexes were used as initial approximate values for the calculations. The initial values were, how-

TABLE I

STABILITY CONSTANTS OF THE MOLYBDENUM(VI)–DTPA COMPLEXES

Complex	$(MoO_3)_2HA^{4-}$	$(MoO_3)_2A^{5-}$	$MoO_3H_3A^{2-}$	$MoO_3H_2A^{3-}$	MoO_3HA^{4-}	MoO_3A^{5}
Notation, Fig. 2	I	—	II	III	IV	V
Constant	K_1	K_2	K_3	K_4	K_5	K_6
log K	15.01	—	8.53	7.31	4.87	2.55

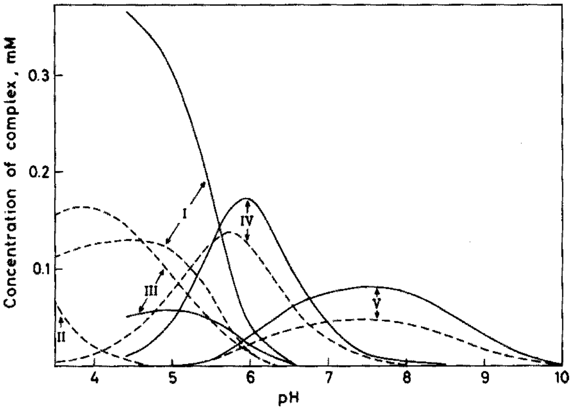

Fig. 2. The concentration of $(MoO_3)_2HA^{4-}$ (I), $MoO_3H_3A^{2-}$ (II), $MoO_3H_2A^{3-}$ (III), MoO_3HA^{4-} (IV) and MoO_3A^{5-} (V) drawn as a function of pH for a 2:1 mixture (full curves) and a 1:1 mixture (dashed curves) of molybdate and DTPA.

ever, of little importance, as the method would almost always converge, when the proper molybdate–DTPA mixtures and pH regions were chosen.

The final stability constants are given in Table I. No evidence was found for the formation of the $(MoO_3)_2A^{5-}$ complex, but the presence of all the other complexes was confirmed. To visualize the results, the concentration of the five complexes is drawn as a function of pH in Fig. 2, for a 1:1, as well as for a 2:1 mixture of molybdate and DTPA. The mononuclear complexes MoO_3HA^{4-} and MoO_3A^{5-} are seen to predominate in the pH regions around 6 and above 7, respectively, both for the 1:1 and the 2:1 mixture. At pH values below 5.5, however, the concentration of the predominating species depends markedly on the magnitude of C_M/C_A. Thus, in the 1:1 mixture the concentrations of the binuclear complex $(MoO_3)_2HA^{4-}$ and the mononuclear complex $MoO_3H_2A^{3-}$ are seen to be of the same order of magnitude, whereas for the 2:1 mixture, the binuclear complex is clearly dominant. The mononuclear complex $MoO_3H_3A^{2-}$ is obviously present in small amounts at pH values above 3.5.

From the curves in Fig. 2 it can be concluded that the stability of the five binuclear and mononuclear complexes formed between molybdenum(VI) and DTPA is of the same order of magnitude. In alkaline solution the concentration of the binuclear complex is negligible, because the concentration of H_5A (seen eqn. 1) is negligible at these pH values. The mononuclear complexes containing few or no protons are consequently favoured.

TTHA complexes

The titration curves of TTHA, and of 1:1, 2:1 and 3:1 mixtures of molybdate and TTHA, are drawn in Fig. 3. The curves are similar to those obtained for the molybdate–DTPA system. The four curves almost coincide above $a=4$. Similar to the DTPA system, one has to consider the following equilibria:

$$2\,MoO_4^{2-}+H_6A=(MoO_3)_2H_2A^{4-}+2\,H_2O \tag{10}$$

$$2\,MoO_4^{2-}+H_5A^{-}=(MoO_3)_2HA^{5-}+2\,H_2O \tag{11}$$

$$2\,MoO_4^{2-}+H_4A^{2-}=(MoO_3)_2A^{6-}+2\,H_2O \tag{12}$$

$$MoO_4^{2-}+H_6A=MoO_3H_4A^{2-}+H_2O \tag{13}$$

$$MoO_4^{2-}+H_5A^{-}=MoO_3H_3A^{3-}+H_2O \tag{14}$$

$$MoO_4^{2-}+H_4A^{2-}=MoO_3H_2A^{4-}+H_2O \tag{15}$$

$$MoO_4^{2-}+H_3A^{3-}=MoO_3HA^{5-}+H_2O \tag{16}$$

$$MoO_4^{2-}+H_2A^{4-}=MoO_3A^{6-}+H_2O \tag{17}$$

where H_6A represents the TTHA. The stability constants K_{10-17} of the eight possible complexes (three binuclear and five mononuclear) are defined by the eqns. (10)–(17).

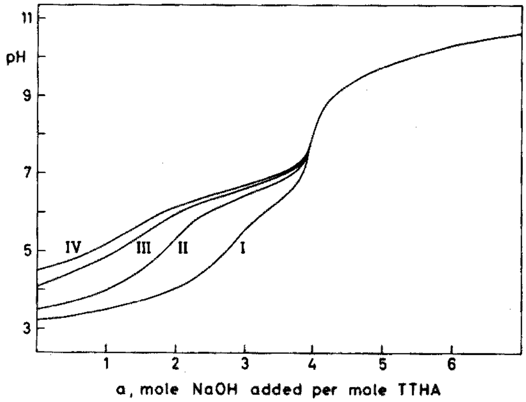

Fig. 3. Titration curves of $5\cdot10^{-4}$ M TTHA (I), and of 1 : 1 (II), 2 ; 1 (III) and 3 : 1 (IV) mixtures of molybdate and TTHA.

The equations defining the relationship between a and pH for the molybdate–TTHA system are completely analogous to eqns. (7)–(9). The procedure for the calculation of the stability constants is also the same as that outlined for the DTPA complexes.

The dissociation constants of the TTHA, which were needed for the calculations, were determined separately, from the titration curve of TTHA. The dissociation constants were calculated by means of a simplified version of the more general computer program which was used for the calculation of the stability constants of the complexes. The following pk values were found for the TTHA: 2.46, 2.84, 4.33, 6.33, 9.48 and 10.13.

The final stability constants of the molybdenum(VI)–TTHA complexes are given in Table II. As seen from that Table, the presence of all the eight possible com-

TABLE II

STABILITY CONSTANTS OF THE MOLYBDENUM(VI)–TTHA COMPLEXES

Complex	$(MoO_3)_2H_2A^{4-}$	$(MoO_3)_2HA^{5-}$	$(MoO_3)_2A^{6-}$	$MoO_3H_4A^{2-}$	$MoO_3H_3A^{3-}$	$MoO_3H_2A^{4-}$	MoO_3HA^{5-}	MoO_3A^{6-}
Notation, Fig. 4	I	II	III	IV	V	VI	VII	VIII
Constant	K_{10}	K_{11}	K_{12}	K_{13}	K_{14}	K_{15}	K_{16}	K_{17}
log K	13.81	11.78	8.42	7.45	6.88	5.64	3.16	3.14

plexes was confirmed. The $(MoO_3)_2A^{6-}$ complex was, however, just on the limit of detection, and the stability constant of that complex should consequently be regarded with some suspicion. In Fig. 4 the concentration of the eight complexes is drawn as a function of pH, for a 2:1 mixture of molybdate and TTHA.

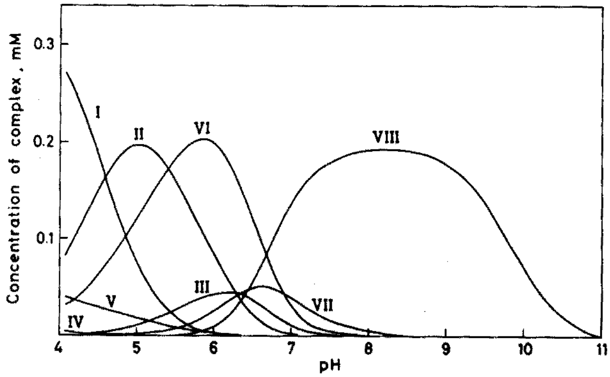

Fig. 4. The concentration of $(MoO_3)_2H_2A^{4-}$ (I), $(MoO_3)_2HA^{5-}$ (II), $(MoO_3)_2A^{6-}$ (III), $MoO_3H_4A^{2-}$ (IV), $MoO_3H_3A^{3-}$ (V), $MoO_3H_2A^{4-}$ (VI), MoO_3HA^{5-} (VII) and MoO_3A^{6-} (VIII) drawn as a function of pH for a 2:1 mixture of molybdate and TTHA.

As can be seen from the Figure, the mononuclear complexes MoO_3A^{6-} and $MoO_3H_2A^{4-}$ predominate at pH values above 5.5, the first being dominant in alkaline solution, where the concentration of all the other complexes is negligible. At pH values below 5.5, the binuclear complexes $(MoO_3)_2H_2A^{4-}$ and $(MoO_3)_2HA^{5-}$ predominate. The general picture is not much altered in the case of 1:1 mixture of molybdate and TTHA. The main changes occur at pH values below 6. Here the concentration of $MoO_3H_3A^{3-}$ is increased, whereas the concentration of the three binuclear complexes is decreased.

There seems to be no great difference between the stability of the eight molybdenum(VI)–TTHA complexes. The formation of the binuclear species is favoured in more acidic solution, as would be expected from eqns. (10)–(12).

There are no dramatic differences in the stability of the molybdenum complexes of TTHA, compared to the complexes of DTPA. But of course, there exist more protonated species for the TTHA system than for the DTPA system. The most marked difference in stability is found for the MoO_3A complexes of DTPA and TTHA.

The author thanks the Geigy Chemical Company, Basel, for a gift of the TTHA sample. He also wishes to thank his wife Tone Lund for performing the titrations.

SUMMARY

The complex formation of molybdenum(VI) with diethylenetriaminepentaacetic acid (DTPA) and with triethylenetetraminehexaacetic acid (TTHA), has been studied by means of potentiometric pH titrations. The presence of five molybdenum(VI)–DTPA complexes, as well as eight Mo(VI)–TTHA complexes has been established. The stability constants of the series of protonated mononuclear and binuclear complexes have been calculated by means of a least-squares method, utilizing a high-speed digital computer.

RÉSUMÉ

Une étude est effectuée sur la formation des complexes du molybdène(VI) avec l'acide diéthylène triaminopentacétique (DTPA) et avec l'acide triéthylènetétraminohexacétique (TTHA), par titrage potentiométrique du pH. On a ainsi pu constater la présence de cinq complexes molybdène(VI)–DTPA et de huit complexes molybdène(VI)–TTHA. Les constantes de stabilité ont été calculées à l'aide d'un ordinateur digital.

ZUSAMMENFASSUNG

Mit Hilfe potentiometrischer pH-Titrationen wurde die Komplexbildung von Molybdän(VI) mit Diäthylentriaminpentaessigsäure (DTPA) und mit Triäthylentetraminhexaessigsäure (TTHA) untersucht. Es wurde festgestellt, dass fünf Molybdän(VI)–DTPA-Komplexe und acht Mo(VI)–TTHA-Komplexe vorliegen. Die Stabilitätskonstanten für die protonisierten einkernigen und zweikernigen Komplexe wurden nach der Methode der kleinsten Quadrate unter Anwendung eines Digitalrechners berechnet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A STUDY OF THE RUTHENIUM–2,2′,2″-TERPYRIDINE SYSTEM

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(Received 6th August 1970)

The compound 2,2′,2″-terpyridine is a tridentate ligand which was originally proposed by Moss and Mellon[1] as a colorimetric reagent for iron. This ligand is also a bivalent Bronsted base whose acid–base constants have recently been determined[2]. The study of its complexes with ruthenium described here is part of an investigation of the complexes of this element with ferroin-type ligands.

Very few references are found in the literature relating to the ruthenium–2,2′2″-terpyridine system: for the intensely colored ruthenium(II) complex, which can be used for the spectrophotometric determination of the element, a metal–ligand ratio of 1:2 is usually attributed, by analogy with the corresponding iron(II) complex. The ruthenium(III) complex has not been characterized. With regard to the redox characteristics of the RuL_2^{3+}/RuL_2^{2+} system, Dwyer and Gyarfas[3] noted that the ruthenium(III) complex is rapidly reduced in acidic solution; they determined approximate formal potentials of the RuL_2^{3+}/RuL_2^{2+} couple, by adding to solutions of the reduced form quantities of cerium(IV) stoichiometrically equivalent to half of the complex present, following the variations of potential in time and extrapolating the measured values to zero time.

EXPERIMENTAL

The ruthenium(II) complex with 2,2′,2″-terpyridine is prepared in the following manner: commercial ruthenium trichloride (Fluka) is heated to boiling in 6 *M* hydrochloric acid for 24 h. The pentachloromonoaquoruthenate(III) that forms[4] is separated as the potassium salt and recrystallized from 6 *M* hydrochloric acid.

To an acid solution of the soluble potassium salt are added a quantity of ligand only slightly greater than the stoichiometric equivalent for the formation of the 1:2 (metal–ligand) complex, and an excess of reducing agent such as sodium hypophosphite or hydroxylammonium chloride. The solution is then heated to 50–60° for several hours. During the heating the pH of the solution is slowly and progressively raised with small additions of a dilute sodium hydroxide solution until neutralization is reached. In this way the ruthenium present is quantitatively transformed into RuL_2^{2+}, which is isolated as an iodide from thoroughly cooled solutions. The solid is dissolved in boiling water and transformed to the corresponding sulfate by addition of a saturated silver sulfate solution. Such a transformation is necessary because iodide ions would interfere in the redox study of the complex.

The investigation was carried out by spectrophotometric, potentiometric, and voltammetric measurements. The potentiometric measurements were made with a

Beckman Expandomatic precision pH meter potentiometer and with glass and platinum indicator electrodes. The spectrophotometric measurements were made with a Beckman DU spectrophotometer and with 1.000-cm silica cells. Finally, the voltammetric measurements were made with a Metrohm E 446 polarograph and with the platinum microelectrode with periodic renewal of the diffusion layer[5].

The buffers used in the spectrophotometric measurements were sodium acetate–sulfuric acid for the pH 1.0–5.2 interval, and potassium dihydrogen phosphate–sodium hydroxide for the pH 5.5–9 interval.

RESULTS AND DISCUSSION

Spectrophotometric study

Spectrophotometric titrations confirmed the 1:2 metal–ligand ratio in the complex formed by ruthenium(II) and 2,2′,2″-terpyridine.

Beer's law was also verified for complex concentrations up to $2.5 \cdot 10^{-4}$ *M*. In contrast to what was found for the corresponding iron(II) complex[2], and to what was expected from the basic character of the ligand, the ruthenium(II) complex is not appreciably dissociated in acidic solution.

With other ruthenium complexes, *e.g.* with 1,10-phenanthroline, it has been noted that the dissociation rate in an acidic environment increases initially with increasing acidity and then decreases with further increments in the hydrogen ion concentration. This decrease is attributed to the passage of the complex to an inert protonated form with increasing acidity. Several authors[6–8] agree with this interpretation, without, however, presenting direct experimental evidence of the existence of the protonated complex. Such evidence is, however, obtainable in the case of the complex of ruthenium(II) with 2,2′,2″-terpyridine.

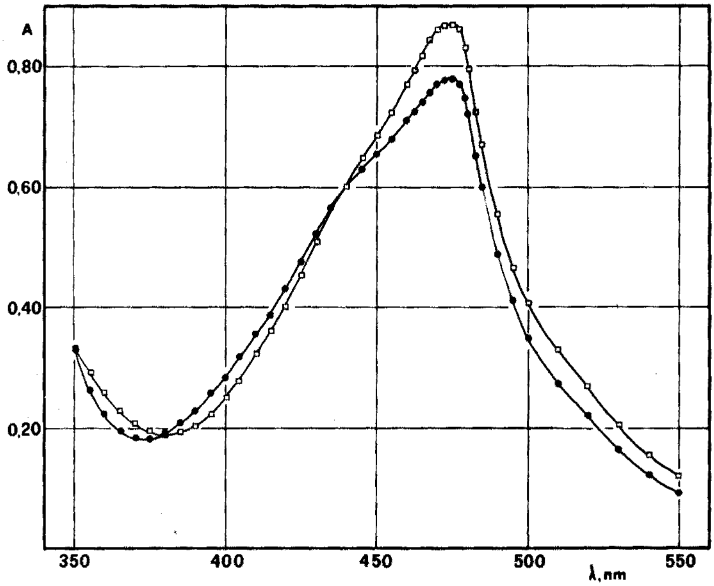


Fig. 1. Absorption spectra from $7 \cdot 10^{-5}$ *M* ruthenium(II). Complex solutions at: (□) pH = 8; (●) pH = 0.

As shown in Fig. 1 the absorption spectrum of this complex varies in the pH 0–6 interval but is constant for pH values above 6. Such a variation can be interpreted as an acid–base equilibrium:

$$\mathrm{RuL_2H}_x^{(2+x)+} \rightleftharpoons \mathrm{RuL}_2^{2+} + x\,\mathrm{H}^+$$

From measurements at pH 0, a molar absorptivity of 11,250 was obtained for the protonated complex and from measurements at pH 8, a molar absorptivity of 12,680 was obtained for the deprotonated complex, in both cases at 475 nm. With these molar absorptivities, the absorption values were calculated when the ratio of the concentrations of the protonated and the deprotonated complexes was, respectively, 1:10 and 10:1. On the pH axis these values were 1.96 units apart, indicating that the acid is monoprotic. Its dissociation constant ($\mathrm{p}K_a$) was found to be 2.9.

If the analytical concentrations of the complex are kept constant, and given the molar absorptivities and the acid dissociation constant, the absorbance values represented by the continuous curve in Fig. 2 can readily be calculated as pH values. The experimental points reported in this figure were obtained from solutions buffered at the indicated pH.

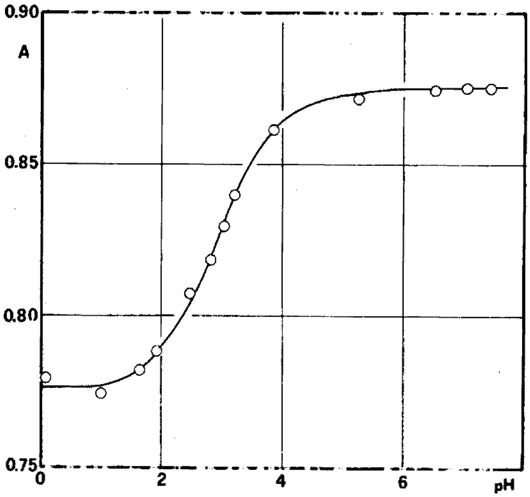


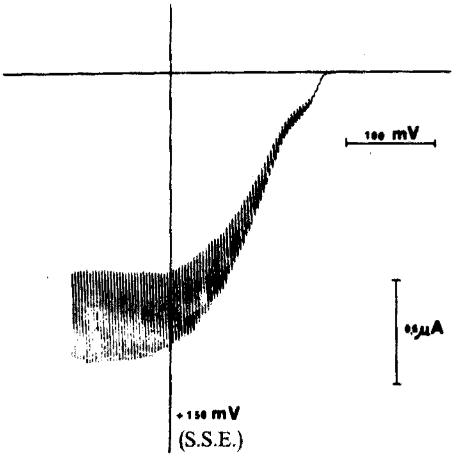
Fig. 2. Absorption variations at $\lambda_{max} = 473$ nm of a $6.9 \cdot 10^{-5}$ M ruthenium(II) complex solution as a function of the pH.

Even if the ionic strength is not rigorously constant in all solutions, this factor is irrelevant in that it has been verified that ionic strength variations of 0.8 M do not produce appreciable variations in absorption spectra. Nor, for that matter, does the complete replacement of acetate ions by equivalent quantities of sulfate and phosphate ions produce appreciable effects, and the eventual formation of ionic couples is, from a spectrophotometric point of view, without influence.

Redox characteristics

In an extension of the measurements made by Dwyer and Gyarfas[3], the marked tendency of ruthenium(III) complexes to be reduced was ascertained with a series of potentiometric titrations of the ruthenium(II) complex. It was found that the end-point and the half-titration point were displaced, respectively, along the volume of titrant added axis and along the potential axis, in relation to the rate at which the titrating agent was added. With an excess of oxidant the ruthenium(III) complex was quantitatively reduced to the corresponding ruthenium(II) complex, in a time depending on the excess of oxidizing agent present and on the acidity of the medium. Identical results were obtained when the water was 90% substituted with methanol or dioxane.

In this series of titrations not even a slight clouding of the solutions was observed when 10^{-3} *M* solutions were used. This clearly indicates that the chemical oxidation–reduction takes place in a homogeneous phase. On the other hand, the redox electrochemical process takes place in a heterogeneous phase. For RuL_2^{2+} solutions the anodic wave of Fig. 3 was recorded with a platinum microelectrode with periodic renewal of the diffusion layer; the rapid rise in current at the foot of the wave is characteristic of the deposition of insoluble products on the electrode, and this is followed by the true wave. At the limiting current of the pre-wave, the electrode appeared to be covered with a red-brown deposit, which gave the characteristic reactions of ruthenium(III) as described by Pascal[9], and which was formed even at temperatures appreciably higher than room temperature (60–70°).



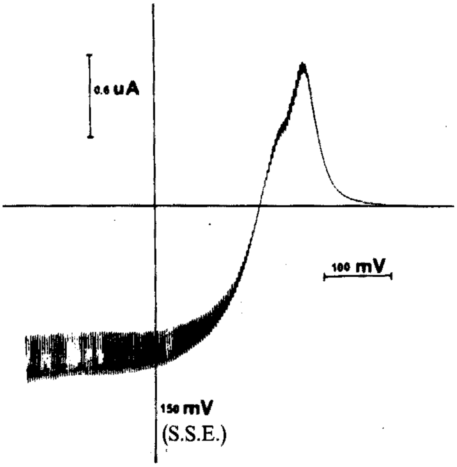


Fig. 3. Voltammetric oxidation curve recorded for $5 \cdot 10^{-4}$ *M* ruthenium(II) complex solutions by polarizing the platinum microelectrode with progressively more positive potentials.

Fig. 4. Voltammetric curve recorded under the conditions of Fig. 3 by polarizing the electrode with progressively less positive potentials.

The presence of ruthenium(III) in the electrode deposit was confirmed by the voltammetric curve (Fig. 4), which was recorded by polarizing the electrode in the direction of decreasing positive potentials. The quantity of electricity involved in the electrodissolution was appreciably less than that involved in the electrodeposition; only when a large excess of complexing agent was present did the amounts tend to be equal, which indicates that the ruthenium complex undergoes chemical alterations during electro-oxidation.

CONCLUSIONS

Previous work on iron and ruthenium complexes with ferroin-type ligands has shown that there is a substantial similarity in the behaviour of the two elements. In the present work on 2,2′,2″-terpyridine, it has been shown that the ruthenium complexes differ from the corresponding iron complexes studied previously, both with respect to lability characteristics in acidic solution and to oxidation–reduction characteristics.

The result of greatest interest is the existence of a protonated ruthenium complex, since such complexes have not been demonstrated for similar ligands such as 2,2′-bipyridine and 1,10-phenanthroline.

Apart from spectrophotometric determinations, iron and ruthenium complexes with ligands of the type considered are often suggested as high-potential redox indicators. Notwithstanding the notable limitations just exponded, the RuL_2H^{3+} complex can be used as a redox indicator. In the titration of iron(II) with cerium(IV), the variation in color at the equivalence point is sharp and persistent for at least 30 sec. A series of titrations showed that the precision is similar to that obtained with ferroin as the indicator.

SUMMARY

The chemical and electrochemical behaviour of the ruthenium(II) and ruthenium(III) complexes with 2,2′,2″-terpyridine has been studied. Spectrophotometric measurements proved the existence of a protonated ruthenium(II) complex with $pK_a = 2.9$. Potentiometric and voltammetric studies showed a difference in the behaviour of the ruthenium(II) complex against chemical and electrochemical oxidation. Potentiometric data showed also that the ruthenium(III) complex may be reduced rapidly and spontaneously.

RÉSUMÉ

Une étude est effectuée sur le comportement chimique et électrochimique des complexes de ruthénium(II) et de ruthénium(III) avec la 2,2′,2″-terpyridine. Les mesures spectrophotométriques prouvent l'existence d'un complexe de ruthénium(II) protoné, avec un $pK_a = 2.9$. Par potentiométrie et par voltammétrie, on observe une différence dans le comportement du complexe de ruthénium(II) lors d'une oxydation chimique ou électrochimique. Les résultats potentiométriques montrent que le complexe de ruthénium(III) peut être réduit rapidement et spontanément.

ZUSAMMENFASSUNG

Es wurde das chemische und elektrochemische Verhalten der Ruthenium(II)- und Ruthenium(III)-Komplexe mit 2,2′,2″-Terpyridin untersucht. Spektrophotometrische Messungen bewiesen die Existenz eines protonisierten Ruthenium(II)-Komplexes mit $pK_a = 2.9$. Potentiometrische und voltammetrische Untersuchungen zeigten unterschiedliches Verhalten des Ruthenium(II)-Komplexes gegenüber chemischer und elektrochemischer Oxidation. Die potentiometrischen Untersuchungen

ergaben ebenfalls, dass der Ruthenium(III)-Komplex schnell und spontan reduziert werden kann.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COMPLEX FORMATION OF VANADIUM WITH THIOGLYCOLLIC ACID

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(Received 2nd October 1970)

Thioglycollic acid (TGA) forms stable complexes with several metals. The formation and composition of the complexes formed with iron[1,2], molybdenum[3], cobalt[4,5], nickel[5,6], zinc[5,7,8], lead[7,8], manganese[5], mercury[8,9], silver[8], cadmium[8] and chromium[10] have been reported in the literature, and TGA has been recommended as a powerful masking agent in spectrophotometric analysis[11,12] and in compleximetric titrations[13].

The reaction between TGA and vanadium was first reported by Ziegler and Rittner[14] who pointed out that vanadate is reduced by TGA and that the vanadyl ions formed react with excess of TGA to form a blue coloured complex. The absorption curve of the complex has a maximum at 620 nm and they recommended TGA as a reagent in the photometric determination of vanadium.

The existence of a vanadium(IV)–TGA complex has not been confirmed by other investigators, and the present work was carried out in order to study the complex formation of vanadium with TGA and to determine the formula of the complex.

EXPERIMENTAL

Instrumentation

A Beckman DB recording spectrophotometer with 1.000-cm glass cells was used for the absorbance measurements. Whenever wanted the absorbance was checked manually with a Zeiss spectrophotometer Model PMQ II. The pH of all solutions was measured with a Beckman Zeromatic pH meter.

Reagents

Thioglycollic acid (80% in water; E. Merck A.G., Germany) was purified and standardized as described previously[10].

Reagent-grade dithiodiglycollic acid (Koch–Light Laboratories Ltd.) was used as a 0.1 *M* stock solution by dissolving the appropriate amount of the acid in air-free distilled water and diluting to 1 l.

A 0.01 *M* vanadyl sulphate stock solution was prepared by dissolving the commercial purum product (Fluka A.G., Switzerland) in distilled water. Any reducible substances were removed by bubbling sulphur dioxide through the solution for 3 h. Excess of sulphur dioxide was then removed with purified nitrogen. The solution was standardized by titration with permanganate[15] and stored in a closed bottle under a nitrogen atmosphere.

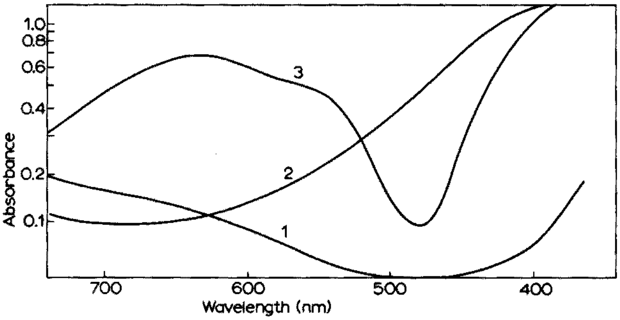
A 0.025 *M* vanadyl stock solution was prepared from vanadium pentoxide (purum product, Fluka A.G.) by drying the product at 500° and dissolving 4.5475 g in 200 ml of 6 *M* sodium hydroxide. The solution was acidified with sulphuric acid and reduced by addition of 200 ml of 1 *M* sodium sulphite. The pH was adjusted to 5.0 and the solution diluted to 2 l with distilled water. The molarity of the two vanadyl stock solutions was checked spectrophotometrically according to Santini *et al.*[16] and gave concordant results.

The primary amine Primene 81-R ($C_{13}H_{27}NH_2$); Rohm and Haas Co., Philadelphia, Pa., U.S.A.) was used without any purification. The remaining chemicals were of reagent grade.

RESULTS AND DISCUSSION

Absorbance spectra

Preliminary experiments indicated that the reaction between vanadium(IV) and TGA is very fast even at room temperature. The absorption curve of the complex measured against distilled water is shown in Fig. 1. Exactly the same curve is obtained after addition of excess of sodium sulphite to the solution. Hence, in order to prevent air oxidation and hydrolysis of vanadium(IV), a stock solution containing 0.1 *M* sulphite was used in most of the following experiments. The same absorption curve is also obtained upon addition of excess of TGA to a solution of vanadium(V), which confirms Ziegler and Rittner's statement[14] that vanadium(V) is reduced by TGA and that the oxidation state of vanadium in the complex is 4.



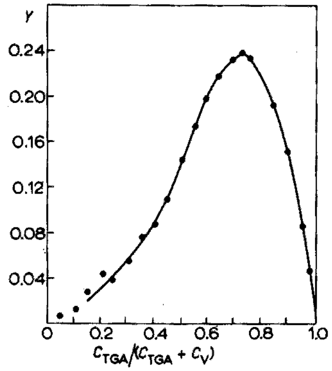


Fig. 1. Absorption curves of $1.2 \cdot 10^{-2}$ *M* vanadium(IV) and 0.24 *M* TGA at pH 3.0 (curve 1), pH 5.0 (curve 2) and pH 11.5 (curve 3).

Fig. 2. Continuous variation curves for vanadium–TGA in 0.1 *M* acetate buffer with pH 5.0. Constant sum of concentrations $C = C_{TGA} + C_V = 1.00 \cdot 10^{-2}$ *M*. Absorbance measured at 630 nm.

The absorption curve exhibits a maximum at 630 nm and the molar absorptivity is 57.5 which is about three times greater than that of vanadyl ions in the absence of TGA. The absorptivity of the complex is very dependent on the pH of the solution and on the excess of TGA present. Thus, at low excess of TGA the absorptivity is independent of pH only in the range 5–6. However, in the presence of 50 times excess of TGA a constant absorptivity is obtained in the whole pH range 4–9. At pH values below 3 and above 11 the same absorption curve is obtained in the presence as in the absence of TGA (Fig. 1), indicating that the complex formation between vanadium(IV) and TGA is restricted to the pH range 4–9.

Composition of the complex

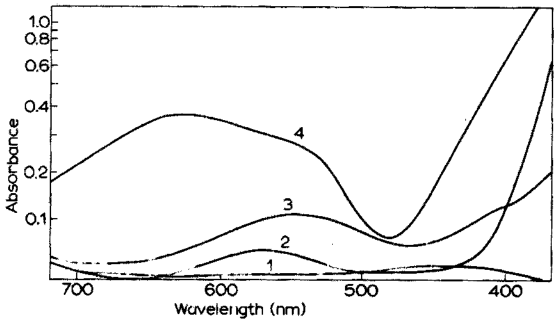
The composition of the complex was first investigated by Job's method of continuous variation[17]. Different ratios of vanadium(IV) and TGA with a constant sum of concentrations, $C = C_V + C_{TGA} = 1.00 \cdot 10^{-2}$ *M*, were mixed in 0.1 *M* acetate buffer, the pH was adjusted to 5.0 and the solutions were diluted to constant volume. The absorbance was measured at 630 nm against a blank containing the same amount of all chemicals except TGA and the difference in absorbance, *Y*, was plotted against the mole ratio. As shown in Fig. 2, a maximum on the curve is obtained where the vanadium and the TGA are present in the ratio 1:2.4. The experiments were repeated by measuring the absorbance at other wavelengths, at other pH values in the range 4–6 and at various total concentrations from $7 \cdot 10^{-3}$ to $2.5 \cdot 10^{-2}$ *M*. In all cases the maximum occurred at the mole ratio 1:2.4, indicating that only one complex is formed in vanadium(IV)–TGA solutions. Because a non-stoichiometric metal/ligand ratio is obtained by this method, the result was checked by performing other experiments.

An attempt to determine the composition of the complex by amperometric titration of vanadium(IV) with TGA failed, because the half-wave potential of TGA and that of the complex are too close to each other.

Potentiometric pH titrations are often a convenient method for investigating the complex formation between metal ions and organic acids. Hence, potentiometric pH titrations of vanadium(IV) in the absence and in the presence of various amounts of TGA were performed, with carbonate-free sodium hydroxide as titrant. In these experiments, the vanadium stock solution without sulphite was employed. The titration showed that hydrogen ions are not involved in the complex formation. The experiment was checked by carefully adjusting a solution of vanadium(IV) (containing 0.1 *M* sulphite) and a solution of TGA to pH 5.0. After mixing the two solutions the pH was still exactly 5.0. The titration curve of vanadium(IV) in the absence of TGA exhibits a buffer region at pH 4.5 corresponding to the formation of vanadium hydroxide. This buffer region is much smaller when TGA is present and it disappears when the mole ratio of vanadium/TGA is 1:2.7. Because 2.7 mole of TGA per mole of vanadium is sufficient to prevent hydrolysis, the vanadium/TGA ratio in the complex is probably 1:2.

TGA is easily oxidized in aqueous solutions and the rate of decomposition is dependent on the pH, temperature, concentration and the presence of some metal ions (copper, iron, cobalt and vanadium) which act as a catalyst in the oxidation[1,10,18–23]. Thiodiglycollic acid, dithiodiglycollic acid, oxalic acid, glycollic acid and hydrogen sulphide have been reported as decomposition products. Hence, an oxidation or decomposition of the reagent may be responsible for the observed non-stoichiometric metal/ligand ratio. Moreover, the ligand in the vanadium complex might be an oxidation product of TGA and not TGA itself.

Consequently, absorption curves of vanadium(IV) in the presence of 15 times excess of glycollic, thiodiglycollic, dithiodiglycollic and oxalic acid, respectively, were recorded. In order to prevent oxidation of the acids, the air was carefully removed from all solutions and the curves were recorded in nitrogen atmosphere against distilled water. As shown in Fig. 3 the same absorption curve of vanadium is observed in the presence of excess of dithiodiglycollic acid (air-free solution) and in the presence of TGA (air present). Further experiments showed that no complex formation occurs on addition of TGA to an air-free solution of vanadium(IV). However, after the solution had been exposed to the air for a few minutes the absorption curve 4, Fig. 3, is obtained. These experiments imply that the ligand in the complex is DTDGA (dithiodiglycollic acid) which is formed by oxidation of TGA. The reaction is very fast, in agreement with the earlier statement that the air oxidation of TGA is catalyzed by vanadium[23].



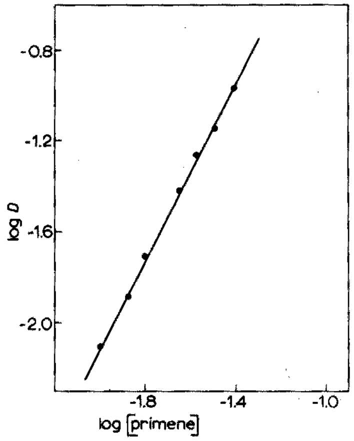


Fig. 3. Absorption curves of $6.6 \cdot 10^{-3}$ *M* vanadium(IV) at pH 5.0 in the presence of 0.1 *M* thiodiglycollic acid (1), 0.1 *M* oxalic acid (2), 0.1 *M* glycollic acid (3), 0.1 *M* dithiodiglycollic acid and 0.1 *M* TGA air present (4).

Fig. 4. Extraction curve of the vanadium–DTDGA complex at pH 5.0 in the presence of various amounts of Primene with 50% n-octanol in benzene.

The above result was checked by titrations with iodate as described by Leussing and Kolthoff[24]. The complex was first prepared at pH 5 by mixing vanadium(IV) with excess of TGA in the presence of air. The complex was then broken down by addition of sulphuric acid to pH 1.0 and the solution was titrated with standard iodate. The result was then compared to a blank containing the same amount of all chemicals except vanadium. The titration was repeated with various total amounts of TGA and of vanadium and showed that 2 moles of TGA per mole of vanadium did not react with iodine. These experiments clearly demonstrate that 2 moles of TGA are oxidized by air to form 1 mole of DTDGA which in turn reacts with 1 mole of vanadium(IV) to form a 1:1 complex.

The vanadium complex prepared with DTDGA as reagent is stable only when air is excluded from the solution. If the solution is exposed to the air, the blue colour turns black in a few minutes and the pH increases. Solutions prepared with excess of TGA are much more stable against air oxidation, probably because the excess of TGA prevents oxidation of the DTDGA in the complex.

The charge type of the complex was determined by the moving boundary method[10,25]. The solution was prepared by mixing vanadium(IV) with 20 times excess reagent and adjusting the pH to 5.0, and placed in the bottom of a U-formed tube. The limbs of the tube were filled with an uncoloured buffer of the same pH. The density of the coloured solution was made slightly higher than that of the uncoloured buffer by addition of sodium sulphate. The greater density of the solution in the bottom of the tube prevented turbulence and mixing of the two solutions, and a very distinct boundary was obtained. Platinum electrodes were placed in the two limbs and connected to a 50-V d.c. source. When the circuit was completed, the blue-coloured complex moved towards the anode, indicating that the complex is negatively charged. The experiment was repeated with other solutions in the pH range 4–6 and the same result was obtained, independently of whether TGA or DTDGA was used as reagent.

Extraction of vanadium

Long-chain amines like Primene 81-R are often used to charge–neutralize anionic complexes and thus enhance their extraction into organic solvents[26]. Experiments showed that the vanadium complex in the presence of Primene is easily extracted into a mixture of n-octanol and benzene. The absorption curve of the complex in the organic phase is the same as in the aqueous phase (Fig. 1) with a maximum at 630 nm. Beer's law is obeyed also in the organic phase, and it was observed that the highest distribution coefficient, $D=18$, is obtained when excess of Primene is present, when the pH of the aqueous phase is 5–7, and when the complex is extracted into a mixture of 50% n-octanol in benzene.

Primene is a primary amine and the reaction must proceed according to:

$$(AB^{n-})_{H_2O}+(nP^+)_{H_2O}\rightleftarrows(P_nAB)_o$$

where AB^{n-} is the vanadium–DTDGA complex, P^+ denotes the adduct-forming agent Primene and the subscript o indicates organic phase.

Hence, the number of negative charges in the complex, n, can be determined from the mole ratio of Primene to vanadium in the organic phase[27,28]. When equilibrium is established between the aqueous and organic phase:

$$\frac{[P_nAB]_o}{[AB^{n-}]_{H_2O}[P^+]^n_{H_2O}}=\frac{D}{[P^+]^n_{H_2O}}=\text{const.}$$

or

$$\log D=n\log[P^+]+\text{const.}$$

where D is the distribution coefficient. Hence, if $\log D$ is plotted against $\log[P^+]$, the value of n can be determined from the slope of the line.

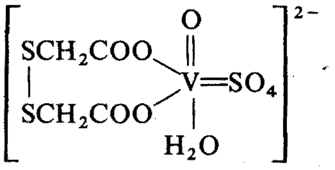
Aliquots of the standard vanadium solution containing 0.1 *M* sulphite, 20 times excess TGA and varying amounts of Primene, were adjusted to pH 5 by addition of sodium hydroxide and diluted to 25 ml with distilled water. The solutions were then extracted with 25 ml of 50% n-octanol in benzene. The absorbance in the organic and in the aqueous phase was measured and the distribution coefficient, D, for each solution was calculated. By plotting $\log D$ against $\log[P]$, where P is the adduct-forming agent Primene, a straight line is obtained (Fig. 4), indicating that only a single species dominates in each phase[28]. The slope of the line is two, which implies that two Primene molecules are coordinated in the complex. Exactly the same result was obtained if the complex in the aqueous phase was prepared from vanadium(V) and excess of TGA or vanadium(IV) and excess of DTDGA. Consequently, the vanadium complex must carry two negative charges in aqueous solutions.

CONCLUSION

It is evident from the experimental results that 2 moles of TGA are oxidized by air (or vanadium(V)) to form 1 mole of DTDGA which reacts with vanadium(IV) to form a blue coloured 1:1 complex. Hydrogen ions are not involved in the reaction which must proceed according to:

$$2HSCH_2COO^- + VO^{2+} + \tfrac{1}{2}O_2 \rightarrow VO(OOCCH_2S\text{–}SCH_2COO) + H_2O$$

The complex carries two negative charges and, therefore, it is probably a mixed ligand complex in which an anion from the electrolyte (for instance sulphate) is coordinated. Similar mixed ligand complexes ($VO(dipy)SO_4$ and $VO(o\text{-}phen)SO_4$) have previously been reported, and by conductance measurements it has been established that they are not dissociated to ions in aqueous solutions[29]. The present work was carried out in sulphate medium, hence the formula of the complex is probably:



The last coordination site is probably occupied by water. The complex is scarcely extracted by benzene, but is easily extracted by a mixture of *n*-octanol in benzene. This is in accordance with Alimarin and Zolotov's statement that coordination-unsaturated chelates are extracted considerably better by alcohols than by hydrocarbons[30].

The rapid oxidation of TGA by air and the formation of a DTDGA complex is probably not unique for vanadium. Cobalt(II) forms a red coloured complex with TGA when air is present[4]. We found that the same absorption curve is obtained after addition of DTDGA to an air-free solution of cobalt(II), indicating that DTDGA is the ligand also in the cobalt complex.

TGA has been recommended as a reagent in spectrophotometric determination of vanadium[14]. The complex formation is very rapid, Beer's law is obeyed and interference from iron, molybdenum, cobalt and chromium can be avoided by addition of ascorbic acid and extraction of the complex with organic solvents in the presence of amines like Primene or Hyamine. However, the low molar absorptivity (57.5) and the unpleasant smell of TGA makes the method rather unattractive for practical analysis.

SUMMARY

The complex formation between vanadium(IV) and thioglycollic acid has been studied by spectrophotometric, potentiometric and extraction methods. Thioglycollic acid is oxidized by air and the oxidation product, dithiodiglycollic acid, reacts with vanadium(IV) to form a blue coloured 1:1 complex. Provided that a large excess of reagent is present, the complex is stable in the whole pH range 4–9. In the presence of long-chain amines like Primene, the complex is easily extracted into a mixture of 50% n-octanol in benzene. The distribution coefficient is 18. The absorption curve in water as well as in the organic phase has a maximum at 630 nm, Beer's law is obeyed and the molar absorptivity in both solvents is 57.5.

RÉSUMÉ

La formation de complexes entre vanadium(IV) et acide thioglycollique a été étudiée par des méthodes spectrophotométriques, potentiométriques et d'extraction. L'acide thioglycollique est oxydé à l'air; le produit d'oxydation, l'acide dithiodiglycollique, réagit avec le vanadium(IV) pour donner un complexe bleu 1 : 1. Ce complexe est stable, en présence d'un grand excès de réactif du pH 4 au pH 9. Il peut être extrait facilement en présence d'amines à longue chaîne, telle que la "Primene", dans un mélange n-octanol–benzène 50%. Le coefficient de partage est de 18. Maximum d'absorption à 630 nm; coefficient d'extinction molaire = 57.5. La loi de Beer peut s'appliquer.

ZUSAMMENFASSUNG

Die Komplexbildung zwischen Vanadin(IV) und Thioglykolsäure wurde mit spektrophotometrischen, potentiometrischen und Extraktionsmethoden untersucht. Thioglykolsäure wird durch Luft oxidiert; das Oxidationsprodukt, Dithiodiglykolsäure, reagiert mit Vanadin(IV) unter Bildung eines blaugefärbten 1 : 1-Komplexes. In Gegenwart eines grossen Reagenzüberschusses ist der Komplex im pH-Bereich 4–9 beständig. In Gegenwart langkettiger Amine wie Primene wird der Komplex leicht mit einem Gemisch von 50% n-Octanol in Benzol extrahiert. Der Verteilungskoeffizient ist 18. Die Absorptionskurve sowohl in Wasser als auch in der organischen Phase hat ein Maximum bei 630 nm. Das Beersche Gesetz ist erfüllt, der molare Extinktionskoeffizient in beiden Lösungsmitteln ist 57.5

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

REACTIONS OF SOME 2-SUBSTITUTED 8-QUINOLINOLS WITH ALUMINIUM(III) IN AQUEOUS SOLUTIONS

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(Received 1st October 1970)

In 1944, Merritt and Walker[1] observed that, although 8-quinolinol yielded an insoluble tris-complex with aluminium in aqueous solution, 2-methyl-8-quinolinol failed to react under similar conditions. Since this early work, several investigators have shown that other 2-alkyl and 2-aryl substituted 8-quinolinols did not react with aluminium[2-5] in aqueous solutions.

Recent investigations by Scherer and Fernando[6,7] have led to the isolation of several hydroxy-complexes and hydroxy-bridged dimers in the reaction of 2-methyl-8-quinolinol with aluminium in non-aqueous solution. An X-ray investigation on one of these complexes[8], a hydroxy-bridged dimer of bis(2-methyl-8-quinolinolato)aluminium(III), has shown it to be an oxo-bridged complex containing two penta-coordinated aluminium atoms. Recent work in these laboratories[9] has shown that tris(2-methyl-8-quinolinolato)aluminium(III) can be precipitated from aqueous solutions by means of very careful pH control.

In order to obtain a better understanding of this rather unusual reaction of 2-methyl-8-quinolinol with aluminium in aqueous solution, it was decided to re-investigate the reactions of some other 2-substituted 8-quinolinols. This paper reports the results of these reactions and the isolation and characterization of any complexes that are produced. The ligands used were 2-phenyl-, 2,3-dimethyl-, 2,5-dimethyl-, 2-methyl-5-chloro-, and 2,3,4-trimethyl-8-quinolinol.

EXPERIMENTAL

Preparation of the ligands

The ligands, 2,3-dimethyl, 2,3,4-trimethyl and 2-methyl-5-chloro-8-quinolinol were prepared by the Doebner–Miller reaction of *o*-aminophenols with the appropriate α,β-unsaturated aldehydes or ketones[10-12], whereas 2,5-dimethyl-8-quinolinol was obtained by a polyphosphoric acid variation of the above reaction[5]. On the other hand, 2-phenyl-8-quinolinol was prepared by the reaction of phenyllithium with 8-quinolinol in ether[10]. The results of analyses on these ligands are shown in Table I. The observed melting points agreed with reported values.

Reaction of the ligands with aluminium(III)

The conditions used for reacting the above ligands with aluminium(III) in aqueous solution were the same as those employed previously in these laboratories for the preparation of tris(2-methyl-8-quinolinolato)aluminium(III)[9], *i.e.* the ligand

TABLE I

ELEMENTAL ANALYSIS OF THE LIGANDS

Substituents	*Formula*		*Elemental analysis*			
			% Carbon	*% Hydrogen*	*% Nitrogen*	*% Chlorine*
2,3-Dimethyl	$C_{11}H_{11}NO$	Calcd.	76.3	6.4	8.1	
		Found	76.1	6.5	8.1	—
2,5-Dimethyl	$C_{11}H_{11}NO$	Calcd.	76.3	6.4	8.1	—
		Found	76.2	6.2	7.4	—
2-Methyl-5-chloro	$C_{10}H_8NOCl$	Calcd.	62.0	4.2	7.2	18.4
		Found	62.1	4.3	7.4	18.9
2-Phenyl	$C_{15}H_{11}NO$	Calcd.	81.1	5.0	6.3	—
		Found	81.2	5.0	6.2	—
2,3,4-Trimethyl	$C_{12}H_{13}NO$	Calcd.	77.0	7.0	7.5	—
		Found	77.3	7.0	7.8	—

in acetic acid was added to an aluminium(III) solution (at 65–70°) and the pH was adjusted with a 1 *M* ammonium acetate–1 *M* ammonia solution. Any material precipitated was collected in a sintered-glass crucible, washed with 1+1 aqueous ethanol, and dried in a desiccator over anhydrous calcium chloride.

Analyses of the complexes

Analyses for carbon, hydrogen and nitrogen were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne University. The aluminium content was determined (i) by ignition to the oxide at 1000° or (ii) by reaction of excess of standard EDTA solution with the aluminium and back-titration with a standard zinc solution. Chlorine was determined by the oxygen-flask method.

Infrared spectra were measured in the range 4000–400 cm^{-1} with a Perkin-Elmer 337 spectrophotometer.

RESULTS AND DISCUSSION

The ligands investigated appear to fall into three classes on the basis of their reactions with aluminium.

Precipitation of tris-chelates

The first class includes the ligands 2,5-dimethyl- and 2-methyl-5-chloro-8-quinolinol, which yield greenish-yellow complexes analysing as $Al(C_{11}H_{10}NO)_3$ and $Al(C_{10}H_7NOCl)_3 \cdot H_2O$, respectively (Table II). Precipitation commenced in both reactions at pH 4.0 and was complete in the range pH 7–8. In the reaction with the chloro-derivative, the ligand was dissolved in ethanol before addition to an aluminium solution which was 0.1 *M* in hydrochloric acid; the temperature was maintained in the range 40–45° since higher temperatures (*e.g.* 65–70°) led to unstable glue-like products.

Mass spectral analyses were carried out but only the 2,5-dimethyl complex

TABLE II

ELEMENTAL ANALYSIS OF ALUMINIUM COMPLEXES WITH 8-QUINOLINOL DERIVATIVES

Ligand in complex		*% C*	*% H*	*% N*	*% Cl*	*% Al*
2,5-Dimethyl-	Calcd.[a]	72.9	5.6	7.7	—	4.9
	Found	72.8	5.8	7.7	—	4.7
2-Methyl-5-chloro-	Calcd.[b]	57.8	3.4	6.8	17.1	4.3
	Found	57.7	3.8	6.7	17.2	4.3
2,3-Dimethyl-	Found	67.5	5.1	6.9	—	7.1
2,3,4-Trimethyl-	Found	71.9	6.3	6.7	—	6.5

[a] For $Al(C_{11}H_{10}NO)_3$.
[b] For $Al(C_{10}H_7NOCl)_3 \cdot H_2O$.

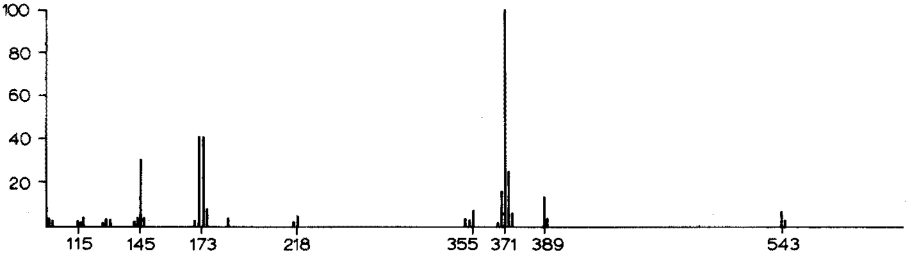


Fig. 1. Mass spectrum of the aluminium chelate of 2,5-dimethyl-8-quinolinol.

yielded a satisfactory spectrum (Fig. 1). The most intense peak, at $m/e = 371$, corresponds to the species $Al(C_{11}H_{10}NO)_2^+$, but a peak was also observed at $m/e = 543$ resulting from the molecular ion $Al(C_{11}H_{10}NO)_3^+$. The reaction, $AlL_3^+ \xrightarrow{-L} AlL_2^+$, is accompanied by the appropriate metastable peak at $m/e = 253.5$. No mass peaks higher than $m/e = 543$ were observed, and those lower than $m/e = 173$ arise mainly from ligand fragments. The 2-methyl-5-chloro complex was found to be thermally unstable above room temperature, and the largest fragment observed in the mass spectrum corresponded to the bis-species, $Al(C_{10}H_7NOCl)_2^+$.

The main features of the infrared spectra for the 2,5-dimethyl and 2-methyl-5-chloro compounds are shown in Figs. 2 and 3, respectively. Absorption bands from the free ligand are absent and infrared patterns characteristic of metal 8-quinolinolates are observed[13]. For example, the spectrum of the 2,5-dimethyl-8-quinolinol complex shows a strong band at 1272 cm^{-1}, which is absent in the spectrum of the free ligand, and a strong band is also observed in both spectra around 1100 cm^{-1}; these bands can be used as evidence of complexation[14,15], the latter being assigned to a C–O–Al stretching frequency[15].

All of the above evidence shows that the aluminium–2,5-dimethyl-8-quinolinol complex has the empirical formula $Al(C_{11}H_{10}NO)_3$. The 2-methyl-5-chloro-8-quinolinol complex is included in this category of compounds because the analytical data indicate a 1:3 ratio between aluminium and the ligand. Furthermore, the complex formed between 2-methyl-8-quinolinol and aluminium in aqueous solution, can also

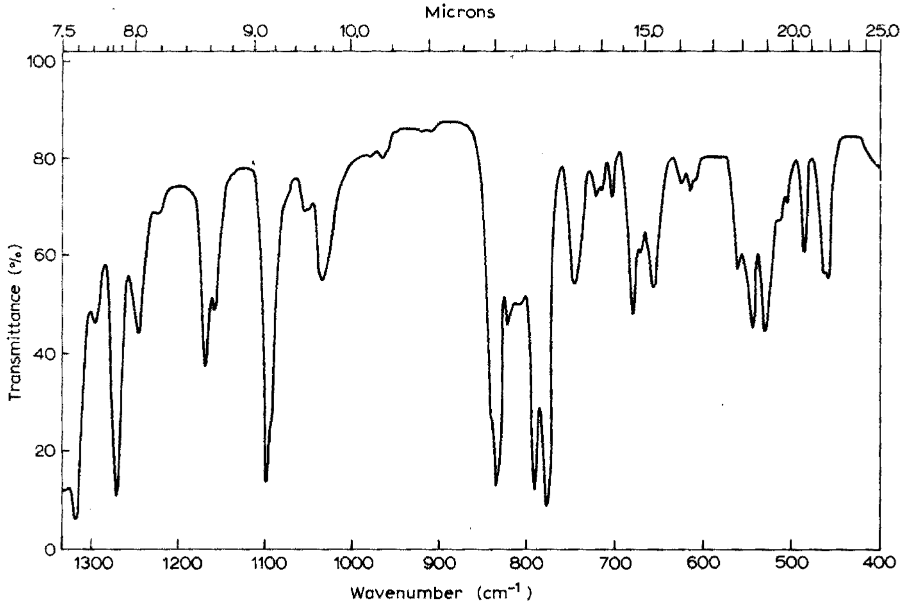


Fig. 2. Infrared spectrum of the aluminium chelate of 2,5-dimethyl-8-quinolinol.

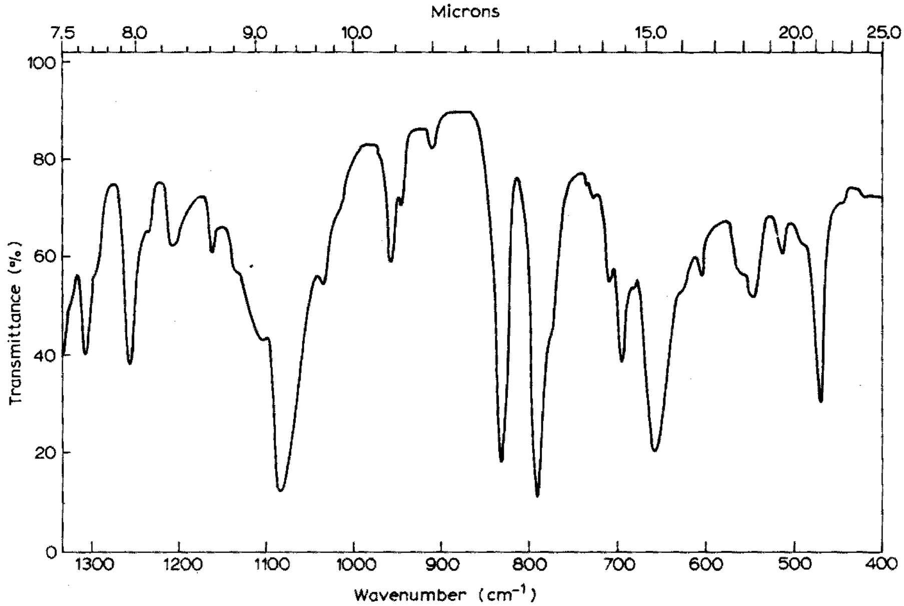


Fig. 3. Infrared spectrum of the aluminium chelate of 2-methyl-5-chloro-8-quinolinol.

be included in this group as all analytical data are consistent with the empirical formula, $Al(C_9H_6NO)_3$[16].

No n.m.r. spectra of these compounds could be obtained because of their poor solubility in the usual solvents.

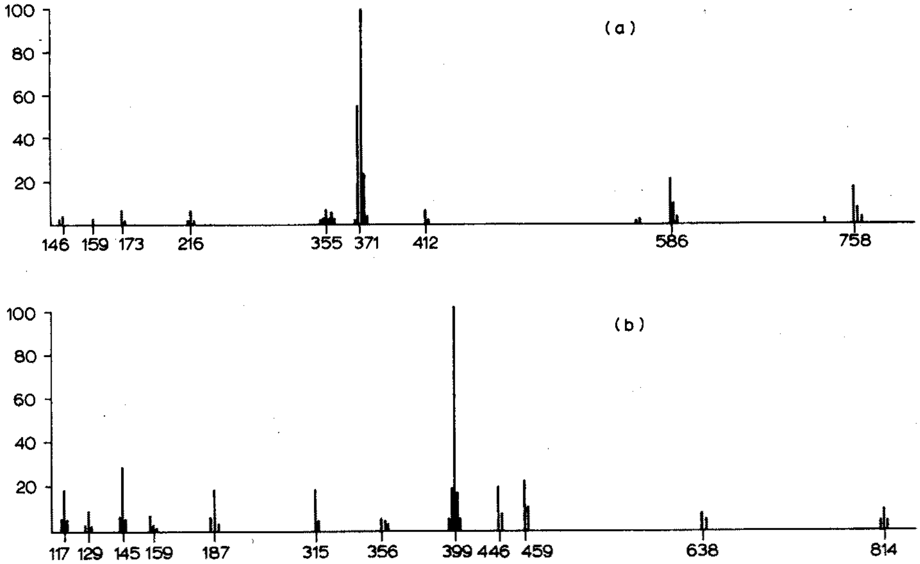


Fig. 4. (a) Mass spectrum of the chelate of 2,3-dimethyl-8-quinolinol. (b) Mass spectrum of the chelate of 2,3,4-trimethyl-8-quinolinol.

Precipitation of bis-chelates

The ligands 2,3-dimethyl- and 2,3,4-trimethyl-8-quinolinol yielded pale-yellow complexes in the pH range 7.5–9.0. The elemental analyses are given in Table II but they only serve to indicate that the complexes have ligand-to-metal ratios of 2:1.

Mass spectral analyses were obtained for samples which had been washed with 1+1 aqueous ethanol in order to remove traces of coprecipitated ligand (Figs. 4a and 4b). In both spectra, the most intense peak corresponds to the fragment ion AlL_2^+ (where L = ligand anion), but a fairly large peak was also found for the molecular ion $Al_2L_4O^+$. It is interesting to note that a mass peak was also observed for the fragment $Al_2L_3O^+$.

In the case of the complex obtained with 2,3-dimethyl-8-quinolinol (Fig. 4a), no mass peaks appeared in the spectrum at $m/e = 543$ corresponding to the tris-complex or at $m/e = 388$ for the monomeric bis-complex. It was also found that the reaction

$$\underset{758}{[AlL_2]_2O^+} \rightarrow \underset{371}{AlL_2{}^+}$$

was accompanied by the appropriate metastable peak at $m/e = 181.6$. All the evidence indicates that the complex formed between 2,3-dimethyl-8-quinolinol and aluminium in aqueous solution has the empirical formula $Al_2(C_{11}H_{10}NO)_4O$.

On the other hand, the spectrum for the complex with 2,3,4-trimethyl-8-quinolinol (Fig. 4b) showed a small peak at $m/e = 585$ corresponding to the ion $Al(C_{12}H_{12}NO)_3^+$, as well as the mass peak at $m/e = 814$ for $Al_2L_4O^+$, mentioned above. There is thus some evidence for the existence of more than one complex of

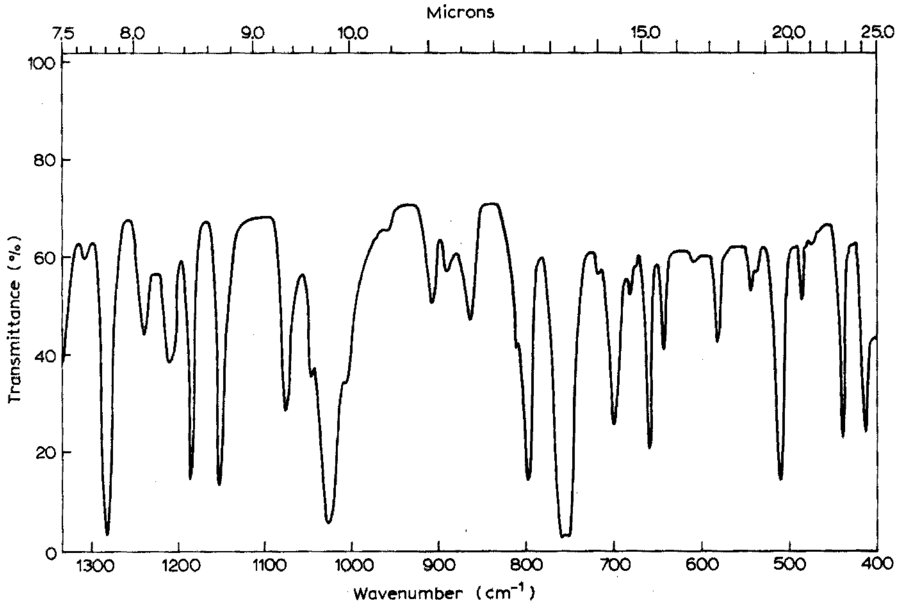


Fig. 5. Infrared spectrum of the chelate of 2,3-dimethyl-8-quinolinol.

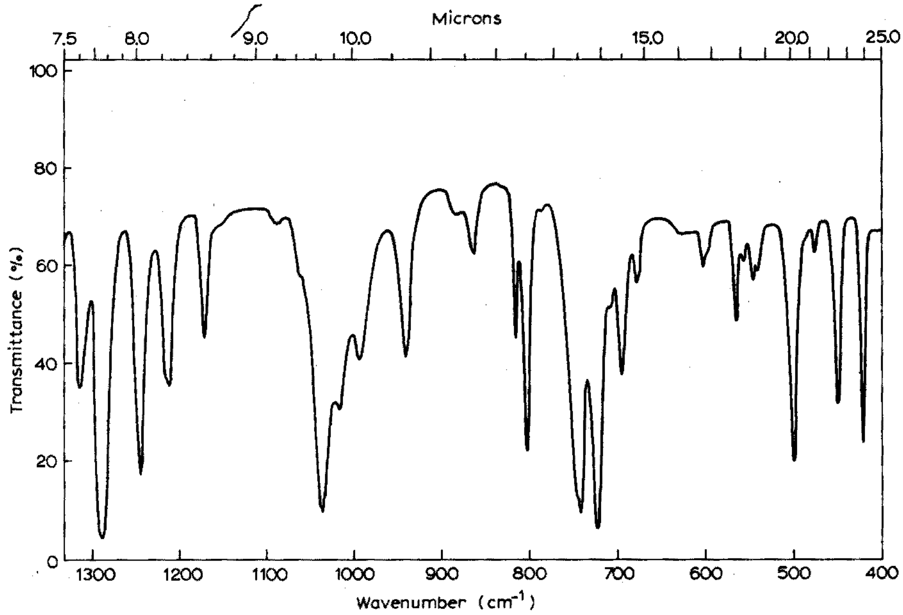
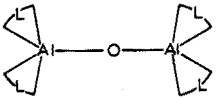


Fig. 6. Infrared spectrum of the chelate of 2,3,4-trimethyl-8-quinolinol.

aluminium(III) with 2,3,4-trimethyl-8-quinolinol. It would appear, however, that the product mixture is predominantly the dimeric bis-complex, since the elemental analyses indicate a ligand:metal ratio of 2:1.

The main features of the infrared spectra are shown in Figs. 5 and 6. Close examination of both spectra indicates that they are very similar with free ligand absorption bands being absent. A strong band is observed between 1280 and 1290 cm^{-1} and, as in the case of the solid-phase reaction between aluminium and 2-methyl-8-quinolinol[14], it is suggested that a band in this region is evidence for complexation. Although the spectra undoubtedly have the characteristic infrared patterns for 8-quinolinolates[13], it is interesting to note that the strong band which normally occurs around 1100 cm^{-1} is not observed in the spectra given here. Instead, a strong band is observed between 1020 and 1040 cm^{-1}. Scherer and Fernando[7] observed an intense band in this region (at 1011 cm^{-1}) for the compound isolated in the reaction of aluminium with 2-methyl-8-quinolinol in non-aqueous solution; this compound was later shown by single-crystal X-ray studies to be μ-oxo-di[bis(2-methyl-8-quinolinolato)aluminium(III)], containing two penta-coordinated aluminium atoms linked by a linear oxo-bridge[8].

All the above evidence suggests that the complexes isolated in the reactions of 2,3-dimethyl and 2,3,4-trimethyl-8-quinolinol with aluminium in aqueous solutions can be formulated as oxo-bridged dimers, with structures similar to μ-oxo-di[bis-(2-methyl-8-quinolinolato)aluminium(III)].



No precipitation

The only ligand which fell into this category was 2-phenyl-8-quinolinol. Various precipitating conditions were attempted without success. Further reactions were attempted in the solid phase. Homogeneous mixtures of anhydrous aluminium(III) chloride, ligand and sodium carbonate were heated for 1 h at 100–110°. Infrared studies on the cooled mixture showed no indication of complexation[14]. Attempts were also made to react the ligand with aluminium(III) chloride in non-aqueous media (chloroform and dimethyl sulphoxide), again without success. It appears that the presence of the large substituent in the 2-position prevents the formation of any complex between 2-phenyl-8-quinolinol and aluminium.

We are grateful to Dr. J. Wunderlich for carrying out the mass spectra of the complexes.

SUMMARY

The ligands 2,5-dimethyl- and 2-methyl-5-chloro-8-quinolinol react with aluminium in aqueous solution to precipitate tris-chelates. Ligands which have a substituent in the 3-position as well as in the 2-position, *viz.*, 2,3-dimethyl- and 2,3,4-trimethyl-8-quinolinol, react with aluminium under similar conditions to precipitate bis-chelates. Mass spectral studies on the latter complexes indicate that they are dimeric and contain an Al–O–Al linkage. Infrared spectra are reported for all of the complexes.

RÉSUMÉ

Les "ligandes" diméthyl-2,5- et méthyl-2-chloro-5-hydroxy-2-quinoléins réagissent avec l'aluminium, en solution aqueuse pour précipiter les trischélates correspondants. Par contre les composés tels que diméthyl-2,3- et triméthyl-2,3,4-hydroxy-8-quinoléine réagissent avec l'aluminium dans des conditions identiques pour précipiter des bis-chélates. Une étude spectrale de masse de ces derniers indique qu'ils sont dimèriques et possèdent une liaison Al–O–Al. Les spectres infra-rouges de tous ces complexes sont donnés.

ZUSAMMENFASSUNG

Die Liganden 2,5-Dimethyl- und 2-Methyl-5-chlor-8-chinolinol reagieren mit Aluminium in wässriger Lösung unter Fällung von Tris-Chelaten. Liganden mit einem Substituenten in der 3-Stellung oder 2-Stellung wie 2,3-Dimethyl- und 2,3,4-Trimethyl-8-chinolinol reagieren mit Aluminium unter ähnlichen Bedingungen unter Fällung von Bis-Chelaten. Massenspektrometrische Untersuchungen der letzteren Komplexe weisen darauf hin, dass sie dimer sind und eine Al–O–Al-Bindung enthalten. Über die Infrarotspektren aller Komplexe wird berichtet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE CHEMICAL ANALYSIS OF TELLURITE–TELLURATE COMPOUNDS

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(Received 14th September 1970)

During the preparation and study of tellurite compounds, the need arose for categorizing the valence state of tellurium in various powders and crystals. This paper describes the automatic methods developed for analyzing cadmium, indium, zinc, and various rare earth tellurite–tellurate compounds (europium, gadolinium, lanthanum, neodymium, thulium, ytterbium and yttrium).

A potentiometric method of end-point detection for EDTA titrations has been described by Reilley *et al.*[1,2]. Gardels and Cornwell[3] described the determination of the stoichiometry of various inorganic compounds by means of automatic potentiometric EDTA titrations for 11 metals. They also described stoichiometry determinations involving automatic redox titrations for chromium, selenium and tellurium. Safronkova and Lyalikov[4] determined tellurium in In–Sb–Te compounds by an iodimetric procedure in which starch was used to indicate the end-point. However, this end-point is not sharp because the solution does not become completely colorless. More recently, Beyak and Jaselskis[5] determined tellurium(VI) in the presence of tellurium(IV) and selenium(VI). Under the experimental conditions described, tellurium(IV) and selenium(VI) were rendered inactive and the tellurium(VI) was determined iodimetrically with a starch end-point. It was found that an iodimetric titration to an amperometric end-point developed by Levin and Swann[6] for the iodimetric determination of sulfide and modified by Gardels and Cornwell[7] for the determination of tellurium in In–Sb–Te, could be used to determine tellurium(VI).

Investigation has shown that the polyvalent metals of tellurite–tellurate compounds may be analyzed by automatic EDTA titrations and the valence state of tellurium categorized by automatic amperometric and potentiometric titrations. For the determination of tellurium(VI) the Bunsen[8] method for determination of active oxygen was used, based upon the following reaction:

$$\mathrm{TeO_4^{2-} + 2HCl \xrightarrow[\text{distil}]{\text{boil}} TeO_3^{2-} + H_2O + Cl_2}$$

The chlorine is swept by a stream of nitrogen into a solution containing excess of potassium iodide. The liberated iodine is titrated with thiosulfate biamperometrically with two indicator platinum electrodes. The titration is performed automatically, *i.e.* the recorder and constant rate burette are started simultaneously giving an L-shape curve, but extrapolation is necessary to determine the end-point. As shown by the above equation, tellurium(VI) can be determined only if the sample is soluble in hydrochloric acid.

Total tellurium and the EDTA-reacting metal ion are determined by fusion of a separate weighed sample with potassium pyrosulfate. Since large amounts of chloride must be avoided in potentiometric EDTA titrations[9,10], this second dissolution is necessary for a total analysis. The interference from sulfate is not as serious. If the sample size is limited, total tellurium, after determination of tellurium(VI), may be determined by biamperometric titration of the sample in the distillation flask. Tellurium(IV) in acid solution is reduced to the metal in an excess of potassium iodide. An equivalent amount of iodine is liberated which is titrated with sodium thiosulfate.

The procedure for the determination of total tellurium after fusing with pyrosulfate is based on the method of Schrenk and Browning[11], in which tellurium(IV) is oxidized to tellurium(VI) and the excess of potassium dichromate is back-titrated with previously standardized iron(II) ammonium sulfate. Cornwell and Cheng[10] have shown that potassium permanganate requires less time for complete oxidation of tellurium than potassium dichromate (15 min *vs.* 60 min). However, frequent standardization is required for accurate results, whereas the use of primary-standard potassium dichromate eliminates this step.

The other metal ion in the tellurite–tellurate system is determined by a back-titration technique; standard zinc solution is used to titrate the excess of EDTA.

EXPERIMENTAL

Reagents

Standard cadmium, indium, tellurium and zinc solutions, 0.01000 *M* were prepared from the pure metal (99.999% purity).

Standard europium, gadolinium, lanthanum, neodymium, thulium, ytterbium and yttrium solutions, 0.01000 *M*, were prepared from rare earth sesquioxides (min. 99.9%, American Potash and Chemical Co.) dissolved in a minimal amount of 1:1 nitric acid.

EDTA solution, 0.05 *M*, was prepared from its disodium salt and standardized potentiometrically against the standard zinc solution.

Standard potassium dichromate solution, 0.01000 *N*, was prepared from primary standard grade potassium dichromate.

Iron(II) ammonium sulfate solution, 0.05 *N*, was prepared from its reagent-grade salt and daily standardized potentiometrically against standard potassium dichromate.

Ammonium acetate–acetic acid buffer[12] was prepared by dissolving 500 g of ammonium acetate in 1 l of water and adding 50 ml of glacial acetic acid.

Sodium thiosulfate solution, 0.1 *N*, was prepared from "Acculute" and standardized biamperometrically against standard tellurium.

Apparatus

The apparatus used for potentiometric determinations was similar to that described by Gardels and Cornwell[3]. The electrodes as described by Cornwell and Cheng[10] were used for all potentiometric titrations.

A Precision Scientific 531365 duo-platinum electrode was used for the amperometric determination of tellurium. This electrode has two platinum wires each about 1 cm long, protruding from a sealed glass unit. The electrode, which was placed at the same position as the indicating electrode for the other titrations, was connected directly to the Radiometer PO_4 Polariter. Automatic plots were made with Sargent Constant Rate Burettes to deliver the titrant.

The distillation equipment (Fig. 1) was adapted from a reflux column designed by Horton and Thomason[13] for the polarographic determination of sulfate. The receiver was a 200-ml tall-form beaker; the top was cut off below the lip to accommodate a machined teflon cap used to prevent any possible air oxidation of the potassium iodide solution. A cap of similar design was made to hold the electrode, delivery tip and degassing tube during the titration of the liberated iodine.

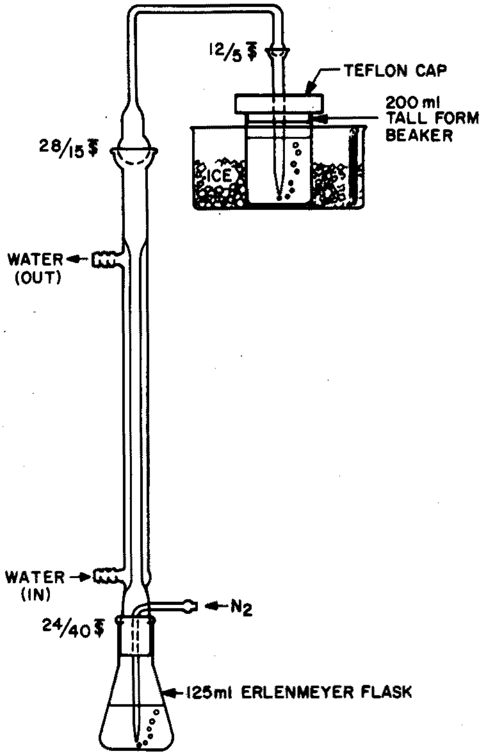

Fig. 1. Distillation apparatus.

Sample preparation

For the potentiometric determination of total tellurium and the associated metal ion, dissolve 200–250 mg of sample in 1:1 nitric acid and dilute to 200 ml. If the samples are not attacked by nitric acid, fuse with 3 g of potassium pyrosulfate in a Vycor crucible. Dissolve the melt in 10% sulfuric acid and dilute to 200 ml.

For the amperometric determination of tellurium(VI), use 200-mg samples weighed directly into the distillation flask, and dissolved in 100 ml of 60% hydrochloric acid.

Determination of complex-forming ion

To a 150-ml beaker containing 10 ml of 10% tartaric acid and 70 ml of water,

TABLE I

RESULTS OF POTENTIOMETRIC EDTA TITRATIONS

Ion	*Standard*	*Taken* (*mg*)	*Found* (*mg*)	*Deviation*	
				(*mg*)	(%)
Cd^{2+}	Cd	5.620	5.623	+0.003	+0.05
		5.620	5.622	+0.002	+0.04
	Cd + 20.01 mg Te	5.620	5.619	−0.001	−0.02
		5.620	5.620	0.000	0.00
In^{3+}	In	5.741	5.741	0.000	0.00
		5.741	5.739	−0.002	−0.04
	In + 20.01 mg Te	5.741	5.743	+0.002	+0.04
		5.741	5.738	−0.003	−0.05
Zn^{2+}	Zn	5.229	5.227	−0.002	−0.04
		5.229	5.227	−0.002	−0.04
	Zn + 20.01 mg Te	5.229	5.229	0.000	0.00
		5.229	5.232	+0.003	+0.06
Eu^{3+}	Eu_2O_3	7.598	7.592	−0.006	−0.08
		7.598	7.597	−0.001	−0.01
	Eu_2O_3 + 20.01 mg Te	7.598	7.599	+0.001	+0.01
		7.598	7.604	+0.006	+0.08
Gd^{3+}	Gd_2O_3	7.862	7.868	+0.006	+0.08
		7.862	7.869	+0.007	+0.09
	Gd_2O_3 + 20.01 mg Te	7.862	7.864	+0.002	+0.02
		7.862	7.868	+0.006	+0.08
La^{3+}	La_2O_3	6.946	6.946	0.000	0.00
		6.946	6.943	−0.003	−0.04
	La_2O_3 + 20.01 mg Te	6.946	6.943	−0.003	−0.04
		6.946	6.947	+0.001	+0.01
Nd^{3+}	Nd_2O_3	7.212	7.214	+0.002	+0.03
		7.212	7.215	+0.003	+0.04
	Nd_2O_3 + 20.01 mg Te	7.212	7.212	0.000	0.00
		7.212	7.209	−0.003	−0.04
Tm^{3+}	Tm_2O_3	8.447	8.440	−0.007	−0.08
		8.447	8.442	−0.005	−0.06
	Tm_2O_3 + 20.01 mg Te	8.447	8.447	−0.005	−0.06
		8.447	8.444	−0.003	−0.04
Yb^{3+}	Yb_2O_3	8.652	8.646	−0.006	−0.07
		8.652	8.648	−0.004	−0.05
	Yb_2O_3 + 20.01 mg Te	8.652	8.645	−0.007	−0.08
		8.652	8.645	−0.007	−0.08
Y^{3+}	Y_2O_3	5.334	5.334	0.000	0.00
		5.334	5.336	+0.002	+0.04
	Y_2O_3 + 20.01 mg Te	5.334	5.334	0.000	0.00
		5.334	5.331	−0.003	−0.06

add a sample aliquot containing 5–15 mg of the complex-forming ion. Add 5 ml of ammonium acetate–acetic acid buffer followed by 3 drops of commercial mercury–EDTA solution (E. H. Sargent). Add a known excess of standardized EDTA solution. Immerse the mercury indicator electrode, saturated calomel electrode and pH combination electrode. After adjusting to pH 5.6 with ammonia solution, obtain a potential–titrant curve with 0.01000 *M* standard zinc solution. From the potentiometric curve, select the end-point and proportional band settings. After preparing another sample as described above, perform an automatic titration.

Determination of total tellurium

To a 400-ml beaker containing 200 ml of water and 10 ml of concentrated sulfuric acid, add a sample aliquot containing 5–15 mg of tellurium. Add a known excess of standard potassium dichromate solution. Stir and allow to stand for 45–60 min. Immerse the platinum ring electrode and the saturated calomel electrode and obtain a potential–titrant curve with previously standardized iron(II) ammonium sulfate solution. From the potentiometric curve, select the end-point and proportional band settings.

TABLE II

RESULTS OF POTENTIOMETRIC TITRATION FOR THE DETERMINATION OF TELLURIUM(IV)

Standard	*Taken (mg)*	*Found (mg)*	*Deviation*	
			(mg)	(%)
Te	8.932	8.925	−0.007	−0.08
	8.932	8.932	0.000	0.00
	8.932	8.939	+0.007	+0.08
	8.932	8.934	+0.002	+0.02
Te+5.620 mg Cd	8.932	8.936	+0.004	+0.04
	8.932	8.932	0.000	0.00
Te+5.741 mg In	8.932	8.930	−0.002	−0.02
	8.932	8.931	−0.001	−0.01
Te+5.229 mg Zn	8.932	8.931	−0.001	−0.01
	8.932	8.940	+0.008	+0.09
Te+7.598 mg Eu	8.932	8.934	+0.002	+0.02
	8.932	8.930	−0.002	−0.02
Te+7.862 mg Gd	8.932	8.928	−0.004	−0.04
	8.932	8.926	−0.006	−0.07
Te+6.946 mg La	8.932	8.937	+0.005	+0.06
	8.932	8.932	0.000	0.00
Te+7.212 mg Nd	8.932	8.931	−0.001	−0.01
	8.932	8.927	−0.005	−0.06
Te+8.447 mg Tm	8.932	8.935	+0.003	+0.03
	8.932	8.931	−0.001	−0.01
Te+8.652 mg Yb	8.932	8.925	−0.007	−0.08
	8.932	8.939	+0.007	+0.08
Te+5.334 mg Y	8.932	8.937	+0.005	+0.06
	8.932	8.928	−0.004	−0.04

band settings.

Determination of tellurium(VI)

Weigh 200 mg of finely ground sample into a 125-ml Erlenmeyer flask fitted with a 24/40 ground glass joint. Add 100 ml of deaerated 60% hydrochloric acid and immediately connect the flask to the reflux condenser of the distillation system. Purge with nitrogen and heat the sample to boiling, allowing the chlorine to pass into a closed receiver flask containing 100 ml of deaerated and cooled 10% potassium iodide and 1% urea. Continue to heat the sample for 5 min after the first signs of liberated iodine.

Remove the receiver, add 5 ml of hydrochloric acid, and insert the twin platinum electrodes. Apply 110 mV across the electrodes. Start the constant rate burette and recorder simultaneously and titrate to an amperometric end-point with 0.01000–0.10000 *N* sodium thiosulfate. Maintain a stream of nitrogen over the sample throughout the entire titration. Extrapolate the end-point and make volume corrections.

RESULTS AND DISCUSSIONS

The methods were tested by performing titrations on synthetic standards.

TABLE III

RESULTS OF AMPEROMETRIC TITRATIONS FOR THE DETERMINATION OF TELLURIUM(VI)

Standard	*Taken (mg)*	*Found (mg)*	*Deviation*	
			(mg)	(%)
$H_2TeO_4 \cdot 2H_2O$	69.45	69.39	−0.06	−0.08
	69.10	69.20	+0.10	+0.14
	69.31	69.34	+0.03	+0.04
	69.53	69.47	−0.06	−0.09
$H_2TeO_4 \cdot 2H_2O$ + 50 mg Te	68.93	68.85	−0.08	−0.12
	69.21	69.20	−0.01	−0.01
$H_2TeO_4 \cdot 2H_2O$ + 50 mg Cd	68.84	68.82	−0.02	−0.03
	69.37	69.43	+0.05	+0.07
$H_2TeO_4 \cdot 2H_2O$ + 50 mg In	69.00	69.01	+0.01	+0.01
	69.13	69.03	−0.10	−0.14
$H_2TeO_4 \cdot 2H_2O$ + 50 mg Zn	69.60	69.63	+0.03	+0.04
	69.25	69.30	+0.05	+0.07
$H_2TeO_4 \cdot 2H_2O$ + 60 mg Eu_2O_3	69.53	69.45	−0.08	−0.12
	69.34	69.34	0.00	0.00
$H_2TeO_4 \cdot 2H_2O$ + 60 mg Gd_2O_3	69.01	69.00	−0.01	−0.01
	68.73	68.70	−0.03	−0.04
$H_2TeO_4 \cdot 2H_2O$ + 60 mg La_2O_3	68.61	68.63	+0.02	+0.03
	68.37	68.43	+0.06	+0.09
$H_2TeO_4 \cdot 2H_2O$ + 60 mg Nd_2O_3	67.36	67.26	−0.10	−0.15
	69.27	69.20	−0.07	−0.10
$H_2TeO_4 \cdot 2H_2O$ + 60 mg Tm_2O_3	68.33	68.37	+0.04	+0.06
	68.66	68.64	−0.02	−0.03
$H_2TeO_4 \cdot 2H_2O$ + 60 mg Yb_2O_3	69.91	69.92	+0.01	+0.01
	69.19	69.30	+0.11	+0.16
$H_2TeO_4 \cdot 2H_2O$ + 60 mg Y_2O_3	67.55	67.52	−0.03	−0.04
	69.77	69.68	−0.09	−0.13

Tables I–III illustrate the results obtained by potentiometric EDTA, redox and amperometric titrations, respectively. Precision of 0.1–0.2% can generally be obtained. As shown in Table II, the non-oxidizable metallic ions do not interfere with the determination of tellurium with potassium dichromate. In agreement with other authors[3,14], a blank was observed when dichromate was titrated with iron(II) ammonium sulfate. The value of the blank, which is probably caused by the formation and dissolution of the oxide layer on the electrode, was determined by titrating successive aliquots of potassium dichromate added to the same beaker.

Tests for interferences in the determination of tellurium(VI) (Table III) were performed by adding aliquots of rare earth oxides dissolved in 1+1 hydrochloric acid directly to the distillation flask containing weighed portions of telluric acid. Other metals were added as their chlorides. To prevent possible oxidation of any chloride to chlorine, the use of nitric acid was avoided.

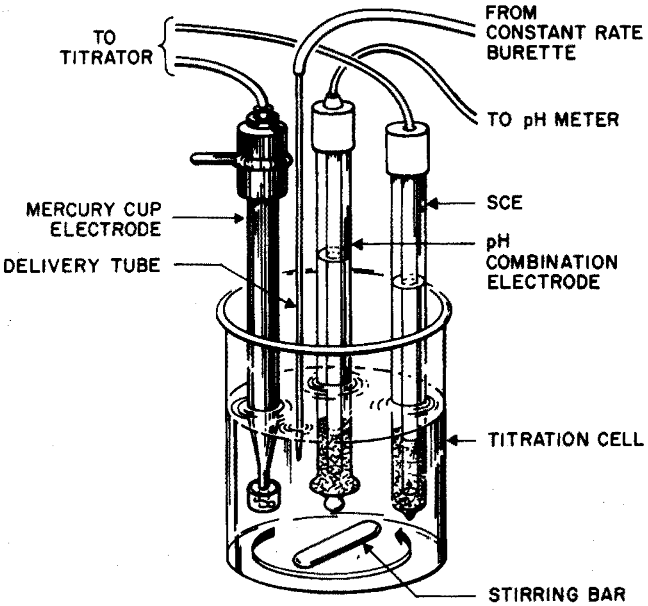

Fig. 2. Titration cell for potentiometric EDTA titrations.

Figure 2 shows the positioning of the electrodes and delivery tip for potentiometric EDTA titrations. Satisfactory results for potentiometric and amperometric determinations were obtained only when the delivery tip was positioned away from, and not in the same plane as, the indicator electrode. Smooth and continuous stirring was essential. The pH combination electrode was not used to monitor pH for redox and amperometric titrations.

The effect of tartaric acid, used to prevent precipitation of the tellurium as tellurium dioxide, on the potential break for EDTA titrations is shown in Fig. 3. Although the magnitude of the potential break is lowered by approximately 30 mV, the curve remains suitable for automatic titrations.

This investigation has shown that tellurites and tellurates may be accurately analyzed by automatic titration techniques. Although the study was limited to the seven rare earths described, the methods cited should be applicable to all type-4*f* rare-earth tellurite–tellurate compounds.

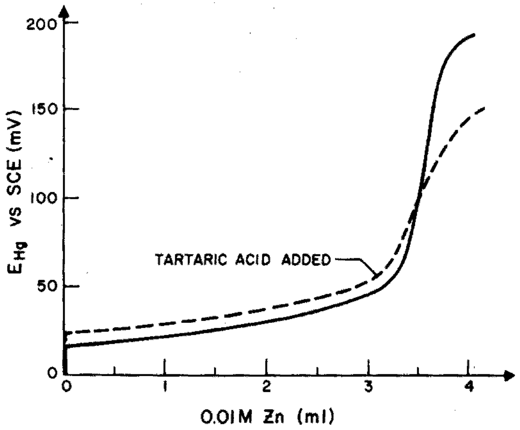

Fig. 3. Effect of tartaric acid on the titration curve of excess EDTA with standard zinc solution.

SUMMARY

Methods have been developed for the analysis of tellurite–tellurate compounds by means of automatic amperometric and potentiometric titrations. Tellurium(VI) is determined by the classical Bunsen method; the chlorine is absorbed in an excess of potassium iodide, and the liberated iodine is titrated automatically with sodium thiosulfate to an amperometric end-point. After fusion with potassium pyrosulfate, total tellurium and the associated metal ion are determined by automatic potentiometric redox and EDTA titrations, respectively.

RÉSUMÉ

Des méthodes sont proposées pour l'analyse de composés tellurite–tellurate, au moyen de titrages ampérométriques et potentiométriques automatiques. Le tellure(VI) est dosé par la méthode classique de Bunsen; le chlore est absorbé dans l'iodure de potassium et l'iode libéré est titré automatiquement par le thiosulfate de sodium, avec point final ampérométrique. Après fusion à l'aide de pyrosulfate de potassium, le tellure total, et l'ion métallique associé, sont dosés par potentiométrie rédox automatique et titrages EDTA, respectivement.

ZUSAMMENFASSUNG

Für die Analyse von Tellurit–Tellurat-Verbindungen wurden Methoden der automatischen amperometrischen und potentiometrischen Titration entwickelt. Tellur(VI) wird nach der klassischen Bunsen-Methode bestimmt. Das Chlor wird in

überschüssigem Kaliumjodid absorbiert und das freigesetzte Jod automatisch mit Natriumthiosulfat bis zu einem amperometrischen Endpunkt titriert. Nach einem Kaliumpyrosulfat-Aufschluss werden das gesamte Tellur und das zugehörige Metallion durch automatische potentiometrische Redox- bzw. EDTA-Titration bestimmt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE USE OF SILICA GEL FOR THE SEPARATION OF TRACES OF URANIUM

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(Received 15th August 1970)

Spectrophotometric and fluorimetric procedures provide the most convenient analytical methods for the determination of traces of uranium. Many organic reagents have been suggested for this purpose, the best being arsenazo III[1]. However, despite the great selectivity of its colour reaction with uranyl ions, a preliminary separation of interfering elements is necessary for the determination of traces of this metal.

In the present paper, which completes previous studies[2-5], the separation of microgram amounts of uranyl ions by sorption on a silica gel column is described, and details of applications to rocks and natural waters are given.

EXPERIMENTAL

Apparatus

Absorbances were measured with a Uvispek (Hilger) spectrophotometer.

The pH values of solutions were measured with a Radiometer pH meter TTT 1. Activity corrections were not applied to concentrated electrolytes. Thus, the pH values measured can be considered as "conditional", related to the given reaction equilibria in the solutions.

Reagents

Arsenazo III was purified as described by Savvin[1]. A 0.25% solution of this dyestuff in 0.02 *M* sodium hydroxide was prepared for the final photometric determination. This solution was stable for at least one week.

Silica gel for the chromatographic separations was prepared as described by Pitra and Štěrba[6] (50–100 mesh). Its specific surface estimated by the method of Sears[7] was about 300 $m^2\ g^{-1}$.

Chromatographic columns were of the usual shape with an internal diameter of 12 mm. They contained 10 ml of the above-mentioned adsorbent. Before use the column was washed with 50 ml of 3 *M* hydrochloric acid and then with water until a neutral reaction was obtained. Finally, the column was washed with the appropriate buffer solution.

The wash solution used for most of the chromatographic separations contained 0.5 *M* sodium chloride, 0.3 *M* ammonium chloride, 0.015 *M* EDTA and 0.015 *M* tartaric acid. The pH value was adjusted to the required value by addition of 4 *M* ammonia solution. All reagents were of analytical-reagent grade.

General spectrophotometric method

The following procedure for the determination of uranium(VI) in weakly acidic solution was used to evaluate the efficiency of the sorption process. The measurements were made in 0.2 *M* monochloracetic acid buffer solution[1,8] or in acetic acid medium[5]. Acetic acid does not influence the colour intensity of the chelate within a wide concentration range (0.5–14 *M*). As the adsorbed uranyl ions can be leached from the column with dilute acetic acid, it is possible to develop the colour reaction immediately in the eluate without any further pH adjustment. The details of the procedure were worked out on the basis of many preliminary experiments.

Procedure. To the acetic acid solution containing 3–50 μg of uranium(VI), add 2 ml of 0.2 *M* EDTA, 2 ml of 0.1 *M* sodium fluoride, 1 ml of 1 % ascorbic acid and 0.5 ml of 0.25% arsenazo III. Dilute the solution to 50 ml in a volumetric flask. Measure the absorbance at 656 nm within 30–120 min after dilution.

RESULTS

The spectrophotometric determination of uranyl ions with arsenazo III

The interferences of Th, Zr, La, Ce(IV), Ti, Al, Fe(III), Ca, Mg on the colour reaction of uranium with arsenazo III were studied in a 2.4 *M* acetic acid medium. The most efficient masking agents proved to be EDTA and sodium fluoride. Because of competition equilibria, their screening effect depended on the amount of the dyestuff added. In the procedure described above, various foreign ions could be present in chromatographic eluate without affecting the determination of uranium. As can be seen from Table I, aluminium(III) and thorium(IV) ions caused some difficulties. The colour reaction of aluminium(III) with arsenazo III was very weak and well masked with EDTA and fluoride. However, aluminium(III) caused the absorbance of the solution to increase because of the equilibrium shift in favour of the coloured uranium complex owing to the consumption of masking agents by aluminium(III). The interference of thorium can be explained similarly.

TABLE 1

INFLUENCE OF SOME METAL IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM
(20 μg U(VI) and 20 ml of 6 *M* acetic acid present; other conditions as in General Procedure)

Metal ion added (μg)	*Error* (%)	*Metal ion added* (μg)	*Error* (%)
100 Th	+ 9.5	5 La + 50 Th +	
50 Th	+ 4.8	+ 10 Zr + 500 Ti	+ 9.3
50 La	+ 19.6	5 La + 50 Th +	
5 La	+ 1.3	+ 10 Zr + 200 Ti	+ 3.3
2000 Ti	+ 6.8	50 Ce(IV)	+ 11.1
500 Ti	+ 1.3	20 Ce(IV)	+ 5.5
200 Ti	− 1.3	1000 Ca	+ 8.2
100 Zr	+ 0.7	1000 Mg	− 0.6
500 Ti + 100 Zr	+ 1.3	1000 Fe(III)	+ 1.3
10 La + 50 Th +		3000 Al	+ 26.6
+ 100 Zr + 500 Ti	+ 18.8	500 Al	+ 8.8
5 La + 50 Th		200 Al	+ 1.3
+ 100 Zr + 500 Ti	+ 12.1	500 Al + 50 Th	+ 14.2
		100 Al + 50 Th	+ 6.1

Sorption of microgram amounts of uranium(VI) on silica gel columns

Uranyl ions were retained when the solution was passed through a silica gel column. The sorption behaviour of uranium is most conveniently illustrated by the sorption curves for different media (Fig. 1). To establish these curves, 200 ml of salt or buffer solution containing 100 μg of uranium(VI) were passed through the silica gel column at a flow rate of 2–3 ml min^{-1}. The column was washed with 100 ml of a solution having the same composition but without uranium(VI), and finally with 100 ml of water. The uranium retained was eluted with 40 ml 3 *M* acetic acid and determined spectrophotometrically.

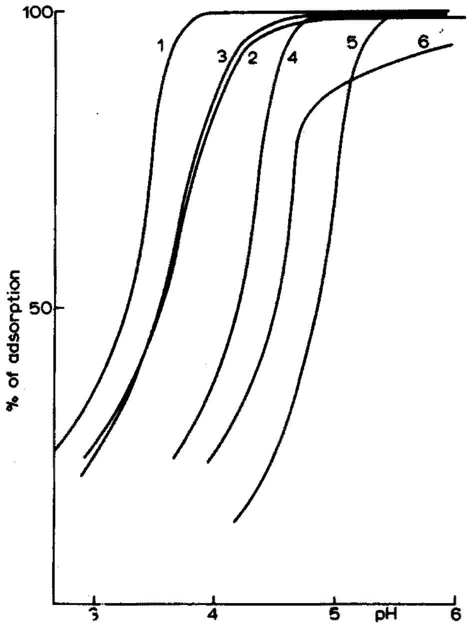

Fig. 1. Adsorption curves of uranium(VI) (100 μg) from different media. (1) 0.1 *M* NH_4Cl; (1) 0.1 *M* NH_4Cl and 0.04 *M* EDTA; (3) 0.5 *M* NaCl, 0.3 *M* NH_4Cl and 0.04 *M* EDTA; (4) 0.5 *M* NaCl, 0.3 *M* NH_4Cl, 0.04 *M* EDTA and 0.03 *M* tartaric acid; (5) 0.25 *M* sodium acetate and 0.04 *M* EDTA; (6) 0.25 *M* sodium formate and 0.04 *M* EDTA.

In media containing uranyl ion and salts such as ammonium or sodium chloride, the extent of adsorption depended only on the pH of the solution. Complete retention was obtained within the pH range 4–9 (Fig. 1, curve 1), but the selectivity was poor, many other ter- and tetravalent cations being retained simultaneously. Masking agents improved the selectivity but the pH limit of quantitative uranium sorption (more than 98%) became higher owing to the simultaneous reaction of uranium(VI) with masking agents. EDTA proved to be the most efficient complexing agent for this purpose; its chelate with uranium(VI) is weak and only a small shift of the pH limit of quantitative sorption (about 0.5 pH unit, see Fig. 1, curve 2) was found. The completeness of uranium adsorption depended neither on the concentration of EDTA (in the studied interval 0.01–0.08 *M*) nor on the volume of the solution (50–250 ml) used for sorption and washing. The concentration of the washing solution also had no effect on retention of uranium(VI). The sorption of some other metal ions (*e.g.* Zr, Ti, Al, Sn) could be further decreased by addition of tartaric acid, though it caused a small additional shift of pH limit (Fig. 1, curves 3 and 4). Ammonium and alkali metal salts did not affect the shape of the sorption curves (Fig. 1, curves 2 and 3). No buffer systems for maintaining the pH values were used because of their tendency to complex formation. Acetates shifted the lower pH limit to 5.5, and the effect of formates was even more pronounced (Fig. 1, curves 5 and 6). The buffer properties of EDTA were sufficient for regulation of the hydrogen ion concentration during the sorption process ($pK_2 = 2.73$; $pK_3 = 6.24$)[9].

The elution of the adsorbed uranyl ions from the silica gel column was very easy. This is the main advantage of this sorbent compared to synthetic ion-exchange resins such as Dowex 50, Dowex A1[8], etc.; 100 μg of uranium(VI) can be completely eluted with about 40 ml of 3 *M* acetic acid[5].

Separation of other elements

The extent of adsorption of elements interfering with the final photometric uranium determination was studied under the optimal conditions found for retention of uranium. As the affinity of most metal ions for silica gel is lower, and their chelates with EDTA and tartaric acid are more stable, than those of uranium, the selectivity of the sorption process for uranium increases both with increasing hydrogen ion concentration and with the use of EDTA and tartaric acid as masking agents.

As the photometric determination requires a highly efficient separation of uranium from accompanying elements, it was necessary to decrease the pH value of the solution as much as possible. The limiting value pH 4.8 (Fig. 1, curve 4) cannot be recommended for routine analysis, for there is a danger of incomplete retention owing to uncontrolled shifts of pH.

The composition of the analysed solutions was chosen according to the presumed application of this procedure. Rock samples are usually decomposed by alkali fusion, which eventually introduces large amounts of neutral salts into the solution. As mentioned previously, high ionic strength did not affect the sorption of uranium (Fig. 1, curves 2 and 3) but could affect the sorption equilibria of other metal ions and the measured pH values. For the usual alkali fusion, the salt concentration in the sorbed solution was estimated to be 0.5 *M* sodium chloride and 0.3 *M* ammonium chloride. The effect of the concentration of the wash solution was also tested, and was found to be important in the case of thorium. The sorption behaviour of large amounts of Al, Fe(III), Ca, Mg and Ti and microgram quantities of Th, Zr, Ce(IV) and La was examined; the amounts of these metals were chosen according to the presumed composition of the rock samples.

To the solution containing the metal ions mentioned, 50 ml of mixed 2 *M* sodium chloride and 1.2 *M* ammonium chloride, 30 ml of 0.2 *M* EDTA (at least 20 ml in excess) and 10 ml of 0.6 *M* tartaric acid were added. After the solution had been adjusted to the desired pH value with 4 *M* ammonia solution, it was diluted to 200 ml and passed through the silica gel column which had been previously washed with the wash solution (p. 335) at a flow rate 2–3 ml min^{-1}. Finally, the column was washed with 100 ml of diluted (1+9) wash solution and with 100 ml of water. Depending on the element to be determined, the elution was performed as follows: (*a*) 40 ml of 3 *M* acetic acid (added in 10-ml portions), to determine uranium and other elements;

(*b*) after (*a*), elution with 50 ml of 3 *M* hydrochloric acid to remove any remaining metals uneluted with acetic acid; (*c*) when the sorption process was to be repeated, the first elution was performed with 27 ml of 3 *M* hydrochloric acid and 40 ml of water. After addition of 20 ml of 0.2 *M* EDTA, 5 ml of 10 *M* sodium hydroxide, 2 ml of 12 *M* ammonia solution and 5 ml of 0.6 *M* tartaric acid, and after the pH had been adjusted appropriately with 4 *M* ammonia solution, the solution was diluted to 100 ml and the sorption process was repeated. For the final elution, acetic acid was used as in (*a*).

The eluate was usually collected in a 50-ml graduated flask and the uranium content was measured spectrophotometrically. Other elements were determined by spectrophotometric[10], compleximetric and atomic absorption methods[11].

TABLE II

SORPTION OF SOME METAL IONS ON SILICA GEL COLUMNS

Mg metal ion added	*% Found in eluate after sorption at*			
	pH 5		*pH 5.5*	
	A[a]	*B*[b]	*A*[a]	*B*[b]
100 Ca	0.006	0.007	—	—
50 Mg	0.007	0.005	—	—
50 Fe(III)	0.012	0.038	0.015	0.044
100 Al	3.81	0.1	3.48	0.1
20 Ti	0.31	1.57	0.43	2.32
1 Zr	0.03	0.2[c]	0.11	0.2[c]
0.5 Th	15.1	0.6	35.3	0.7
0.5 Th	48.0[d]	0.9[d]	88.3[d]	0.7[d]
0.1 La	0.15	2.2	0.45	1.9
0.1 Ce(IV)	0.15	0.4	0.15	1.7

[a] Eluted with 3 *M* acetic acid

[b] Subsequent elution of the rest of retained metal ions with 3 *M* hydrochloric acid.

[c] Subsequent elution with 0.1 *M* oxalic acid.

[d] Diluted wash solution (1 + 9) was used.

The results of these experiments are summarised in Table II, from which the following conclusions can be drawn. The retention of all metal ions decreased with decreasing pH value so that the selectivity of the silica gel for uranium improved; pH 5 proved to be the best. There was a further chromatographic separation during elution of the retained metal ions with acetic acid. It was verified that the concentrated wash solution increased the separation effect for thorium. Finally, the separation effect of simple sorption was sufficient for all the mentioned elements except thorium and aluminium.

The content of thorium and aluminium in the eluate was substantially decreased (Th to 15% and Al to 4% of the original amounts)[*]. However, because of the composition of the sample rock materials and the interferences of these metals in

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[*] The retention of aluminium is not caused by the incomplete formation of the chelate. The sorption ratio was the same even after a preliminary boiling of the solution in the presence of EDTA.

the photometric uranium determination, the simple procedure was not sufficient. A repeated sorption for the separation of uranium from excess of these elements proved to be the most convenient (elution procedure *c*). Even with this repeated sorption procedure, the recovery of uranium exceeded 97% of the original amount, which corresponds to the values obtained from the sorption curves. The separation efficiency of the procedure is illustrated in Table III, where the results of determinations of uranium in presence of aluminium(III) and a mixture of other elements including thorium, are given.

TABLE III

DETERMINATION OF URANIUM AFTER CHROMATOGRAPHIC SEPARATION FROM MIXTURES OF SOME METAL IONS

pH of the sorbed solution	*Number of sorptions*	*U(VI) added* (μg)	*U(VI) found* (μg)	*Error* (%)
5.5[b]	1	20	25.8	+29
5.5[a]	1	20	23.8	+19
5.0[b]	1	20	22.9	+14.5
5.0[a]	1	20	21.9	+ 9.5
5.0[b]	1	0	0.0	0.0
4.8[b]	1	20	20.8	+ 4
4.8[b]	1	0	0.0	0.0
5.0[b]	2	20	20.5	+ 2.5
5.0[a]	2	20	20.1	+ 0.5

[a] The solution contained 100 mg Al.

[b] The solution contained mixture of 100 mg Al; 50 mg Mg; 100 mg Ca; 50 mg Fe(III); 20 mg Ti; 0.5 mg Zr; 0.2 mg Th; 0.1 mg La; 0.1 mg Ce(IV).

Sorption process

Most published papers on the sorption of inorganic ions on silica gel explain the sorption as an ion-exchange reaction between gel and solution. Weakly acidic silanol groups have been proved in the structure of silica gel[12,13], and these confer the character of a weakly acidic cation exchanger. The reaction can be described by the following equation:

$$\geqslant \mathrm{SiOH} + \mathrm{Me}^{+} \rightleftharpoons \geqslant \mathrm{SiOMe} + \mathrm{H}^{+}$$

Compared to strongly acidic cation exchangers, where the sorption of uranium is completely suppressed by EDTA above pH 3[14,15], the affinity of uranyl ions for weakly acidic cation exchangers (*e.g.* Amberlite IRC 50[4,16,17]) and therefore also for silica gel is very high. In this case, the anionic chelates decompose on passage through the gel column and sorption is complete.

Detailed studies of the sorption process showed that EDTA is also partially retained. The silica gel column (10 ml of gel previously washed with redistilled 6 *M* hydrochloric acid and water) was treated with 100 ml of solution containing 0.1 *M* ammonium chloride and 0.001 *M* EDTA (pH 5.5 and 8), then with 100 ml of 0.01 *M* ammonium chloride and finally with 100 ml of water. The EDTA content in the collected effluents was determined titrimetrically with 0.01 *M* zinc acetate to eriochrome black T indicator. The procedure was repeated several times. After the last traces of metal impurities had been removed, the decrease in the EDTA concentration on passage through the column remained constant at the value 0.5–1.2 μmoles of EDTA, which value could not be reduced by further washing. The same procedure was used for the determination of EDTA in the effluent obtained after passing 100 ml of 0.001 M EDTA and 0.1 M ammonium chloride (pH 5.5 and 8) solution containing 7 and 14 mg (30 and 60 μmoles) of uranium(VI), through the column. The results are given in Table IV, from which it is evident that the amount of EDTA contained in the sorbed particles is in a constant ratio to the amount of uranium independently of the pH value in the given range. A similar phenomenon was found during the sorption of aluminium(III) from EDTA medium at pH 5–5.5. The aluminium compounds retained contained an amount of EDTA which represented 80–90% of the theoretical 1:1 molar ratio.

TABLE IV

RETENTION OF EDTA ON SILICA GEL COLUMN

(Reaction conditions are given in the text)

U(VI) added (μmoles)	*EDTA retained on column (μmoles)*	*pH*
0	0.9	5.5
30	6.2	5.5
60	11	5.5
0	1.2	8
30	7.3	8
60	12.3	8

When the uranium–DCTA system was examined no increase of complexing agents was detected in the eluate, indicating that this complex is completely decomposed during the sorption. These experiments proved that the sorption equilibria in the complexing electrolyte media used are more complicated than is suggested by the equation given above. It is evident that the amount of the retained complex-forming agents (EDTA, DCTA) and the composition of the retained particle depend on the stability of the given metal chelate.

THE DETERMINATION OF URANIUM IN ROCKS

The purpose of the work was to establish a reliable but simple analytical method for the routine determination of small amounts of uranium in rocks and waters. In most cases, treatment of the rock sample with inorganic acids (especially a mixture of hydrofluoric acid with an oxidising agent) is sufficient, but the choice depends on the mineralogical character of the material under consideration. For rock samples of an unknown composition alkali fusion is the generally adopted method.

Recommended procedure

If it is known that the particular type of rock can be decomposed with acid, weigh a sample of previously ignited rock into a small platinum dish and decompose by fuming with 2 ml of 14 *M* nitric acid, 3 ml of 18 *M* sulphuric acid and 20 ml of 22 *M* hydrofluoric acid until dense fumes of sulphur trioxide appear. Repeat the fuming step, dissolve the residue in 10 ml of 3 *M* hydrochloric acid and transfer to a 200-ml graduated flask.

For rocks of unknown composition, fuse 0.5–1.5 g of the finely ground sample with 10 g of sodium carbonate in a platinum crucible. Dissolve the melt in 6 *M* hydrochloric acid containing 2–3 ml of 14 *M* nitric acid, and evaporate the solution to dryness. Dissolve the residue in 10 ml of 12 *M* hydrochloric acid and dilute with hot water. Filter off the precipitated silicic acid and wash with 0.5% (v/v) hydrochloric acid and then with hot water. Collect the filtrate in a 200-ml graduated flask. Ignite the filter containing silicic acid in the platinum crucible which was used, and heat the residue with 20 ml of 22 *M* hydrofluoric acid and 0.5 ml of 18 *M* sulphuric acid. It is essential to remove all hydrofluoric acid by fuming. Again fuse the residue with a small amount of 3+1 sodium carbonate–borax, dissolve the melt in 6 *M* hydrochloric acid and add to the main solution. The precipitated silicic acid usually contains a negligible amount of uranium. Dilute the solution in the flask to 200 ml.

Take a suitable aliquot of the solution containing 3–50 μg of uranium(VI) (100 ml maximum) and add 70 ml of 0.2 *M* EDTA and 10 ml of 0.6 *M* tartaric acid solution. Dilute to 200 ml and neutralise to pH 5 with 14 *M* ammonia solution. When 100 ml of the stock solution is taken, the salt concentration after dilution and neutralisation is about 0.5 *M* in sodium chloride and 0.3 *M* in ammonium chloride, the values which were found convenient for the sorption step. Accordingly, the amounts of sodium carbonate and hydrochloric acid used above are essential. If the aliquot taken is less than 100 ml, or if the acid decomposition method is used, appropriate amounts of sodium chloride and ammonium chloride should be added.

Wash the silica gel column with wash solution at pH 5 (p. 335), and then pass the sample solution through the column at a flow rate of 2–3 ml min^{-1}. Wash the column with 100 ml of wash solution (pH 5) and with 100 ml of water. Elute the retained uranium(VI) with 27 ml of 3 *M* hydrochloric acid and 40 ml of water at a flow rate of 1–2 ml min^{-1}. Add 20 ml of 0.2 *M* EDTA, 5 ml of 0.6 *M* tartaric acid, 5 ml of 10 *M* sodium hydroxide and 2 ml of 14 *M* ammonia solution to the eluate and adjust the pH value to 5. Repeat the sorption procedure as described, eluting with 40 ml of 3 *M* acetic acid added in 10-ml portions. Collect the eluate in a 50-ml graduated flask. Add 2 ml of 0.2 *M* EDTA, 2 ml of 0.1 *M* sodium fluoride, 1 ml of 1% (w/v) ascorbic acid and 0.25 ml of 0.5% arsenazo solution. Dilute the solution to the mark, and measure the absorbance at 656 nm.

Results

The proposed method was verified by the analyses of rocks of various composition with uranium contents within the range 10^{-3}–10^{-1}%. The results (Table V) indicated that higher and apparently more correct values (compared with the results of other laboratories) were obtained by alkali fusion, especially for smaller uranium contents. Repeated sorption caused a small decrease in the final values but, according to the results of the preliminary experiments, these values are more correct. On the other hand, for the determination of higher contents of uranium, acid decomposition of samples and even a single sorption are sufficient, for the ratio between uranium and interfering elements is more favorable.

TABLE V

ANALYSES OF ROCK SAMPLES

Decomposition by fusion with Na_2CO_3		*Decomposition by acids*[a]		*Reported*[b] *% U*
Single sorption	*Repeated sorption*	*Single sorption*	*Repeated sorption*	
0.005_4	0.005_0	0.003_8	0.003_8	0.005
0.008_4	0.007_4	—	—	0.008_3
0.019	0.017	0.014	0.014	0.017
0.022	0.020	0.017	0.017	0.021
0.093	0.090	0.094	0.092	0.096
0.104	0.098	0.107	0.100	0.105

[a] Decomposition after igniting.
[b] Standard value reported by uranium industry.

THE DETERMINATION OF URANIUM IN NATURAL WATERS

The proposed method also proved to be useful for the determination of trace amounts of uranium in natural waters. Silica gel is most advantageous for highly mineralised waters because alkali- and alkaline-earth metal ions are not retained in the presence of EDTA within a broad range of hydrogen ions concentration (pH 4–9). Except for special cases such as mining waters, one sorption is sufficient for isolation of uranium.

Recommended procedure

To 100–2000 ml of the sample water (containing 3–50 μg U) add 20 ml of 12 *M* hydrochloric acid and 5 ml of 14 *M* nitric acid and evaporate the solution to dryness. Dissolve the residue in 5–10 ml of 12 *M* hydrochloric acid and after dilution with water, filter off the silicic acid. Treat the filtrate as described above.

Results

The results obtained were verified by parallel analyses of the same samples with the chelating resin Dowex A1 for the preliminary concentration of uranium[8].

This study has confirmed the reliability of silica gel for the separation of trace quantities of uranium. Further improvements and simplification of the analytical procedure can be expected by the introduction of new masking agents and by an increase of the selectivity in the final determination.

SUMMARY

A simple chromatographic procedure for the separation of trace amounts of uranium has been developed. From the solution containing EDTA and tartaric acid at pH 5, uranyl ions are selectively retained on a short silica gel column and are later eluted with 3 *M* acetic acid. The uranium content is measured spectrophotometrically with arsenazo III directly in the eluate without further pH adjustment. The effects of aluminium and thorium are discussed in detail. The method is applied to the determination of microgram amounts of uranium in rocks and underground waters.

RÉSUMÉ

Une méthode chromatographique simple est proposée pour la séparation de traces d'uranium. Les ions uranyle en solution contenant EDTA et acide tartrique, au pH 5 sont sélectivement retenus sur une colonne de silicagel; ils sont élués au moyen d'acide acétique 3 *M*. La teneur en uranium est déterminée spectrophotométriquement à l'aide d'arsenazo III, directement dans l'éluat sans ajustement de pH. On examine l'influence de l'aluminium et du thorium. Cette méthode a été appliquée au dosage d'uranium, en quantités de l'ordre du microgramme, dans des roches et des eaux souterraines.

ZUSAMMENFASSUNG

Es wurde ein einfaches chromatographisches Verfahren für die Abtrennung von Spurenmengen Uran entwickelt. Auf einer kurzen Silicagel-Säule werden Uranylionen aus einer EDTA- und weinsäurehaltigen Lösung bei pH 5 selektiv zurückgehalten und später mit 3 *M* Essigsäure eluiert. Der Urangehalt wird direkt im Eluat ohne weitere pH-Einstellung spektrophotometrisch mit Arsenazo III bestimmt. Die Einflüsse von Aluminium und Thorium werden im einzelnen erörtert. Die Methode wird auf die Bestimmung von Mikrogramm-Mengen Uran in Gesteinen und unterirdischen Wässern angewendet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BARIUM AND STRONTIUM IN SILICATES

A STUDY ON THE DEVELOPMENT OF ANALYTICAL METHODS

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This paper describes a long-term study at The Pennsylvania State University of various techniques used to determine barium and strontium in rocks and minerals, supplemented by the development by B. P. Fabbi in the Menlo Park laboratories of the U.S. Geological Survey of a new X-ray method for these elements. The aims have been to discover and correct systematic errors in the various methods, to evaluate methods in terms of speed and reliability, to obtain accurate values for barium and strontium in several standard rocks and minerals, to show how effective a combination of techniques and disciplines can be in the solving of analytical problems, and to estimate the effect of sample inhomogeneity on analytical error.

Similar collaborative efforts have been made with respect to other constituents of silicates. These have been reported rather briefly[1,2]. The work with barium and strontium may serve as an example of such efforts; it is worth reporting in detail because of the unusual range of techniques applied, and because there still remains some doubt concerning the barium and strontium contents of several of the most widely distributed reference samples. For example, the "preferred values" for strontium in the G. F. Smith limestones reported by Ingamells and Suhr[3] are now known to be in error (see Table I).

EXPERIMENTAL

Most of the methods used in this study have been described before, and will be outlined only briefly. Those wishing to make use of them are referred to the original papers and texts. Details are given of modifications and improvements not reported elsewhere.

Chemical methods (Chromate, sulfate)

The separation and determination of barium as chromate, and of strontium as nitrate, have been described by Maxwell[4].

Procedure. Fuse the sample (usually 1 g) with sodium carbonate and peroxide,

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TABLE I

PRELIMINARY EFFORTS TO DETERMINE BARIUM AND STRONTIUM

Sample no.	*G*-1	*W*-1	*T*-1	*Syenite*-1	*Sulfide ore*-1
(*BaO in rocks*) (*Results from Ingamells and Suhr*[1])					
Chemical	0.11 0.13	0.02	0.09 0.08	0.04	0.04
Spectrographic	0.12	0.015	0.055	0.026	0.019
(*SrO in rocks*) (*Results from Ingamells and Suhr*[1])					
Chemical (flame)	0.02	0.02	0.04 0.04	0.03	0.02
Spectrographic	0.031	0.021	0.033	0.028	0.011
Sample no	400	401	402	403	
(*SrO in limestones*) (*Results from Ingamells and Suhr*[3])					
Chemical (flame)	0.09	0.03	0.03	0.08	
Spectrographic	0.13	0.018	0.012	0.043	
A.a. spectrometry (unpublished, 1970)	0.083	0.015	0.0125	0.049	
Sample no.	4-216	4-218	4-220	60-1240	
(*Ba in rocks*) (*Unpublished results, from Table II*)					
Gravimetric as chromate	0.37	1.07	0.63	2.87	
Gravimetric as sulfate	0.19	1.04	0.58	2.41 2.42	
Emission spectrometric	0.210	1.08	0.58	2.35	

leach with water, and filter. Treat the residue with dilute sulfuric acid in 50% ethanol, adding calcium (as carbonate) if little or none is present in the sample. Filter off the precipitated sulfates, convert to carbonates, dissolve in acid, and remove iron, alumina, and other elements of the ammonia group by ammonia precipitation, using bromine to bring down manganese. Precipitate the barium as chromate from acetate-buffered solution, ignite and weigh $BaCrO_4$. Recover strontium (and calcium) from the filtrate with ammonium carbonate, convert the carbonates to nitrates, and separate strontium from calcium with fuming nitric acid, to determine strontium by flame photometry.

Some barium determinations were made by a modified procedure in which the initial attack was with sodium peroxide instead of carbonate. This has the advantage that less silica remains in the initial barium sulfate precipitate. Few gravimetric determinations of strontium were attempted. In most instances, flame photometry of the neutral nitrate solution resulting from the above procedure was used (see below).

In many instances the weighed barium chromate was impure and was converted to sulfate as follows.

Procedure. Treat the weighed barium chromate with 5–10 ml of 1:1 hydrochloric acid, and heat until solution is complete, adding a little 3% hydrogen peroxide to reduce chromium and manganese. Occasionally some material (presumably Cr_2O_3) remains undissolved. Remove it by filtration. Evaporate the solution to small volume (about 1–2 ml), dilute to 50–100 ml, and heat to boiling. Add dropwise 10–20 ml of 10% (by volume) sulfuric acid, interrupting the addition while the precipitate is forming. Digest hot until the barium sulfate has settled, then cool and let stand overnight. Filter, and wash with a minimum of 1% sulfuric acid. Ignite and weigh barium sulfate. If the barium content of the sample is more than a few tenths of a percent the product should be purified. To do this, treat the ignited barium sulfate with 1–2 ml of concentrated hydrochloric acid, dilute to the same volume as before, and add sulfuric acid as before. Again filter, ignite, and weigh.

Attempts to determine barium as sulfate without the preliminary separation as chromate led to very poor results because of gross contamination by iron, silicon, calcium, and rare earths, and methods based on this principle were abandoned.

TABLE II

DETERMINATION OF BARIUM IN ROCKS BY DIFFERENT METHODS

(Reported as % Ba)

Sample	*Isotope dilution*		*Gravimetric*		*Spectrographic*[a]	*Spectrometric*[a]	*X-r.f. direct dilution*[a]
	D.H.A.	*F. Tan*	*as CrO_4*	*as SO_4*			
W-1	0.0167	0.0171	0.018		0.013	0.0167	0.017
G-1	0.1072	0.1058	0.10 0.12		0.11	0.103	0.106
T-1	0.0582	0.0576	0.08 0.07		0.049	0.055	0.059
GR	0.1057				0.099	0.100	0.106
GA	0.0840		0.07	0.08	0.083	0.080	0.088
GH			0.01		0.0020	0.002	0.001
BR	0.1088	0.1061	0.19	0.13	0.099	0.105	0.115
S-1			0.036		0.023	0.029	0.0229
S.O.-1			0.036		0.017	0.022	0.020
G-2	0.1903	0.1857 0.1811		0.16	0.17	0.184	0.190
PCC-1					0.001	0.002	<0.001
DTS-1					0.001	0.002	0.002
GSP-1	0.1319	0.1316		0.11	0.11	0.133	0.125
BCR-1	0.0695	0.0687		0.06	0.060	0.070	0.070
AGV-1	0.1228	0.1241		0.12	0.11	0.123	0.124
U.S.S.R.						0.121	0.124
Or-1	0.7371 0.7380 0.7302	0.7102	0.70			0.699	0.719
Px-1	0.00524					0.003	0.001
Ab-1						0.002	0.002
4-216			0.37	0.19		0.210	0.168
4-218		1.1554	1.07	1.04		1.08	1.06
4-220			0.63	0.58		0.58	0.552
60-1240			2.87	2.41 2.42		2.35	2.947

[a] Usually used as a secondary method.

Flame emission photometry

Of numerous procedures investigated, only that with a cool flame as described by Ingamells[5], and the neutral nitrate solution of calcium and strontium resulting from the procedures above, was successful.

Procedure. Dissolve the precipitated calcium and strontium carbonates (obtained by adding ammonium carbonate to the filtrate from the barium chromate) in dilute nitric acid. Evaporate to dryness in platinum, and dry in the oven at 135°. Dissolve the nitrates in water, and dilute to 50 ml in a volumetric flask. Determine the calcium concentration in the solution and dilute 25 ml of it to 50 ml, adding enough standard calcium nitrate solution to bring the final concentration of calcium to a standard value, preferably 1000 p.p.m.; this compensates for the interference of calcium with the strontium determination. Determine the strontium content with the cool flame

TABLE III

DETERMINATION OF STRONTIUM IN ROCKS BY DIFFERENT METHODS

(Reported as % Sr)

Sample	*Isotope dilution*		*Flame after chem. sepn.*	*Spectrographic*[a]	*Spectrometric*[a]	*X-r.f.*		*Atomic absorption*
	D.H.A.	*F. Tan*				*Fusion*	*Direct dilution*[a]	
W-1		0.0196 0.0197 0.0200	0.017	0.018	0.0175	0.017	0.018	0.019
G-1	0.0256	0.0256 0.0265 0.0257	0.017	0.026	0.0241	0.023	0.023	0.024
T-1	0.0380	0.0373	0.034	0.028	0.0347	0.037	0.034	0.034
GR	0.0588			0.057	0.0517	0.060	0.055	0.053
GA	0.0301		0.028	0.027	0.0295	0.025	[b]	0.032
GH			0.003	0.0008	<0.002	0.001	0.000	0.000
BR	0.1372	0.1332	0.139		0.133	0.116	0.146	0.149
S-1			0.025	0.024	0.0216	0.019	0.019	0.021
S.O.-1			0.017	0.0093	0.0100	0.005	0.004	0.017
G-2	0.0479	0.0475	0.049	0.042	0.0443	0.043	[b]	0.045
PCC-1				<0.0005	<0.002	<0.001	<0.001	—
DTS-1				<0.0005	<0.002	<0.001	<0.001	—
GSP-1	0.0235	0.0259	0.025	0.018	0.0223	0.023	0.025	0.025
BCR-1	0.0336	0.0348	0.044	0.028	0.0330	0.029	0.040	0.032
AGV-1	0.0677	0.0670	0.066	0.065	0.0628	0.064	0.069	0.067
U.S.S.R.	0.1668				0.145	0.159	0.163	0.164
Or-1	0.0345	0.0368			0.0298	0.033	0.027	0.036
Px-1	0.0291				0.0300	0.025	0.023	0.032
Ab-1					0.0046	0.005	0.006	0.006
4-216			0.089		0.0913	0.076	0.090	0.095
4-218		0.1356	0.119		0.138	0.120	0.119	0.148
4-220			0.101		0.109	0.095	0.107	0.115
60-1240			0.074		0.106	0.082	0.106	0.114

[a] Usually used as a secondary method.
[b] Used as a calibrating standard.

using standards with the same calcium content as the unknown, and the SrOH band at *ca.* 605 nm.

Emission spectrography

The early spectrographic work was accomplished by modifications of the methods of Joensuu and Suhr[6]. The spectrographic results in Tables II and III were obtained by the method for trace elements described by Ingamells and Suhr[1], slightly modified.

Procedure. Mix the sample with internal standard-buffer (Lu_2O_3 in $Na_2B_4O_7$) and graphite in the ratio of 1:1:2 and pack the mixture into 1/8-in preformed electrodes (total charge about 30 mg). Burn to completion in a Stallwood jet using an 86:14 argon–oxygen mixture flowing at 6 l min^{-1}.

Standard procedures were used to develop and read the photographic plates. All samples were burned in triplicate and the averages taken. Standards were synthetic and consisted of varying amounts of strontium and barium carbonate in a sintered oxide–carbonate mixture of approximately 1:1 granite–diabase composition.

Emission spectrometry

The emission–spectrometric–spark–solution procedure has been described by Suhr and Ingamells[7].

Procedure. Fuse 0.1000 g of sample with 0.500 g of lithium metaborate in a graphite crucible at 950° for 10 min. Pour the melt into 50.0 ml of 3% nitric acid containing cobalt nitrate, used as an internal standard. Excite the sample solution with an a.c. spark, using a rotating disc electrode. Read out voltage ratios, which are directly proportional to concentration.

Standardization may be accomplished by the use of standard samples, or of synthetic rock solutions to which known amounts of barium and strontium have been added. The latter alternative was used in this work. Standard solutions of barium and strontium nitrates, containing the proper amounts of lithium metaborate, nitric acid, and cobalt nitrate, were added to aliquots of a stock rock solution, made from a synthetic "rock" containing no strontium or barium. The "rock" contained 60% SiO_2, 15% Al_2O_3, 5% Fe_2O_3, 5% $CaCO_3$, 5% MgO, 5% NaCl and 5% KCl; all these chemicals were Johnson–Matthey SpecPure compounds.

Isotope dilution mass spectrometry

The instrument used to obtain the isotope dilution results reported in Tables II and III was a 6-in, 60° sector, triple-filament surface ionization mass spectrometer of Bureau of Standards design, equipped with an expanded scale recorder[8]. The appropriate masses (136/138 for barium and 86/88 for strontium) were scanned magnetically, and concentration was calculated from signal ratios.

Procedure. To 20–200 mg (depending on the expected barium or strontium concentration) of sample in a platinum dish, add a little water and accurately measured portions of calibrated spike solutions (^{136}Ba and ^{86}Sr). Treat with 30 ml of hydrofluoric acid and 5 ml of perchloric acid, cover with a Teflon cover, and digest to decompose the sample. Uncover, and evaporate slowly to fumes of perchloric acid. Repeat the treatment with hydrofluoric acid; then evaporate to dryness, and heat until perchloric acid fumes are no longer evolved. Cool, add about 10 ml of 0.5 *M* hydrochloric acid, and digest for about 30 min, or until dissolution is complete.

This solution was used without further treatment for the barium determination. For strontium, ion exchange in Vycor columns filled with Dowex 50W, 12% cross-linked, 200–400 mesh resin, was used for separation.

Before loading, the rhenium filaments were examined in the spectrometer for barium and strontium background. The barium results had to be corrected for a blank amounting to about 0.8 μg of barium per determination. Pure spikes, carried through the whole chemical procedure, were used to establish the blank correction.

X-ray spectrography

Two sample preparation techniques were used: pelleting after fusion[1] and direct dilution[9-11].

Fusion method. Mix 0.2 g of sample with 2 g of $LiBO_2$ and fuse in graphite at 950°. Crush and grind the resulting bead, mix with 10% of its weight in methyl cellulose, and pelletize, using a methyl cellulose backing.

The fusion method was used only for strontium: the dilution put barium, except in high-barium samples, below the detection limit. Synthetic standards were used for strontium, and only a background correction was made.

Direct dilution. Grind 0.5 g of sample for 10 min in a mixer-mill, hand-grind the product with 0.5 g of chromatographic cellulose powder in a mortar and pestle, return the mixture to the vial and regrind for 5 min on the mixer-mill, then pelletize at 30,000 psi, using a methyl cellulose backing.

Correction for the direct interference of titanium on barium and matrix corrections for mass absorption of strontium radiation are necessary[11].

Atomic absorption spectrometry

The method has been described by Medlin *et al.*[12].

Procedure. Prepare sample and synthetic standard solutions as described for emission spectrometry. Add lanthanum nitrate solution to minimize aluminum interference and aspirate into an acetylene–air flame adjusted for maximum sensitivity. This procedure works only for strontium.

RESULTS AND DISCUSSION

Preliminary method development

At the beginning of this study, only two methods for barium and for strontium in rocks and minerals were available—the classical gravimetric and flame photometric method[4] and emission spectrography, with either the procedure of Joensuu and Suhr[6] or that of O'Neil and Suhr[13]. The classical method is long and arduous, and the earlier spectrographic results were not very accurate, for reasons which are more apparent now than they were then.

Table I shows results by these methods on five standard silicate samples and four standard limestone samples, as reported by Ingamells and Suhr[1,3]. It is evident that they are not very satisfactory. When the same method for barium was applied to certain other samples (Table I), agreement was even worse. Frequent use of the spectrograph revealed faults in the classical gravimetric method for barium. Rare earths and manganese were found in the weighed barium chromate, and analysis by chemical methods showed that it sometimes contained too much chromium. These faults in the chemical method were partially corrected by converting the barium chromate to sulfate before weighing. A better correlation between spectrographic and chemical results was then obtained, but discrepancies nevertheless remained.

In the determination of high barium contents (0.1%) in several rocks, a deficiency in the spectrographic procedure was uncovered. Standards with varying amounts of barium in a synthetic rock base were prepared. After analysis by the spectrographic procedure of Joensuu and Suhr[6], the intensity ratio of Ba 4130 to the internal standard Co 4110 was computed and plotted *vs.* concentration. This working curve was used to determine barium in previously analysed (by gravimetry) rocks. Except in the case of a high barium sample (2.71% BaO by gravimetry, weighed as sulfate), all values obtained were too high. However, a plot of gravimetric values *vs.* intensity ratios showed a remarkably linear relationship (Fig. 1).

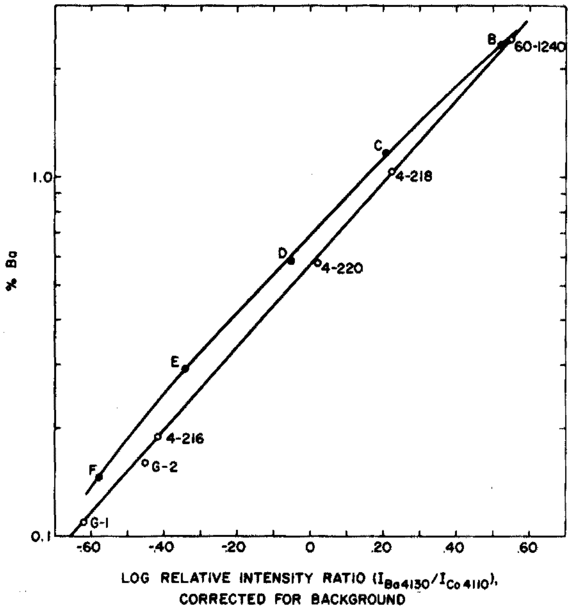

Fig. 1. Spectrographic working curve for barium. Points B–F are synthetic standards, others are chemical values in various rocks.

It seemed probable that there was a difference between the background generated by the synthetic standards and by the rocks. This is illustrated by the agreement between standard B and rock 60-1240, for which the Ba 4130 lin intensity was considerably above background and background correction was very minor. Background corrections made at several other wavelengths were similar, and the conclusion was that, with the Ba 4130 line, synthetic standards are not useful. Consequently, it was considered advisable to use chemically analysed rock samples as standards.

Similar discrepancies were registered when comparisons were made between the spectrographic and the flame photometric (after chemical separation) strontium values. With strontium, it was believed (erroneously) that the flame values were inferior, because of the long process used to collect the strontium, and because the necessary correction for calcium interference did not inspire confidence. No attempts were made at this stage, therefore, to improve the agreement between the spectrographic and the flame photometric values for strontium. The comparison of results (Table I) by the two methods was less than satisfying.

Another method was required to resolve the issue, and the rather limited success of the emission spectrographic, flame photometric, and classical methods led to an investigation of other techniques.

Preliminary efforts to resolve the difficulty by means of X-ray fluorescence spectrography were not encouraging, and this approach was dropped for the time being. After more standards were available, improved sample preparation methods were devised, and matrix effects became better understood, Fabbi[11] was able to use X-ray spectrography successfully for both barium and strontium.

A considerable effort was made to use neutron activation analysis to determine barium. Results were not satisfactory. Chemical separations were necessary, and those that were devised failed to separate the rare earth elements from the barium; there was also difficulty in determining the chemical yield. The activated rare earths give γ-ray spectra which made it impossible, with the available counting equipment (NaI(Tl) scintillation detector), to resolve the signal caused by barium. This approach was therefore abandoned. With the development of lithium-drifted germanium γ-ray detectors, barium is now easily measured[14,15] above about 200 p.p.m., with a detection limit of *ca.* 5 p.p.m.[16]. Strontium has also been accurately determined in rocks by neutron activation[16].

Some time was spent in attempts to determine barium and strontium by flame emission spectrometry, avoiding chemical separations by using whole rock solutions. Both low- and high-temperature flames were used. Results were not acceptable. Sensitivities were low, and interferences could not be overcome.

Later developments

Acquisition of a direct-reading emission spectrometer and the development of a rapid solution technique for silicates[7] made further work possible. The numerous analysed samples accumulated during the chemical and spectrographic work made it easy to establish the viability of the spark-solution spectrometric technique. It was relatively simple to add known amounts of barium and strontium to prepared rock solutions, and this gave emission spectrometry the character of a primary method. It did not take long to confirm that chemical results for barium by the modified technique, with barium sulfate as a weighing form, were low because of solubility losses, and that the flame photometric results for strontium were more accurate than had been supposed.

While emission spectrometric results for barium and strontium seemed satisfactory and precision was good (relative deviation about 5%), uncertainties remained. Before experience with the new method was accumulated, there was doubt about the extent of line interference and matrix effects. In order to confirm the values obtained for the various reference samples, which were in general higher than those by the other two methods, and to extend accuracy by the order of magnitude which seemed possible, a further umpire technique was required.

Isotope dilution mass spectrometry is widely used in geochronology to determine strontium and was easily extended to determine barium as well. Accordingly, these elements were determined by this technique in most of the available samples. Preliminary results confirmed the reliability of the emission spectrometric values. The comparative results in Tables II and III illustrate this. Some minor interferences (*e.g.* that of zirconium on barium) in the spectrometric procedure were detected, but none proved serious.

X-Ray fluorescence and atomic absorption equipment are commonly available. Accordingly, the numerous analysed samples obtained during the work described above were used to establish the conditions necessary for the accurate determination of strontium by X-ray methods and by atomic absorption spectrometry. Kerber and Barnett[17] have shown that barium is determinable to about 1 p.p.m. in aqueous solutions by atomic absorption spectrometry, but attempts to determine it in lithium metaborate–nitric acid solutions were not entirely successful. While as little as 25 p.p.m. barium in rocks could be detected, results were erratic, and a recommended procedure cannot be given. The addition of 1,000 p.p.m. potassium to suppress the ionization of barium in a nitrous oxide–acetylene flame did not resolve the difficulty.

Routine determination of both barium and strontium by direct dilution X-ray methods is completely satisfactory if adequate standards are available and if the precautions suggested by Fabbi[11] are observed.

TABLE IV

PREFERRED VALUES FOR BARIUM AND STRONTIUM

(By isotope dilution mass spectrometry except where noted)

Sample	*Weight(%)*	
	Sr	*Ba*
W-1	0.0198	0.0169
G-1	0.0259	0.107
T-1	0.0377	0.0579
GR	0.0588	0.106
GA	0.0301	0.0840
GH	0.0008[a]	0.0020[a]
BR	0.135	0.108
S-1	0.019[b]	0.023[a,b]
S.O.-1	0.0093[a]	0.020[b]
G-2	0.0477	0.186
PCC-1	<0.0005[a]	0.001[a]
DTS-1	<0.0005[a]	0.001[a]
GSP-1	0.0247	0.132
BCR-1	0.0342	0.0691
AGV-1	0.0674	0.124
U.S.S.R.	0.167	0.124[b]
Or-1	0.1357	0.729
Px-1	0.0291	0.0052
Ab-1	0.005[c]	0.002[b,c]

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[a] Emission spectrography.

[b] X-ray fluorescence spectrography.

[c] Emission spectrometry.

TABLE V

METHOD FOR ESTIMATING ACCURACY AND PRECISION (EXAMPLE)

	% Sr			*Δ Pref. − calc.*	*Δ Pref. − X-r.f.*
	X-r.f. (Fusion)	*Pref.*	*Recalc.*		
W-1	0.017	0.0198	0.01923288	0.00056712	0.0028
G-1	0.023	0.0259	0.02565232	0.00024768	0.0029
T-1	0.037	0.0377	0.04063104	−0.00293104	0.0007
GR	0.060	0.0588	0.06523892	−0.00643892	−0.0012
GA	0.025	0.0301	0.02779214	0.00230786	0.0051
GH	0.001	0.0008	0.00211435	−0.00131435	−0.0002
BR	0.116	0.1352	0.12515377	0.01004623	0.0192
S-1					
S.O.-1	0.005	0.0093	0.00639398	0.00290602	0.0043
G-2	0.043	0.0477	0.04705048	0.00064952	0.0047
PCC-1					
DTS-1					
GSP-1	0.023	0.0247	0.02565232	−0.00095232	0.0017
BCR-1	0.029	0.0342	0.03207177	0.00212823	0.0052
AGV-1	0.064	0.0674	0.06951855	−0.00211855	0.0034
U.S.S.R.	0.159	0.1668	0.17115982	−0.00435982	0.0078
Or-1	0.033	0.0357	0.03635140	−0.00065140	0.0027
Px-1	0.025	0.0291	0.02779214	0.00130786	0.0041
Ab-1	0.005	0.005	0.00639398	−0.00139398	0.0000
			Sum Δ	0.04032090	0.063200
			Average Δ, $\bar{\Delta}P$	0.00252005	$\bar{\Delta}A$ 0.003950

Evaluation of results

To provide an objective evaluation of the results, the values obtained for barium and for strontium by the various methods in the primary mode were recalculated, the preferred values (Table IV) being used to calibrate. A sample calculation is shown in Table V, the X-ray results for strontium being taken as an example. Column 1 in this Table contains the reported values by this method, and column 2 the preferred values. The former are treated as instrument readout, and a linear regression analysis yields the recalculated values in column 3. Column 4 gives the differences between the preferred and the recalculated values, ΔP, and column 5 the differences between the preferred and the original values, ΔA. An average of ΔP, taken without regard to sign, gives a measure of the precision of the method; an average of ΔA, in which the addition is algebraic, gives a measure of accuracy. Several other methods for evaluating the data were attempted, but proved less than satisfactory.

The comparison of methods, summarized in Table VI, gives $\bar{\Delta}P$ and $\bar{\Delta}A$ for each method, and also a "time factor" which is the estimated number of minutes per completed determination to the nearest order of magnitude. The time factor for emission spectrometry is low because the equipment is automated, sample preparation is rapid, and as many as 20 elements are read in the same operation. Obviously,

TABLE VI

COMPARISON OF METHODS

Method	$\bar{\Delta}P$	$\bar{\Delta}A$	*Time factor*	*Sample weight (mg)*
Barium (%)				
X-ray fluorescence	0.0026	−0.0002[a]	100	500
Emission spectrometry	0.0026	−0.0023	10[b]	20
Emission spectrography	0.0043	−0.0081	100	10
Grav. as chromate	0.0173	+0.0109	10000	1000
Grav. as sulfate	0.0119	−0.0069	10000	1000
Strontium (%)				
Emission spectrometry	0.0026	−0.0035	10[b]	20
Emission spectrography	0.0030	−0.0032	100	10
Flame photometry	0.0039	+0.0010	10000	1000
X-r.f. Direct dilution	0.0037	−0.0012[a]	100	500
X-r.f. Fusion	0.0025	−0.0040	100	200
Atomic absorption	0.0031	+0.0005	100	20

[a] This value should be interpreted in light of the fact that the method was calibrated with analysed standards.
[b] Takes into account the fact that up to 20 elements may be determined in the same operation.

similar automation of the other methods would increase their speed, and the time factors given refer only to the equipment and procedure actually used.

The sample weight required by a method is sometimes of importance. Emission spectrography, emission spectrometry, and atomic absorption spectrophotometry can be used to obtain satisfactory results with only a few milligrams of sample. On the other hand, a method which can only use a small sample is at a serious disadvantage when samples are inhomogeneous[18-20].

Excluding isotope dilution mass spectrometry, which is considered the reference method, it can easily be seen that atomic absorption spectrometry gives the best values for strontium and that the precision of all the methods is about the same. For barium, the classical methods are poor, and either X-ray or emission spectrometry can be recommended. Classical gravimetry is better suited to the determination of larger percentages than are present in most rocks: a reason for its poor showing in this study is that the method is used near the limit of its sensitivity.

The methods for barium and strontium are believed to have been refined until sampling error and analytical error are, in general, of comparable magnitude. The point has been reached where further improvement in accuracy and precision will require careful attention to sampling problems[21-23].

It is necessary to distinguish between primary and secondary methods. The distinction is not always clear-cut, but, in general, primary methods are those which do not rely on other methods for accuracy. Secondary methods compare unknowns with analysed standards. Consequently, the accuracy of secondary methods can be no greater than that of the primary methods used to generate the standards. On the other hand, secondary methods are commonly of high precision, usually because they involve fewer analytical steps and are therefore less subject to operator error.

Many instrumental methods can be used in either the primary or the secondary mode, depending on whether natural or synthetic standards are chosen. With synthetic standards, there is danger of introducing a bias into the results because the standards and the unknowns are not prepared in an identical manner. There is also a danger that matrix effects and elemental interferences may go undetected if relatively simple synthetic standards are used. This is illustrated by the early spectrographic work with barium and strontium.

A common convention is to refer to an instrumental technique as though it were a complete description of a method. This convenient practice has been followed in this paper; however, it should be recognized that a method includes many steps. The instrumental readout may not be critical to the accuracy of the results: the preparatory procedure may have faults which cause losses of the element in question, the reagents used may be contaminated, or sampling problems may exist. Variance in the results cannot rightfully be attributed to the instrumental technique in such cases. A comparison of methods such as the one attempted here should not be accepted as an evaluation of instrumental techniques alone. The quality of the results is due as much to the improvement of sample preparation procedures and the elimination of interferences and contaminants as it is to the selection and proper adjustment, maintenance, and skilful use of the instruments.

To say that strontium in silicates may be determined by flame emission spectrometry, by the method described in this paper, is obviously correct, but only if the designation "flame emission spectrometry" is tacitly understood to include the long separatory process which must precede the determination. Rapid methods involving flame emission spectrometry of whole rock solutions are, in our experience, thoroughly inferior.

Similarly, while atomic absorption and emission spectrometric results for strontium are comparable in terms of precision, this merely reflects the fact that both readout devices use the same sample solution.

CONCLUSIONS

While earlier work (by classical gravimetry, emission spectrography, and flame emission spectrometry) did not result in an ability to produce highly reliable and accurate strontium and barium determinations, it did serve the function of providing a series of samples in which the concentration of these elements was at least approximately known. It also developed a system of collaboration between disciplines which has proven to be very useful.

Work with the direct-reading emission spectrometer showed that earlier conclusions regarding the discrepancies between emission spectrographic and classical methods for barium were only partially correct. It also indicated that strontium values obtained by flame emission after chemical separation, which had been discounted, were in fact good enough to warrant reporting to three places instead of two. This emphasizes the value of a third technique in deciding which of two others that are in disagreement may be taken as the more accurate. No one would suggest that strontium in rocks be routinely determined by the tedious method used to produce the flame results, but this did serve a useful purpose by inspiring confidence in the emission spectrometric technique.

TABLE VII

SAMPLE DESCRIPTIONS

Abbreviation	*Description*	*Source*
G-1	Granite	U.S. Geological Survey[24,25]
W-1	Diabase	
G-2	Granite	
GSP-1	Granodiorite	
AGV-1	Andesite	
BCR-1	Basalt	
PCC-1	Peridotite	
DTS-1	Dunite	
GR	Granite	Petrographic and Geochemical Research Center, Nancy, France[26]
GA	Granite	
GH	Granite	
BR	Basalt	
S-1	Syenite	Canadian Association for Applied Spectroscopy[27,28]
S.O.-1	Sulfide ore	
T-1	Tonalite	Geol. Survey of Tanzania[29]
U.S.S.R.	Syenite	Leningrad State University[30]
Or-1	Adularia	Pennsylvania State University[20]
Ab-1	Albite	
Px-1	Pyroxene	
4-216	Minette	Pennsylvania State University (local samples only)
4-218	Syenite	
4-220	Syenite	
60-1240	Limonitic rock	
400	Dolomite	G. Frederick Smith Chemical Co.[31]
401	Limestone	
402	Limestone	
403	Limestone–Dolomite	

The isotope dilution mass spectrometry values for barium and strontium are arbitrarily assumed to be reliable, and the preferred values given in Table IV are for the most part those obtained by this technique. The several standards used are identified in Table VII.

Attainable sampling precision depends on the weight of sample taken for analysis and on the condition of the element of interest in the sample[19,20]. It is probable that the barium and strontium in most standard rocks are present as minor constituents in feldspars. This makes the sampling problem somewhat less intractable than would be the case for elements (*e.g.* zirconium) that commonly occur as major constituents of specific minerals. Nevertheless, the possibility that at least some of the variations that appear in Tables II and III are due to sampling error should not be discounted.

There are indications that some of the reference samples are less homogeneous with respect to barium and strontium than others. For example, the spread in results by all methods for strontium in BCR-1 is $0.028-0.044=0.016$, while the same methods applied to AGV-1 give a spread of $0.063-0.069=0.006$. Estimated standard deviations for a few samples are given in Table VIII. While these cannot, of course, be taken as conclusive evidence of inhomogeneity, they may provide an impetus

TABLE VIII

ESTIMATED STANDARD DEVIATIONS (ALL METHODS)[a]

	$\bar{x}$	$s(Ba)$	R	$\bar{x}$	$s(Sr)$	R
G-1	0.1074	0.0064	6.0	0.0241	0.0028	11.6
T-1	0.0613	0.0104	17.0	0.0346	0.0031	9.0
BR	0.1220	0.0316	25.9	0.1362	0.0108	7.9
G-2	0.1802	0.0112	6.2	0.0455	0.0027	5.9
GSP-1	0.1236	0.0109	8.8	0.0235	0.0025	10.6
BCR-1	0.0664	0.0050	7.5	0.0343	0.0054	15.7
AGV-1	0.1207	0.0054	4.5	0.0661	0.0020	3.0

[a] $\bar{x}$ = average of all results.
s(Ba) = estimated standard deviation.
R = relative deviation in %

toward further investigation of sampling problems, or at least a warning that such problems may exist.

Most of this work was done in the Mineral Constitution Laboratories of the Pennsylvania State University. The direct dilution X-ray technique was developed by B. P. Fabbi, of the U.S. Geological Survey, to whom we are indebted for permission to include his results. The work was financed in part through a National Science Foundation Grant no. GP-3853, to S. S. Goldich and C. O. I. Our thanks go to the many people who assisted: to H. Van der Graaf and W. Miller, Pennsylvania State University, for neutron activation analyses, to C. Randall for maintenance and modification of instruments, to M. L. Keith for advice with fluxes, to S. Neil for various computations, and to R. B. Ellestad and E. H. Oslund, University of Minnesota, for early gravimetric results.

SUMMARY

Barium and strontium in silicates have been determined by a number of methods, and their contents in several standard samples are reported. Instrumental techniques evaluated include isotope dilution mass spectrometry, flame emission and absorption spectrometry, emission spectrography and spectrometry, X-ray fluorescence spectrography, and neutron activation analysis. Classical gravimetric methods are reported. Two X-ray fluorescence procedures were used; one involves fusion with lithium metaborate and yields only strontium values. The other uses a direct dilution technique and gives results for both barium and strontium. In practice, this method requires a suite of analyzed standards, which should be generally similar in composition to the unknown. Strontium can be satisfactorily determined by atomic absorption spectrometry in whole-rock solutions, but there are difficulties in determining barium in this way. Emission spectrometry, with a spark-solution technique and automated equipment, gives rapid and accurate results for both barium and strontium. Flame emission spectrometry, neutron activation analysis, and classical gravimetric methods are not satisfactory as practicable routine methods for barium and strontium in silicate rocks. Conslusions are that barium and strontium may be

satisfactorily determined by several methods, and that refinement of these methods is possible to the point where sampling error, rather than analytical error, may often determine variance in the results.

RÉSUMÉ

Une étude est effectuée sur les possibilités de dosage du baryum et du strontium dans des silicates. Les techniques instrumentales examinées comprennent: dilution isotopique, spectrométrie de masse, spectrométrie d'émission de flamme et d'absorption, spectrographie et spectrométrie d'émission, spectrographie de fluorescence aux rayons-X et analyse par activation neutronique. Les méthodes gravimétriques classiques sont reportées. Deux procédés par fluorescence aux rayons-X sont utilisés: l'un comprend la fusion avec le métaborate de lithium, et ne fournit que des valeurs pour le strontium; l'autre consiste en une technique directe par dilution et fournit des résultats pour le baryum et le strontium. Le strontium peut être dosé par absorption atomique, mais le dosage du baryum offre certains difficultés.

ZUSAMMENFASSUNG

Barium und Strontium in Silicaten wurden nach verschiedenen Methoden bestimmt, die Gehalte in einigen Standardproben werden angegeben. Zu den instrumentellen Verfahren gehörten Isotopenverdünnungsmassenspektrometrie, Flammenemissions- und -absorptionsspektrometrie, Emissionsspektrographie und -spektrometrie, Röntgenfluoreszenzspektrographie und Neutronenaktivierungsanalyse. Es wird über klassische gravimetrische Methoden berichtet. Zwei Röntgenfluoreszenzverfahren wurden angewendet; das eine enthält einen Aufschluss mit Lithiummetaborat und ergibt nur Strontiumwerte; das andere ist eine direkte Verdünnungsmethode und ergibt Werte für Barium und Strontium. In der Praxis erfordert diese Methode eine Reihe von analysierten Vergleichsproben, die in der Zusammensetzung der unbekannten Probe ähnlich sein sollten. Strontium kann durch Atomabsorptionsspektrometrie in Lösungen des gesamten Gesteins bestimmt werden, jedoch ist die Bestimmung von Barium auf diesem Wege schwierig.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A NEW SPECIFIC COLOUR REACTION FOR SUBSTITUTED AROMATIC ALDEHYDES WITH DIPHENYLAMINE AND ITS USE FOR THEIR DETECTION AND DETERMINATION

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(Received 10th September 1970)

Numerous tests for the detection of aldehydes have been described in the literature[1]. Feigl *et al.*[2] have developed a method for the detection of various aromatic aldehydes as well as for unsaturated aliphatic aldehydes based on the formation of Schiff's bases with N,N-dimethyl-*p*-phenylenediamine in the presence of acids. A spot test has been given by Anger and Ofri[3] for the detection of aromatic aldehydes along with polysaccharides, pentoses, hexoses, celluloses, ethers and esters of celluloses and N-arylidene compounds. A general test based on the characteristic yellow colour formation between aldehydes and chlorite in neutral or acidic medium is described by Hashmi *et al.*[4], but this is not applicable to aldehydes such as anisaldehyde, vanillin, acrolein, *p*-dimethylaminobenzaldehyde, glucose, veratraldehyde, and glyceraldehyde. Billman *et al.*[5] used molybdosilicic acid and its sodium salt for the detection of aldehydes and cyclic ketones containing at least one α-hydrogen atom. An ion-exchange method has been described by Tsuji[6]. Other tests for the detection and determination of aliphatic and cyclic aldehydes have also been reported[7-13].

However, there are few selective methods for the detection and determination of substituted aromatic aldehydes. Schiff's bases are formed by the condensation of aldehydes and primary amines but no such formation has been reported with secondary amines. During studies on the dectection of diphenylamine[14], it was found that hydrogen ions are necessary to bring about the condensation of the amine with *p*-dimethylaminobenzaldehyde which results in the formation of a bluish-green colour. An effort was therefore made to develop a new colour reaction for the detection and determination of substituted aromatic aldehydes with diphenylamine in the presence of hydrochloric acid. The method developed is described in this paper, and a mechanism for the colour reaction is discussed. The proposed test was found to be highly selectice for aromatic aldehydes containing hydroxy or methoxy groups or groups containing nitrogen atoms.

EXPERIMENTAL

Apparatus

Colorimetric determinations of aldehydes were made with a Bausch and Lomb Spectronic 20 or a Hilger and Watts Spekker colorimeter.

Reagents and chemicals

All the reagents and chemicals were obtained from E. Merck or B.D.H. Solutions (1.0% w/v) of diphenylamine, salicylaldehyde, *p*-dimethylaminobenzaldehyde and *o*-vanillin, and a 0.5% (w/v) solution of anisaldehyde were prepared in ethanol.

Detection of substituted aromatic aldehydes

To a few drops of an ethanolic solution of the substance to be tested, add 1–2 drops of hydrochloric acid (d. 1.16) in a microtest tube followed by 2 drops of 1% diphenylamine solution in ethanol. Heat the mixture for 2 min. A red colour is obtained with the aldehydes substituted with hydroxy or methoxy groups. *p*-Dimethylaminobenzaldehyde gives a green coloured solution. In the case of nitroaldehydes green coloured precipitates are obtained instead of a clear solution.

Determination of substituted aromatic aldehydes

Anisaldehyde. Acidify an ethanolic solution containing 1.25–10.0 mg of anisaldehyde with 6 ml of concentrated hydrochloric acid and add 2 ml of 1% diphenylamine solution. Dilute to volume with ethanol in a 10-ml standard flask. Heat the solutions for 30 min in a water bath at 60–70°. After cooling, measure the absorbance at 520 nm.

Salicylaldehyde. Use an ethanolic solution containing 2.0–9.0 mg of salicylaldehyde, and proceed exactly as described for anisaldehyde, except that only 1.0 ml of diphenylamine solution is necessary.

p-Dimethylaminobenzaldehyde. To 2.5–15.0 mg of *p*-dimethylaminobenzaldehyde, add 1 ml of concentrated hydrochloric acid followed by 0.5 ml of 1% diphenylamine solution. Dilute to volume with ethanol in a 10-ml standard flask. Measure the absorbance at 435 nm.

o-Vanillin. To 2.5–15.0 mg of *o*-vanillin, add 5.0 ml of concentrated hydrochloric acid and 2.0 ml of 1% diphenylamine solution. Proceed as described for anisaldehyde.

In all cases, Beer's law was obeyed within the limits mentioned for each compound.

RESULTS

Detection

The following substituted aromatic aldehydes gave a positive test by the recommended procedure:

anisaldehyde, salicylaldehyde, *p*-dimethylaminobenzaldehyde, *o*-vanillin, *o*-nitrobenzaldehyde and *m*-nitrobenzaldehyde.

The following substances gave no colour.

Hydrocarbons and their derivatives: benzene, bromobenzene, nitrobenzene, carbon tetrachloride, chloroform, cyclohexane and toluene.

Aliphatic saturated and unsaturated aldehydes: formaldehyde, acetaldehyde, crotonaldehyde and chloral hydrate.

Ketones: acetone, ethyl methyl ketone, cyclohexanone, methyl isobutyl ketone, diisobutyl ketone, benzophenone, acetophenone and benzil.

Alcohols: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, isoamyl, *tert*-amyl, glycerol and ethylene glycol.
Acids: acetic, benzoic, formic, propionic, oxalic, sulphanilic and tartaric acid.
Amides: formamide, chloral formamide, acetamide, benzamide, *n*-butyramide, propionamide, oxamide, nicotinamide and phthalimide.
Aliphatic and aromatic amines: methyl-, dimethyl- and trimethylamine; monoethanol-, diethanol- and triethanolamine; ethylenediamine, aniline, diethylaniline, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, benzidine, *p*-toluidine, 1-naphthylamine, 2-naphthylamine and *o*-phenylenediamine.
Anilides: acetanilide, *p*-bromoacetanilide, carbanilide, oxanilide and phenylurea.
Ethers: anisole, dioxane, ether, and *p*-nitroanisole.
Nitriles: benzonitrile, chloroacetonitrile and cyanoacetic acid.
Esters: methyl acetate, methyl benzoate, benzyl benzoate, diethyl malonate and *n*-tributylphosphate.
Phenols: *m*-cresol and phenol.
Heterocyclic bases: pyridine and piperidine.

Various carbohydrates gave characteristic colours when they were heated with diphenylamine in presence of hydrochloric acid (d. 1.16). Sucrose, raffinose, glucose,

TABLE I

LIMITS OF IDENTIFICATION OF ALDEHYDES

Aldehydes	*Amount detected* (μg)	*Colour obtained*	*Limiting proportion*
Anisaldehyde	5	Red	$1:4\cdot10^3$
o-Vanillin	10	Red	$1:1\cdot10^3$
m-Nitrobenzaldehyde	10	Green ppt.	$1:1\cdot10^3$
p-Dimethylaminobenzaldehyde	1	Green	$1:1\cdot10^4$
o-Nitrobenzaldehyde	10	Green ppt.	$1:1\cdot10^3$
Salicylaldehyde	5	Red	$1:4\cdot10^3$

TABLE II

DETECTION OF ANISALDEHYDE IN PRESENCE OF FOREIGN SUBSTANCES

Foreign substance	*Amount added* (μg)	*Anisaldehyde detected* (μg)	*Foreign substance*	*Amount added* (μg)	*Anisaldehyde detected* (μg)
Acetic acid	400	5	Glycerol	200	5
Acetone	500	5	Methanol	500	5
Acetanilide	100	10	Methylamine	100	5
Aniline	100	10	Nitrobenzene	500	5
Anisole	500	5	Phenol	500	5
Benzene	500	5	Pyridine	100	5
Carbon tetrachloride	1000	5	Sucrose	50	10

TABLE III

DETECTION OF *p*-DIMETHYLAMINOBENZALDEHYDE (DAB) IN PRESENCE OF FOREIGN SUBSTANCES

Foreign substance	*Amount added (μg)*	*DAB detected (μg)*	*Foreign substance*	*Amount added (μg)*	*DAB detected (μg)*
Acetic acid	100	1	Methanol	500	1
Acetaldehyde	100	1	Methylacetate	100	1
Acetone	500	1	Methylamine	200	1
Anisole	200	2	Nitrobenzene	100	1
Aniline	150	2	Phenol	200	1
Acetanilide	200	1	Sucrose	50	10
Benzene	400	1			

TABLE IV

DETERMINATION OF ALDEHYDES

Aldehyde	*Amount taken (mg)*	*Amount found (mg)*	*% Error*
Anisaldehyde	2.50	2.50	0.0
	3.50	3.43	−2.0
	4.50	4.68	+4.0
	5.00	5.00	0.0
	6.50	6.56	+0.9
	7.50	7.50	0.0
	9.00	9.06	+0.7
	9.50	9.21	−3.0
Salicylaldehyde	3.0	3.0	0.0
	9.0	8.7	−3.3
	6.0	6.0	0.0
	0.0	0.0	0.0
	2.0	2.1	+5.0
p-Dimethylamino-benzaldehyde	2.5	2.50	0.0
	5.0	5.30	+6.0
	6.0	6.25	+4.1
	8.0	8.44	+5.5
	10.0	10.0	0.0
	12.5	12.50	0.0
	0.0	0.0	0.0
	10.0	10.0	0.0
o-Vanillin	2.2	2.13	−3.1
	5.0	5.0	0.0
	7.2	7.13	−1.0
	0.0	0.0	0.0
	4.0	4.0	0.0
	3.0	2.9	−3.3
	10.0	10.0	0.0
	1.0	1.05	+5.0

fructose, melezitose, mannose and cellobiose gave blue colours, whereas arabinose and xylose gave yellow colours, and rhamnose an orange colour.

Limits of identification. The limits of identification of various aldehydes were determined with the results shown in Table I.

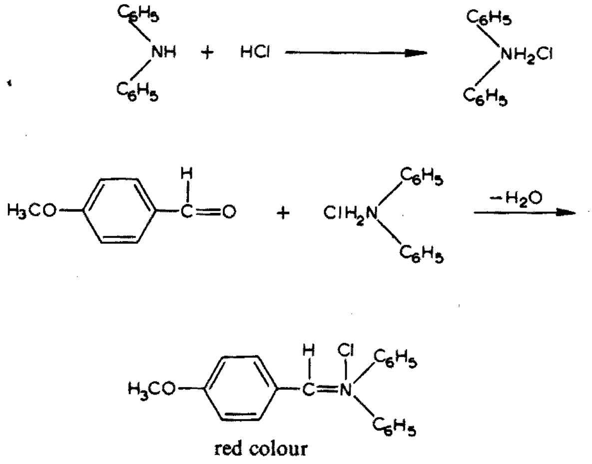
Detection of substituted aromatic aldehydes in presence of foreign substances. The interferences of various foreign substances in the test procedure were checked for small amounts of the aldehyde in presence of a large excess of these substances. The minimum amounts of anisaldehyde and *p*-dimethylaminobenzaldehyde which could be detected are shown in Tables II and III, respectively. The limiting proportions were $1{:}4\cdot10^3$ for the red colour formed with anisaldehyde, and $1{:}1\cdot10^4$ for the green colour formed with *p*-dimethylaminobenzaldehyde in all cases.

Determination

To check the validity and the reproducibility of the recommended procedure of determination, several unknowns were run. The results are summarized in Table IV. The red or yellow colours formed were found to be stable for up to 4 h.

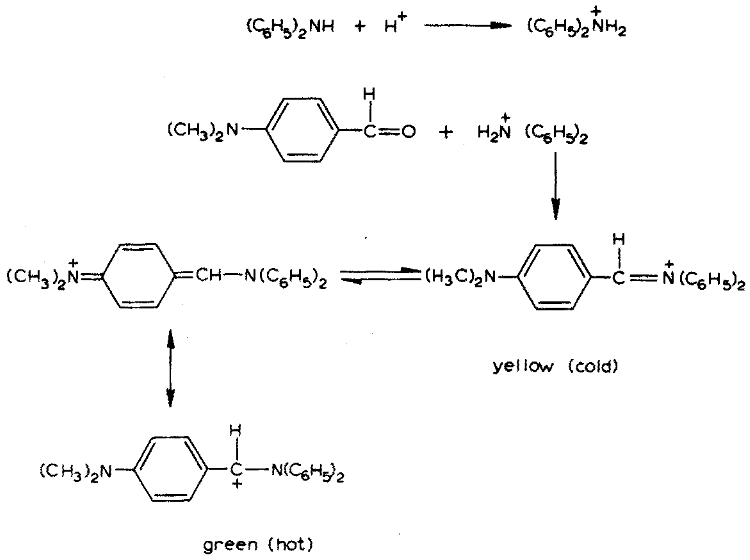
DISCUSSION

Substituted aromatic aldehydes containing hydroxy or methoxy groups form red colours when they are heated with diphenylamine in presence of hydrochloric acid. The mechanism of the reaction may be postulated as follows:



Diphenylamine first reacts with hydrochloric acid to form diphenylamine hydrochloride which condenses with aldehydes losing one mole of water. The red coloured compound is not adsorbed either on cation-exchange or on anion-exchange resins which clearly shows that it has no charge.

However, substituted aromatic aldehydes containing a nitrogen atom react with $(C_6H_5)_2\overset{+}{N}H_2$ ions and lose one water molecule. The resulting product is yellow in the cold and turns green on heating. The green product is adsorbed on a cation-exchange resin which shows that the species is positively charged[14].



The authors thank Dr. S. M. F. Rahman, Head of the Chemistry Department, for providing research facilities and encouragement. The Council of Scientific and Industrial Research (India) is thanked for financial assistance to S.C.S.

SUMMARY

A new highly selective colour reaction for the detection and determination of substituted aromatic aldehydes with diphenylamine in presence of hydrochloric acid is described. Successful colorimetric determinations of milligram amounts of anisaldehyde, salicylaldehyde, *p*-dimethylaminobenzaldehyde and *o*-vanillin were achieved. Substituted aromatic aldehydes containing methoxy or hydroxy groups form a red colour and the others containing a nitrogen atom form green coloured products on heating with diphenylamine and concentrated hydrochloric acid. Tentative mechanisms for the two colour reactions are proposed.

RÉSUMÉ

On décrit une nouvelle réaction colorée, très sélective pour la détection et le dosage d'aldéhydes aromatiques substitués, au moyen de diphénylamine, en présence d'acide chlorhydrique. Des résultats satisfaisants ont été obtenus lors du dosage d'anisaldéhyde, de salicylaldéhyde, de *p*-dimethylaminobenzaldéhyde, et d'*o*-vanilline, en quantités de l'ordre du milligramme. Les aldéhydes aromatiques substitués renfermant des groupes méthoxy ou hydroxy donnent une coloration rouge; les autres, avec atome d'azote, donnent des colorations vertes, par chauffage avec la diphénylamine et l'acide chlorhydrique concentré. Des mécanismes sont proposés.

ZUSAMMENFASSUNG

Es wird eine neue hochselektive Farbreaktion beschrieben für den Nachweis und die Bestimmung von substituierten aromatischen Aldehyden mittels Diphenylamin in Gegenwart von Salzsäure. Milligramm-Mengen von Anisaldehyd, Salicylaldehyd, *p*-Dimethylaminobenzaldehyd und *o*-Vanillin wurden mit Erfolg colorimetrisch bestimmt. Substituierte aromatische Aldehyde mit Methoxy- oder Hydroxygruppen ergeben eine Rotfärbung, die anderen, die ein Stickstoffatom enthalten, bilden grün gefärbte Produkte beim Erhitzen mit Diphenylamin und konzentrierter Salzsäure. Es werden versuchsweise Mechanismen für die beiden Farbreaktionen vorgeschlagen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DUAL-WAVELENGTH SPECTROPHOTOMETRY
PART II. THE DETERMINATION OF MIXTURES

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(Received 4th October 1970)

In a previous paper[1], a general method of dual-wavelength spectrophotometry for analytical applications was described. In this method, light from a highly stabilized tungsten–iodide lamp or deuterium lamp is divided into two beams with wavelengths of λ_1 and λ_2 in two grating monochromators. The two light beams of different wavelength from the two gratings are time-shared through a single cell by means of a rotating sector and the difference between the absorbances at wavelengths λ_1 and λ_2 is measured. In the classical method, it is usual to measure the absorbance of the sample solution against a reference solution set to read zero. Generally, in the dual-wavelength method, λ_1 is regarded as the reference wavelength and λ_2 as the analytical or measurement wavelength. A schematic representation of the principle of the method is shown in Fig. 1.

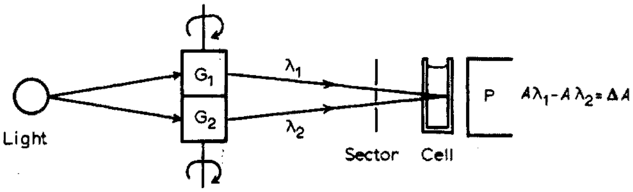
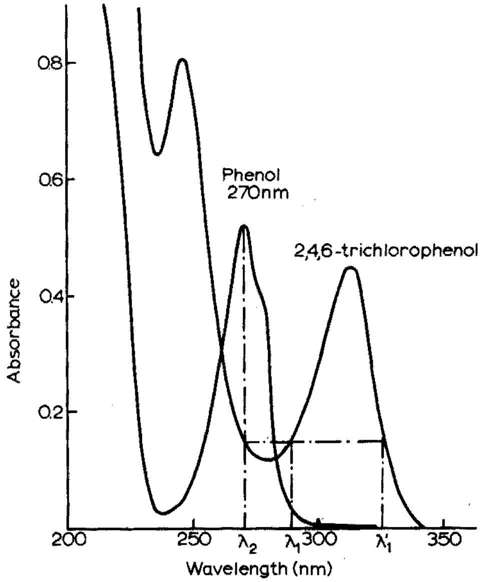


Fig. 1. Principle of dual-wavelength spectrophotometry. (G_1, G_2) Grating; (P) photomultiplier.

Instruments of this new type can be easily used as the classical double-beam recording spectrophotometer by self-rocking of two gratings so that $\lambda_1=\lambda_2$. A detailed description of the apparatus is available in the previous paper[1].

Spectrophotometric analysis for two components generally requires the solution of simultaneous equations[2]. Many schemes have been proposed to simplify the calculations and to lessen the amount of time[3].

When the dual-wavelength measurement is applied, the simultaneous determination of mixtures, or masking of the diverse components, can be done very easily and accurately without any calculations. Suppose that a two-component sample contains X and Y. If it is desired to determine Y by eliminating the influence of X, two wavelengths at which X shows the same absorbance are selected from its absorption spectrum. At these wavelengths, the baseline in the dual-wavelength measurement remains level in spite of variations in the concentration of X because $\Delta A_{\lambda_1-\lambda_2}$



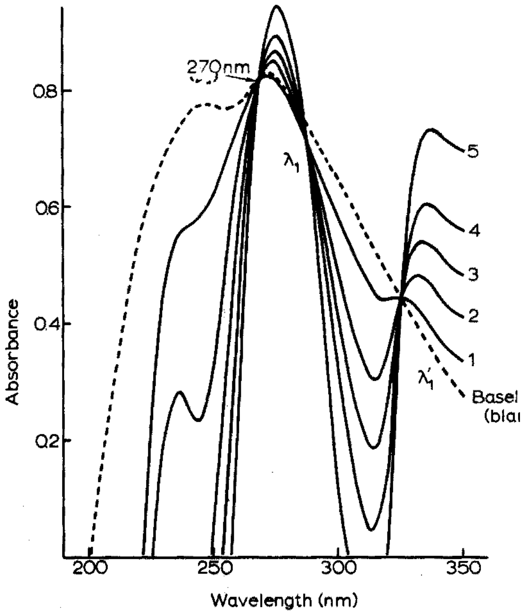


Fig. 2. Selection of λ_1 and λ_2 by drawing figures. Determination of phenol in the presence of 2,4,6-trichlorophenol. $\lambda_1 = \lambda_2$, 30 p.p.m. of each component.

Fig. 3. Selection of λ_1 and λ_2 from absorption spectra with λ_2 fixed (270 nm) and λ_1 as the scanning wavelength. 2,4,6-Trichlorophenol (p.p.m.): (1) 10, (2) 20, (3) 30, (4) 40 and (5) 50.

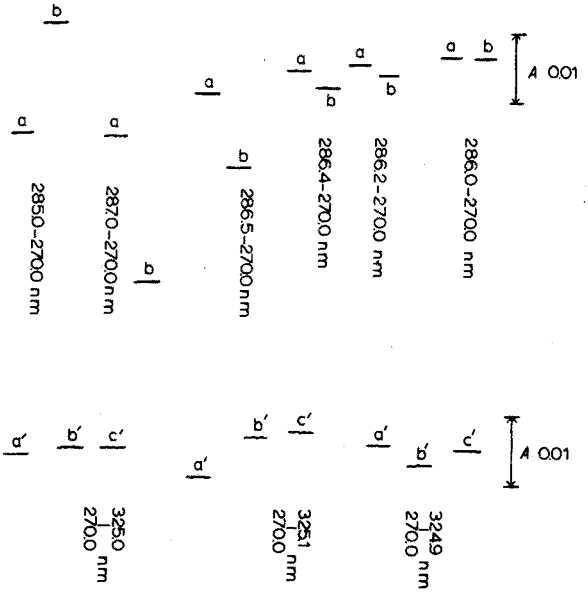


Fig. 4. Precise method for selection of λ_1 and λ_2. (a, a') Water; (b, b') 50 p.p.m. 2,4,6-trichlorophenol; (c') 100 p.p.m. 2,4,6-trichlorophenol.

equals zero. The wavelengths λ_1 and λ_2 are selected according to the shapes of the absorption spectra of the two components. The wavelengths chosen must satisfy the following two fundamental conditions:

1. the coexisting component must show the same absorbance at those wavelengths ($\Delta A_{\lambda_1-\lambda_2}=0$),so that variations in its concentration may have no influence on the measurement;

2. the differential absorbance of the other component to be determined between those wavelengths must show an adequate value.

EXPERIMENTAL

Reagents

Phenol, *o*-, and *p*-nitrophenol, 2,4,6-trichlorophenol, iso- and terephthalic acid were purified by the usual manner. All other reagents used were prepared from high-purity materials or purified reagents, and all solutions were prepared with re-distilled water.

Apparatus

A Hitachi 356 two-wavelength spectrophotometer was used with 1-cm quartz cells. This apparatus can be used both as a dual-wavelength and as a classical double-beam recording spectrophotometer.

RESULTS AND DISCUSSION

The most important feature of the determination of mixtures is the selection of the optimal wavelengths for λ_1 and λ_2, and this procedure is quite simple.

Initial selection of approximate values for λ_1 and λ_2

This can be done either by drawing figures or by scanning the mixture with one wavelength fixed. As an example of the first method, the determination of phenol in the presence of 2,4,6-trichlorophenol can be considered. Figure 2 shows the absorption spectra of phenol and 2,4,6-trichlorophenol in aqueous solution. If the wavelength of maximum absorbance for phenol at 270 nm is chosen as the analytical wavelength, a line is drawn from this peak to the *x*-axis. A point of intersection is then obtained on the absorption spectrum of 2,4,6-trichlorophenol, and from this point, a line horizontal to the *x*-axis is drawn. Another absorption point (or several similar points) λ_1 or λ_1' is thus obtained. At the combination λ_1–λ_2 or λ_1'–λ_2, the baseline does not change when the concentration of 2,4,6-trichlorophenol is altered, *i.e.* $A_{\lambda_1}-A_{\lambda_2}=\Delta A=0$. Accordingly, any variation in the concentration of the trichlorphenol has no influence on the determination of phenol. Of course, at the combination of λ_1 and λ_2 selected, the ΔA value for phenol should be sufficiently large. From Fig. 2, the combination 270–286 (or 325) nm would be selected for this system. Generally, the selection of the combination of λ_1 and λ_2 depends on the shape of each spectrum. If the maximum absorbance wavelength cannot be used as the analytical wavelength, any other suitable wavelength on the absorption spectra can be selected (see the iso- and terephthalic acid system below).

Although in the above description, λ_1 and λ_2 are determined from a single

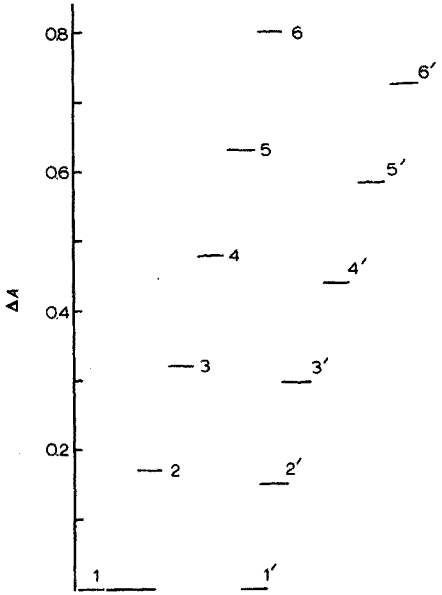


Fig. 5. Determination of phenol in the presence of 2,4,6-trichlorophenol.
$\lambda_1=286.0$ *nm*, $\lambda_2=270.0$ *nm*
(1) Phenol 0 p.p.m. + 2,4,6-trichlorophenol 50 p.p.m.
(2) Phenol 10 p.p.m. + 2,4,6-trichlorophenol 40 p.p.m.
(3) Phenol 20 p.p.m. + 2,4,6-trichlorophenol 25 p.p.m.
(4) Phenol 30 p.p.m. + 2,4,6-trichlorophenol 20 p.p.m.
(5) Phenol 40 p.p.m. + 2,4,6-trichlorophenol 10 p.p.m.
(6) Phenol 50 p.p.m. + 2,4,6-trichlorophenol 50 p.p.m.
$\lambda_1=325.0$ *nm*, $\lambda_2=270$ *nm*
(1′) Phenol 0 p.p.m. + 2,4,6-trichlorophenol 0 p.p.m.
(2′) Phenol 10 p.p.m. + 2,4,6-trichlorophenol 0 p.p.m.
(3′) Phenol 20 p.p.m. + 2,4,6-trichlorophenol 40 p.p.m.
(4′) Phenol 30 p.p.m. + 2,4,6-trichlorophenol 30 p.p.m.
(5′) Phenol 40 p.p.m. + 2,4,6-trichlorophenol 50 p.p.m.
(6′) Phenol 50 p.p.m. + 2,4,6-trichlorophenol 20 p.p.m.

concentration of 2,4,6-trichlorophenol, it is also possible to use several samples of various concentration. This method then enables any changes in the soluble species, caused by polymerization, dissociation or other chemical or physical effects, to be easily checked from the shapes of the spectra. Initially, it is necessary to choose an analytical wavelength from the normal absorption spectrum of phenol; as mentioned above 270 nm was selected. The fixed wavelength λ_2 is then dialled at 270 nm, and absorption spectra of various concentrations of 2,4,6-trichlorophenol are measured, λ_1 being the scanning wavelength. Several isosbestic points can then be observed on the baseline, *i.e.* the differential absorbance ΔA between 270 nm and these points is zero. Spectra obtained in this way for 2,4,6-trichlorophenol are shown in Fig. 3.

Precise method of selecting suitable wavelengths

Here, the changes in the differential absorbance in response to some variation in the concentration of 2,4,6-trichlorophenol are measured 5 or 6 times in the vicinity of the temporary wavelength settings, so that λ_1 and λ_2 can be finally set at wavelengths which minimize changes in the difference of absorbance.

Advantageously, wavelength λ_1 is first altered forward or backward by about 1 nm so that the direction and size of the change in the differential absorbance ΔA can be observed. Then both wavelengths are finely adjusted successively until the differential absorbance becomes zero despite variations in the concentration of 2,4,6-trichlorophenol. An example of the procedure for selecting λ_1 and λ_2 is shown in Fig. 4.

With a scale range of 0.1 absorbance unit, this procedure presents few problems. But when the range is 0.01 absorbance unit for full scale, great prudence is needed. Since the absorbance scale is expanded 100-fold compared with that of ordinary spectrophotometers, a very slight displacement in the absorption cell can produce a considerable error caused by regularly reflected light from the transmission surface of the cell. However, with careful experiment, the variation of the baseline can be limited within about 0.0003 absorbance unit (see sections on nitrophenol and phthalic acid below). By this procedure, suitable combinations of λ_1–λ_2 were established as 286.0–270.0 nm or 325.0–270.0 nm for the determination of phenol in the presence of 2,4,6-trichlorophenol. In the case of determinations of another component, the optimal selection of λ_1–λ_2 can be established by a similar procedure. Figure 5 shows some data for the determination of phenol in the presence of 2,4,6-trichlorophenol.

Determination of o- *and* p-*nitrophenol mixtures*

By dual-wavelength measurements, even if the absorption spectra of two components are quite similar, it is possible to determine each component accurately without trouble. Figure 6 shows the absorption spectra of *o*- and *p*-nitrophenol in aqueous solution. The procedures for the selection of λ_1 and λ_2 are shown in Figs. 7 and 8; finally, 431.4–400 nm was selected as the most suitable combination.

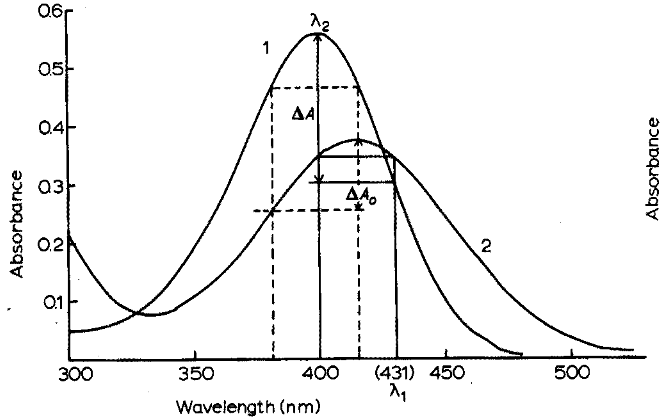
Data for the determination of *o*-nitrophenol in the presence of various amounts of *p*-nitrophenol are shown in Fig. 9.

Determination of terephthalic acid in the presence of isophthalic acid

Figure 10 shows the absorption spectra of both compounds in the wavelength range of 240–320 nm. It can be seen from the spectrum of isophthalic acid that the wavelengths to be selected lie in a shoulder portion at 260–280 nm. For example, λ_2 is set at the peak position of isophthalic acid (277 nm) and λ_1 is temporarily set at 263 nm which is known to give the same absorbance as at 277 nm. For the purpose of masking the coexisting isophthalic acid, the wavelengths between which the differential absorbance equals zero, in spite of variations in its concentration must be established. Figure 11 shows the precise method for the selection of λ_1 and λ_2.

Since the difference between absorbances at two wavelengths is measured in the dual-wavelength technique, the results are scarcely affected by external factors. Therefore, highly sensitive measurements are possible by utilizing this feature. In Fig. 12, the results for a full-scale range of 0.01 are shown. The calibration curve shows excellent linearity, while the noise level is only about 0.0002 absorbance unit. Some typical results are shown in Table I.

Studies on the application of the dual-wavelength method to multicomponent mixtures are now in progress.



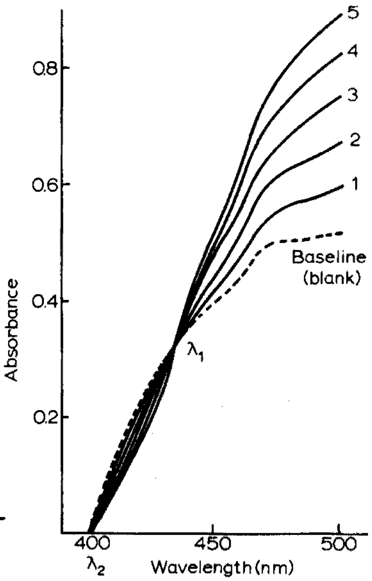


Fig. 6. Absorption spectra of *o*- and *p*-nitrophenol. (1) $3 \cdot 10^{-5}$ *M* *p*-nitrophenol; (2) $8 \cdot 10^{-5}$ *M* *o*-nitrophenol. pH 10, $\lambda_1 = \lambda_2$. (----) For the determination of *p*-nitrophenol in the presence of *o*-nitrophenol.

Fig. 7. Selection of λ_1 and λ_2 from absorption spectra with λ_2 fixed (400 nm) and λ_1 as the scanning wavelength. *o*-Nitrophenol: (1) $2 \cdot 10^{-5}$ *M*; (2) $4 \cdot 10^{-5}$ *M*; (3) $6 \cdot 10^{-5}$ *M*; (4) $8 \cdot 10^{-5}$ *M*; (5) $10 \cdot 10^{-5}$ *M*.

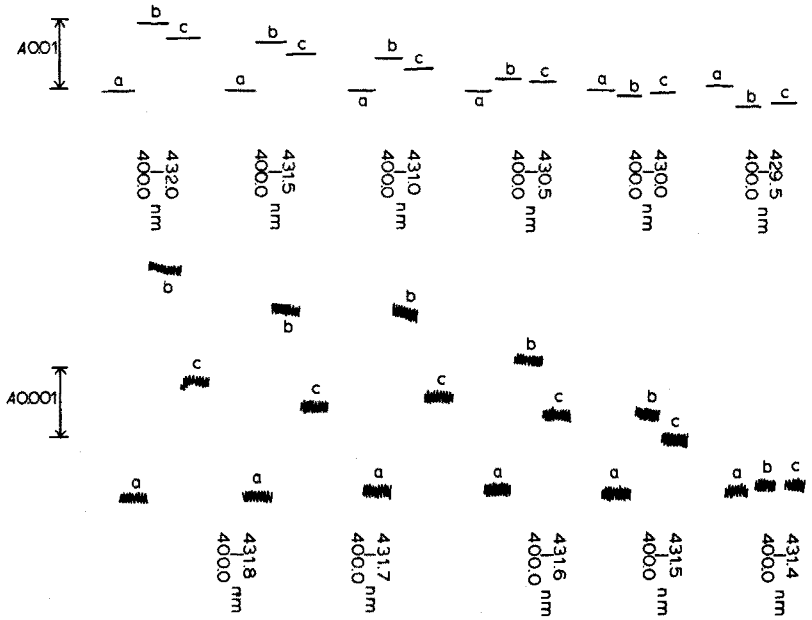


Fig. 8. Precise method for selection of λ_1 and λ_2. *o*-Nitrophenol: (a) $4 \cdot 10^{-5}$ *M*, (b) $8 \cdot 10^{-5}$ *M*, (c) $12 \cdot 10^{-5}$ *M*.

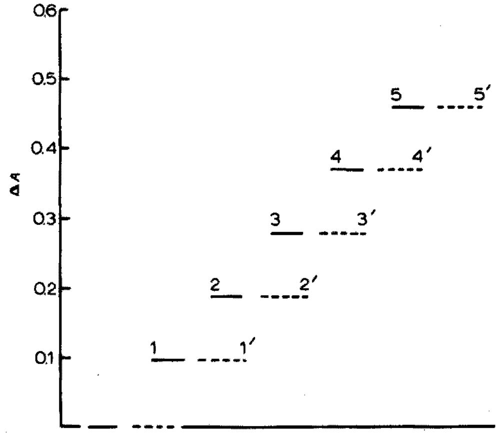


Fig. 9. Determination of *p*-nitrophenol in the presence of *o*-nitrophenol. $\lambda_1 = 431.4$ nm; $\lambda_2 = 400.0$ nm. *p*-Nitrophenol: (1) $1 \cdot 10^{-5}$ *M*; (2) $2 \cdot 10^{-5}$ *M*; (3) $3 \cdot 10^{-5}$ *M*; (4) $4 \cdot 10^{-5}$ *M*; (5) $5 \cdot 10^{-5}$ *M*.
(1′) *p*-Nitrophenol $1 \cdot 10^{-5}$ *M* + *o*-nitrophenol $6 \cdot 10^{-5}$ *M*
(2′) *p*-Nitrophenol $2 \cdot 10^{-5}$ *M* + *o*-nitrophenol $10 \cdot 10^{-5}$ *M*
(3′) *p*-Nitrophenol $3 \cdot 10^{-5}$ *M* + *o*-nitrophenol $2 \cdot 10^{-5}$ *M*
(4′) *p*-Nitrophenol $4 \cdot 10^{-5}$ *M* + *o*-nitrophenol $4 \cdot 10^{-5}$ *M*
(5′) *p*-Nitrophenol $5 \cdot 10^{-5}$ *M* + *o*-nitrophenol $8 \cdot 10^{-5}$ *M*

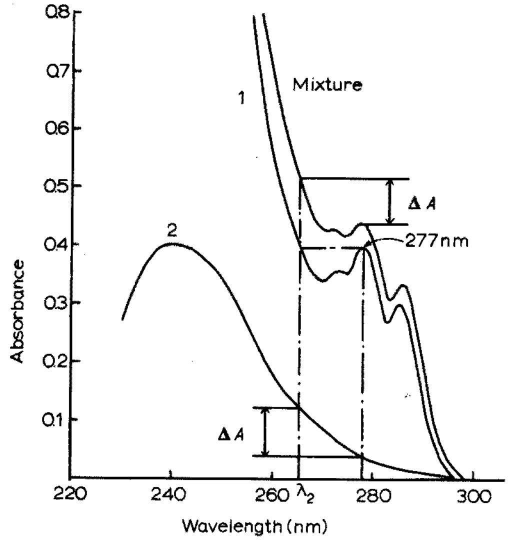


Fig. 10. Absorption spectra of iso- and terephthalic acid. (1) Isophthalic acid, 10 mg/100 ml; (2) Terephthalic acid, 0.5 mg/100 ml. $\lambda_1 = \lambda_2$.

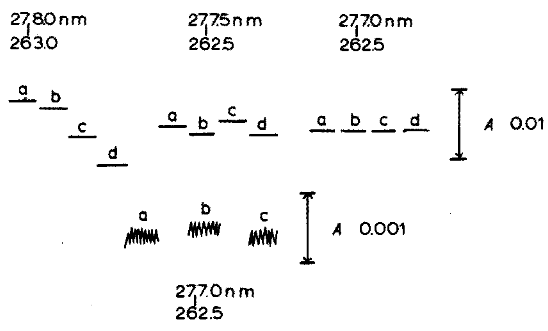


Fig. 11. Precise method for selection of λ_1 and λ_2. Isophthalic acid: (a) 25 mg ml^{-1}; (b) 20 mg ml^{-1}; (c) 15 mg ml^{-1}; (d) 10 mg ml^{-1}.

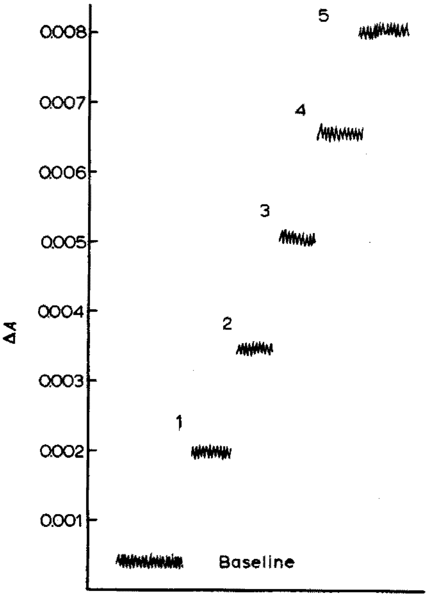


Fig. 12. Determination of terephthalic acid with the full scale. $A = 0.01$. Isophthalic acid, 20 mg/100 ml. Terephthalic acid: (1) 0.01 mg, (2) 0.02 mg, (3) 0.03 mg, (4) 0.04 mg, (5) 0.05 mg/100 ml. λ_1–$\lambda_2 = 262.5$–277.0 nm.

TABLE I

DETERMINATION OF TEREPHTHALIC ACID IN THE PRESENCE OF ISOPHTHALIC ACID

(λ_1–λ_2, 277.0 nm–262.5 nm)

Isophthalic acid (mg/100 ml)	*Terephthalic acid (mg/100 ml)*	ΔA	*Terephthalic acid found (mg/100 ml)*	*Error (%)*
20	0.10	0.012	0.10	±0.0
20	0.20	0.024	0.20	±0.0
20	0.30	0.0368	0.302	+0.5
20	0.40	0.0492	0.402	+0.5
20	0.01	0.0015	0.0095	−0.5
20	0.02	0.0032	0.0205	+2.5
20	0.03	0.0046	0.030	±0.0
20	0.04	0.0062	0.0405	+1.3
20	0.05	0.0077	0.050	+0.0

The authors thank Dr. K. Yasuda and Mr. T. Honkawa for their helpful discussion and remarks, and Mr. R. Komori for his assistance in obtaining spectra and in the preparation of this manuscript.

SUMMARY

A simple rapid spectrophotometric method for the determination of two-component systems by means of a dual-wavelength method is described. By proper selection of the combination of two wavelengths λ_1 and λ_2, one component can be masked instrumentally even when its concentration varies. The component to be determined is measured as follows: two light beams of different wavelengths λ_1 and λ_2 from two gratings are time-shared through a single cell by means of a rotating sector and the difference between the absorbance at wavelengths λ_1 and λ_2 is measured. Analysis of mixtures of *o*- and *p*-nitrophenol, and of iso- and terephthalic acid, is discussed.

RÉSUMÉ

Une méthode spectrophotométrique simple et rapide est décrite pour le dosage de systèmes à deux composants, à l'aide de la technique à deux longueurs d'onde. Par combinaison de deux longueurs d'onde λ_1 et λ_2, un composant peut être masqué instrumentalement, même si sa concentration varie. On examine l'analyse de mélanges d'*o*- et de *p*-nitrophénols et d'acides iso- et téréphtalique.

ZUSAMMENFASSUNG

Es wird ein einfaches und schnelles spektrophotometrisches Verfahren für die Bestimmung von Zweikomponentensystemen mit Hilfe einer Zwei-Wellenlängen-Methode beschrieben. Durch sorgfältige Auswahl der Kombination zweier Wellenlängen λ_1 und λ_2 kann eine Komponente sogar bei wechselnder Konzentration instrumentell maskiert werden. Die zu bestimmende Komponente wird folgendermassen gemessen: von zwei Gittern gelangen zwei Lichtstrahlen verschiedener Wellenlänge λ_1 und λ_2, mittels eines rotierenden Sektors zeitlich unterteilt, durch eine einzige Küvette; die Differenz zwischen den Extinktionen bei den Wellenlängen λ_1 und λ_2 wird gemessen. Die Analyse von Gemischen von *o*- und *p*-Nitrophenol und von Iso- und Terephthalsäure wird diskutiert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

UNSATURATED N-ARYLHYDROXAMIC ACIDS AS COLORIMETRIC REAGENTS FOR VANADIUM(V)

SPECTROPHOTOMETRIC DETERMINATION WITH N-PHENYL-3-STYRYLACRYLOHYDROXAMIC ACID

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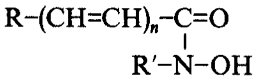
(Received 12th August 1970)

N-Phenylbenzohydroxamic acid (PBHA) has been well established as a reagent for the solvent extraction and spectrophotometric determination of vanadium(V)[1-3]. The striking selectivity of the method for vanadium(V) reaction, especially the freedom from the interference of iron(III), enables the direct determination of vanadium(V) in steels[4,5], alloys[6], ores[1,2], blood, urine and plant products[7] and other complex materials[8]. This and the other excellent qualities of PBHA as a reagent for vanadium(V) have led to several systematic studies for better reagents among the family of hydroxamic acids. Over 150 analogous N-substituted hydroxamic acids have been examined in this laboratory[9-15], and several others elsewhere[16-18], and N-phenylcinnamohydroxamic acid (PCHA)[12,19] has elicited special interest. This reagent retains all the useful features of PBHA as a reagent for vanadium(V) but excels it in the sensitivity and selectivity of the reaction. The molar absorptivity of the vanadium complex of PCHA is 6300 l mole^{-1} cm^{-1} compared to 4650 l mole^{-1} cm^{-1} for the PBHA complex, both being measured at their wavelengths of maximum absorbance. Moreover, the PCHA method can tolerate large amounts of zirconium(IV), which interfere in the determination of vanadium(V) with PBHA. The improved sensitivity of the reaction as reflected by the conspicuous increase in molar absorptivity may presumably be attributed to the increased conjugation in PCHA caused by the CH=CH linkage. A number of unsaturated N-arylhydroxamic acids of the general formula I have therefore been synthesized and examined as possible reagents for vanadium(V):



$$\begin{array}{l} R\text{–}(CH{=}CH)_n\text{–}\underset{\displaystyle R'\text{–}N\text{–}OH}{\underset{|}{C}}{=}O \end{array} \qquad I$$

where n is 1 or 2; R is methyl, phenyl, 2-furyl, *p*-methoxyphenyl or 3,4-methylenedioxyphenyl; and R′ is phenyl, *o*-, *m*- or *p*-tolyl or *p*-chlorophenyl.

This study has shown that by a judicious choice of the substituents for attaching to the hydroxamic acid functional grouping, –CO(NOH)–, it is possible to develop superior chromogenic reagents for vanadium(V). Of the 23 hydroxamic acids examined here, 20 showed better sensitivity for vanadium(V) reactions than PBHA. The molar absorptivities for the reactions of vanadium(V) with nine hydroxamic acids reached a new high mark of 7500 l mole^{-1} cm^{-1}. Detailed studies with N-phenyl-3-

styrylacrylohydroxamic acid (PSAHA) showed that the determination of vanadium(V) with this new hydroxamic acid possesses all the merits of PBHA with additional qualities of enhanced selectivity and sensitivity.

EXPERIMENTAL

Apparatus

The spectra of the vanadium(V) complexes were scanned on a Perkin-Elmer Model 350 recording spectrophotometer and measurements at constant wavelengths were performed on a Unicam SP 500 spectrophotometer with 10-mm matched silica cells.

Reagents and solutions

The preparation and physical characteristics of the reagents have been described earlier[13]. Solutions (0.1 % w/v) of N-arylhydroxamic acids in ethanol-free chloroform were used for all extraction work. Commercial chloroform was washed free of alcohol with distilled water and distilled after dyring over fused calcium chloride. Standard vanadium solution was prepared from A.R. ammonium metavanadate and standardized titrimetrically with potassium permanganate.

Analytical procedure

Transfer an aliquot of vanadium solution to a separating funnel and add dilute potassium permanganate solution dropwise until a faint pink colour persists to ensure complete oxidation of vanadium to the pentavalent state. Adjust the acidity to about 4 *M* in a final volume of 25 ml with concentrated hydrochloric acid and distilled water and then add 8–10 ml of reagent solution.

Shake vigorously for 2–3 min and allow the phases to separate. Dry the chloroform extract over anhydrous sodium sulphate and transfer to a 25-ml volumetric flask. Repeat the extraction twice to ensure complete recovery of vanadium. Dilute the extracts to 25 ml with chloroform and measure the absorbance spectrum of the coloured extract with the reagent solution in the reference cell.

Colour reaction

In general, the reactions of N-arylhydroxamic acids with vanadium(V) were similar to that of PBHA[1-3]. The chloroform solution of any particular hydroxamic acid reacted with vanadium(V) in solutions containing more than 2 *M* hydrochloric acid to give a coloured extract (see Table I). The same complex was formed if the hydrochloric acid concentration of the aqueous phase was more than 2 *M*, as was evidenced by the absorbance spectra; the wavelength of maximum absorbance of the coloured extract did not vary with change of hydrochloric acid concentration of the aqueous phase, although the molar absorptivity varied.

Several organic solvents such as chloroform, carbon tetrachloride, benzene, *o*-dichlorobenzene, diethyl ether and ethyl acetate, extracted the complex from the aqueous phase. However, chloroform was found to be the most suitable solvent because of its very favourable distribution ratio. The chloroform must be free from ethanol, otherwise the extracts were unstable; extracts containing ethanol gradually acquired a reddish brown colour and recorded shifts in spectral characteristics. Other

TABLE I

SPECTRAL CHARACTERISTICS OF COLOURED VANADIUM(V)–N-ARYLHYDROXAMATES IN CHLOROFORM

(Extracted from 4 *M* hydrochloric acid)

No.	*Hydroxamic acid*	*Colour of chloroform extract*[a]	*Wavelength of maximum absorption (nm)*	*Molar absorptivity*[b]
1.	N-Phenylbenzo-	V	530	4650
2.	N-Phenyl-3-styrylacrylo-	BV	555	7500
3.	N-Phenyl-*p*-methoxycinnamo-	BV	570	7500
4.	N-*m*-Tolyl-*p*-methoxycinnamo-	BV	570	7500
5.	N-*p*-Tolyl-*p*-methoxycinnamo-	BV	570	7500
6.	N-*p*-Chlorophenyl-*p*-methoxycinnamo-	BV	570	7400
7.	N-Phenyl-3,4-methylenedioxycinnamo-	BV	570	7400
8.	N-*m*-Tolyl-3,4-methylenedioxycinnamo-	BV	570	7500
9.	N-*p*-Tolyl-3,4-methylenedioxycinnamo-	BV	570	7500
10.	N-*p*-Chlorophenyl-3,4-methylenedioxycinnamo-	BV	570	7400
11.	N-Phenylcinnamo-	BV	540	6300[c]
12.	N-*o*-Tolylcinnamo-	BV	530	6300
13.	N-*m*-Tolylcinnamo-	BV	540	6200
14.	N-*p*-Tolylcinnamo-	BV	555	6500[b]
15.	N-*p*-Chlorophenylcinnamo-	BV	535	6300
16.	N-Phenyl-2-furanacrylo-	BV	560	6200
17.	N-*m*-Tolyl-2-furanacrylo-	BV	570	6300
18.	N-*p*-Tolyl-2-furanacrylo-	BV	570	6300
19.	N-*p*-Chlorophenyl-2-furanacrylo-	BV	570	6100
20.	N-Phenylsorbo-	BV	550	5500
21.	N-*m*-Tolylsorbo-	BV	550	5500
22.	N-*p*-Tolylsorbo-	BV	555	5500
23.	N-*p*-Chlorophenylsorbo-	BV	550	5100
24.	N-Phenylcrotono-	V	535	4400
25.	N-*p*-Tolylcrotono-	V	540	4800
26.	N-*p*-Chlorophenylcrotono-	V	530	4400

[a] V = violet; BV = bluish violet.
[b] The average of 12 measurements of 4 samples.
[c] Ref. 12.
[d] Ref. 6.

alcohols such as methanol, propanols, butanols, amyl alcohol, *n*-hexanol and *n*-octanol, etc., when added to the chloroform extracts also exhibited similar behaviour.

RESULTS AND DISCUSSION

The spectral characteristics of the vanadium(V) complexes of the various

N-arylhydroxamic acids studied are recorded in Table I. Their absorbance bands are generally broad and the maxima are present between 530 and 570 nm (Fig. 1). These spectra show strong bathochromic and hyperchromic effects with respect to that of PBHA. Evidently, the effects of the $\pi \rightarrow \pi$ and $n \rightarrow \pi$ systems present in conjugation with the functional carbonyl group in the ligand molecules are transmitted in the spectra of the respective vanadium(V) complexes. During the analyses of various steel samples (p. 384), it was, however, noticed that the selectivity of the vanadium(V) reaction was entirely unaffected only in the case of N-phenyl-3-styrylacrylohydroxamic acid (PSAHA). In other cases various degrees of interference from alloyed metal ions were observed; the extracts usually turned red.

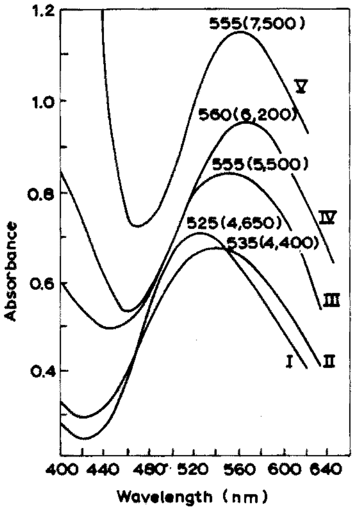


Fig. 1. Absorption spectra of complexes of vanadium(V) (0.00781 g vanadium per l) from 4 *M* HCl with chloroform containing (I) PBHA, (II) N-phenylcrotonohydroxamic acid, (III) N-phenylsorbohydroxamic acid, (IV) N-phenyl-2-furanacrylohydroxamic acid, (V) N-phenyl-3-styrylacrylohydroxamic acid.

Determination of vanadium(V) with PSAHA

The effects of the following variables in the reaction of PSAHA with vanadium(V) were investigated.

Beer's law and precision studies. The system obeys Beer's law over the range 0.7–8.4 $\mu g\ ml^{-1}$ of vanadium at 555 nm. The optimal working range is about 1.4–4.9 μg of vanadium per ml. The sensitivity of the reaction, as defined by Sandell[20] is 0.0068 $\mu g\ V\ cm^{-2}$ at 555 nm.

For testing the precision of the recommended analytical procedure, seven concentration levels of vanadium were chosen and ten determinations were made at each level. The absorbance of each extract was measured at least three times and averaged. The standard deviation, σ, in terms of the absorbance was calculated. The data on relative standard deviation[21] presented in Table II show that vanadium can be determined with good precision. High values for the relative standard deviation at the level of 17 p.p.m. of vanadium(V) are primarily due to the low sensitivity of spectrophotometer for light coloured solutions[22].

Effect of acidity. The position of the absorbance band of the chloroform extracts

TABLE II

CALIBRATION CURVE DATA AND RESULTS OF PRECISION STUDIES

Vanadium(V) (μg/25 ml of chloroform)	*Absorbance at 555 nm*[a]	*Standard deviation σ (in absorbance)*	*Relative standard deviation (%)*
17.0	0.100	0.0050	5.00
34.7	0.202	0.0036	1.78
86.8	0.510	0.0052	1.02
98.4	0.580	0.0052	0.90
121.5	0.712	0.0058	0.82
173.6	1.040	0.0080	0.77
208.3	1.252	0.0097	0.77

[a] Average of 10 analyses of the same sample.

remained unaltered when the aqueous solutions were 2–10 *M* in hydrochloric acid, but the maximum colour intensity was obtained when the acid concentration lay between 2.5 and 8 *M*. Only hydrochloric acid was suitable for adjusting the acidity, but other acids such as sulfuric, nitric, and perchloric, could be tolerated when their concentration in the aqueous phase was less than 1 *M*. In practice, the measurements were made in solutions which were 4 *M* in hydrochloric acid.

Effect of reagent concentration. The optimum concentration of the reagent solution was 0.1 % w/v and maximum colour development took place when the mole ratio of vanadium to reagent was 1:10. Larger excesses of reagent could be used. In practice, for each milligram of vanadium about 60 mg of reagent, corresponding to about 1:12 mole ratio of vanadium to PSAHA, were employed.

Effect of volume, ionic strength and temperature of aqueous phase. The volume of the aqueous phase was varied between 5 and 75 ml without effect. For convenience and uniformity, the volume of the aqueous phase was adjusted to approximately 25 ml before extraction.

Variation of the ionic strength of the aqueous phase from 2.5 to 8 gram moles per litre with hydrochloric acid and potassium chloride, caused no adverse effect on the absorbance of the coloured system. In fact, the extraction of the bluish violet complex into the chloroform layer was facilitated at high ionic strengths owing to the salting-out effect.

Variation in the temperature of the aqueous phase from 20° to 40° did not produce any measurable change in the absorbance of the chloroform extracts.

Extraction time and stability of colour. Extraction of the coloured complex from the aqueous phase was quantitative in one equilibration step of 1–2 min under the conditions recommended in the analytical procedure. The chloroform extracts of the complex were stable for several days, if stored in a cool dark place in stoppered bottles.

Effect of diverse ions

The effects of various ions on the determination of vanadium with PSAHA were almost the same as those found with PBHA[2,3] or PCHA[12]. Titanium(IV), zirconium(IV) and molybdenum(VI) which interfered in the determination of vanadium with PBHA were tolerated in larger amounts in the method with PSAHA. The following ions did not interfere with the determination of 86.8 µg V in 25 ml:

Al^{3+} (20 mg), Ba^{2+} (20 mg), Ca^{2+} (20 mg), Cd^{2+} (20 mg), Co^{2+} (20 mg), Cr^{3+} (20 mg), Cu^{2+} (30 mg), Fe^{3+} (30 mg), Hg^{2+} (20 mg), Mn^{2+} (20 mg), MoO_4^{2-} (5 mg), Ni^{2+} (20 mg), NH_4^+ (50 mg), Pb^{2+} (20 mg), Th^{4+} (20 mg), UO_2^{2+} (20 mg), Ti^{4+} (10 mg), WO_4^{2-} (10 mg), Zn^{2+} (20 mg), Zr^{4+} (20 mg), acetate (20 mg), citrate (20 mg), tartrate (20 mg), phosphate (30 mg), fluoride (30 mg).

Phosphoric acid was used to keep tungstate in solution and sodium fluoride as masking reagent for titanium. Under the experimental conditions, thiocyanate completely masked vanadium(V) and seriously interfered. Reducing agents obviously interfered with the determination of vanadium but these were easily eliminated during the step of oxidation of vanadium to the pentavalent state.

Some oxidising agents such as potassium dichromate and potassium permanganate attacked the reagent and the oxidation products gave a brown colour in the chloroform layer. In such cases, the oxidising agent was reduced with an excess of iron(II) sulfate and the reduced vanadium was then oxidised with a solution of potassium permanganate and the determination completed by the recommended analytical procedure.

Silver(I), lead(II), mercury(I), thallium(I) and tungstate formed precipitates with hydrochloric acid. These precipitates were removed by centrifuging and washing before extraction of vanadium. If necessary, the precipitates were also separately shaken with hydrochloric acid and the reagent solution to extract any coprecipitated vanadium, but usually only a negligible amount of vanadium was retained.

Analysis of steels

To test the reliability of the method, three steel samples obtained from the Bureau of Analysed Samples Ltd. (Middlesbrough, Yorks) were analysed for vanadium. The results presented in Table III show that vanadium can be determined in B.C.S. steels precisely and accurately. Several other spectrophotometric methods for determination of vanadium necessitate prior separation of iron and other alloying metals by precipitation, electrolysis at the mercury pool cathode, ion exchange or solvent extraction[20,23]. The method adopted here is direct and involves no such additional steps. Arsenic, cobalt, copper, carbon, chromium, manganese, molyb-

TABLE III

ANALYSIS OF B.C.S. STEELS FOR VANADIUM

No.	*B.C.S. steel*	*Percentage of vanadium*		*Standard deviation*	*Relative error of average*
		Certified	*Found*[a]	*σ*	(%)
224	Cr–V steel	0.240	0.238	0.0052	0.83
252	Low alloy	0.460	0.465	0.0080	1.09
241/1	High speed	1.570	1.560	0.0097	0.64

[a] Average of 3 determinations.

denum, nickel, phosphorus, sulfur, silicon, tin and tungsten present in B.C.S. steels did not interfere.

The authors thank the authorities of Government Science College, Jabalpur for facilities and the University of Jabalpur for partial financial support.

SUMMARY

The reactions of 23 unsaturated N-arylhydroxamic acids with vanadium(V) have been investigated in strong hydrochloric acid media to find more sensitive reagents among the family of hydroxamic acids. This study shows that the vanadium complexes of 9 new reagents have molar absorptivities around 7500 l $mole^{-1}$ cm^{-1}. This value is considerably larger than that obtained for the vanadium complex of N-phenylbenzohydroxamic acid ($\varepsilon = 4650$). A rapid spectrophotometric method for the determination of vanadium(V) is described, employing the most promising of these reagents, N-phenyl-3-styrylacrylohydroxamic 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

On examine les réactions de 23 acides N-arylhydroxamiques non saturés, avec le vanadium(V), en milieu acide chlorhydrique concentré, afin de trouver quels sont les réactifs présentant la meilleure sensibilité. Neuf nouveaux réactifs ont un coefficient d'extinction molaire d'environ 7500 ($\varepsilon = 4650$ pour le réactif habituel du vanadium(V)). On propose une méhode spectrophotométrique rapide pour le dosage du vanadium(V), à l'aide de l'acide N-phényl-3-styrylacrylohydroxamique). La selectivité est très bonne, en présence de fer(III), aluminium(III), chrome(III), nickel(II), cobalt(II) et manganèse(II).

ZUSAMMENFASSUNG

Die Reaktionen von 23 ungesättigten N-Arylhydroxamsäuren mit Vanadin(V) sind in stark salzsaurem Medium mit dem Ziel untersucht worden, empfindlichere Reagenzien aus der Familie der Hydroxamsäuren zu finden. Diese Untersuchung ergibt, dass neun neue Reagenzien molare Extinktionskoeffizienten für Vanadin(V) um 7500 l mol^{-1} cm^{-1} haben. Dieser Wert ist erheblich grösser als der mit PBHA ($\varepsilon = 4650$), dem für die Bestimmung von Vanadin(V) üblichen Reagenz. Mit dem meistversprechenden dieser Reagenzien, N-Phenyl-3-styrylacrylhydroxamsäure, wird eine schnelle spektrophotometrische Methode für die Bestimmung von Vanadin(V) entwickelt. Die Methode ist hochselektiv und erlaubt die Gegenwart grosser Mengen verschiedener Ionen, die gewöhnlich in vanadinhaltigen Materialien enthalten sind, wie Eisen(III), Aluminium(III), Chrom(III), Nickel(II), Kobalt(II), Zink(II) und Mangan(II).

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COLORIMETRIC DETERMINATION OF ACONITIC ACID IN SUGAR CANE JUICE

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(Received 14th September 1970)

The determination of aconitic acid (1-propene-1,2,3-tricarboxylic acid) in the sugar industry is presently a laborious chore accomplished by the decarboxylation of the lead precipitate as described by Ambler and Roberts[1]. Since 1950 alternative methods have been proposed based on chromatographic procedures[2,3], but none has been widely accepted for other than research applications. Very recent attempts to use gas chromatography appear promising, but the work has not yet been published[4].

Poe and Barrentine[5] have recently suggested a colorimetric method for the determination of aconitic acid in sorgo juice and then applied the technique to the determination of that acid in the oat plant[6]. The method is based on the Furth and Herrmann reaction[7] in which color is formed in the presence of pyridine and acetic anhydride. Several other spectrophotometric methods based on this reaction have been proposed for the determination of various carboxylic acids[8-13], although with widely different reaction conditions, reagent proportions, and results. In some cases, samples were analyzed as aqueous solutions while Poe and Barrentine[5] felt that water was the only compound which interfered with color development. Part of this disagreement is probably due to the fact that different investigators selected different wavelengths to monitor. It is interesting that water is also considered to interfere with the determination of aconitic acid by the decarboxylation procedure[1].

The colorimetric reaction has been known in the sugar cane industry but has been thought to be only a qualitative test for aconitic acid. The presence of aconitic acid is indicated by the yellow-golden color formed immediately upon adding pyridine and acetic anhydride to an acid-containing sample of juice, syrup, or molasses. Usually proportions are not carefully measured and the color is considered to be unstable since it darkens to the color of "iodine" on standing[14].

In this paper the method of Poe and Barrentine is modified and applied to sugar cane juice in such a manner that the color formed can be used to determine the juice acid content.

EXPERIMENTAL

Materials

A gallon of representative Louisiana sugar cane juice was obtained from the Audubon Sugar Factory, Louisiana State University, Baton Rouge.

Reagents used were acetic anhydride (99.8 %; J. T. Baker), pyridine (Matheson, Coleman and Bell), 2-butanone (Eastman Organic Chemicals) and *trans*-aconitic acid (K and K Laboratories, Plainview, N.Y.).

Separation of aconitic acid from sugar cane juice

The method of Poe and Barrentine was used to extract aconitic acid from sugar cane juice with slight modification. Centrifuge *ca.* 100 ml of juice for 10 min at 10,000 r.p.m. to separate suspended impurities and organics, and then filter with suction through Whatman No. 4 filter paper. Adjust the pH of this clarified juice from 5.35 to 1.3 with several drops of concentrated sulfuric acid, using a pH meter. After allowing a few minutes for complete conversion of aconitates to aconitic acid, centrifuge the juice again. Shake 5 ml of the resulting juice with 20 ml of 2-butanone for 15 min and separate the layers by centrifuging.

Drying of 2-butanone aliquots

Place a suitable aliquot of the 2-butanone layer in a 20 × 150 mm test tube and evaporate to dryness using a Buchler Evaporator as described previously[15]; alternatively use a steam bath and stream of air[5]. For the particular juice used in this investigation, an aliquot of 0.2 to 0.4 ml gave a suitable color intensity. For other juice samples from more mature canes than are harvested in Louisiana, this aliquot size could vary. In general, three aliquots were dried for each sample run.

Preparation of aconitic acid standards

trans-Aconitic acid was used to prepare standard acid samples; the color reaction is identical with both the *cis* and the *trans* isomers[5]. A great deal of difficulty was experienced in preparing solutions of aconitic acid in acetic anhydride as described by Poe and Barrentine[5]. Not only is the acid slow to dissolve, but reaction accompanies dissolution since the color produced is very similar to the color produced by the Furth–Herrmann reaction although it is not as intense as when pyridine is present. Thus it was difficult to decide exactly when the pyridine should be added, and this interfered with the timing between mixing of reactants and reading on the spectrophotometer. Results were extremely erratic. The difficulty was found to be due to the use of an ultrasonic vibrator by Poe and Barrentine to effect rapid dissolution of the acid in acetic anhydride without the problem of color formation[16].

In an effort to overcome this difficulty and in order to produce a standard solution which would be stable for a number of days without color formation, aconitic acid was dissolved in diethyl ether (40 μg/ml). Triplicate aliquots of this solution from 0.05 to 10 ml were placed in test tubes and dried at room temperature to give aconitic acid residues ranging from 2 to 400 μg per sample. The first three samples were of 2, 4, and 20 μg respectively and then others increased in 20-μg increments.

Color production and determination

Mix 0.5 ml of pyridine with one pint (473 ml) of acetic anhydride. This mixture can be prepared at any time and does not deteriorate on standing. Fill the reservoir of a 10-ml automatic burette fitted with a three-way stopcock, with the mixture. Add 10-ml portions to sample and standard test tubes at 1-min intervals. Immediately after the addition, cap the tubes with plastic disposable Kim-Pak closures and place on a Buchler Evaporator shaker for 10 min (used only for thoroughly mixing the samples at this point). Leave for exactly 45 min after the addition of the pyridine–acetic anhydride, and then read the samples at 1-min intervals on a Beckman DB spectrophotometer at 550 nm. Use the pyridine–acetic anhydride mixture in the reference cell.

RESULTS

The absorbance of the color formed from the reaction of acetic anhydride–pyridine with aconitic acid was monitored at 550 nm as suggested by Poe and Barrentine[5,6]. A linear calibration curve was obtained from 20 to 400 μg per sample, a significantly broader range than they obtained; this is probably due to the modification in the procedure. Data representing the average values for triplicate samples are summarized in Table I. A least squares analysis of data points from 20 to 200 μg was performed on a card-programmed Wang Model 360 electronic calculator. The linear relationship between A, the absorbance, and C, the concentration of aconitic acid in μg per sample was found to be: $A = 0.002883C - 0.050083$.

In agreement with the results of Poe and Barrentine for sorgo juice, no appreciable aconitic acid was extracted from the unacidified sugar cane juice. No investiga-

TABLE I

ABSORBANCES OF ACONITIC ACID SAMPLES

(Each sample represents the average value of triplicate runs with the absorbance being calculated from observed percent transmissions)

Aconitic acid (μg/sample)	*Absorbance*	*Aconitic acid (μg/sample)*	*Absorbance*
20	0.025	160	0.417
40	0.072	180	0.469
60	0.115	200	0.529
80	0.177	280	0.749
100	0.231	320	0.879
120	0.288	360	0.991
140	0.343	400	1.105

TABLE II

PERCENT RECOVERIES FOR ACONITIC ACID EXTRACTED FROM MOLASSES WITH 2-BUTANONE

Aconitic acid (mg/5 ml sample)		*Recovery (%)*	*Aconitic acid (mg/5 ml sample)*		*Recovery (%)*
Added	*Found*		*Added*	*Found*	
0	10.2	—	5.0	15.2	100
1.0	11.2	100	6.0	16.0	97
2.0	12.3	105	7.0	16.2	86
3.0	13.0	93	8.0	17.6	93
4.0	13.9	93			

tion was made of the extractability at any pH other than 1.3. Similarly, the reaction of aliquots from multiple extractions with 2-butanone failed to produce the pink-purple color when mixed with pyridine–acetic anhydride, thus indicating no detectable residual aconitic acid in the aqueous phase. To investigate the effectiveness of this extraction procedure further, sugar cane juice samples to which had been added known amounts of aconitic acid were analyzed. The data obtained (Table II) indicated an average recovery of 96% which agrees with the 97% obtained by Poe and Barrentine[5].

From the amount of aconitic acid in the aliquot analyzed the total amount present in the 2-butanone layer can be calculated. Knowing the density of the juice, which was determined experimentally as 1.0788 g ml^{-1}, the aconitic acid content on a whole juice basis was calculated as 0.20%. For this calculation the small amount of sulfuric acid used to adjust the acidity of the juice was assumed to have a negligible effect on the 5-ml volume analyzed. This result is in agreement with other established methods[17].

DISCUSSION

The use of esters of aconitic acid as plasticizers[18-20] has led to numerous efforts to produce the acid by methods other than the dehydration of citric acid[21-24]. In 1944, it was demonstrated that commercial quantities of the acid could be obtained as alkaline earth salts from second or B molasses[25]. A detailed description of the dicalcium magnesium aconitate precipitation process has been given[26]. Other economically feasible recovery methods have been also suggested for commercial use in the sugar cane industry[27].

Unfortunately, the practical application of these methods is hampered by the lack of rapid analytical techniques for aconitic acid in the juice, syrup, and molasses. Decarboxylation of lead aconitate and various chromatographic procedures do give results, but not until usually several days after they are needed. Knowledge of the concentration of aconitic acid is important to acid recovery procedures and to other sugar plant operations. The acid is known to affect clarification procedures[3], for example by decreasing the decolorizing capacity of bone char; it evidently affects the formation of crystalline sugar[5], and probably affects sedimentation rates, centrifuging, and other operations in the sugar industry. Thus if improved methods of operation are desired, analytical results are vital during the actual operation.

There are at least nine different carboxylic acids in sugar cane juice including, in order of their abundance, aconitic, citric, malic, oxalic, glycollic, mesaconic, succinic, fumaric, and syringic[4]. While both aconitic and citric acids have been found to undergo the Furth–Herrmann reaction (as well as itaconic and fumaric acids), the successful application of the method to sugar cane juice is governed by two other considerations: (*a*) the selection of the proper wavelength at which to read samples[5], and (*b*) the relative concentrations of the acids found in the juice, aconitic being about 75 to 90% of all acids present[3,15]. Also it is possible that not all acids present will undergo the color reaction since tartaric and *l*-malic acids give only clear solutions with acetic anhydride and pyridine[3].

The method of analysis presented can provide an accurate aconitic acid determination in less than 1 h. After 2-butanone extraction and evaporation of the sample, the time expended per sample consists only of the time necessary to add the reaction mixture of pyridine and acetic anhydride and then the time necessary to read the absorbance on a spectrophotometer.

The authors wish to thank the staff of the United States Department of Agriculture, Cotton Insects Research Branch, Baton Rouge, La., for use of materials, facilities, and equipment. Dr. John Seip and Mr. Fred L. Gayle of the Audubon Sugar Mill, Louisiana State University, are cordially thanked for supplying samples and for useful discussions. The technical assistance of Mr. Frank Nelson and Miss Madeleine Crozat is sincerely appreciated.

SUMMARY

The Poe–Barrentine method of determining aconitic acid in sorgo juice has been modified and extended to sugar cane juice. A stock solution of aconitic acid in ethyl ether is used to prepare standard samples which are then dried and reacted with a mixture of acetic anhydride and pyridine for the Furth–Herrmann reaction. After each sample has stood for 45 min, its absorbance is read at 550 nm to give a standard plot which is linear from 20 to 200 μg of acid. For cane juices, after acidification to pH 1.3 with sulfuric acid, the sample is extracted with 2-butanone, the extract is dried, and the reaction is accomplished in the same manner.

RÉSUMÉ

Une méthode est proposée pour le dosage colorimétrique de l'acide aconitique dans les jus de sucre de canne. On utilise une solution d'acide aconitique dans l'éther éthylique pour préparer des échantillons standards, qui sont ensuite séches et traités par un mélange d'anhydride acétique et de pyridine (réaction Furth–Herrmann). Après 45 minutes, on mesure l'absorption à 550 nm, linéaire de 20 à 200 μg d'acide. Les jus de caune à analyser sont acidifiés à $pH = 1.3$ à l'aide d'acide sulfurique, extraite au moyen de butanone-2, séchés et traités comme les standards ci-dessus.

ZUSAMMENFASSUNG

Die Poe–Barrentine-Methode zur Bestimmung von Aconitsäure in Sorghosaft ist modifiziert und auf Zuckerrohrsaft erweitert worden. Eine Stammlösung von Aconitsäure in Äthyläther wird für die Herstellung von Vergleichsproben verwendet, die dann getrocknet und mit einem Gemisch von Acetanhydrid und Pyridin zur Furth–Herrmann-Reaktion umgesetzt werden. Nach 45minütigem Stehen wird die Extinktion jeder Probe bei 550 nm ermittelt, wobei von 20 bis 200 μg Säure eine lineare Eichkurve erhalten wird. Im Falle von Zuckerrohrsaft wird die Probe mit Schwefelsäure auf pH 1.3 angesäuert, mit 2-Butanon extrahiert, der Extrakt getrocknet und die Reaktion in gleicher Weise ausgeführt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

1-(2-CARBOXY-4-SULPHONATOPHENYL)-3-HYDROXY-3-PHENYLTRIAZENE AS A SPECTROPHOTOMETRIC REAGENT FOR THE DETERMINATIONS OF COPPER(II) AND PALLADIUM(II) IN PRESENCE OF OTHER IONS AND IN TERNARY MIXTURES WITH IRON, MOLYBDENUM AND VANADIUM

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(Received 15th September 1970)

1-(2-Carboxy-4-sulphonatophenyl)-3-hydroxy-3-phenyltriazene has already been suggested[1] for the spectrophotometric determination of iron(III), molybdenum(VI) and vanadium(V) in the presence of each other. In this present investigation, the reagent has been used for the spectrophotometric determination of copper(II) and palladium(II) in presence of other ions and for the determination of copper(II), palladium(II) and vanadium(V); copper(II), palladium(II) and molybdenum(VI); palladium(II), iron(III) and vanadium(V); and palladium(II), molybdenum(VI) and vanadium(V) in the presence of each other. The reagent is highly selective in its reaction towards palladium.

Light yellow and golden yellow 1:2 complexes are formed by copper and palladium, respectively, with the reagent. In the respective pH regions of 4.8–8.4 and 4.2–8.0, Beer's law is obeyed within the optimum metal ion concentration ranges of 0.3–3.0 p.p.m. and 0.4–5.0 at 400 and 410 nm, respectively. The molar absorptivities and sensitivities of reaction are 15333 and 0.0043 μg cm^{-2} for copper, and 20222 and 0.0055 μg cm^{-2} for palladium.

EXPERIMENTAL

Chemicals and reagents

Reagent solutions, solutions of diverse ions and the apparatus used were the same as used previously[1].

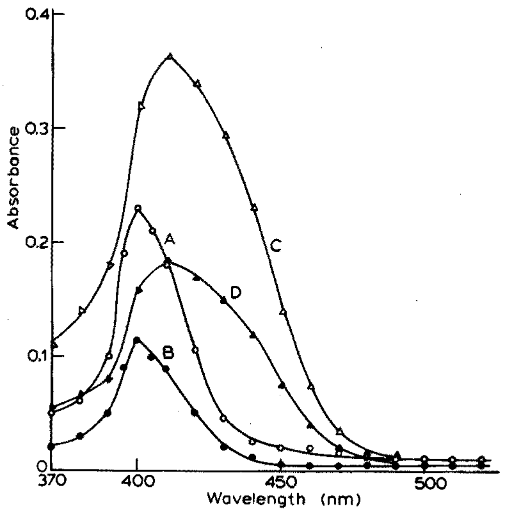
A standard solution of copper sulphate was prepared from a weighed sample of electrolytic copper, after dissolving in nitric acid, fuming with sulphuric acid and diluting it with water to a definite volume.

The standard solution of palladium chloride was prepared by dissolving palladium chloride of Analar quality in a definite volume of 0.1 *M* hydrochloric acid; the palladium content of the solution was determined by the dimethylglyoxime method[2].

Weaker solutions of the metal ions were made by appropriate dilution, as required.

Absorbance curves

Copper(II). To the solution containing 25 or 12.5 μg of copper in a 50-ml beaker was added 4 ml of the reagent solution (0.1 % w/v) and dilute hydrochloric acid to adjust its pH to 5–6. The solution was then diluted to 25 ml in a volumetric flask and its absorbance was measured against the reagent solution as blank. The colour systems corresponding to 1.0 and 0.5 p.p.m. of copper(II) ions show maximum absorbances at 400 nm (Curves A and B, Fig. 1).



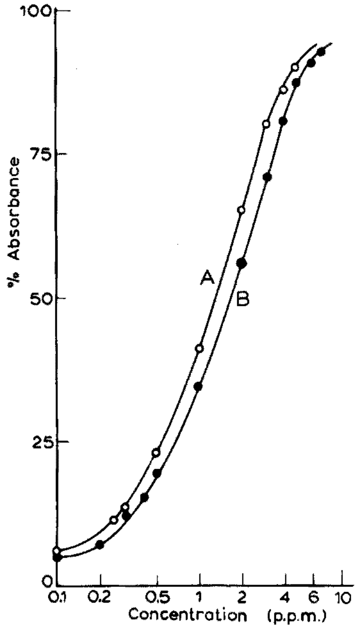


Fig. 1. Absorption spectra of the copper and palladium complexes. (A) Copper(II) 1.0 p.p.m.; (B) copper(II) 0.5 p.p.m.; (C) palladium(II) 2.0 p.p.m.; (D) palladium(II) 1.0 p.p.m.

Fig. 2. Ringbom plots. (A) Copper(II); (B) palladium(II).

Palladium(II). In the same way as above the solution containing 50 or 25 μg of palladium(II) was mixed with 5 ml of the reagent solution (0.1 % w/v) and after adjustment of its pH to about 5.5, the solution was diluted to 25 ml in a volumetric flask and its optical density was measured against the reagent solution. Curves C and D in Fig. 1, corresponding to 2 and 1 p.p.m. of palladium(II), indicate maximum absorbance at 410 nm.

Effect of pH, reagent and time

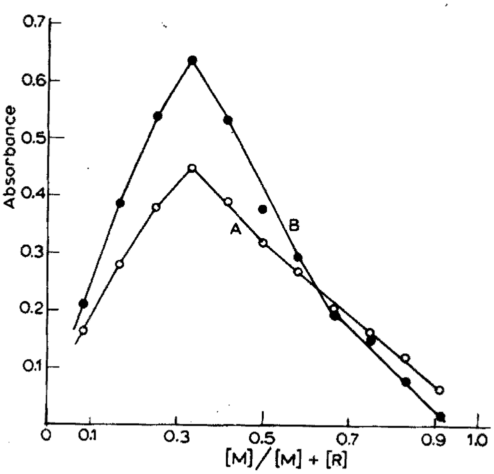
For complete colour development, 1 p.p.m. of copper(II) and 2 p.p.m. of palladium(II) required, respectively, 3 and 4 ml of 0.1 % (w/v) reagent solution and the colour intensities of the systems so produced remained constant for 15 and 12 h in the optimum pH ranges of 4.8–8.4 for copper and 4.2–8.0 for palladium.

Beer's law, optimum range, photometric error, sensitivity and molar absorptivity

The systems obeyed Beer's law over the ranges 0.1–3.0 p.p.m. of copper and

0.2–5.0 p.p.m. of palladium. From the steepest slope of the curves drawn on plotting percent absorbances against log concentrations, the optimal concentration ranges[3] appear to be 0.3–3.0 and 0.4–5.0 p.p.m., respectively (Fig. 2, A, B).

The percent relative errors ($dc/c \cdot 100$) per 1% absolute photometric error[4] for the systems are 2.69 for copper(II) and 2.71 for palladium(II). The sensitivities[5] for $\log I_0/I = 0.001$ were calculated to be 0.0043 μg cm^{-2} of copper(II) and 0.0055 μg cm^{-2} of palladium(II) with molar absorptivities of 15333 and 20222, respectively.



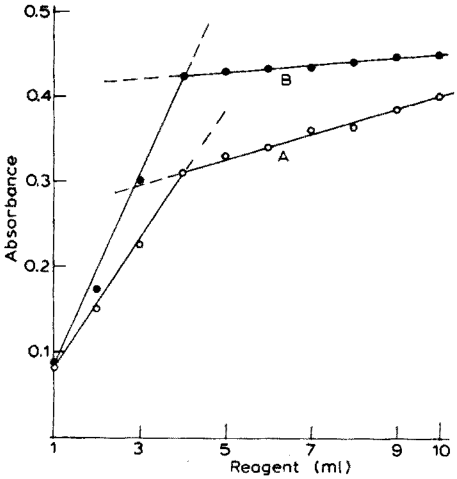


Fig. 3. Job's method. (A) Copper(II) = reagent = $2.0 \cdot 10^{-4}$; (B) palladium(II) = reagent = $2.5 \cdot 10^{-4}$.

Fig. 4. Molar ratio method. (A) Copper(II) = reagent = $3.0 \cdot 10^{-4}$, 2 ml of Cu(II) solution used; (B) palladium(II) = reagent = $3.0 \cdot 10^{-4}$, 2 ml of Pd(II) solution used.

Composition of the complexes

The composition of the copper and palladium complexes was determined by a modified Job's method[6] of continuous variation and by the molar ratio method[7]. The procedure followed was the same as described earlier[1].

By Job's method, the peaks of the curves obtained at 400 nm and 410 nm, respectively (Fig. 3), indicate that copper and palladium combine with the reagent in the ratio of 1:2.

For the molar ratio method, solutions at their optimal pH values were prepared with varying ratios of reagent to metal ion, keeping the concentration of the metal ions constant. The curves obtained (Fig. 4), show sharp breaks at metal-to-reagent mole ratios of 1:2 for both copper(II) and palladium(II).

Degree of dissociation and stability constants

The degree of dissociation, α, was calculated from Harvey and Manning's equation[8], and the stability constants as evaluated from the equation $K = (m\alpha c)^m \cdot (n\alpha c)^n / c(1-\alpha)$, where $m = 1$, $n = 2$ for both copper(II) and palladium(II) are given in Table I.

The stability constants of the complexes were also evaluated from a study of the absorbances of complementary mixtures of non-equimolar solutions of the metal

TABLE I

STABILITY CONSTANTS OF THE COPPER(II) AND PALLADIUM(II) COMPLEXES BY THE HARVEY–MANNING METHOD

Complex	E_m	E_s	c	α	K
Cu(II)	0.40	0.31	$3\cdot10^{-4}$	0.225	$5.2\cdot10^{-9}$
Pd(II)	0.45	0.425	$3\cdot10^{-4}$	0.055	$5.5\cdot10^{-11}$

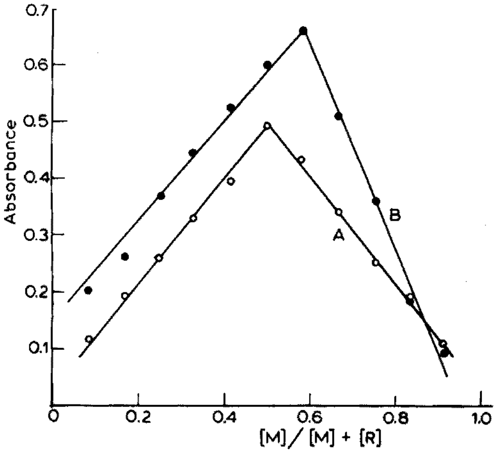


Fig. 5. Job's method of measurement of dissociation constant. (A) Copper(II) $= 1.5\cdot10^{-4}$; reagent $= 4.5\cdot10^{-4}$; (B) palladium(II) $= 1.5\cdot10^{-4}$; reagent $= 4.5\cdot10^{-4}$.

TABLE II

STABILITY CONSTANTS OF THE COPPER(II) AND PALLADIUM(II) COMPLEXES BY THE MAJUMDAR–SEN METHOD

Metal concn. (*c*)	*Reagent* concn.	m	n	P	x	K *at* 31°
Cu(II) $1.5\cdot10^{-4}$	$4.5\cdot10^{-4}$	1	2	3	0.5	$4.21\cdot10^{-9}$
Pd(II) $1.5\cdot10^{-4}$	$4.5\cdot10^{-4}$	1	2	3	0.418	$1.64\cdot10^{-11}$

ions and the reagent (Fig. 5). The colour of the solutions was developed as described previously. The dissociation constants as calculated from the equation[9] are reported in Table II.

Effect of various ions

To evaluate the tolerance limits for different ions, solutions containing either 1 p.p.m. of copper(II) or 2 p.p.m. of palladium(II) and varying amounts of other ions were analysed as described above. Absorbance errors above 0.005 were considered to indicate interference.

In the copper(II) system, EDTA, oxalate, thiosulphate, Fe^{3+}, V^{5+}, Ni^{2+}, Co^{2+}, Mo^{6+} and Pd^{2+} interfered. The system, however, tolerates the presence of the following ions, the tolerance limits of which in p.p.m. are given in parentheses:

citrate (100), tartrate (400), thiocyanate (300), Th^{4+} (300), Zn^{2+} (350), Ce^{3+} (30), Mg^{2+} (100), UO_2^{2+} (150), Al^{3+} (30), Hg^{2+} (200), Mn^{2+} (100), WO_4^{2-} (30), Ca^{2+} (200), Ti^{4+} (80), Be^{2+} (300), Sr^{2+} (350), As^{3+} (200), Pt^{4+} (180), La^{3+} (40), Cr^{3+} (50), Ba^{2+} (250) and Cd^{2+} (300). Molybdenum(VI) can be tolerated upto 50 p.p.m. if measured at pH 6.3–7.5. Li^+, Na^+, K^+, Br^-, I^-, Cl^-, F^- and PO_4^{3-} do not interfere.

In the palladium(II) colour system, only EDTA, $S_2O_3^{2-}$, Cu^{2+}, Fe^{3+}, Mo^{6+} and V^{5+} interfere, while the tolerance limits as given in parentheses in p.p.m. for other ions are: Al^{3+} (50), UO_2^{2+} (200), Mg^{2+} (150), Hg^{2+} (240), Ce^{3+} (40), WO_4^{2-} (100), Zn^{2+} (300), Th^{4+} (250), Ca^{2+} (240), Ti^{4+} (100), Be^{2+} (350), Sr^{2+} (300), As^{3+} (160), Pt^{4+} (120), Cr^{3+} (80), La^{3+} (60), Mn^{2+} (80), Cd^{2+} (240) and Ba^{2+} (360). At pH 4.2–4.5, Ni^{2+} (20) and Co^{2+} (30) also are tolerated. Li^+, Na^+, K^+, Br^-, I^-, SCN^-, F^-, PO_4^{3-}, oxalate, tartrate and citrate have no interfering effect.

In presence of oxalate ion (or 20 mg of oxalic acid), however, Cu^{2+}, Fe^{3+}, Mo^{6+} and V^{5+} can be tolerated upto limits of 80, 100, 200 and 50 p.p.m., respectively.

DETERMINATION OF METAL IONS IN TERNARY MIXTURES

For the determination of (i) copper(II), palladium(II) and vanadium(V), (ii) copper(II), palladium(II) and molybdenum(VI), (iii) palladium(II), iron(III) and vanadium(V), and (iv) palladium(II), molybdenum(VI) and vanadium(V) in presence of each other, the same procedure as described for the absorbance measurement of the colour systems was followed with the addition of complexing agents.

To the sample solution were added 8 ml of the reagent solution (0.25% w/v) and distilled water, to dilute to 25 ml, after adjustment of the pH of the solutions to the appropriate values as stated below. The measurements were made at 410 nm and not at 400 nm because the reagent absorbance was found to be less at the former region.

Determination of copper(II), palladium(II) and vanadium(V)

First, in an aliquot of the solution the total absorbance (*A*) caused by all three metal ions was measured, the pH of the solution being maintained at 5–7.

TABLE III

DETERMINATION OF COPPER(II), PALLADIUM(II) AND VANADIUM(V)

Amount present (p.p.m.)	*Cu(II) found (p.p.m.)*	*Pd(II) found (p.p.m.)*	*V(V) found (p.p.m.)*
1.0 Cu(II) 1.0 Pd(II) 2.0 V(V)	1.03	0.937	2.05
0.50 Cu(II) 0.50 Pd(II) 3.0 V(V)	0.472	0.522	3.02
1.0 Cu(II) 0.5 Pd(II) 2.0 V(V)	1.01	0.467	1.956

The absorbance (*B*) of only vanadium was then measured in a second aliquot, treated with 5 ml of 1 % sodium thiosulphate solution and adjusted to pH 3.0–3.7. Finally, the absorbance (*C*) of the third aliquot, adjusted to pH 4.5–7.0 after the addition of 15 mg of oxalic acid, gave the amount of palladium present. Thus, $A-(B+C)$ gives the amount of copper. The results are shown in Table III.

Determination of copper(II), palladium(II) and molybdenum(VI)

The absorbance (*A*) caused by molybdenum(VI) was measured first in an aliquot after the addition of sodium thiosulphate solution (5 ml of 1 %) and adjustment of the pH to 3.0–3.7. In another aliquot, the absorbance (*B*) of palladium was measured after the addition of oxalic acid (20 mg) and adjustment of the pH to 4.2–6.5. Thirdly, in another aliquot, the absorbance (*C*) arising from both copper and palladium was measured, keeping molybdenum out of reaction at pH 5.5–7.0 with sodium fluoride (5 ml of 1 %). $C-B$ gave the amount of copper present (Table IV).

TABLE IV

DETERMINATION OF COPPER(II), PALLADIUM(II) AND MOLYBDENUM(VI)

Amount present (p.p.m.)	*Cu(II) found (p.p.m.)*	*Pd(II) found (p.p.m.)*	*Mo(VI) found (p.p.m.)*
1.0 Cu(II) 1.0 Pd(II) 4.0 Mo(VI)	1.04	0.931	3.76
0.5 Cu(II) 0.5 Pd(II) 2.0 Mo(VI)	0.5	0.494	1.952
0.5 Cu(II) 1.0 Pd(II) 4.0 Mo(VI)	0.488	0.989	3.88

TABLE V

DETERMINATION OF PALLADIUM(II), IRON(III) AND VANADIUM(V)

Amount present (p.p.m.)	*Pd(II) found (p.p.m.)*	*Fe(III) found (p.p.m.)*	*V(V) found (p.p.m.)*
1.0 Pd(II) 2.0 Fe(III) 2.0 V(V)	0.943	2.06	2.00
0.5 Pd(II) 1.0 Fe(III) 2.0 V(V)	0.494	1.04	1.956
0.5 Pd(II) 2.0 Fe(III) 1.0 V(V)	0.505	2.01	0.977

Determination of palladium(II), iron(III) and vanadium(V)

The absorbance (*A*) of the three metal ions was measured in an aliquot at pH 4.2–4.5. Then, in another aliquot, the absorbance (*B*) for palladium was measured after the addition of oxalic acid (20 mg) and adjustment of the pH to 4.2–7.5. In the same way, the amount of vanadium present was determined by measuring the absorbance (*C*) of another aliquot to which had been added sodium thiosulphate solution (5 ml of 1%) with adjustment of the pH to 3.0–3.7. $A-(B+C)$ gave the amount of iron(III) present (Table V).

Determination of palladium(II), molybdenum(VI) and vanadium(V)

The absorbance (*A*) arising from palladium(II) was measured first in an aliquot after the addition of 20 mg of oxalic acid and adjustment of the pH to 4.2–7.5. The absorbance (*B*) of both palladium(II) and vanadium(V) was next measured in an aliquot after addition of 2 ml of 1% sodium fluoride and adjustment of the pH to 5.0–6.5. Thirdly, in another aliquot, the absorbance (*C*) arising from both molybdenum(VI) and vanadium(V) was measured, palladium being masked at pH 3.0–3.7 by sodium thiosulphate (5 ml of 1%). By subtracting *A* from *B*, the amount of vanadium(V) (*D*) was obtained, and subtraction of *D* from *C* gave the amount of molybdenum(VI) (Table VI).

TABLE VI

DETERMINATION OF PALLADIUM(II), MOLYBDENUM(VI) AND VANADIUM(V)

Amount present (p.p.m.)	*Pd(II) found (p.p.m.)*	*Mo(VI) found (p.p.m.)*	*V(V) found (p.p.m.)*
1.0 Pd(II) 4.0 Mo(VI) 2.0 V(V)	0.97	4.00	2.00
0.5 Pd(II) 3.0 Mo(VI) 1.0 V(V)	0.478	2.945	1.03
1.0 Pd(II) 4.0 Mo(VI) 2.0 V(V)	0.989	4.07	2.01

SUMMARY

Methods for the spectrophotometric determination of copper(II) and palladium(II) in presence of other ions and of colour-forming metal ions in ternary mixtures have been developed with 1-(2-carboxy-4-sulphonatophenyl)-3-hydroxy-3-phenyltriazene as the reagent. The reagent forms 1:2 complexes with both copper(II) and palladium(II) with dissociation constants of the order of 10^{-9} and 10^{-11}, respectively. The systems obey Beer's law with optimal ranges of 0.3–3.0 p.p.m. and 0.4–5.0 p.p.m.; the sensitivities are 0.0043 and 0.0055 μg cm^{-2} and the molar absorptivities are 15333 and 20222, respectively. The reagent is highly selective for palladium.

RÉSUMÉ

Des méthodes sont décrites pour le dosage spectrophotométrique du cuivre(II) et du palladium(II), en présence d'autres ions, en utilisant comme réactif le 1-(2-carboxy-4-sulfonatophényl)-3-hydroxy-3-phényltriazène. Ce réactif forme des complexes 1 : 2, soit avec le cuivre, soit avec le palladium, avec des constantes de dissociation de l'ordre de 10^{-9} et 10^{-11}, respectivement. La loi de Beer s'applique de 0.3 à 3.0 p.p.m. et de 0.4 à 5.0 p.p.m.; les sensibilités 0.0043 et 0.0055 μg cm^{-2} et les coefficients d'extinction molaire 15333 et 20222, respectivement. Ce réactif est très sélectif pour le palladium.

ZUSAMMENFASSUNG

Es wurden Methoden entwickelt für die spektrophotometrische Bestimmung von Kupfer(II) und Palladium(II) in Gegenwart anderer Ionen und farbbildender Metallionen in ternären Gemischen; als Reagenz wurd 1-(2-Carboxy-4-sulphonatophenyl)-3-hydroxy-3-phenyltriazen verwendet. Es bildet 1 : 2-Komplexe mit Kupfer(II) und Palladium(II) mit Dissoziationskonstanten in der Grössenordnung 10^{-9} bzw. 10^{-11}. Das System gehorcht dem Beerschen Gesetz bei optimalem Bereich von 0.3–3.0 p.p.m. bzw. 0.4–5.0 p.p.m.; die Empfindlichkeiten sind 0.0043 und 0.0055 μg cm^{-2}, die molaren Extinktionskoeffizienten 15333 und 20222. Das Reagenz ist für Palladium hochselektiv.

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Anal. Chim. Acta, 53 (1971) 393–400

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANALYSIS WITH A Po–Be SOURCE:

THE MEASUREMENT OF PROMPT GAMMA-RAYS

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(Received 20th September 1970)

The measurement of γ-rays following inelastic neutron scattering with an accelerator as a source of neutrons is a well known technique in nuclear structure physics[1]. This method has also been explored as a tool for materials analysis by Schrader and Stinner[2], who investigated the sensitivity of the method to the presence of quantities of several common elements added to a sand carrier. The application of this method (again with an accelerator as a source of neutrons) to coal analysis[3] and to lunar and planetary[4] probes has also been reported.

The present work is mainly concerned with the measurement of the intensity of prompt γ-rays from elements and compounds with a Po–Be neutron source. This method has potential applications in the extractive and allied industries for quality control and materials analysis. Here the technique of prompt γ-ray measurement could be used in the rapid analysis of bulk quantities of material. The task of selecting samples representative of a process stream would be minimized by the large sample size (kg-range) and in general the samples would require no time-consuming preparation. Additional advantages of this method are that the destruction of the sample is not involved and that all the operations could be carried out automatically with consequent savings in man-power.

The choice of a radioactive neutron source as opposed to that of an accelerator was prompted by several considerations. An accelerator is appreciably more expensive in capital cost, in maintenance and also in operation than a radioactive neutron source. In general the lack of output stability dictates the use of a beam monitor with attendant increase in complexity and cost, whereas the stability of a radioactive source can normally be relied upon. Neutrons produced by the $d(t,n)^4He$ reaction have an energy of *ca.* 14 MeV and often result in the simultaneous production of several neutron-induced reactions from each nucleide. This can easily lead to the production of γ-rays of the same energy from different nucleides in the sample *e.g.* the $^{28}Si(n,p)^{28}Al$ and $^{31}P(n,\alpha)^{28}Al$ reactions. This problem is less likely to arise if neutrons of lower energy (such as those obtainable from a radioactive neutron source) are used, since the $(n,p\gamma)$ and $(n,\alpha\gamma)$ reactions will be inhibited over the $(n,n'\gamma)$ reaction by the Coulomb barrier associated with the emergent charged particles. The mean energy of neutrons from a Po–Be neutron source is *ca.* 4 MeV with only a few per cent of neutrons with an energy greater than 8 MeV[5].

Activation methods involving the detection of delayed radiation require the use of a larger neutron source than that needed for the measurement of prompt radiation: these measurements usually entail a period of irradiation followed by a period of counting at a point remote from the source. The (n,n′γ) reaction and to a lesser extent the (n,pγ), (n,αγ) and (n,γ) reactions are responsible for the production of prompt γ-rays from radioactive neutron sources. In addition, "prompt" γ-ray spectra obtained in the presence of the neutron source will contain small contributions of "delayed" radiation associated with neutron activation of the sample.

A Po–Be neutron source was used because of the low γ-ray yield, although the relatively short lifetime of 138 days was a disadvantage. The neutron source, which was originally 1 Ci in strength, had an emission rate of about $2.5 \cdot 10^6$ n sec^{-1}.

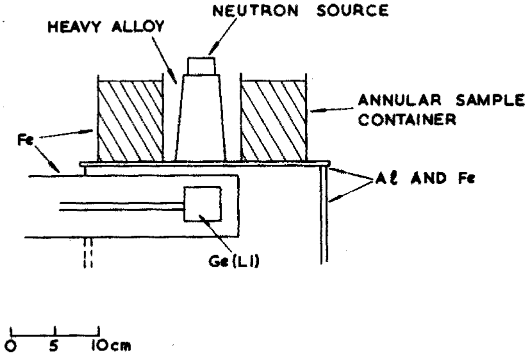
The measurements were made with a Ge(Li) detector and subsequently repeated with a NaI(Tl) detector.

Additional measurements have also been made in order to test the usefulness of this method as a tool in chemical analysis. These measurements comprise an examination of effects caused by the presence of moisture in the sample, and an investigation of the linearity of response to changes in the ratio of constituent elements in a two-element mixture.

EXPERIMENTAL

Prompt gamma-rays with a Ge(Li) detector

The geometrical arrangement used in the detection of γ-rays with a Ge(Li) counter is shown in Fig. 1. A Heavy Alloy shield limits the number of direct neutrons and γ-rays reaching the detector from the source. The sample has a ring geometry rather similar to that commonly used in early (n,n′γ) experiments with Van de Graaff accelerators[1], and is symmetrically disposed with respect to the source and detector. Samples were placed in steel containers, which were in the form of hollow right circular cylinders of inner and outer diameter 8.5 and 24 cm, respectively, and which had a length of 10.2 cm or 12.7 cm according to the quantity of material under investigation. The mechanical supports for the sample and shield were as light as possible to minimize the "sample-out" background. The Po–Be source, which was contained in a 1.2-cm diam. and 2.0-cm long cylinder was readily detachable from a steel clip at-



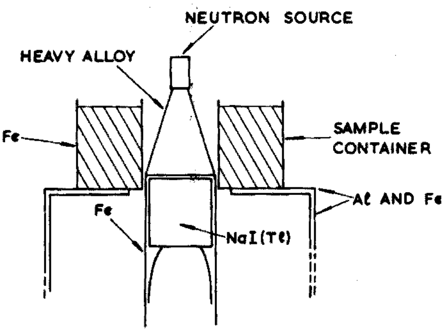


Fig. 1. General experimental arrangement with a Ge(Li) detector.

Fig. 2. General experimental arrangement with a NaI(Tl) detector.

tached to the Heavy Alloy shield. The Ge(Li) detector was of the trapezoidal type with a volume of *ca.* 30 cm^3 and an energy resolution of 5 keV at 1.33 MeV.

Prompt gamma-rays with a NaI(Tl) detector

The geometrical arrangement used in the detection of γ-rays with a 7.6 cm × 7.6 cm NaI(Tl) crystal and photomultiplier (Fig. 2) is rather similar to that used with the Ge(Li) detector except that the Heavy Alloy shield is of different dimensions. Again, the sample is symmetrically disposed between the Po–Be neutron source and the detector.

RESULTS

Ge(Li) detector

Gamma-ray spectra obtained from nineteen elements and compounds are shown in Fig. 3 and the intensities of the principal γ-rays (together with the counting errors) associated with each substance are listed in Table I in units of counts kg^{-1} min^{-1} Ci^{-1}. In each case the γ-ray intensity was obtained as an integration over the full-energy peak. Since the measurements were made over an extended period, the γ-ray intensities were normalized to 1 Ci of Po–Be in order to correct for the decay of the neutron source. The counting errors also have the magnitude appropriate to

TABLE I

MEASUREMENTS MADE WITH A Ge(Li) DETECTOR

Material	*γ-Ray*	*Reaction, if not (n, n'γ)*	*Intensity*[a] *(counts kg^{-1} min^{-1} Ci^{-1})*	*Peak / back-ground*	*Sample weight (kg)*	*Counting time (min)*
H_3BO_3	^{7}Li(0.46)	^{10}B(n,α)^{7}Li	210±10	2.0:1	2.5	180
CaF_2	^{19}F(1.35, 1.36)	[a]	29± 2	1.5:1	1.0	121
NaCl	^{23}Na(0.44)		180± 5	2.6:1	3.0	78
	^{35}Cl(1.76)		14± 1	1.7:1		
MgO	^{24}Mg(1.37)		58± 2	3.1:1	1.25	78
Al_2O_3	^{27}Al(1.01)		21± 0.8	2.1:1	3.0	60
SiO_2(sand)	^{28}Si(1.77)		27± 0.7	4.8:1	5.0	26
Kaolin	^{28}Si(1.77)		18± 3	1.5:1	1.0	33
KH_2PO_4	^{31}P(1.27)		31± 1.8	1.6:1	1.0	108
S	^{32}S(2.23)		32± 1.3	3.6:1	2.0	188
K_2CO_3	^{40}Ar(1.46)	^{40}K(E.C.)^{40}Ar	22± 1.2	2.4:1	1.5	61
$CaCO_3$ (marble)	^{40}K(0.77)	^{40}Ca(n,p)^{40}K	6± 0.4	1.4:1	5.6	136
TiO_2	^{48}Ti(0.98)		43± 2.5	1.8:1	0.5	147
CuO_3	^{50}Cr(1.45)		48± 0.7	4.7:1	3.0	180
Mn	^{55}Mn(0.86)		55± 5	1.9:1	1.0	51
Fe (nails)	^{56}Fe(0.84)		116± 2	5.0:1	6.0	114
Ni	^{58}Ni(1.45)		61± 2	2.4:1	1.0	128
Cu	^{63}Cu(0.96)		61± 3.5	2.4:1	1.5	95
Zn	^{64}Zn(0.99)		28± 3	1.4:1	1.5	145
$SnCl_2 \cdot 2\,H_2O$	^{120}Sn(1.17)		18± 3	1.2:1	0.5	216

[a] Activation by the (n,p) reaction adds an additional contribution to the γ-ray intensities.
[b] Intensity obtained as the sum of unresolved γ-ray peaks.

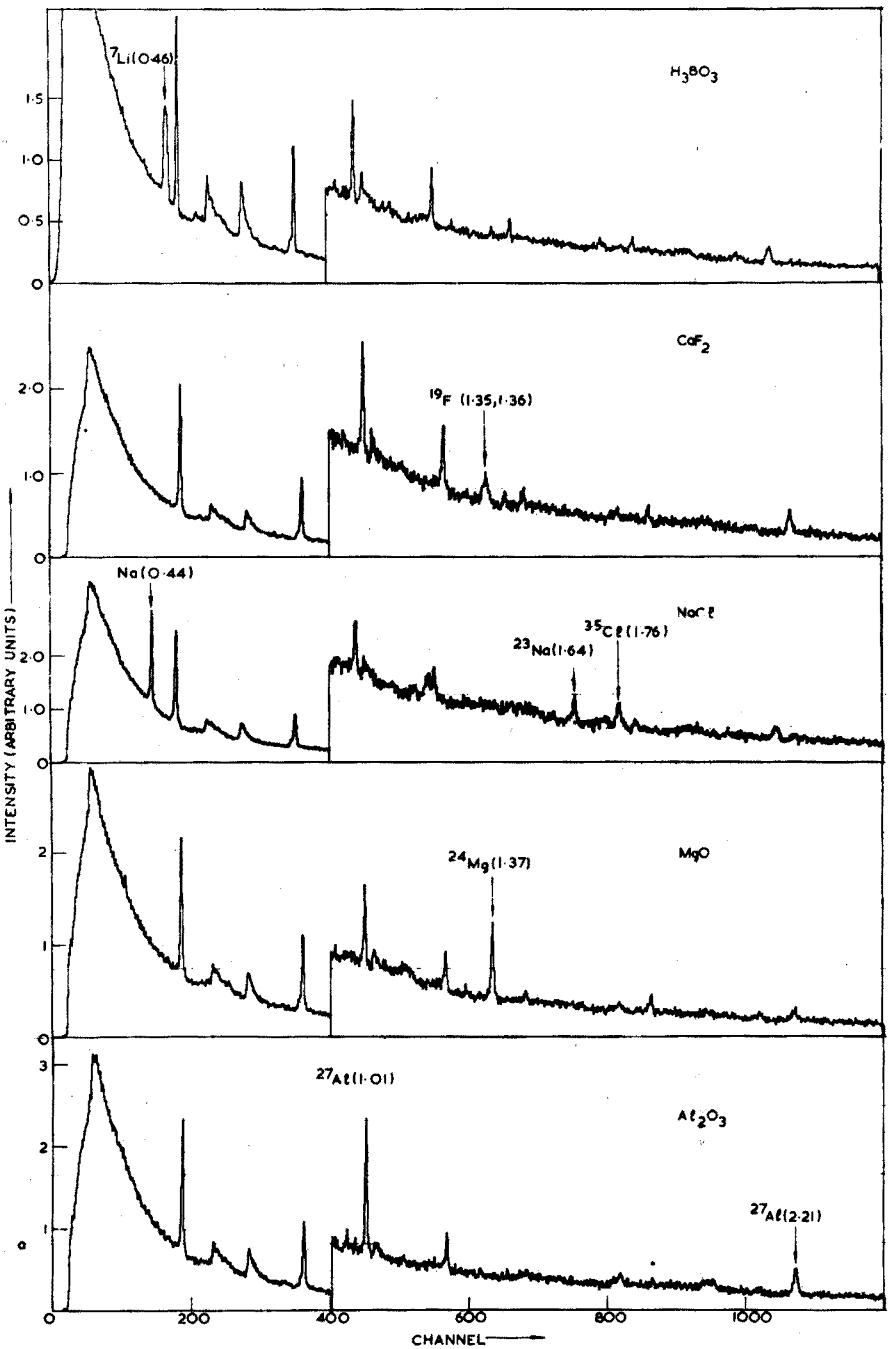

^{7}Li(0·46)
H$_3$BO$_3$
1·5
1·0
0·5
0
CaF$_2$
^{19}F (1·35, 1·36)
2·0
1·0
0
Na(0·44)
NaCl
^{35}Cl(1·76)
^{23}Na(1·64)
2·0
1·0
0
INTENSITY (ARBITRARY UNITS)
MgO
^{24}Mg(1·37)
2
1
0
^{27}Al(1·01)
Al$_2$O$_3$
^{27}Al(2·21)
3
2
1
0
200
400
600
800
1000
CHANNEL

Fig. 3A.

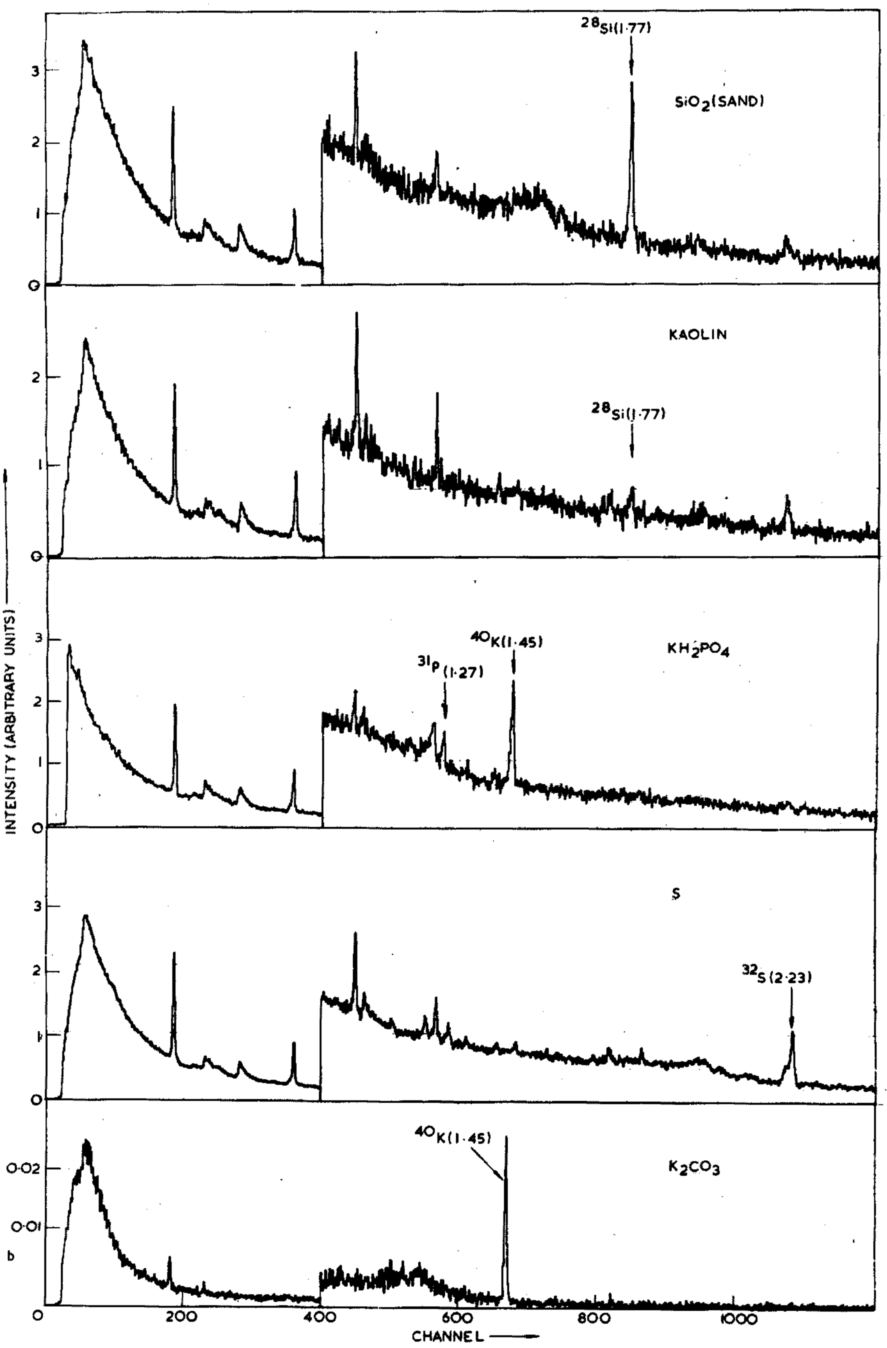

^{28}Si(1·77)
SiO$_2$(SAND)
KAOLIN
^{28}Si(1·77)
^{40}K(1·45)
^{31}P(1·27)
KH$_2$PO$_4$
S
^{32}S(2·23)
^{40}K(1·45)
K$_2$CO$_3$
INTENSITY (ARBITRARY UNITS)
0
1
2
3
0·01
0·02
b
0
200
400
600
800
1000
CHANNEL

Fig. 3B.

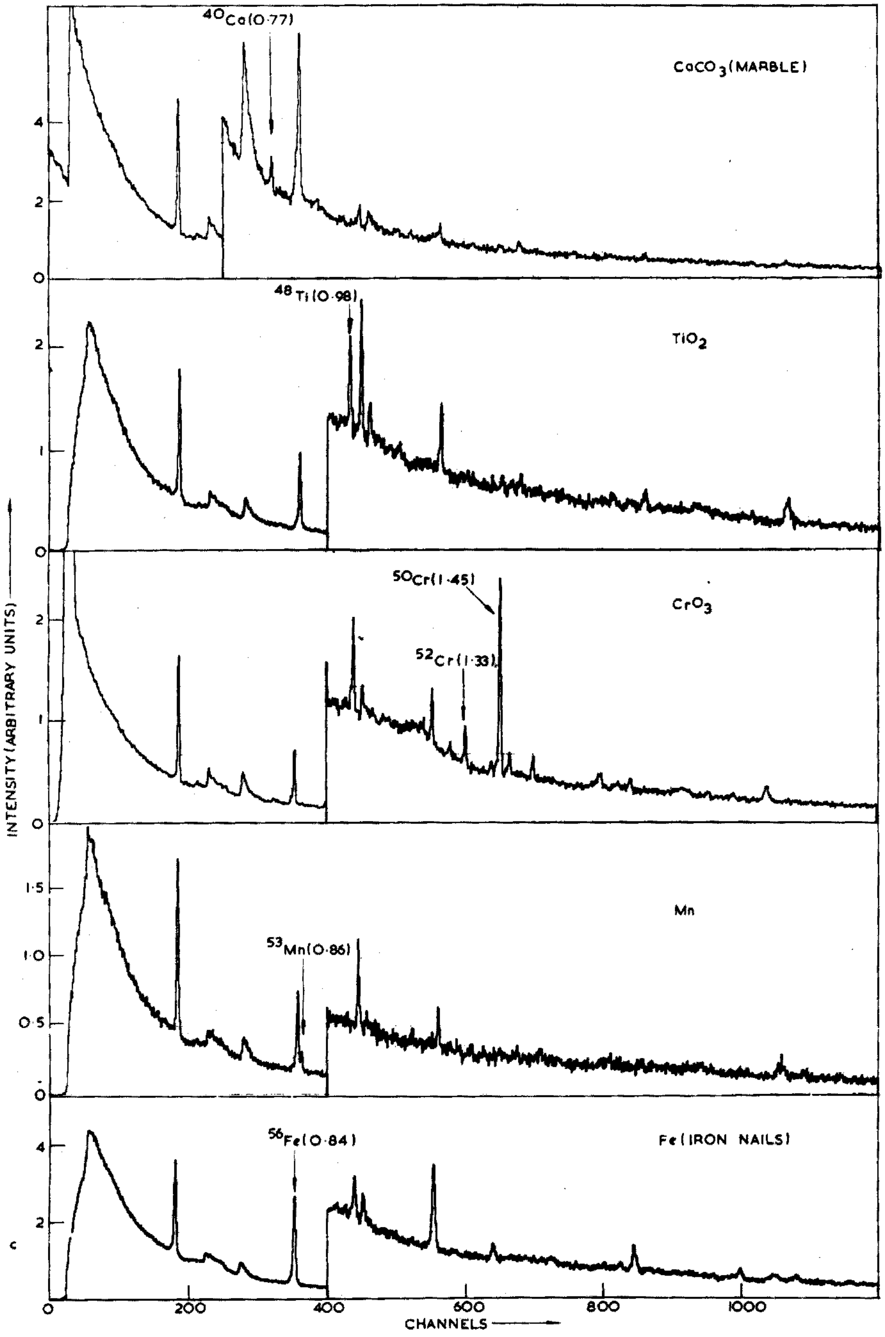

40Ca(0·77)
CaCO3(MARBLE)
4
2
0
48Ti(0·98)
TiO2
2
1
0
50Cr(1·45)
CrO3
52Cr(1·33)
2
1
0
Mn
53Mn(0·86)
1·5
1·0
0·5
0
56Fe(0·84)
Fe(IRON NAILS)
4
2
INTENSITY (ARBITRARY UNITS)
0
200
400
600
800
1000
CHANNELS

Fig. 3C.

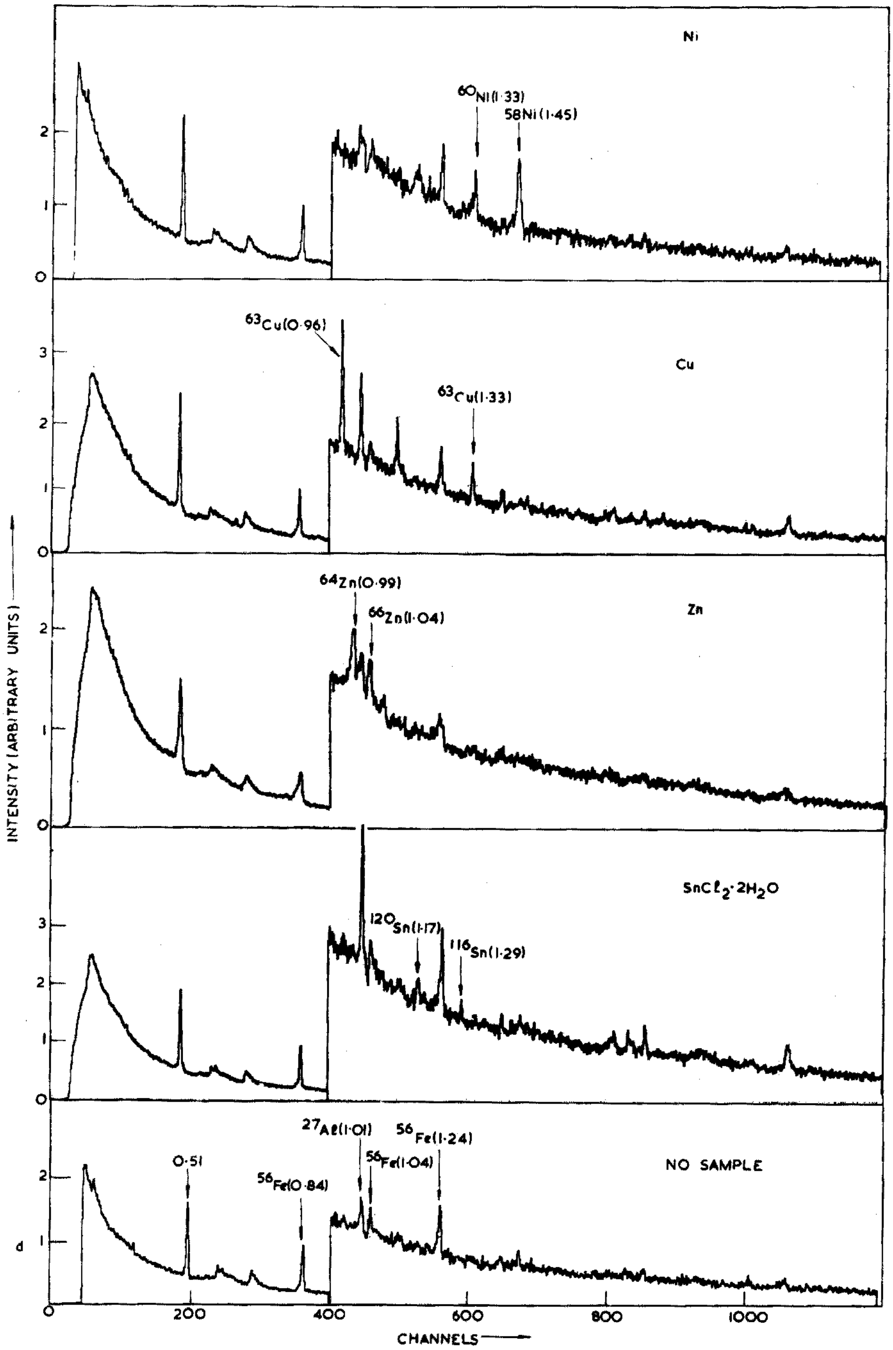


Fig. 3. Spectra of γ-rays from 19 elements and compounds obtained with a Po–Be neutron source with a Ge(Li) detector.

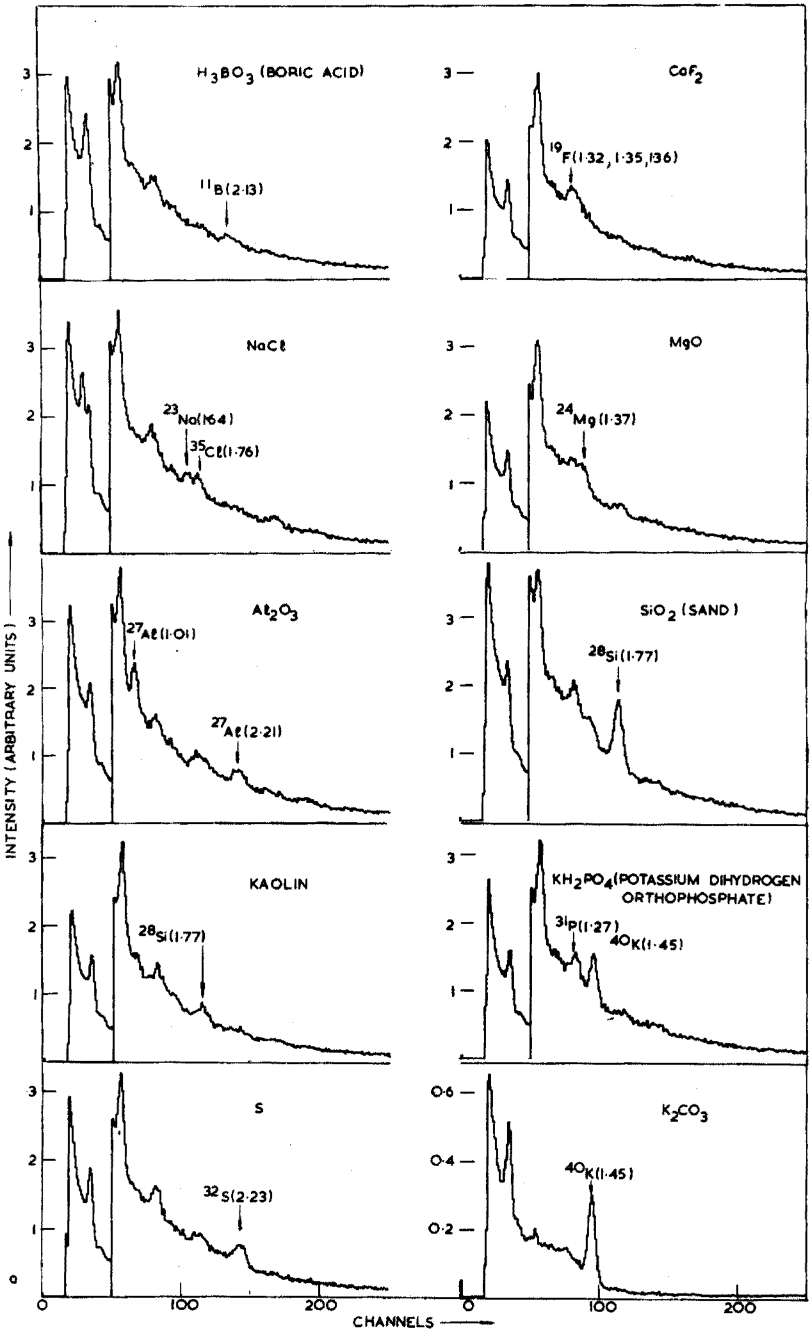

H_3BO_3 (BORIC ACID)
^{11}B(2·13)
CaF_2
^{19}F(1·32, 1·35, 1·36)
NaCℓ
^{23}Na(1·64)
$^{35}Cℓ$(1·76)
MgO
^{24}Mg(1·37)
$Aℓ_2O_3$
$^{27}Aℓ$(1·01)
$^{27}Aℓ$(2·21)
SiO_2 (SAND)
^{28}Si(1·77)
KAOLIN
^{28}Si(1·77)
KH_2PO_4(POTASSIUM DIHYDROGEN ORTHOPHOSPHATE)
^{31}P(1·27)
^{40}K(1·45)
S
^{32}S(2·23)
K_2CO_3
^{40}K(1·45)
INTENSITY (ARBITRARY UNITS)
0
1
2
3
0·2
0·4
0·6
0
100
200
CHANNELS

Fig. 4A.

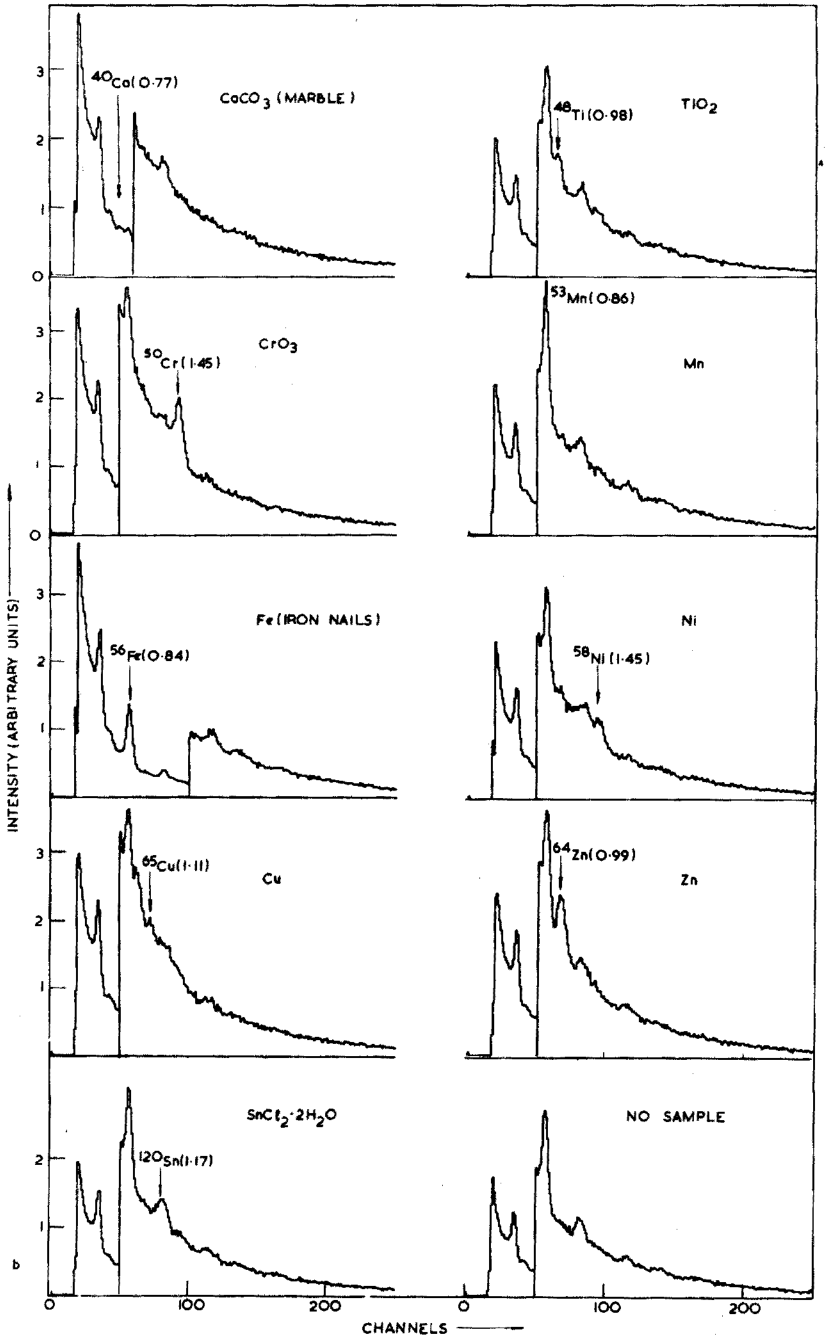


Fig. 4. Spectra of γ-rays from 19 elements and compounds obtained with a Po–Be neutron source and a NaI(Tl) detector.

a 1 Ci neutron source. The ratio of the peak height to the background is also given for each γ-ray.

From element to element the γ-ray intensity is seen to vary rather widely: this effect is partly due to lack of correction for the energy dependence of the full-energy detection efficiency. Similarly, no correction has been made for multiple scattering of neutrons in the sample and for the self-absorption of γ-rays. For the majority of the materials considered here, the strongest peak in the γ-ray spectrum arises from the (n,n'γ) reaction. However, additional contributions to these peaks will be associated with β-decay following activation by the (n,p) reaction. Since these additional contributions will depend on the life-times of the activated nuclei, the counting periods for each measurement are listed in Table I.

An important exception to the observation that reasonable γ-ray intensities are obtained from the more common light elements is provided by calcium where the γ-radiation is particularly weak. The natural activity from ^{40}K enabled potassium to be assayed with the present arrangement by the simple expedient of counting the 1.46-MeV γ-ray from the ^{40}K activity with the neutron source removed.

The problems encountered in γ-ray intensity measurement appear to increase progressively with increasing atomic weight. Difficulties arise from extra complexity in the γ-ray spectra owing to increases in level density, from increases in the number of stable isotopes amongst even Z nuclei and also from greater self-absorption of γ-rays

TABLE II

MEASUREMENTS MADE WITH A NaI(Tl) DETECTOR

Material	*γ-Ray*	*Reaction, if not (n,n'γ)*	*Intensity*[a] *(counts kg^{-1} min^{-1} Ci^{-1})*	*Peak/ back-ground*	*Sample weight (kg)*
H_3BO_3	^{11}B(2.14)		250 ± 125	1.25:1	2.5
CaF_2	^{19}F(1.32, 1.35, 1.36)	[b]	750 ± 750	1.10:1	0.5
NaCl	^{23}Na(1.64)		300 ± 90	1.15:1	3.0
	^{35}Cl(1.76)		300 ± 75	1.21:1	
MgO	^{24}Mg(1.37)		1,900 ± 400	1.31:1	0.8
Al_2O_3	^{27}Al(1.01)		600 ± 75	1.23:1	3.0
SiO_2 (sand)	^{28}Si(1.77)		900 ± 45	2.00:1	5.0
Kaolin	^{28}Si(1.77)		800 ± 200	1.20:1	1.0
KH_2PO_4	^{31}P(1.27)		800 ± 200	1.15:1	1.0
S	^{32}S(2.23)		850 ± 125	1.53:1	1.9
K_2CO_3	^{42}Ar(1.46)	^{40}K(E.C.)^{40}Ar	560 ± 35	5.90:1	1.0
$CaCO_3$ (marble)	^{40}K(0.77)	^{40}Ca(n,p)^{40}K	400 ± 150	1.28:1	5.0
TiO_2	^{48}Ti(0.98)		1,200 ± 350	1.15:1	0.5
CrO_3	^{50}Cr(1.45)		1,450 ± 150	1.67:1	3.0
Mn	^{55}Mn(0.86)		1,600 ± 550	1.29:1	1.0
Fe (nails)	^{56}Fe(0.84)		3,600 ± 200	2.06:1	3.0
Ni	^{58}Ni(1.45)		1,400 ± 400	1.29:1	1.0
Cu	^{64}Cu(1.11)		1,600 ± 250	1.12:1	2.0
Zn	^{64,66,68}Zn(0.99, 1.04, 1.08)	[b]	3,200 ± 250	1.45:1	1.0
$SnCl_2 \cdot 2\,H_2O$	^{120}Sn(1.17)		600 ± 600	1.20:1	0.5

[a] Activation by the (n,p) reaction adds an additional contribution to the γ-ray intensities. All measurements made in 512-sec counting periods.

[b] Intensity obtained as the sum of unresolved γ-ray peaks.

in the sample. It can be concluded that the present technique is more applicable to the analysis of the lighter nuclei.

NaI(Tl) detector

Gamma-ray spectra obtained from the same nineteen substances are shown in Fig. 4 and the intensities of the principal γ-rays are listed in Table II. The presentation is similar to that of the Ge(Li) detector. Here again the errors associated with the γ-ray intensities exclude those of systematic origin and are almost entirely due to background subtraction. At the time at which these measurements were made the strength of the Po–Be source was about 0.15 Ci. It can be seen that the γ-ray intensities are much greater for the NaI(Tl) detector than the Ge(Li) detector, as would be expected when relevant factors such as the ratio of the sensitive volumes (*ca.* 10) are taken into account. The increased detection efficiency does not adequately compensate for the worsened energy resolution of the NaI(Tl) detector (6% at 1.33 MeV). The more general observations made in the previous paragraph also appear to apply for the γ-ray spectra obtained with the NaI(Tl) detector.

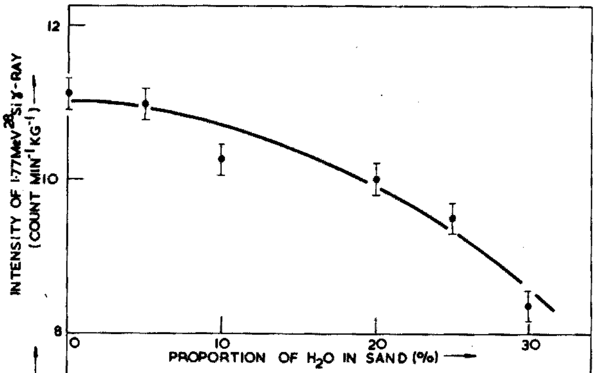
Effect of moisture

In the industrial environment many materials undergoing processing contain appreciable quantities of moisture. It was thought worthwhile to consider the applicability of the method to moist samples, since it is obviously desirable to avoid having to remove the moisture. The need for such an investigation was originally prompted by the qualitative observation that the 1.77-MeV γ-ray from a sample of sand (contained in a 10-l cylindrical glass beaker) became much weaker on the addition of water. The explanation for this effect is that moderation of the neutrons by the H present in the water results in the reduction of the average neutron energy and also in the attenuation of the neutron flux available for the ^{28}Si(n,n′γ)^{28}Si reaction. The reduction of the energy of the incident neutrons is accompanied by the reduction of the strength of the 1.77-MeV silicon γ-ray, and for neutrons of energy below 1.84 MeV, the ^{28}Si(n,n′γ)^{28}Si reaction is energetically impossible.

A set of measurements were made with a 4-kg annular-shaped sample of sand (SiO_2) to which was added various quantities of water. It was observed that no appreciable volume change took place as the weight of the moisture was raised to 30%. The effect of the moderation of the fast neutrons on the intensity of the ^{28}Si γ-ray observed with the Ge(Li) detector is shown in Fig. 5, where the ordinates are plotted on an extended scale. It must be supposed that the variation of intensity with moisture content would be very dependent on the sample geometry, particularly with regard to the mean path length which would be traversed by the primary neutrons in the absence of interaction within the sample. In the present measurement the intensity of the 1.77-MeV γ-ray is reduced by 10% at a moisture level of 20%.

An additional measurement was made which suggested that at a moisture level of 20% the effect of non-uniformity in the distribution of moisture throughout the sample was negligible. The annular-shaped sample holder was divided into two equal parts by a plane through the axis of cylindrical symmetry. Moist and dry samples were placed in the two parts of the container. No discernible difference was observed between the γ-ray intensity obtained under the conditions described and the γ-ray intensity observed with a uniform distribution of moisture.

It should be pointed out that although the effect of moisture on the γ-ray intensity is significant in the present geometry it can be envisaged that in certain circumstances the magnitude of the effect will be reduced, if the analysis procedure is merely to measure the ratio of the intensity of two γ-rays from different elements present in a mixture. This point would appear to merit further investigation.



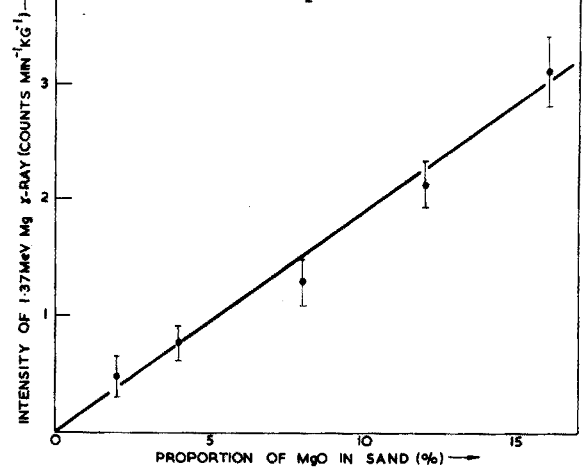


Fig. 5. Intensity of the 1.77 MeV ^{28}Si γ-ray from sand (SiO_2) as a function of moisture content.

Fig. 6. Intensity of the 1.37 MeV ^{24}Mg γ-ray as a function of the proportion of magnesium oxide in a mixture of sand (SiO_2) and magnesium oxide.

Measurement of mixtures

Measurements have also been made to investigate the linearity and sensitivity of response of the Ge(Li) detector to changes in the proportion of one material in a two-material mixture. Small measured quantities of magnesium oxide were added to 4 kg of dry sand (SiO_2) and compared with the intensities of the 1.37-MeV γ-ray from ^{24}Mg. As can be seen from Fig. 6 no significant departure from linearity can be observed.

On the assumption of a linear response to the amount of magnesium oxide present the sensitivity of the measurements varies from 19% at a level of 4% MgO to

9% at a level of 10% MgO. The use of a stronger neutron source would of course lead to a much higher sensitivity; the present measurements were made with 0.3 Ci of Po–Be during a counting period of 180 min.

DISCUSSION

The sensitivity of the prompt γ-ray measurements with a very small neutron source and the Ge(Li) detector (*ca.* 5%) is rather modest. The use of a much larger radioactive neutron source, say in the range 10 to 100 Ci should result in a much improved sensitivity (*ca.* 1%) especially if used in conjunction with a high-resolution (*ca.* 3 keV) Ge(Li) detector. A further improvement in sensitivity could be obtained by the addition of an anti-coincidence shield with NaI detectors. Such systems, which have frequently been described[6-9], can lead to a very marked reduction in the intensity of the Compton distribution but at the cost of considerable extra complexity in the electronics.

Reference has already been made in this paper to neutron activation analysis. This approach has the advantage over the present method that the γ-ray counting does not take place against a background of source or accelerator neutrons and γ-rays. Furthermore, for a given rate of counting, higher sensitivity is available from neutron activation although a rather larger neutron source would be required. This is because a careful choice of irradiation and counting times should result in an enhancement of the desired γ-ray peak against the background of a relatively simple spectrum. In the activation method significant errors may result from small changes in sample geometry or from inhomogeneity in the sample composition. This can arise if considerations of counting efficiency lead to an arrangement whereby the sample partly surrounds the source during irradiation and partly surrounds the detector during counting. It follows then that the detected γ-ray intensity from a particular sample element is highly dependent on the separation between the sample element and the source, and between the sample element and the detector. This problem hardly arises, however, if the sample is symmetrically disposed with respect to the source and detector in a manner similar to that used in the present work (Figs. 2 and 3) for prompt γ-ray measurements. The measured γ-ray intensity is then largely independent of sample inhomogeneity and small changes in geometry.

In any discussion of the relative merits of the present method in relation to such established techniques as X-ray fluorescence and the electron microprobe, mention should be made of the fact that these methods both demand the preparation of samples with a high degree of surface uniformity, and that the measurements are only sensitive to a depth of a few thousand Ångstrom below the surface. The relatively wide range of applicability of these techniques is offset to a certain extent by the cost and complexity of the apparatus required. The time spent in sample preparation would appear to be a disadvantage in the use of these methods in "on-line" applications. Slow neutron activation, which involves the use of a reactor, is of course unsuitable for "on-line" use.

Although the present method does not have the potential accuracy of such techniques as the electron microprobe, X-ray fluorescence and certain chemical analytical methods, it does have substantial advantages. One of these is simplicity. It should be possible to operate a radioactive neutron source γ-ray spectrometer with a minimum of maintenance and with only the occasional intervention of skilled personnel. When this advantage is added to simplicity of sample preparation, rapidity of measurement, the non-destructive nature of the method, and the fact that the measurements have an almost uniform sensitivity over kilogram quantities of sample material, it would seem that a substantial case has been made for further development. A certain degree of attention would have to be directed to the moisture content of the sample material, although it should be emphasized that the effect of moisture content on the γ-ray intensity is critically dependent on the geometry.

SUMMARY

Measurements of prompt γ-rays arising from the neutron irradiation of nineteen elements and compounds with a Po–Be source have been made with a Ge(Li) detector and also a NaI(Tl) detector. The intensities of the strongest γ-rays present in each substance have been obtained in units of counts $\mathrm{kg}^{-1}\ \mathrm{min}^{-1}\ \mathrm{Ci}^{-1}$. The effect on the γ-ray intensity of the presence of moisture in a sand (SiO_2) sample has also been investigated.

RÉSUMÉ

Des mesures de rayons ont été effectueés, après irradiation neutronique de 19 éléments et composés avec une source Po–Be, et détecteur Ge(Li) ou NaI(Tl). On examine également l'influence de l'humidité sur l'intensité du rayonnement gamma, lors de l'analyse d'un échantillon de sable (SiO_2).

ZUSAMMENFASSUNG

Mit einem Ge(Li)- und einem NaJ(Tl)-Detektor wurden die γ-Strahlen gemessen, die bei der Neutronenbestrahlung von neunzehn Elementen und Verbindungen mit einer Po–Be-Quelle entstehen. Es wurden die Intensitäten der stärksten γ-Strahlung in jeder Substanz in den Einheiten Impulse $\mathrm{kg}^{-1}\ \mathrm{min}^{-1}\ \mathrm{Ci}^{-1}$ erhalten. Der Einfluss von in einer Sand(SiO_2)-Probe enthaltener Feuchtigkeit auf die γ-Strahlenintensität wurde ebenfalls untersucht.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF MERCURY IN NATURAL WATERS AND EFFLUENTS BY FLAMELESS ATOMIC ABSORPTION SPECTROPHOTOMETRY

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(Received 22nd August 1970)

Considerable work has been done during recent years on the flameless cold-vapour atomic absorption method for determinations of traces of mercury. Kimura and Miller[1] were the first to use the reaction between mercury(II) and tin(II), which produces elementary mercury, as a means of isolating the metal from its matrix. Poluektov *et al.*[2], however, applied the same principle combined with direct light absorption measurements in the evolved vapour for mercury determinations. Since then, numerous methods based on the same principle but differing in sensitivity and type of sample have appeared in literature. Recently, Lindstedt[3] described urine analysis in detail, Magos and Cernik[4] dealt with biological samples and Hatch and Ott[5] and Dyvik[6] with metals and rocks.

Little work has been done for water, effluent and sewage analysis. Igoshin and Bogusevich[7] used the described principle in their work on water analysis but reported the relatively low sensitivity 14 $\mu g\ l^{-1}$. They also described a preconcentration step, in which mercury sulphide was precipitated on cadmium sulphide, and were then able to determine smaller quantities.

The limitation in sensitivity is, according to several authors, caused by the high blank value. To reach a lower detection limit, purification of chemicals would thus be necessary. A means of reducing some of this contamination has been used at this Institute during the last three years and mercury determinations have been carried out in natural waters, effluents, sewage, sodium hydroxide, sulphuric acid and to some extent baby food. The modifications and refinements developed in order to reach a detection limit of 0.02 μg mercury per litre are described in this paper.

FACTORS INFLUENCING THE RESULTS

Sample treatment

For such a simple matrix as water, the interferences mentioned by Poluektov *et al.*[2] and by Lindstedt[3] need not be taken into consideration unless industrial waste water, possibly containing organic solvents, noble metals or halides other than chloride, is to be analysed.

Igoshin and Bogusevich[7] state that after storage for 6–8 days, natural water loses mercury by adsorption to the walls of the container. In an acidic solution, however, in the presence of permanganate, there is no such loss even after boiling. The treatment proposed and used by these authors was therefore adopted in the present work. There is also another reason for undertaking this treatment. Natural Scandinavian waters are normally acidic and contain very little calcium but considerable amounts of organic humus compounds. These compounds could also contain or adsorb strongly some of the mercury present. The simplest way of ensuring a quantitative determination is thus to digest the sample with permanganate–sulphuric acid. This same mixture, but in considerably higher concentrations has also been shown[8] to decompose organic mercurials such as methyl- and phenylmercury.

It is of importance to use as small amounts of reagents as possible in order to reduce the blank value. In the case of effluents and sewage containing relatively high concentrations of oxidizable matter, considerably more permanganate might have to be added to prevent decoloration and thereby incomplete oxidation.

Stability of standard solutions

Lindström[9] has discussed the losses caused by evaporation of metallic mercury from extremely dilute neutral standard solutions of mercury compounds. Shimomura *et al.*[10] recommended the use of complex-forming agents, such as iodide or cyanide, or oxidants to prevent this. Other workers prepare dilute standard solutions daily in acidic medium which also tends to reduce volatilization. In this work sulphuric acid and potassium permanganate were added in the same concentrations as used for digestion of samples.

The stability of 0.1-p.p.m. mercury standards in 1 *N* solutions of hydrochloric acid, nitric acid and sulphuric acid, as well as the sulphuric acid–potassium permanganate mixture, were tested by means of a radioactive mercury-203 tracer. None of the four solutions stored in open bottles changed their activity appreciably within one week of preparation.

Reagent contamination

When the present method of analysis is used, mercury can be shown to be present in almost any type of chemical. It is important therefore to remove as much of this "blank" mercury as possible in order to increase the signal-to-blank ratio. This should, if possible, be done without time-consuming and difficult reagent purification procedures.

In this laboratory, a simple method was used for eliminating the contribution from the tin(II) chloride solution in hydrochloric acid and from the sulphuric acid added in order to prevent precipitation of tin hydroxides. The two reagents were mixed with known amounts of distilled water and the contaminating mercury present, reduced to the elementary state, was stripped by bubbling air through the solution. The potassium permanganate used for digestion cannot be purified in this manner. If necessary, the traces contained in the sulphuric acid used for digestion and in other reagents not used as oxidants, can be removed in the described way after addition of a small amount of tin(II) chloride. However, the main contamination found in this work, was in the tin(II) chloride and reagent-grade hydrochloric acid.

EXPERIMENTAL

Equipment and reagents

A Perkin-Elmer Model 303 atomic absorption spectrophotometer equipped with an automatic recorder readout accessory and a Hitachi-Perkin-Elmer Recorder Model 159 together with a Westinghouse hollow-cathode lamp and a 8.7-cm long square gas cell made of PVC of 4.8-cm^2 cross-section with quartz windows was used. All chemicals were of reagent-grade quality.

Mercury solutions. A 1000 p.p.m. stock solution was prepared from 0.1354 g of mercury(II) chloride dissolved in 100 ml of 0.5 *M* sulphuric acid. A 0.1 p.p.m. standard solution was prepared by dilution of the stock solution and final addition of 1.0 ml of 1 + 1 sulphuric acid and 0.5 ml of aqueous 2%(*w*/v) potassium permanganate solution per 100 ml as preservative.

Aeration apparatus

A system similar to that used by Lindstedt[3] was used. Air from a gas cylinder passes through a flow meter at the rate of 0.5 l min^{-1} into a 100-ml wash bottle equipped with a glass sinter of coarse porosity. Through a tube filled with ascarite to absorb water and fumes of acid or sulphur dioxide, the air containing mercury vapors released in the wash bottle, enters the gas cell where the mercury concentration is monitored. The flask is equipped with ground-glass joints on inlet and outlet in order to ensure rapid and air-tight connections and also to make bypassing of the wash bottle possible.

Procedure

To a 1-l water sample add 10 ml of 1 + 1 sulphuric acid and 5 ml of aqueous 2% (w/v) potassium permanganate solution. Mix well and let stand for 24 h at room temperature. The solution is then ready for mercury determination. For effluent and sewage add more permanganate if decoloration occurs. Run a blank containing all the reagents used in the same way.

Introduce 30 ml of distilled water, 2 ml of 1 + 1 sulphuric acid and 2 ml of 10% (*ω*/v) tin(II) chloride dihydrate solution in 1 *M* hydrochloric acid into the wash bottle. Mix well and connect the flask to the aeration apparatus. After 2 min, or when the recorder pen has returned to the base line, disconnect the flask, add 50 ml of the well mixed sample, close the flask, shake well for 20 sec and connect it to the aeration apparatus. Record the mercury peak, using scale expansion 10, damping 1, and speed low on the recorder. In case of foaming add a drop of tri-*n*-butyl phosphate. For samples with a high mercury content either reduce the scale expansion or use a smaller sample aliquot. In this case take care to adjust the total volume in the fask to 84 ml by adding distilled water, as this would otherwise change the sensitivity. A smaller volume causes a higher absorption peak.

After 2 or 3 min, when the recorder pen has returned to the base line, disconnect the flask, add a suitable small volume of standard solution, *e.g.* 0.1 ml of 0.1-p.p.m. mercury solution which does not change the total volume appreciably. This amount of mercury (0.01 μg) produces about 20% absorption at scale expansion 10. Repeat the procedure for new aliquots of standard solution as soon as the recorder pen has returned to the base line.

After conversion of the measured peak values of percentage absorption to absorbance, subtract the blank value and evaluate the concentration of mercury in the sample from the calibration graph which is usually a straight line. For absorption values smaller than 10% at scale expansion 1, the conversion to absorbance is unnecessary.

Decomposition of methylmercury contaminated samples

To test the completeness of decomposition of organic mercurials, some samples of lake water known to be contaminated by methylmercury from a fungicide were analysed by the described procedure and by the method of Lindstedt[3], which involves very much higher concentrations of potassium permanganate and sulphuric acid.

By Lindstedt's method, 2.44 p.p.m. mercury was found in one sample, a value which, as discussed above, is considered to be the true analysis. With the described method, decoloration of the permanganate occurred and only 1.1 p.p.m. mercury was measured. Since there was obviously too much oxidizable matter in this sample in relation to the amount of potassium permanganate, five times as much permanganate was added to a new sample aliquot. After 20 h, the analysis showed a mercury content of 2.36 p.p.m. and no decoloration. The excellent agreement between the two procedures was taken as evidence of complete decomposition also by the more dilute digestion mixture.

RESULTS AND DISCUSSION

The proposed method has been used in the analysis of natural waters, effluent, sewage, sodium hydroxide and sulphuric acid. Results obtained by other workers[3-5,9] have shown good agreement between the flameless atomic absorption technique and dithizone extraction or neutron activation methods. Though the same high sensitivity was not achieved by these authors, there is good reason to believe that their results are also applicable to lower concentrations, an argument strongly supported by the results found by means of the described procedure.

Several standard aliquots could be reduced and measured after each other or after or before sample aliquots in the same way as described in the procedure, without any kind of memory effect or irregularity, and with a relative standard deviation of 4.9% in measurements of 0.01 μg of mercury.

Experiments showed that samples containing organomercurials such as methylmercury were also completely decomposed by the described treatment. The measured mercury content in some contaminated samples of waste water was the same whether the samples were digested or not, indicating that all the mercury was present in an ionic or at least easily reducible form. Some values measured in casual samples of drinking water are listed in Table I.

TABLE I

MEASURED ABSORPTION AND DETERMINED CONCENTRATION OF MERCURY IN LAKE WATER (SCALE EXPANSION 10)

Sample	*Aliquot (ml)*	*Absorption (%)*	*Total amount (ng)*	*μg l^{-1}*
0.050 p.p.m. standard	0.100	10.0	5.0	—
0.050 p.p.m. standard	0.010	1.2	0.5	—
Blank	50	0.3	0.01	—
øen, 4 m depth	50	9.0	4.4	0.088
Gjersjøen 4 m depth	50	6.7	3.2	0.064
Aurevann	50	3.3	1.5	0.030

The author is indebted to Dr. F. Dyvik, to the Norwegian Zinc Company A/S and to the Royal Norwegian Council for Scientific and Industrial Research for support of this work.

SUMMARY

A rapid and extremely sensitive method for the determination of mercury concentrations as low as 20 ng l^{-1} in water is described. The samples are digested with a mixture of potassium permanganate and sulphuric acid, in order to decompose organic compounds containing or adsorbing mercury and to avoid adsorption on the walls of the container as well as losses by volatilization. The recommended concentration of permanganate is shown to decompose methylmercury compounds completely. After digestion the analysis is carried out by the cold-vapour atomic absorption technique.

ZUSAMMENFASSUNG

Es wird eine schnelle und extrem empfindliche Methode für die Bestimmung von Quecksilberkonzentrationen in Wasser bis zu 20 ng l^{-1} herab beschrieben. Die Proben werden mit einem Gemisch von Kaliumpermanganat und Schwefelsäure digeriert, um die organischen Verbindungen zu zersetzen, die das Quecksilber enthalten oder adsorbieren, und um Adsorption an den Gefässwandungen sowie Verluste durch Verflüchtigung zu vermeiden. Die empfohlene Permanganatkonzentration zersetzt Methylquecksilberverbindungen vollständig. Nach der Vorbehandlung wird die Analyse nach dem flammenlosen Kaltdampf-Atomabsorptionsverfahren durchgeführt.

RÉSUMÉ

Une méthode rapide et extrèmement sensible est décrite pour le dosage du mercure, à des concentrations de l'ordre de 20 ng l^{-1}. Les échantillons sont traités par un mélange de permanganate de potassium et d'acide sulfurique, afin de décomposer les composés organiques et d'éviter une adsorption sur les parois du récipient, de même que des pertes par volatilisation. La concentration de permanganate recommendée permet la décomposition totale des composés méthylmercure. L'analyse est finalement effectuée par absorption atomique sans flamme.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A SIMPLE DEMOUNTABLE HOLLOW-CATHODE TUBE FOR THE ANALYSIS OF SOLUTIONS

APPLICATION TO LEAD IN BIOLOGICAL MATERIALS

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(Received 11th September 1970)

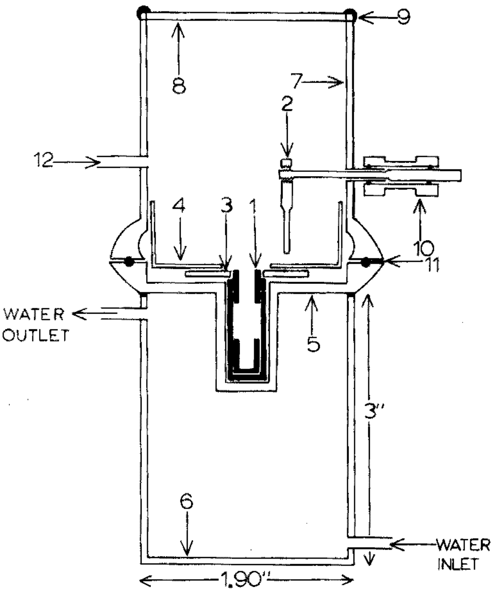
The hollow-cathode excitation source introduced by Paschen in 1905[1] has found increasing use in recent years for the emission spectroscopic trace analysis of metals and non-metals[2-4]. This highly energetic, controllable excitation source has been shown to yield better sensitivity for many elements[5], particularly non-metals. The rapid development in the field of atomic absorption spectroscopy has contributed considerably to the revival of interest in the hollow-cathode excitation source.

The analysis of solutions by this technique presents certain difficulties owing to the low pressure environment of the hollow-cathode tube. A few investigators[6,7] have reported such solution analyses, including an earlier study from this laboratory[8]. In the present investigation, a shielded graphite cathode which is suitable for analysis of the acidic residue from wet-ashed biological materials is described. To facilitate such analyses, a very simple demountable hollow-cathode tube assembly has been constructed which allows a stabilized discharge, high emission intensity, and a short turn-around time. Characteristics of this hollow-cathode excitation system are demonstrated for standard solutions and biological samples.

EXPERIMENTAL

Hollow-cathode source

The demountable hollow-cathode tube previously used[8] was quite suitable for emission analysis but subsequent experience with the hollow-cathode excitation technique indicated that design improvements could be made, including simplification. Construction of the previous tube was laborious, the numerous vacuum-seal points presented potential leak sites, and the cathode was not directly accessible for cooling. The tube design used in the present investigation is shown in Fig. 1. The stainless steel cathode holder block was machined to mate with a 40-mm i.d. glass joint (Kontes Glass Co.), with a Viton O-ring and pinch clamp for the vacuum seal. A brass water jacket (solder connection) permitted water cooling of the cathode holder block, as well as the graphite cathode assembly which could be slipped into the cathode holder cavity. The demountable stainless steel anode was attached to the glass envelope with a 0.25-in Cajon Ultra Torr fitting, and the front of the glass tube was sealed with a quartz optical grade window using silicon rubber. The discharge was localized between the anode and cathode cavity by shielding the cathode holder block with a center drilled quartz disc flush against the holder and a 1.5-in diameter glass shield which extended over the cathode–anode interspace. The cathode–anode distance was normally set at about 1 cm. Compared to the previous tube, the present tube can operate at high currents, owing to the water cooling capabilities. Our power supply was limited to 200 mA capacity, but higher currents could be used with no damage to the tube. A higher signal-to-background ratio was also observed, but increased ease of operation was perhaps the greatest advantage.



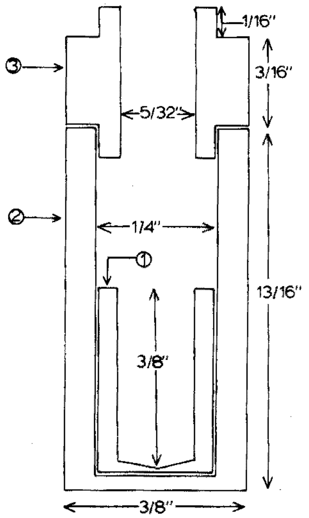


Fig. 1. Demountable hollow-cathode source showing (1) graphite cathode assembly, (2) stainless steel demountable anode, (3) quartz disc shield, (4) outer glass envelope shield, (5) stainless steel cathode block, (6) brass water jacket, (7) O-ring vacuum glass connector, (8) quartz window, (9) Silicone rubber seal, (10) Ultra Torr vacuum connection, (11) Viton O-ring, and (12) gas inlet.

Fig. 2. Graphite hollow-cathode assembly showing (1) inner electrode (sample receptor), (2) outer graphite electrode, and (3) graphite assembly cap.

The assembled hollow-cathode tube was used in both the horizontal and vertical modes. The latter was more convenient with respect to shield placement and access to the cathode cavity, as well as general ease of demounting, and was used for all the data reported here. The water-jacketed cathode holder was kinematically mounted on a 65-mm Ealing Tri-Rack flat-bed carrier which was movable along an Ealing 500-cm triangular steel optical bench. A front surface mirror mounted at a 45° angle to the vertical hollow-cathode tube directed the emission radiation through two quartz focussing lenses and into the spectrometer. The spectrometer, readout, and vacuum system have been previously described[8].

Hollow-cathode assembly

The cavity in the stainless steel cathode holder was intended to accommodate many different types of cathodes, including those of pure metal to act as a line source for atomic absorption. For the analysis of solutions, possibly of small volume, the assembly shown in Fig. 2 was used. The outer graphite electrode acts as a housing which fits into the holder cavity. The smaller inner electrode contains the sample deposition and, upon ion bombardment, allows the production of an atomic vapor which is advantageously concentrated within the assembly by the bayonet friction fitting cap. The inner analytical electrode was discarded after each run, but the outer graphite electrode and cap could be used for 10–15 runs before significant background from residual amounts of the trace test element appeared.

Reagents

All chemicals used in this study were reagent-grade. The graphite hollow-cathode assemblies were machined from "Ultra Purity" spectroscopic grade electrodes (Ultra Carbon Corporation, Bay City, Mich.). Standard solutions were prepared by dilution of Fisher atomic absorption standards. The laboratory distilled water was further purified by passage through a mixed ion-exchange bed and used for dilution of standards and final rinsing of glassware.

Procedure

A series of standard solutions of the analyte was prepared, each containing an added carrier salt concentration of 1000 p.p.m. lithium and 500 p.p.m. potassium. The small inner graphite cathodes were dip-coated with collodion over the entire extra-cavity surface to prevent the loss of test solution by diffusion through the porous graphite. The treated electrodes were air-dried, followed by the addition of 0.1-ml increments of the test solution which were dried under an infrared lamp. Four such increments were normally used. The cathode with the dry residue was heated for a few minutes in a muffle furnace at 450° to destroy the collodion coating, to expel any last traces of water, and to aid in degassing the graphite.

The electrode was then transferred to the larger graphite electrode and the assembly inserted into the cathode block. After tube assembly and evacuation, the system was flushed with argon filler gas, re-evacuated, and filled with argon to a pressure of 35 mm oil (16 mm oil = 1 mm Hg). The discharge was initiated at low currents and quickly increased to the 200-mA working current. The low p.p.m. and sub-p.p.m. concentrations of test element produced a pronounced emission maximum, subsequently falling off to background within minutes. Blanks were run for each sample to determine any background contribution caused by carrier salt, cathode, or sample treatment. Experimental parameters such as wavelength, slit width, current, and fill gas, were optimized in preliminary studies with standard solutions.

RESULTS AND DISCUSSION

Problems related to solution analysis

The transition from solution sample to a test element film deposited in the cathode cavity requires the consideration of several factors. An inert, pure metal hollow cathode with a simple emission spectrum would seem ideal as a deposition site, but this may depend upon the salt content of the solution. In a sample containing no particularly high elemental concentrations, the deposited sample film will normally cause no discharge problems, but small changes in major component concentration may significantly alter the analyte discharge environment with a subsequent change in test element emission intensity. Conversely, a high salt content which allows a certain spectroscopic tolerance in the concentration variation of major constituents may produce a sample film which essentially acts as an insulator either to prevent discharge initiation or at least to create erratic behavior. Graphite, as a hollow-cathode medium, has several advantages. It is obtainable in high purity, in many physical forms ranging from blocks to powders, and has a relatively simple emission spectrum.

A further significant advantage of graphite is the fact that it is unaffected by acidic or basic solutions that could seriously react with various metals. Initially an attempt was made to use a suitably drilled graphite rod as a receptor for the solution sample, but the porosity of the graphite transmitted the solution through the rod, resulting in sample loss. Pressed graphite pellets, with the sample solution applied dropwise and dried on the pellet surface, were then used but the high carrier salt content created discharge stability problems. The next approach was the formation of a homogeneous slurry of the sample solution and graphite powder which was dried and pressed into a pellet for analysis. A stable, reproducible discharge resulted, but in addition to reduced sensitivity, the inconvenient and time-consuming preparation step was a marked disadvantage. The method as finally evolved makes use of collodion-coated thin-wall graphite electrodes which prevent sample diffusion out of the electrode but do not cause all of the carrier salt to deposit as a non-conducting surface layer. With this arrangement, it was possible to produce uniform elemental sensitivities with a minimum of pretreatment steps.

Spectroscopic buffer

In an earlier investigation[8] a carrier salt was used to impede the loss of test element from the cathode cavity during discharge by producing a more even and controlled volatilization. In applying the method to biological samples, the high concentrations of sodium and potassium, which may vary from sample to sample, caused changes in analyte emission intensity. The alkali halide carrier salt content which could be tolerated with stainless steel electrodes was not sufficient to provide a constant sample matrix. However, with the graphite electrodes, it was discovered that a very high added carrier salt concentration of up to 5000 p.p.m. in the sample solution still allowed a stable discharge. This was used to advantage by preparing various combinations of alkali halide salts to act as both a carrier salt and a spectroscopic buffer to negate the variation of intrinsic concentrations of these species in biological samples. Best results in terms of precision and buffer action in the presence of variable sodium and potassium concentrations, were obtained with a stock solution from which each sample solution was made to be 1000 p.p.m. in lithium chloride and 500 p.p.m. in potassium chloride.

Studies with lead solutions

Working solutions of lead at the low p.p.m. range were used to optimize experimental parameters, including choice of filler gas, gas pressure, and tube current. The 405.8-nm emission line provided the best combination of sensitivity and freedom from interference. All solutions contained the previously described carrier salt. The emission response of a lead solution in the hollow-cathode discharge is shown in Fig. 3 along with a blank comparison of the carrier salt.

The ability of the method to eliminate problems caused by variation of sodium and potassium was of particular interest since the method was to be eventually applied to biological samples. Test solutions of lead plus carrier salt were doped with increasing amounts of sodium and potassium from 0 to 400 p.p.m., a concentration which was expected to be beyond the upper limit to be encountered after digestion and dilution of the biologicals. The carrier salt seemed to act as an effective discharge saturation buffer, because repeated test measurements showed no significant change in lead emission as the alkalis were added. The variation to be encountered in real biological samples would normally be less than these extreme conditions and should be effectively neutralized.

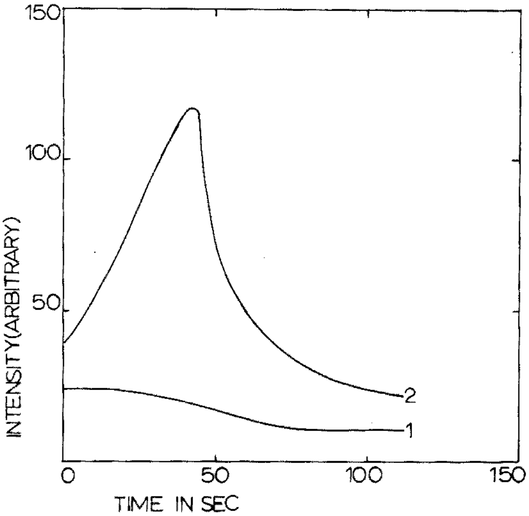


Fig. 3. Emission response of 405.78-nm lead line for (1) cathode-carrier salt background and (2) a 0.20 p.p.m. standard lead solution with added carrier (1000 p.p.m. lithium, 500 p.p.m. potassium in solution). Filler gas, argon at 35 mm oil (16 mm oil = 1 mm Hg); slit width, 0.05 mm; tube current, 200 mA.

Lead in biological materials

Lead is of obvious interest in biological samples. Although lead is almost always present in tissues, its concentration is quite low, leading to digested samples in which lead is at the sub-p.p.m. level. This may impose serious sensitivity requirements unless concentration steps are taken, such as extraction. Hollow-cathode excitation was used to establish a working curve from lead standard solutions to cover the 0–1 p.p.m. range, with a limit of acceptable accuracy and precision ($\pm 6\%$) encountered at the 0.1-p.p.m. level.

Samples of human hair and cat liver tissue were analyzed for lead by the described method after wet digestion by a procedure previously described[8]. Table I shows the values obtained for the hair samples and tissue samples. Dry sample weights ranged from 0.2–0.5 g with a dilution after digestion to 5 or 10 ml in a volumetric flask.

In order to define more clearly the accuracy and efficiency of the technique for these sample types, recovery studies were made to determine the effect of the digested sample on lead emission. Aliquots of a digested sample were taken with increasing amounts of lead added, followed by emission analysis of each. Two hair samples and one liver sample were used with recovery values of 93.0, 99.5, and 92.3% obtained.

TABLE I

LEAD ANALYSES IN THREE DIFFERENT HAIR SAMPLES AND ONE LIVER SAMPLE AS DETERMINED BY HOLLOW-CATHODE EXCITATION

Sample	*Lead concentration ($\mu g\ g^{-1}$, dry wt.)*
Hair III	4.10
Hair II	8.10
Hair	7.03
Liver tissue	2.00

The biological analyses are presented not to suggest any particular significance of lead in these samples, but rather to show that the hollow-cathode excitation technique could be used to obtain such data from small portions of samples containing low lead concentrations. The very simple design of the demountable tube eliminates serious instrumental problems and allows stable operation. It has been very useful in our laboratory as a complementary technique to atomic absorption.

This work was supported by Grant No. GM-14569, USPHS.

SUMMARY

A simple, demountable hollow-cathode excitation source for the analysis of solutions is described which allows water cooling, high emission intensity, discharge shielding, and extreme ease of operation. A graphite hollow-cathode assembly is shown which is particularly suitable for the analysis of acidic digestion residues. A high salt concentration can be used with the tube, allowing a lithium and potassium carrier salt–spectroscopic buffer which controls effects caused by matrix variation. Analyses of lead in biological materials are used to demonstrate the capabilities of the tube.

RÉSUMÉ

Une source d'excitation à cathode creuse, simple et démontable, est décrite pour l'analyse de solutions; elle permet le refroidissement à l'eau, une intensité d'émission élevée et une extrême facilité d'opération. Une cathode creuse de graphite convient particulièrement bien pour l'analyse de résidus de digestion acide. De fortes concentrations de sels ne gènent pas, permettent d'utiliser des tampons spectrocopiques au lithium ou au potassium pour contrôler l'influence des variations de la matrice. On démontre les possibilités de ce tube par des analyses de plomb dans des matières biologiques.

ZUSAMMENFASSUNG

Für die Analyse von Lösungen wird eine einfache, demontierbare Hohlkathodenanregungsquelle beschrieben, die Wasserkühlung, hohe Emissionsintensität, Entladungsabschirmung und sehr leichte Handlabung ermöglicht. Die gezeigte Graphithohlkathodenanordnung eignet sich besonders für die Analyse von Rückständen von Säurebehandlungen. Es sind hohe Salzkonzentrationen möglich, so dass durch Anwendung von Lithium- und Kaliumträgern als salzspektroskopische Puffer Matrixeffekte beseitigt werden können. Analysen von Blei in biologischem Material zeigen die Leistungsfähigkeit der Anregungsröhre.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

VOLLAUTOMAT ZUR SAUERSTOFFBESTIMMUNG IN ORGANISCHEN SUBSTANZEN MIT KOLORIMETRISCHER ENDPUNKTSINDIKATION

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(Eingegangen den 2. September 1970)

In Ergänzung zur ersten Mitteilung über die automatische Sauerstoffbestimmung[1] in organischen Substanzen soll hier über eine Apparatur berichtet werden, die als Vollautomat bezeichnet werden kann. Von dem Automaten selbst werden dabei nur die wesentlichen Unterschiede zu dem Prototyp ausführlicher beschrieben. Näher beleuchtet werden soll hier vor allem die Erfassung und Verarbeitung der anfallenden Daten. Nachdem sich die von uns entwickelten Automaten zur N, CH und O-Bestimmung im Routinebetrieb bewährt hatten, war eine automatische Verarbeitung der Analysendaten naheliegend. Grundsätzlich ist eine solche Messwertverarbeitung nach drei Verfahren möglich:

1. dem Analogverfahren;
2. der Analogspeicherung und anschliessender Digitalauswertung off-line;
3. der on-line Digitalauswertung, wobei das analoge Messsignal automatisch digitalisiert, korrigiert und ausgewertet wird.

Die primäre Frage war also das System: ein "Grossrechner" oder aber für jede Apparatur ein preiswerter kleiner Tischrechner. Hier wie dort wird die menschliche Arbeitskraft entlastet, die Analyse beschleunigt und auch die Überwachung auf ein Minimum reduziert. Voraussetzung war die elektrische Ausgabe sowohl des Wägeergebnisses als auch der Messergebnisse.

Die einfachste Lösung war zunächst der Einsatz eines Kleinstkomputers. Die von der Büromaschinen-Industrie preiswert angebotenen Klein- und Kleinstrechner können allerdings wegen ihrer geringen Speicherkapazität und der relativ langen Rechenzeit nicht simultan für mehrere Analysenautomaten eingesetzt werden. Ihr Vorteil ist aber die einfache Programmierung und die Tatsache, dass die Ergebnisse in allen Fällen sofort greifbar sind. Für umfangreiche Aufgaben oder aufwendigere Rechenprogramme kann off-line ein grösserer Rechner in Anspruch genommen werden. Als Kleinstrechner wurde die Combitron S der Firma Diehl, Nürnberg, gewählt. Diese vollelektronische mit elektromechanischem Druckwerk ausgerüstete Maschine ist von der Ausstattung her gerade passend. Auch die Speicherkapazität ist mit 10 Konstanten- und 10 Programmspeichern mit jeweils 10 Befehlen, also 100 Programmschritten, ausreichend. Die Rechenprogramme können mittels Lochstreifenleser eingegeben werden.

APPARATUR

Dieser Combitron S Rechner wurde in den beschriebenen Automaten zur

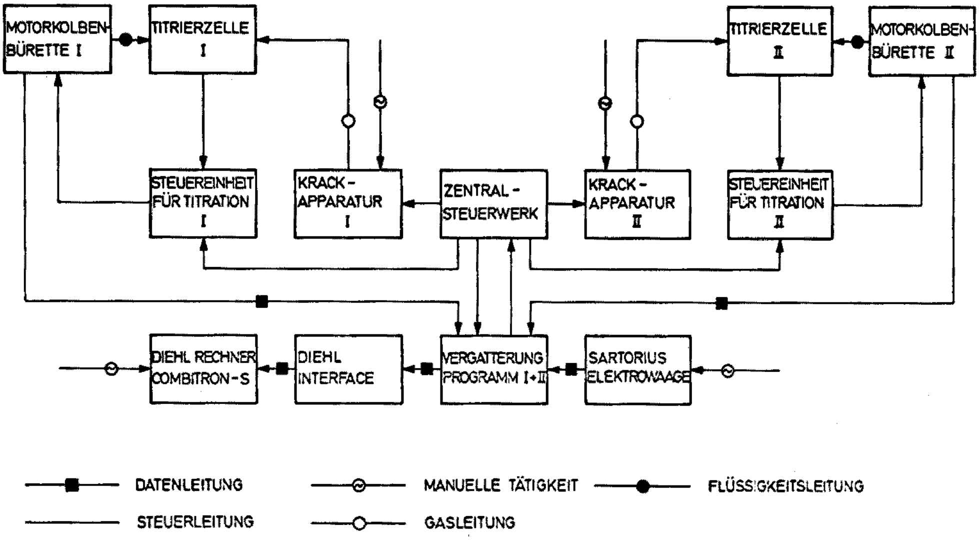


Abb. 1.

Sauerstoffbestimmung integriert (Abb. 1). Als Elektrowaage wurde das Modell 4125 der Firma Sartorius verwendet, mit dem gute Erfahrungen gesammelt werden konnten. Gegenüber der ursprünglichen Anordnung der Apparatur mussten dabei folgende Änderungen vorgenommen werden:

1. Die Motorkolbenbüretten wurden zur Datenerfassung mit induktiven Impulsgebern ausgerüstet. Die Impulszahl ist der verbrauchten Menge Titrierlösung proportional.
2. In die Gattereinheit (Verriegelungseinheit) wurden 2 elektronische Zähler eingebaut, die die Impulse beider Büretten zählen.
3. Da eine eventuelle Blindwertkorrektur wegen der begrenzten Speicherkapazität nicht über den Rechner vorgenommen werden kann, wurde diese Möglichkeit an der Gattereinheit geschaffen. Über Schalter können die dem Blindwert äquivalenten Impulse bis zu einer Dekade unterdrückt werden, sodass nut die korrigierten Volumenwerte anstehen.
4. Die Eingabe der Gewichte als elektrische Grössen erfolgt ebenfalls über die Verriegelungseinheit. Über je eine Drucktaste werden die Tara- und Bruttowerte vom Digitalvoltmeter der Waage übernommen. Ein eingebautes Netzwerk sorgt dabei für die logische Verknüpfung der Gewichte und Volumina.
5. Zur Umsetzung der parallel im BCD-Code anstehenden Messwerte in den seriellen Maschinencode der Combitron S war ein Interface notwendig, das von der Firma Diehl lieferbar ist.

PROGRAMMABLAUF

Mit dieser hier aufgezeigten, geänderten Anordnung ergibt sich nun folgender Programmablauf (Abb. 2). Das für die Sauerstoff-Bestimmung erstellte Rechenpro-

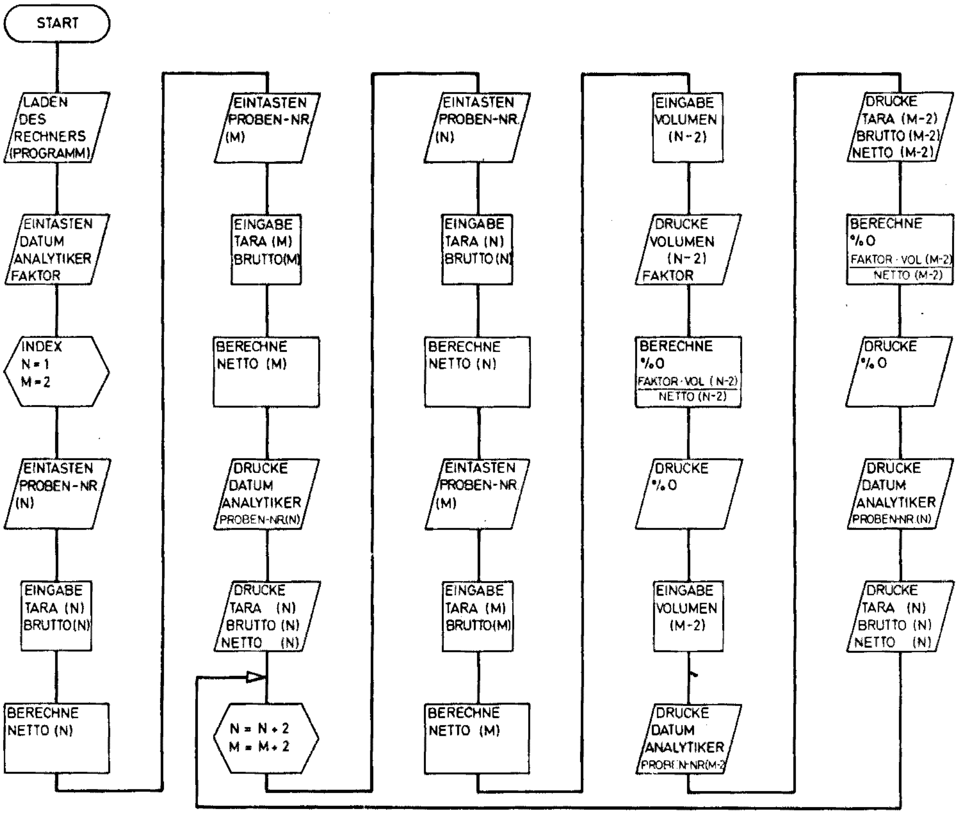
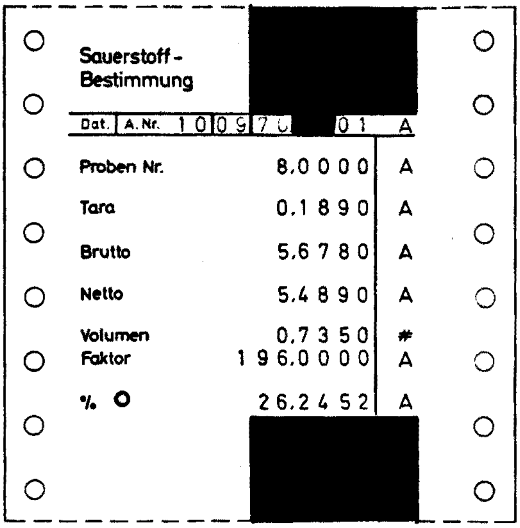


Abb. 2.

gramm wird manuell oder mittels eines Lochstreifenlesers (Dilektor) in den Rechner eingegeben. Zusätzlich werden Datum und Analytiker-Nummer sowie der Faktor der Titrierlösung als Konstanten gespeichert. Für die Einwaage wird die Proben-Nummer eingegeben, das Taragewicht des Schiffchens bzw. der Kapillare ermittelt und durch Druck der Taste an der Gattereinheit in der Rechenspeicher übertragen. Die Eingabe des Bruttogewichtes erfolgt entsprechend. Nach Eingabe der Nummer der nächsten Probe über die Tastatur des Rechners wird die zweite Einwaage ausgeführt, und die Werte werden ebenfalls gespeichert. Während die Substanzen 1 und 2 in den Einschleusgabeln der beiden Krackapparaturen luftfrei gespült werden, werden die Proben 3 und 4 eingewogen. Vor Eingabe der Nummer der 3. Probe wird durch Tastendruck der Maschine ein Sprungbefehl erteilt, wodurch das Programm in die Schleife, in den eigentlichen, sich stets wiederholenden Operationscyclus eintritt. Dieser Tastendruck ist nur einmal im Verlauf eines Arbeitstages auszuführen, wobei gleichzeitig Datum, Analytiker-Nummer sowie Proben-Nummer, Tara-, Brutto- und Netto-Gewicht der 1. Probe ausgedruckt werden. Um die beiden letzten Analysen eines Arbeitstages zu erhalten, werden zur Beendigung des Cyclus zwei Einwägevorgänge simuliert.

ANALYSENPROGRAMME

Bei Start 1 des Programmes werden die elektronischen Zähler der Bürettenwerte automatisch auf Null gestellt und gesperrt. Der weitere Vorgang ist mit dem beschriebenen[1] Vorbereitungsprogramm identisch. Mit dem Start des Analysenprogrammes wird die Sperre der elektronischen Bürettenzähler aufgehoben, und die Verbrennungsautomaten werden, wie beschrieben[1], in Gang gesetzt. Nach Ablauf der programmierbaren Spülzeit gibt das Zentralsteuerwerk dem Rechner den Befehl, das Volumen der ersten Bürette im Zähler abzufragen. Anschliessend erfolgen (Abb. 3) die Berechnung des Prozentgehaltes und Ausdruck auf einem Endlosformular. Nach Ausdrucken des Ergebnisses gibt das Interface dem Rechner den Befehl, 15 Leerzeilen zu drucken, wodurch das Endlosformular weitertransportiert und so das Analysenprotokoll entsprechend übersichtlich wird. Ein Papiervorschub ohne Ausdruck ist bei der Diehl-Rechenmaschine nicht möglich. Die Endlosformulare sind daher an dieser Stelle geschwärzt. Nach Weitertransport druckt der Rechner zeilenrichtig den Kopf des nächsten Formulares sowie die 2. Einwaage. Nach Abfragen des zweiten Bürettenwertes, was mit zeitlicher Verzögerung über das Leitwerk gesteuert wird, erfolgen die Berechnung der zweiten Analyse, Ausdruck des Ergebnisses, erneuter Leertransport und Ausdruck der folgenden Einwaage bis zur Nettozeile. Damit kann der nächste Zyklus gestartet werden.



Sauerstoff-Bestimmung

Dat. | A.Nr. 1 0 | 0 9 | 7 0 | 0 1 A

Proben Nr.	8,0000	A
Tara	0,1890	A
Brutto	5,6780	A
Netto	5,4890	A
Volumen	0,7350	#
Faktor	196,0000	A
% O	26,2452	A

Abb. 3.

Das genaue Zeitprogramm ist aus Abb. 4 zu ersehen. Die Gesamtanalysendauer für die Doppelanalyse beträgt je nach Wahl der variablen Zeitglieder 14–18 Min. Gegenüber der klassischen Zimmermann–Unterzaucher-Methode ergibt dies eine Steigerung der Analysenzahl von—im ungünstigsten Falle—100%. Bei leicht verkrackbaren Substanzen ist dieses Verhältnis noch besser.

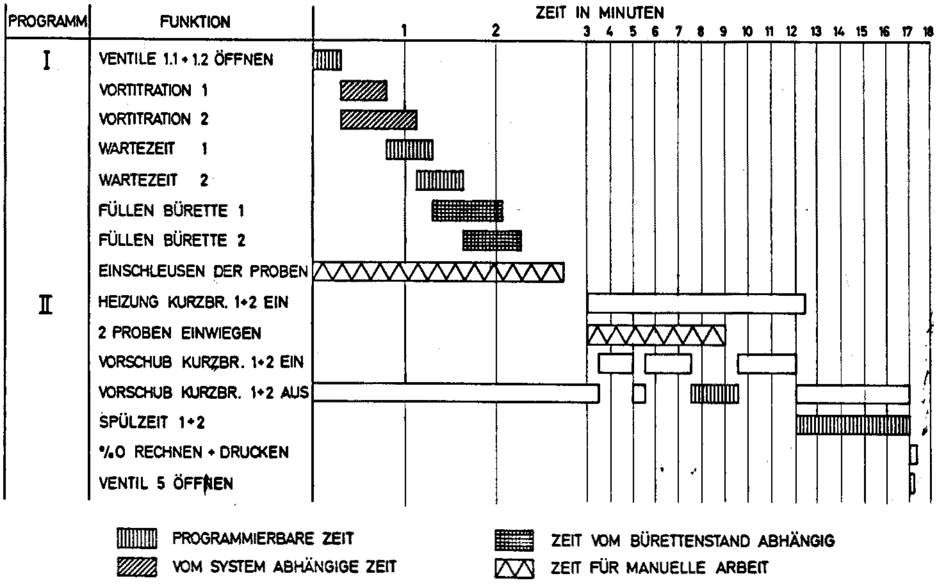


Abb. 4.

Im Routinebetrieb kann für diesen Fall mit 50 Analysen pro Automat und Arbeitstag gerechnet werden. Zur Erzielung eines optimalen Analysendurchsatzes empfiehlt sich eine individuelle Programmierung der Apparatur entsprechend den Krackeigenschaften der zu analysierenden Substanzen. Mögliche Fehler bei der Pyrolyse sind dadurch weitgehend ausgeschlossen, wodurch Sicherheit und Genauigkeit der Analysen wesentlich erhöht werden. Bei Verwendung eines solchen "Proben-Programmes" kann nun auch bei der Sauerstoff-Bestimmung angelerntes Personal in grösserem Umfange eingesetzt werden.

DISKUSSION

Für kleinere Laboratorien mit nur wenigen Apparaturen für die einzelnen Elemente ist die skizzierte "kleine" Lösung mit Kleinstrechnern sicherlich optimal. Überschreitet jedoch das Labor eine bestimmte Grösse, dann ist die Verwendung von Tischrechnern aus organisatorischen Gründen nicht mehr rationell. In diesem Falle wird ein grösserer Rechner rentabel, der den Probeneingang, die Registrierung und Erstellung von Arbeitslisten, das Zusammensuchen der Einzeldaten der Proben und die Analysenerledigung mitübernehmen könnte. Dieser Rechner sollte 8–16 K Kernspeicher haben. Ob er autark eingesetzt wird oder als Terminal zu einer grösseren EDV-Anlage fungiert, muss von Fall zu Fall entschieden werden. Letzteres hätte den Vorteil, dass genügend Speicher vorhanden sind, die über eine ausreichend lange Zeit belegt bleiben können. Den folgenden Anforderungen müssen beide Systeme genügen:

1. Sie müssen einen optimalen Organisationsablauf des Laborbetriebes gewährleisten, wozu gehören: Erfassung der Proben und Erstellung von Arbeitslisten; Identifizierung der Proben und Zuordnung der entsprechenden Messwerte; vorrangige

Ausgabe der berechneten Testwerte für jeden einzelnen Automaten; automatische Fehlermeldung bei unzulässigen Differenzen von Doppelbestimmungen und Überschreiten der 100%-Grenze bei Addition der Einzelkomponenten; eventuelle automatische Kontrolle aller notwendigen Parameter wie Druck, Temperatur, Strömungsgeschwindigkeit, etc.; Meldung bei zeitlicher Verzögerung der Eilanalysen.

2. Muss der Rechner den Besteller umfassend und schnell informieren. Dies geschieht durch: Erstellung von Ausgabelisten bzw. direkte Übermittlung der Analysendaten über Fernschreiber; Errechnung der Summenformel und automatische Qualitätskontrolle bestimmter Substanzen.

3. Muss der Rechner alle verwaltungstechnischen Arbeiten übernehmen. Er muss die Abrechnung der Analysen vornehmen und die Besteller entsprechend belasten sowie jede gewünschte Statistik liefern.

Eine solche Universallösung stellen wir uns als Endstufe vor. Dass diese Entwicklung Zeit braucht, steht ausser Diskussion. Sie wird aber notwendig sein.

Herrn Kranz sei auch an dieser Stelle für wertvolle Unterstützung bei allen Rechenproblemen gedankt.

ZUSAMMENFASSUNG

Es wird über einen Vollautomaten zur Sauerstoff-Bestimmung in organischen Substanzen berichtet. Eine hohe Analysenzahl wird durch elektronisch gesteuerten Parallelbetrieb von 2 Krackapparaturen und 2 Automaten zur Titration der gebildeten Kohlensäure unter Integration eines Tischrechners und einer Elektrowaage in das System erreicht. Der gesamte Analysencyclus einschliesslich der logischen Verknüpfung von Proben-Nummern, der Volumina sowie der auf Tastendruck selbsttätig übertragenen Gewichte läuft automatisch ab. Das Ergebnis wird auf einem Endlosformular ausgedruckt. Die Anzahl von Fehlanalysen wird durch individuelle Programmierung der Apparatur entsprechend den Krackeigenschaften der Substanzen auf ein Minimum herabgesetzt.

SUMMARY

A completely automated method for the determination of oxygen in organic compounds is described. Parallel operation of two pyrolysis apparatus and two automatic titrators, with inclusion of a print-out desk calculator and an electrobalance, is electronically controlled, so that the total cycle, including the print-out of sample number, volume and sample weight, proceeds automatically. A single analysis requires 14–18 min, and the number of erroneous determinations is kept to a minimum by individual programming of the apparatus according to the pyrolysis properties of the compounds.

RÉSUMÉ

Une méthode entièrement automatique est décrite pour le dosage de l'oxygène dans des composés organiques. Deux appareils de pyrolyse et deux titreurs automatiques, avec pupitre calculateur imprimant et électrobalance sont contrôlés électro-

niquement; le cycle total comprenant impression du numéro de l'échantillon, du volume et du poids, s'effectue automatiquement. Une analyse se fait en 14 à 18 min; le nombre d'erreurs est réduit au minimum par programmation individuelle de l'appareil, suivant les propriétés pyrolytiques des composés.

LITERATUR

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

A comparative study of turbulent, premixed and separated flames in atomic fluorescence analyses, with reference to the determination of zinc

Atomic fluorescence has been thoroughly established as an analytical method since the first communication was published by Winefordner and Vickers[1] in 1964. Detailed discussions of the theory and investigations of the parameters involved can be found in the works of Winefordner *et al.*[2-5], Jenkins[6] and West *et al.*[7,8]. In experimental work the accent has been placed on excitation sources, means of atomizing and various flame types.

Turbulent and premixed flames have been applied to a wide range of elements. Omenetto and Rossi[9], Klaus[10] and Winefordner and Staab[2] successfully used turbulent total consumption burners for the determination of Zn, Cd, Hg, Fe, Mg, Cu, etc. The use of premixed laminar burners, separated and unseparated has been described by West[7,11,12] for the elements Cd, Zn, Hg and Tl. In a recent paper, Cresser and West[13] examined the effect of flame composition and burner type on the interferences and sensitivity of zinc determinations.

The aim of this communication is to present a comparison of turbulent, premixed and separated flames in fluorescence work and to point out some important flame parameters affecting detection limits. The effects of disturbing elements on the detection limits were not investigated.

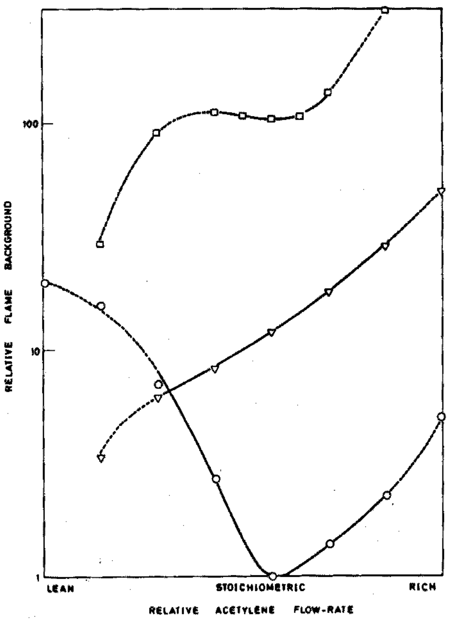
Experimental

The experimental arrangement employed for this study was similar to that described by Winefordner and Vickers[1]. The source was placed at right angles to the monochromator. No lenses were used and the slits of the monochromator and source were mounted as near as possible to the flame.

The fluorescence signal produced in any one of the flames was evaluated by using zinc as analytical element. Zinc was chosen because of the availability of high-intensity sources, and its large absorption cross-section for resonance radiation. A Philips zinc vapour discharge lamp, operated from the mains, was used. The highest fluorescence yield was obtained at a current of 0.7 A.

The apparatus further consisted of a Zeiss PMQ II monochromator with a selected 931 A photomultiplier as detector. The multiplier current was digitized and the results printed.

Turbulent flames were produced by using a Zeiss total-consumption nebulizer burner. Premixed laminar flames were produced by means of a standard Varian Techtron nebulizing chamber combined with a circular thermal-emission burner head. A similar nebulizing chamber was attached to a separated flame burner head built in our workshop according to the description given by West *et al.*[12]. Argon was used to effect separation. The latter two flames were operated with acetylene as fuel and air as oxidant, but in the Zeiss burner pure oxygen was used as oxidant. The argon as well as the oxidant and fuel gases were monitored by pressure gauges and rotameters.



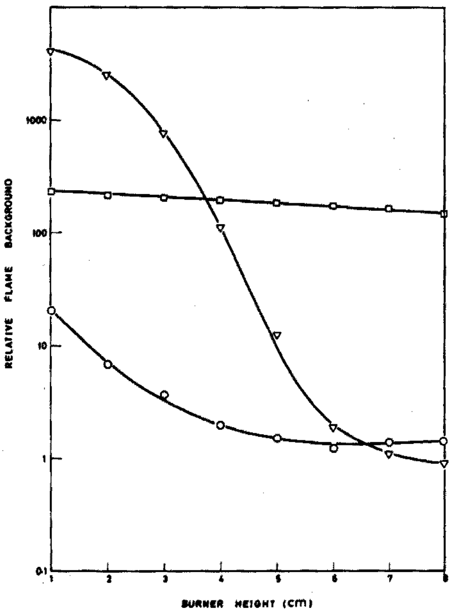
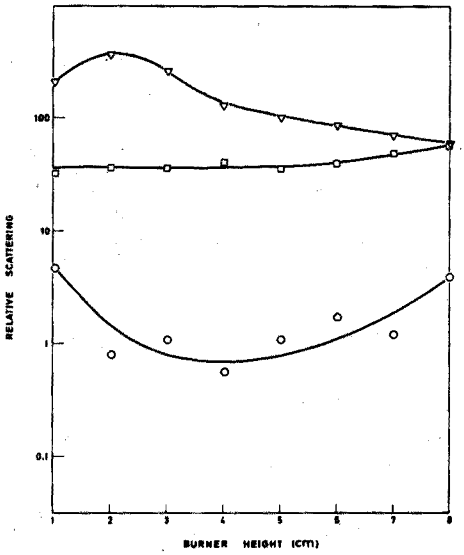


Fig. 1. Flame background *vs.* acetylene flow-rate. Burner height 5 cm, wavelength 213.9 nm and bandwidth 3.7 nm. The dotted lines indicate regions of instability. (○) Separated flame; (▽) turbulent flame; (□) premixed flame.

Fig. 2. Flame background *vs.* burner height. Stoichiometric gas mixtures, wavelength 213.9 nm and bandwidth 3.7 nm. Symbols as in Fig. 1.



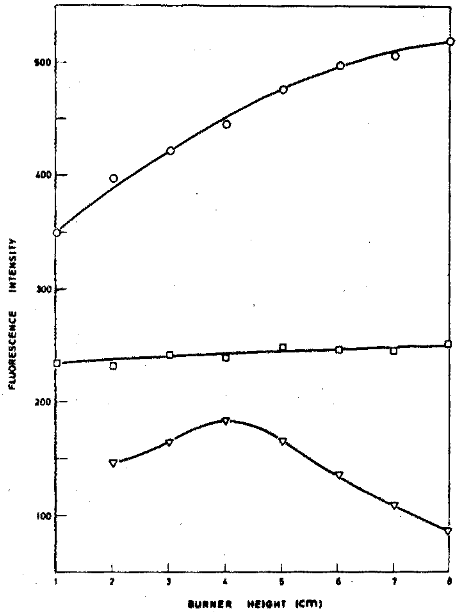


Fig. 3. Scattering *vs.* burner height. Stoichiometric gas mixtures, 213.9 nm and bandwidth 3.7 nm. Deionized water nebulized into the flame. Symbols as in Fig. 1.

Fig. 4. Fluorescence *vs.* burner height for a 1-p.p.m. zinc solution. 213.9 nm, stoichiometric gas mixtures and bandwidth 3.7 nm. Symbols as in Fig. 1.

Standards were prepared by dissolving Specpure zinc oxide (Johnson, Matthey and Co.) in as little hydrochloric acid as possible. A stock solution of 1000 p.p.m. was prepared, and further dilutions were made to give standards ranging from 1000 p.p.m. down to 0.0001 p.p.m. Zn.

For each set of parameters, ten successive readings were taken. The average, standard deviation and percentage standard deviation of each set were then calculated. These results formed the base for comparing the properties of the different flames.

The flames were adjusted to give minimum flame background and maximum stability. It was found that optimum conditions were obtained when an approximately stoichiometric gas mixture was used. Deviation from this condition resulted in a loss of fluorescence as well as instability of the flame, as is shown in Fig. 1.

In this study, burner height implies the distance between the top of the luminous primary zone and the middle of the monochromator slit. Flame background was measured by positioning the burner in front of the slit, without nebulizing any matrix. A decrease of 30–60% in background was encountered when deionized water was nebulized into the flame. Scattering was measured with the light source in its proper position and the appropriate burning conditions while deionized water was nebulized into the flame.

Results and discussion

Flame background. The flame backgrounds emitted by the three flames were measured against burner height and wavelength. The results for the first mentioned are given in Fig. 2, which shows that the turbulent and separated flames exhibit distinct zones of low flame background between 5 and 8 cm burner height. Flame background tends to grow excessive below a burner height of 5 cm in both cases. The premixed flame has a high flame background at all usable burner heights. It is thus possible to select regions of minimum flame background for the turbulent and separated flames. This is not the case for the premixed flame.

Flame background against wavelength was measured at various burner heights. All three flames show similar characteristics at all usable burner heights, namely peaks in the region of the OH-bands, and a steadily increasing general background from 200.0 to 300.0 nm. The background flattens out from *ca.* 330.0 nm except in the case of the turbulent burner where a slight increase is evident from 400.0 to 500.0 nm. For all wavelengths, the flame backgrounds for the premixed, turbulent and separated flames are in the approximate ratio 100 : 10 : 1, respectively, for equal fluorescence signals derived from a 1-p.p.m. zinc solution.

No emission of the zinc resonance line 213.9 nm was observed in any of the flames even when a solution of 1000 p.p.m. zinc was nebulized.

Scattering. Flame cells of varying refractive indices give rise to scattering of the primary excitation beam. The scattering characteristics of the various flames are shown in Fig. 3. The premixed burner displays a fair amount of scattering with a slight increase at large burner heights. This is due to the loss of laminar flow, which thus causes more scattering. The effect of turbulency is clearly illustrated in the turbulent flame, with its pronounced scattering. Direct nebulization into the latter flame, without any selection of droplet sizes, causes further variation of refractive index, and thus increased scattering. With the separated flame scattering is considerably less and showed some increase below the reaction zone as well as higher in the flame.

Fluorescence. The fluorescence intensities obtained for the various flames at the resonance wavelength for zinc, using a 1-p.p.m. solution, for various burner heights, are shown in Fig. 4. These measurements were made with a slit width of 2 mm, which represented a spectral bandwidth of 3.7 nm. The fluorescence proved to be fairly constant over a wide range of burner heights. The superiority of the separated flame is clearly illustrated in Fig. 4.

Working curves and detection limits

Working curves for the various flames obtained for zinc are given in Fig. 5. The working curve of the separated flame displays linearity over a slightly wider concentration range than the other two.

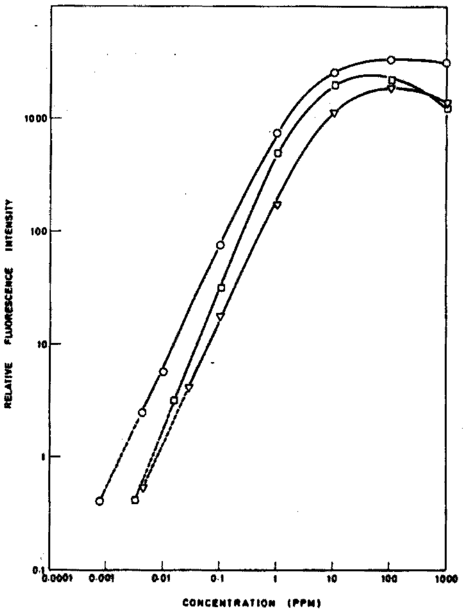


Fig. 5. Working curve plots for the Zn 213.9-nm line. Stoichiometric gas mixtures, 5-cm burner height and bandwidth 3.7 nm. (○) Separated flame; (∇) turbulent flame; (□) premixed flame.

TABLE I

DETECTION LIMITS AND LIMITS OF DETECTABILITY FOR ZINC ATOMIC FLUORESCENCE

Flame	*Limit of detectability (p.p.m.)*	*Detection limit (p.p.m.)*
Separated	$4.2 \cdot 10^{-3}$	$7.9 \cdot 10^{-4}$
Premixed	$1.6 \cdot 10^{-2}$	$3.2 \cdot 10^{-3}$
Turbulent	$2.8 \cdot 10^{-2}$	$4.6 \cdot 10^{-3}$

Detection limits were determined according to the criteria laid down by Winefordner and Staab[2]. The limits of detectability were determined as the signal which could be detected with a 99.5% confidence level and a coefficient of variance of 5%. These results are given in Table I.

Conclusion

The separated flame produces an interconal zone with very low and highly stable radiative background. This advantage follows from the fact that the flame is sealed off from the surrounding atmosphere. The elimination of high background noise thus achieved makes possible very low detection limits with this flame. The premixed flame with its noisy background is clearly not advisable in atomic fluorescence determinations at very low concentrations. The turbulent flame with oxy–acetylene is superior to the premixed flame, as far as strength of fluorescence signal is concerned, but has a large noisy scattering component which adversely affects low detection limits.

The fact that the separated flame can be used with a great variety of gas mixtures, should make it applicable to the analysis of a wide range of elements by atomic fluorescence spectrometry.

The authors wish to thank the South African Council for Scientific and Industrial Research for a grant in aid of this research. They also wish to thank Mr. T. Monaci for constructing the separated flame burner and auxiliary apparatus.

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(Received 14th September 1970)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

An automatic method for the determination of hydrogen sulphide in natural waters

The most sensitive method for the determination of hydrogen sulphide is based on the reaction of N-1-dimethyl-*p*-phenylenediamine with hydrogen sulphide in the presence of iron(III) to form methylene blue[1]. A modified procedure has been applied to sea water by Fonselius[2], and the method has also been used for the determination of hydrogen sulphide in gases[3,4]. The formation of methylene blue is specific for hydrogen sulphide and has advantages over the usual iodimetric titration methods, which are time-consuming and not very sensitive, as well as inselective unless prior separation of metal sulphide is used. The methylene blue method is now applied as a standard procedure for the determination of hydrogen sulphide in sea water.

However, the methylene blue method is far too sensitive to be applied without modification for the entire range of concentration expected (0–500 μg at. H_2S–S per l). Previous experiments showed that Beer's law is only obeyed up to about 60 μg at. H_2S–S per l for the direct determination. Increasing the amount of reagents did not improve the linear range, hence a technique was developed which allowed dilution of the sample before the formation of the methylene blue without any loss of the sulphide by evaporation or oxidation. This could be done by immediate stabilization of the sampled sulphide as zinc or cadmium sulphide which was then kept in colloidal solution with gelatine. The analysis could then be continued either directly, or after proper dilution if the concentration exceeded 50 μg at. H_2S–S per l, *i.e.* if the absorbance exceeded 0.8 in a 1-cm cuvette. The initial formation of colloidal metal sulphide opened a way for the automation of the dye formation and the photometric determination by means of the Auto Analyzer technique.

Experimental

Sampling technique. The water sample for the determination of the hydrogen sulphide is taken with the same precautions as for the determination of oxygen[5]; 50–60-ml glass bottles with glass stoppers are sufficient. The neck of the bottle and the stopper should be shaped so that no air bubbles are trapped after stoppering. Immediately after the sampling (before stoppering), 1 ml of the zinc or cadmium chloride–gelatine solution is added to the bottom of the sample with a syringe. The bottle is then stoppered, after the water in the bottle neck has been replaced without trapping air, and shaken for about 30 sec. Stored in the dark, the colloid is stable for at least 24 h. In saline waters cadmium sulphide remains colloidal longer, whereas zinc sulphide tends to coagulate and precipitate. (Other colloid protectants may improve the stability of the colloidal sulphide.) The samples are then inserted into the Technicon sampler and diluted automatically to the proper concentration range.

Equipment. The Technicon AutoAnalyzer consists of the following modules: a sampler II, proportioning pumps with manifolds as shown in Fig. 1, colorimeter with a 660-nm filter and a 50-mm flow cell; a recorder and a range expander. The sample cycle is set at the rate of 20 per h.

Reagents. For the N-1-dimethyl-*p*-phenylenediamine dihydrochloride solution, dissolve 1 g of reagent in 500 ml of 6 *M* hydrochloric acid. Dilute 10 ml of the prepared stock solution to 120 ml with distilled water.

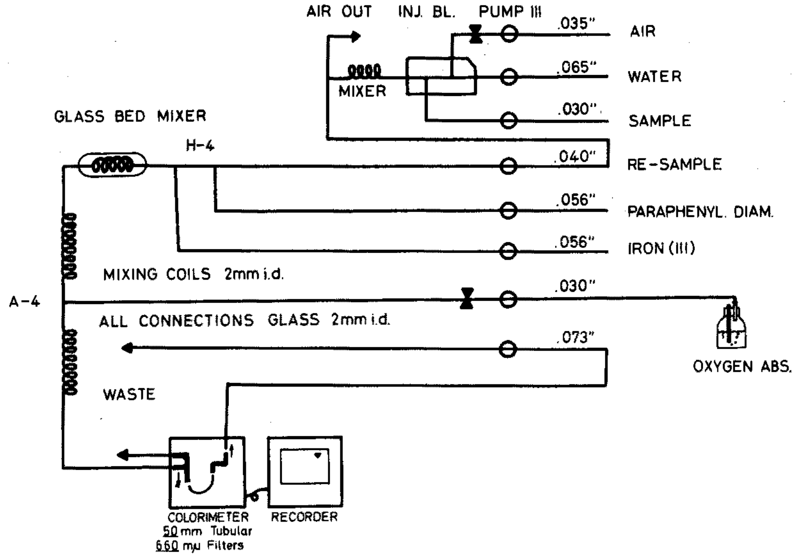

Fig. 1. Flow diagram of the hydrogen sulphide manifold.

For the iron(III) solution, dissolve 8 g of iron(III) chloride in 500 ml of 6 M hydrochloric acid. Dilute 10 ml of the stock solution to 120 ml with distilled water.

For the stabilizer solution, dissolve 7 g of zinc chloride in 400 ml of water, add 50 ml of 1% (w/v) gelatine solution and dilute to 500 ml.

Standard solution. Dissolve *ca.* 1 g of sodium sulphide nonahydrate (4 mg at. S^{2-}–S) in 100 ml of deoxygenated water (by boiling or by stripping with nitrogen). Use only large transparent crystals which have been washed with water and dried with filter paper. Transfer 10 ml of this solution to 1 l of a deoxygenated solution containing 0.2 g of zinc chloride and 2 g of gelatine. Stored in a brown glass bottle, this solution is stable for about 14 days.

To standardize the solution, pipette 50 ml into a 25-ml Erlenmeyer flask, and add 10 ml of a standard 0.0100 N potassium iodate solution and *ca.* 100 mg of potassium iodide. After dissolution, add 2 ml of 1 M sulphuric acid and, after 5 min, titrate the liberated iodine with standard 0.02 N thiosulphate solution. Carry out a blank titration on 100 ml of distilled water instead of the sulphide solution. Calculate the content of the sulphide solution from

$$\text{ml } S_2O_3^{2-}\cdot N\cdot 10^4 = C_{H_2S}\ (\mu\text{g at. } H_2S\text{–S } l^{-1})$$

(N = normality of the thiosulphate solution).

Pipette appropriate amounts of this diluted standard into 100-ml volumetric flasks and dilute to the mark with deoxygenated water (Fig. 2).

Results and discussion

The manifold. A modification of the AutoAnalyzer technique which normally involves immediate segmentation of the sample stream, must be applied for the determination of hydrogen sulphide. When the strongly acidic reagents are added, the colloidal metal sulphide is dissolved and the hydrogen sulphide tension in the liquid phase increases to very high values. If a gas phase were present (air segments), the hydrogen sulphide would tend to escape into the gas phase until equilibrium was reached. On the other hand, the concentration of the hydrogen sulphide in the liquid phase is diminished (to almost zero) by the formation of the methylene blue. The rate of the dye formation would then be controlled by the very slow re-entry of the hydrogen sulphide from the gas phase into the acid liquid phase. Accordingly, the sample stream is best segmented first when the methylene blue formation is nearly complete and there is almost no free hydrogen sulphide in the liquid phase.

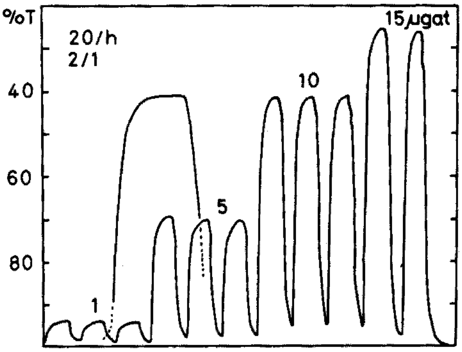

Fig. 2. Calibration record and steady state record for the concentration range 0–15 μg at. H_2S–S l^{-1}.

TABLE 1

LINEAR RANGES OF CALIBRATION CURVES WITH DIFFERENT TUBE SIZES

Sample tube (in.)	0.030	0.030	0.030	0.030
Dilution tube (in.)	0.081	0.100	0.100	0.100
Resample tube (in.)	—	0.081	0.030	0.040
Linear range (μg at. H_2S–S l^{-1})	0–50	0–100	0–200	0–300
Approximate absorbance at top of range	0.250	0.320	0.350	0.500

Beer's law. In the manual method, deviation from Beer's law at high concentration of hydrogen sulphide is observed. Similar results were also found when samples containing more than 30 μg at. H_2S–S l^{-1} were automatically analyzed without dilution. However, with a simple automatic dilution technique, as adopted in the present manifold, a linear calibration curve in the range of 0–300 μg at. H_2S–S l^{-1} can be achieved. With different combinations of tubing sizes, the manifold can be modified for any specific range required. Typical examples are shown in Table I.

Effect of acidity and temperature. The formation of methylene blue depends both on the temperature of the reaction and the acidity of the reagents. The reaction is faster at higher temperature and acidity, but the possibility of hydrogen sulphide escaping from the acid solution into the vapor phase before reacting increases and the reproducibility of the results is poor. Tests showed that the absorbance of the methylene blue solution was essentially constant when the acidity lay in the range 0.4–1 *M*. The results showed that the acidity of the reagent employed would give maximum color development without loss of hydrogen sulphide during the reaction.

Accuracy of the method. Replicate analyses of sea water samples containing sulphide of concentration of 1 μg at. H_2S–S per l with a 2 × range expander were done; the coefficient of variation of the results is ±0.8%. The sensitivity is 0.2 μg at. H_2S–S per l.

It seems possible with this method to collect water samples, stabilize the hydrogen sulphide and analyze the sulphide in a central laboratory.

We wish to express our sincere thanks to the Technicon Corporation for providing an AutoAnalyzer unit, and to the National Science Foundation and to the German Research Association (Grant Gr320/1) for financial support (Grant GA 1261).

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(Received 1st October 1970)

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Identification of impurities in crude TNT by tandem GC–MS technique

Analysis of the impurities in crude TNT has been a major concern in explosive laboratories. Several procedures have been developed to determine nitroaromatic impurities by using thin-layer chromatography[1], infrared spectroscopy[2], nuclear magnetic resonance[3], and gas chromatography[4,5]. Among these procedures, the gas chromatographic method is by far the most efficient and quantitatively accurate. However, a major limitation of gas chromatography is that positive identification is lacking; the presence of some unexpected impurities often jeopardizes the analysis. Since crude TNT is usually a highly complex mixture, it would be desirable if these GC-separated components could be identified with a mass spectrometer. The tandem GC–MS technique is now a widely used technique in many laboratories[6,7]. We have employed this technique to establish a more reliable GC method for the analysis of crude TNT by positively identifying each separated component with a high-resolution mass spectrometer.

Apparatus

A Consolidated Electrodynamics Corp. Model 21-110B high-resolution mass spectrometer was used. The mass spectra were recorded on photoplates and then processed via a real time–time-shared computer–comparator system[8].

The gas chromatograph was a Model 881 (Perkin Elmer Corp.) with a flame ionization detector. A 10′ × 3/16″ 15% SE30 column was used. Helium was the carrier gas and the flow rate was maintained at 60 cm^3 min^{-1}. The inlet temperature was 220°. The column temperature was maintained either isothermally at 180° or was programmed from 150° to 200° with a heating rate of 4° min^{-1}.

The gas chromatograph was connected to the mass spectrometer via a Biemann-Watson molecular separator[9]. A needle valve was placed between the gas chromatograph and the molecular separator to split *ca.* 50% of the GC effluent into the molecular separator. Another needle valve was placed between the molecular separator and the mass spectrometer to adjust the amount of sample introduced into the mass spectrometer. The ion source pressure was controlled at *ca.* $8–10 \cdot 10^{-6}$ mm Hg during the GC–MS operation. The temperature of the molecular separator, needle valves, and connection lines (Pyrex glass) was maintained at *ca.* 250°.

Reagents

The sources of crude TNT samples were military-grade TNT, extract from military-grade Composition B pellet, and Eastman Kodak Corp.

The impurities in the crude TNT were concentrated by fractional crystallization from ethanol and benzene. About 90% of the 2,4,6-trinitrotoluene was removed from each sample before the GC–MS investigation.

Results and discussion

Figure 1 shows a gas chromatogram of a crude TNT sample (>90% of 2,4,6-TNT removed). This chromatogram was obtained by programming the column temperature as described above. An excellent separation was obtained under these

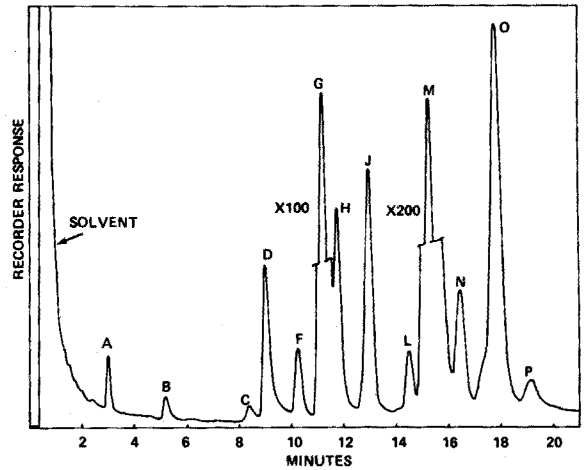

Fig. 1. A typical chromatogram. $T_i = 220°$; $T_d = 210°$; $T_c = 150°–200°$ (programmed). Sensitivity, ×20; sample size, 2 µl 5% solution.

column conditions, which were also used for the acquisition of mass spectra in this work. The major peaks are designated alphabetically according to their elution order. Sixteen components from crude TNT samples were identified; Table I lists the name of the peak designated, its relative retention time, the exact mass of molecular ion determined by mass spectrometer, the most likely elemental composition found by computer, deviation of the theoretical mass of this elemental composition from the observed mass expressed in milli-mass units, and the compound identified. In case of 2,4,6-trinitroxylene, because no molecular ion was observed, the highest fragment ion is listed in Table I. The relative retention time of a peak is based on the retention time obtained at a column temperature maintained isothermally at 180° and then normalized against the retention time of 2,3,4-trinitrotoluene. The 2,3,4-trinitrotoluene is used because of its long retention time and its lack of interference from other peaks. Since the major objective of this work is the identification of impurities rather than the analysis of samples, the quantitative aspect of the identified components will not be discussed in this paper.

Based on the elemental composition of the molecular ion of unknown peaks, peaks *C* and *D* can be recognized as dinitrobenzenes, peaks *E*, *F*, *G*, *H*, and *I* as dinitrotoluenes, peak *L* as trinitrobenzene, and peaks *M*, *O*, and *P* as trinitrotoluenes. After a further comparison of the MS fragmentation pattern and GC retention time of these peaks with those of pure materials, peaks *C–I*, *L*, *M*, *O*, and *P* were identified as shown in Table I.

TABLE I

COMPONENTS IDENTIFIED FROM CRUDE TNT SAMPLES

GC peak	*Relative retention time*	*Molecular ion found*	*Elemental composition*	*Deviation*[a]	*Identified as*
A	0.07	98.0751	$C_6H_{10}O$	1.9	Cyclohexanone
B	0.14	135.0128	C_7H_5NS	−1.4	Benzothiazole
C	0.24	168.0160	$C_6H_4N_2O_4$	−1.1	*p*-Dinitrobenzene
D	0.27	168.0142	$C_6H_4N_2O_4$	−2.9	*m*-Dinitrobenzene
E	0.28	182.0322	$C_7H_6N_2O_4$	−0.6	2,6-Dinitrotoluene
F	0.32	182.0348	$C_7H_6N_2O_4$	2.0	2,5-Dinitrotoluene
G	0.37	182.0338	$C_7H_6N_2O_4$	1.0	2,4-Dinitrotoluene
H	0.40	182.0310	$C_7H_6N_2O_4$	−1.8	2,3-Dinitrotoluene
I	0.45	182.0330	$C_7H_6N_2O_4$	0.2	3,4-Dinitrotoluene
J	0.48	222.0886	$C_{12}H_{14}O_4$	−0.6	Diethylphthalate
K	0.54	173.0463	$C_{10}H_7NO_2$	−1.4	α-Nitronaphthalene
L	0.59	213.0035	$C_6H_3N_3O_6$	1.4	1,3,5-Trinitrobenzene
M	0.66	227.0163[b]	$C_7H_5N_3O_6$	−1.5	2,4,6-Trinitrotoluene
N	0.77	224.0281[c]	$C_8H_6N_3O_5$	−2.6	2,4,6-Trinitroxylene
O	0.88	227.0177	$C_7H_5N_3O_6$	−0.1	2,4,5-Trinitrotoluene
P	1.00	227.0175	$C_7H_5N_3O_6$	−0.3	2,3,4-Trinitrotoluene

[a] Deviation = (theoretical mass − mass found) · 1000 given in milli-mass units.

[b] Molecular ion is observed only from intensely exposed spectrum. Otherwise, the highest mass is 210.0151 ($C_7H_4N_3O_5$), which is $(M-OH)^+$.

[c] The highest fragment ion.

It is known that the mass spectra of nitrotoluenes are strongly influenced by the position of functional groups[10]. For instance, *o*-nitrotoluene has a rather weak molecular ion but shows a very intense $(M-OH)^+$ ion. On the other hand, *m*-nitrotoluene and *p*-nitrotoluene have strong molecular ion and lose an O, NO, or NO_2 radical instead of an OH radical. These fragmentation rules can be used as simple criteria to determine the presence of a nitro group at the *ortho* position. The highest fragment ion observed from peak *N* was *m/e* 224.0281 ($C_8H_6N_3O_5$), which undoubtedly is a $(M-OH)^+$ fragment ion. This peak was identified as 2,4,6-trinitroxylene.

Peaks *A*, *B*, *J*, and *K* are neither nitrobenzenes nor nitrotoluenes. The GC–MS combination is especially useful in the identification of these peaks. After a peak has been identified by the mass spectrometer, this structure can be reconfirmed by the GC retention time of pure material. Peak *A* is cyclohexanone, which is most likely a contaminant in solvents used. Peak *B* was observed in many crude TNT samples, and was identified as benzothiazole. Peak *J* was identified as diethylphthalate, which probably was used as a plasticizer. Peak *K* was found in the Composition B pellet, and was identified as α-nitronaphthalene.

In conclusion, the GC–MS technique has allowed a reliable GC analytical method to be established for determining impurities in crude TNT. Although this technique is not necessary for routine analysis, it certainly should be extensively employed whenever the identity of a GC peak is questioned.

The author acknowledges the invaluable assistance of F. C. Rauch and members of his laboratory for furnishing crude TNT samples. This work was supported by Picatinny Arsenal, U.S. Army Munitions Command.

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(Received 10th September 1970)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

Microgasometric determination of nitrate by reduction with sulphamic acid

Stoichiometric reduction of the nitrate group is difficult owing to the various oxidation states of nitrogen; depending on the reducing agent and conditions, NO_2, NO, N_2O, N_2 and NH_3 can be formed[1]. Microgasometric determinations of nitrate as nitric oxide by reduction with mercury, iodine, iron(II), titanium(III), iodide ion, and hydroquinone[2,3], and as nitrous oxide by reduction with urea[4] or formic acid[5], have been proposed. Reduction with sulphamic acid to nitrous oxide is also possible. The simple procedure is described in this communication.

Apparatus and chemicals

The reaction vessel (10 × 2 cm) is provided with a small glass funnel and two side-arms, one of which is connected through a bubbler to a Dewar flask containing solid carbon dioxide, and the other to a conventional 1.5-ml micronitrometer containing 50% (w/v) potassium hydroxide[4].

Unless otherwise specified, all the chemicals were of analytical grade. The purity of all the nitrate samples (not less than 99.5%) was confirmed by the standard nitrometer method[6].

Procedure

Introduce 3–5 mg of the nitrate sample into the reaction vessel, and add 10–20 mg of sulphamic acid. Displace the air with carbon dioxide for about 5 min until no air bubbles are collected in the nitrometer. Introduce about 5 ml of concentrated hydrochloric acid through the small funnel. Gently heat the reaction mixture for 5 min with a microburner. Sweep the gaseous products into the nitrometer by passing carbon dioxide for 5 min at a rate of 100 bubbles $\min^{-1}$. After a further 5 min, record the volume of the gas liberated. Carry out a blank experiment under identical conditions.

Calculate the nitrogen content from the equation:

$$\% \text{ nitrogen} = 17.08\,(V_1 - V)(P - p)/(273 + T)\,W$$

where V_1 ml is the volume measured, V ml is the blank, P mbar is the atmospheric pressure, p mbar is the vapour pressure of the potassium hydroxide solution at $T°$, and W mg is the sample weight.

Results

The results of the determination of some nitrate samples by reduction with sulphamic acid are given in Table I. With the organic nitrates, the average absolute error was ±0.07% and the mean recovery 99.71%; for inorganic nitrates, the corresponding figures were ±0.10% and 99.01%.

Nature of the reaction

Sulphamic acid quantitatively reduces the nitrate function to nitrous oxide; one mole of the gas is liberated per mole of the nitrate group indicating that the sulphonamide–nitrogen is involved in the reduction process. Reduction of potassium nitrate, in strong acid media, showed that at least an equivalent amount of sulphamic acid is required for quantitative reaction. The reaction can be represented by the equation:

$$HSO_3NH_2 + KNO_3 + HCl \rightarrow H_2SO_4 + N_2O + KCl + H_2O$$

The gaseous reduction product was shown to be pure nitrous oxide; it was recovered quantitatively after passing through a trap containing manganese dioxide or a saturated solution of iron(II) sulphate, and it liberated iodine when passed through hydriodic acid solution. Formation of sulphuric acid was proved by qualitative tests[7].

TABLE I

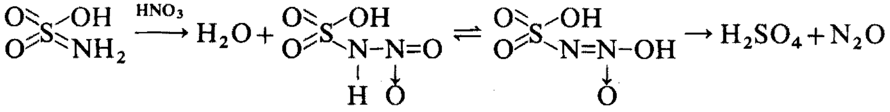
MICROGASOMETRIC DETERMINATION OF SOME NITRATE SAMPLES BY REDUCTION WITH SULPHAMIC ACID

Sample	*Nitrate-nitrogen (%)*		*Recovery (%)*
	Calculated	*Found*	
Urea nitrate[a]	11.38	11.27 11.41	99.03 100.26
Guanidine nitrate[a]	11.47	11.40 11.33	99.39 98.78
Nitron nitrate[a]	3.73	3.69 3.80	98.93 101.88
Potassium nitrate	13.85	13.83 13.71	99.86 98.99
Silver nitrate	8.24	8.28 8.11	100.49 98.42
Barium nitrate	10.71	10.64 10.59	99.35 98.88
Cadmium nitrate tetrahydrate[b]	9.08	8.98 9.00	98.90 99.12
Bismuth nitrate pentahydrate[b]	8.66	8.49 8.52	98.04 98.38
Lanthanum nitrate hexahydrate[b]	9.70	9.60 9.58	98.97 98.76

[a] Prepared by standard method.
[b] Purified by several recrystallizations.

The reaction does not proceed through the formation of ammonium nitrate; the amount of the (NH_2-containing) basic form of sulphamic acid is not sufficient to permit the production of ammonium salt by hydrolysis[8].

The reduction of the nitrate group with sulphamic acid most probably proceeds through nitration of the sulphonamide–nitrogen to give a nitramine group which decomposes to nitrous oxide:



$$\mathrm{O_2S(OH)NH_2} \xrightarrow{\mathrm{HNO_3}} \mathrm{H_2O} + \mathrm{O_2S(OH)}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\underset{\mathrm{O}}{\underset{\downarrow}{\mathrm{N}}}=\mathrm{O} \rightleftharpoons \mathrm{O_2S(OH)N}=\underset{\mathrm{O}}{\underset{\downarrow}{\mathrm{N}}}-\mathrm{OH} \rightarrow \mathrm{H_2SO_4} + \mathrm{N_2O}$$

This scheme is supported by the quantitative liberation of nitrous oxide from α-aminocarboxylic acids on treatment with nitric acid[9], and by the fact that the nitramine group quantitatively loses nitrous oxide on treatment with strong acids through the tautomeric form N-nitronic acid[10].

Reaction medium

Reduction of potassium nitrate with sulphamic acid in acetic, sulphuric, and hydrochloric acid media was studied to determine the most suitable medium. In glacial acetic acid no reduction occurred; concentrated sulphuric acid was suitable for inorganic samples, but not for organic samples. Hydrochloric acid was suitable for both organic and inorganic nitrate samples, reduction being complete within 5 min. In general, as the acid concentration decreased the rate of reduction decreased.

Interferences

Some organic compounds containing different types of nitrogen-containing groups were subjected to the procedure. Nitro (*m*-dinitrobenzene), hydrazo (hydrazobenzene), amine (*p*-aminoacetophenone), oxime (α-benzoinoxime), amide (oxamide) and hydrazine (phenylhydrazine hydrochloride) compounds showed no reaction

Inorganic oxidants, such as potassium dichromate, potassium iodate, ammonium metavanadate, iron(III), copper(II), and chromium(III) ions, gave no gaseous products with sulphamic acid, but potassium permanganate, cerium(IV), and mercury(II) oxidised sulphamic acid to nitrogen.

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(Received 13th July 1970)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A sealed glass ampoule for use with a commercial differential scanning calorimeter

Since the introduction of the first commercial differential scanning calorimeter[1], the Perkin-Elmer model DSC-1, and later DSC-1B, many successful attempts have been made to extend the application of this instrument[2-4]. The thermal analysis of high vapour pressure solids and liquids was made possible with the introduction of volatile sample pans[5]. However, these volatile sample pans still have certain limitations. The pans are only capable of withstanding an internal pressure of about 30 to 40 p.s.i. after sealing and, further, the use of aluminum for the manufacture of the pan limits its use to non-corrosive liquids and solids. The introduction of gold pans has helped to minimise the limitations but only at a considerable increase in capital expenditure. A capillary tube sample holder for differential scanning calorimetry has been reported[6] which enables thermal analysis studies to be made on corrosive substances. This paper describes the design and manufacture of a sealed glass ampoule which can be used with the Perkin-Elmer model DSC-1 and DSC-1B. Results are included which indicate that quantitative measurements can be made with the glass ampoules at high internal pressures and with highly corrosive compounds.

Ampoule design

The ampoule design is shown in Fig. 1. The size of the glass ampoule was limited both by the dimensions of the sample holder and by the dimensions of the low-temperature cover supplied with the instrument. The height above the sample holder with the low-temperature cover is less than that with the transparent cover. The glass ampoules were manufactured from Kimble Standard Flint Glass tubing (Kimble Glass Company), type R6 (8 mm o.d. × 6 mm i.d.) although other types of soda glass

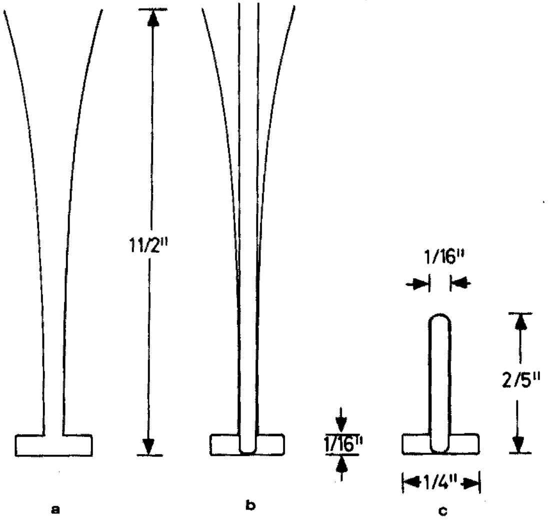

Fig. 1. Ampoule design.

could also be used. The ampoule is first blown into the shape as shown in Fig. 1a. A hollow plug, sealed at one end, is then made using the same glass so that it fits into the stem of the ampoule as in Fig. 1b. The substance under analysis is introduced into the ampoule and the plug inserted. The ampoule base is cooled with a suitable coolant and the stem is then sealed with a small flame to give the finished ampoule, Fig. 1c. The glass ampoules were manufactured so that the base of the ampoule was as thin and as flat as possible so that the area in contact with the sample holder was maximal. This was best achieved with flint glass. Ampoules manufactured in an identical manner from borosilicate glass were not as efficient because it was difficult to obtain a flat base. This was due to the higher softening temperature of borosilicate glass as compared to flint glass which resulted in greater heat loss during manufacture. As a result, the borosilicate glass ampoules could not retain their heat long enough for a perfectly flat base to be formed. Generally ampoules manufactured from borosilicate glass had concave bases. The capacity of the glass ampoule is approximately 0.025 cm^3 and the thickness of the base of the ampoule, in contact with the sample holder, is 0.001 (±0.0001) in.

Results and discussion

Results obtained for the sealed glass ampoules were compared with results obtained for the volatile sample pans supplied with the instrument. Although flint glass is a very much poorer conductor of heat than aluminium, it is evident from the following results that quantitative measurements can be made with glass ampoules. A comparison of the shape of the peaks obtained with the volatile sample pans and the glass ampoules is shown in Fig. 2. It is evident that the poor heat conductivity of the glass produces a broadening of the peak. Quantitative results (Table I) indicate that the broadening (w2/w1) is constant for different phase changes. A comparison of the temperature calibration of the instrument with the volatile sample pans and the glass ampoules is shown in Fig. 3; obviously, heat changes produced in the sample take slightly longer to be detected in the glass ampoules than in the aluminum pans. This difference is small and is due to the difference in the heat conductivity of the two materials. Although there were slight differences in the sizes of the ampoules, the

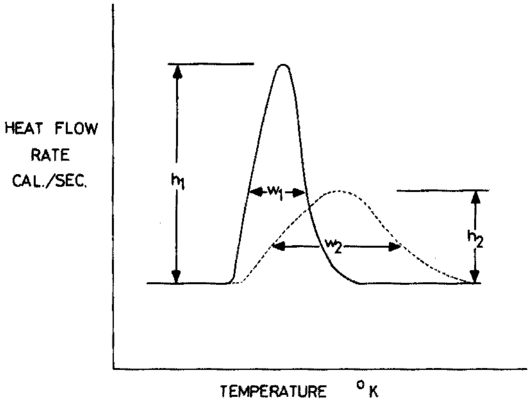

Fig. 2. Peak shape. (——) Transition in volatile sample pans; (------) transition in glass ampoules.

TABLE I

EFFECT OF GLASS AMPOULES ON THE PEAK SHAPE OF THE ENDOTHERMS OBTAINED ON HEATING AMMONIUM NITRATE[a]

Transition[b]	*Peak width at half-peak height*		$\frac{w2}{w1}$
	Aluminium (w1)	*Glass* (w2)	
β-Rhombic to α-rhombic	2.13	5.34	2.51
Rhombohedral to cubic	3.82	9.74	2.55
Cubic to liquid (fusion)	4.43	11.55	2.60

[a] Peaks obtained with 7.4 mg of ammonium nitrate. Both samples were initially melted and cooled before analysis to ensure that they were in the same crystalline form.

[b] Ref. 1.

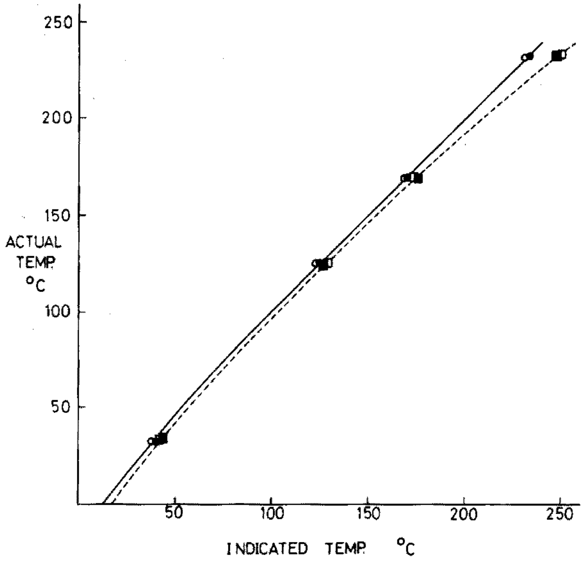

Fig. 3. Temperature calibration. (●) and (○) Transitions in volatile pans scanned at 10° min^{-1} and 2.5° min^{-1}, respectively; (■) and (□) transitions in glass ampoules scanned at 10° min^{-1} and 2.5° min^{-1}, respectively.

TABLE II

HEATS OF FUSION[a]

Compound	*Temperature* (°)		ΔH (*cal g*$^{-1}$)	
	Observed	*Ref.*[b]	*Observed*	*Ref.*[b]
Bromine	-7.5[c]	-7.3	15.9	16.2
Tin	231.9[d]	231.9	13.7	14.0
o-Nitrophenol	42.5	42.8	27.3	26.8
Stearic acid	63.5	64.0	47.3	47.6

[a] Determined from peak area, with a planimeter, with 10–15 mg of sample.

[b] Ref. 7.

[c] Temperature of fusion of mercury ($-38.9°$)[b] and water (0°)[b] used as the calibration.

[d] Reference temperature.

reproducibility of the temperature calibration was ±0.5° for a particular phase change.

The heats of fusion of several compounds were determined. The results (Table II) indicate that good quantitative results can be obtained with glass ampoules. The heats of fusion of corrosive substances, such as bromine, can be determined in this way. In an earlier design, the glass ampoules were manufactured without the glass plug. Heats of fusion which were measured with these ampoules tended to be less than the values reported in the literature, because the heated compound condensed in the cooler parts of the stem, resulting in a removal of compound from the immediate vicinity of the sample holder. The introduction of the glass plug prevented this compound loss. Glass ampoules, filled with air, were capable of being heated at 10° $\min^{-1}$ to 500° without any apparent distortion of the ampoule base. Further, water-filled ampoules were found to be capable of withstanding internal pressures of over 500 p.s.i. before fracture.

This work indicates that the application of the Perkin-Elmer DSC-1 and DSC-1B can be extended by the use of the glass ampoules. An obvious advantage over the volatile sample pans is that phase changes can actually be observed in the ampoules when the transparent cover is used. This will be an advantage in phase studies where heat changes associated with solid–liquid or solid–solid phase changes can be distinguished simply by viewing the sample. With a slight modification to the design of the ampoule, the ampoule and contents could easily be sealed under vacuum. Further, the thermal analysis of low-vapour-pressure solids could be observed in a small open glass beaker without the necessity of sealing in an ampoule.

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(Received 24th June 1970)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

The use of fluorescence in determining formation constants of complexes
Part I. Complexes which do not fluoresce

The general theory involved in the use of chelates has been discussed extensively by Martell and Calvin[1], Sen[2], Rossotti and Rossotti[3], and by Ringbom[4-6], who has has emphasized conditional constants. Holme and Langmyhr[7] have extended the ideas of Asmus[8] with regard to the use of linear methods of plotting to determine the composition of complexes. Momoki *et al.*[9] used "normalized absorbance" to describe curved plots obtained with weak complexes, and Freiser *et al.*[10] have discussed the problems involved in spectrophotometric measurements of complexes. Logarithmic plots have been used[11]. Dean and Harris[12] have suggested a method for improving end-point detection in cases in which a pronounced curve appears in the graph which is to be extrapolated. Hannema and Den Boef[13] have discussed the errors involved.

Several years ago the writer[14] showed that it is possible to carry out titrations of cations forming non-fluorescing complexes with the 8-quinolinol-5-sulfonate anion ($OxSO_3$) by using weaker complexes that would fluoresce when exposed to ultraviolet light. This work was done at or above pH 7, under conditions such that ML_2 complexes were formed for all of the cations involved.

The work reported in this paper was done at lower pH values, chosen such that not all the non-fluorescing complex will be in the ML_2 form.

Experimental

8-Quinolinol-5-sulfonic acid (Eastman Kodak Co.) was used without further purification. All titrations and volume measurements involving this solution were carried out with a McCluskey buret (Scientific Glass Apparatus, Co., Inc., Bloomfield, N.J.) which is an automatic zeroing reservoir buret designed to protect the solution from atmospheric contamination.

Palladium chloride was obtained from A. D. Mackay Co., New York. Other salts were reagent-grade hydrated sulfates. Approximately 10^{-3} *M* salt solutions were prepared from more concentrated solutions which had been standardized against 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, with the exception of the copper ion solutions. These were taken as the ultimate standards, the titrating solutions being standardized against copper sulfate pentahydrate.

Buffer solutions were prepared by partial titration of acetic acid solutions with carbonate-free sodium hydroxide solutions, with a Corning expanded-scale pH meter to follow the titrations.

Titration method. A pipetted sample of the $10^{-3}M$ copper(II) or palladium(II) solution was placed in a beaker, along with another pipetted sample of the aluminum(III) solution. To this mixture there was added distilled water plus buffer solution, with a final dilution to a definite volume before beginning the titration. The method has been described previously[14], increments of titrant being added, and the fluorescence being measured after each addition, using a Turner 110 fluorimeter. The result of such a titration may be seen in Fig. 1. A careful account of the amount of solution was kept in the case of beaker titrations, so that final concentrations could be calculated. In addition, after preliminary runs in beakers, solution mixtures in 100-ml volumetric flasks were run, in which the only variable from flask to flask was the $OxSO_3$ concentration.

Discussion

When a cation such as copper(II), which forms a strong, non-fluorescing complex with $OxSO_3$, is placed in solution with a cation forming a weaker complex which fluoresces, titration curves are produced such as are shown in Fig. 1. If the pH of the solution is high enough, the point at which the fluorescent portion of the curve extrapolates to zero may be taken as the end-point for a titration in which the non-fluorescing complex has the formula ML_2; very reproducible results can be obtained. As the pH is lowered, reaction (1) below will shift toward the right, and a mixture of ML and ML_2 forms in the solution.

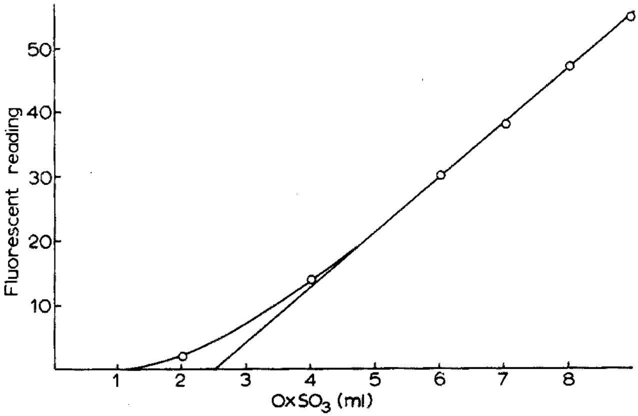

Fig. 1. Titration of Cu(II) with $OxSO_3$ in the presence of Al(III) at pH 4.

$$ML_2 + H^+ = ML + HL \tag{1}$$

In the case of $OxSO_3$ at pH 4, the predominant acid species formed is H_2L, so that the reaction can be taken to be

$$ML_2 + 2\,H^+ = ML + H_2L \tag{2}$$

Figure 1 shows the titration of 2 ml of $1 \cdot 10^{-3}M$ copper(II) with $1.25 \cdot 10^{-3}M$ $OxSO_3$ at pH 4. Extrapolation to the x-axis indicates that 2.50 ml of the titrant are equivalent to the copper(II) present, while the formation of CuL_2 requires 3.20 ml. Writing the reverse of reaction (2) as the formation reaction for CuL_2 from ML and H_2L, the conditional constant will be

$$K_2^* = \frac{(CuL_2)(H^+)^2}{(CuL)(H_2L)} = K_2 \cdot K_{a_1} \cdot K_{a_2} \tag{3}$$

where K_2 is the second formation constant for ML_2[15], and K_{a_1} and K_{a_2} are the two constants involved in the stepwise dissociation of the acid H_2OxSO_3.

The number of millimoles of ML and of ML_2 can be calculated by a method similar to the well known carbonate–bicarbonate calculation.

$$\Sigma\,\mathrm{L} = (2.4)(1.25)(10^{-3}) = 3.125(10^{-3}) = \mathrm{ML} + 2\,\mathrm{ML}_2 \tag{4}$$

$$\Sigma\,\mathrm{Cu} = (2)(1)(10^{-3}) = 2(10^{-3}) = \mathrm{ML} + \mathrm{ML}_2 \tag{5}$$

Subtracting (5) from (4) $1.125(10^{-3}) = \mathrm{ML}_2$

and . $0.875(10^{-3}) = \mathrm{ML}$

Since one molecule of H_2L reacts for each molecule of ML

$$0.875(10^{-3}) = \mathrm{H_2L}$$

After converting to concentrations (mole l^{-1}) by dividing these millimole values by the final volume in ml, these values may be substituted in eqn. (3) along with the (H^+) to give a value of $K_2^* = 2.28 \cdot 10^{-3}$.

Taking logarithms in eqn. (3)

$$\log K_2^* = \log K_2 + (\log K_{a_1} + \log K_{a_2}) \tag{6}$$

For H_2OxSO_3, the sum of the acidity terms in the bracket is 12.86, which gives a value for log K_2 of 10.22, as compared with 10.1 given by Sillén and Martell[15].

The above experiments with copper(II) were carried out to test the method with reference to known data. Similar experiments were carried out with palladium(II) in place of copper(II), resulting in a value of log $K_2 = 8.54$ for $Pd(OxSO_3)_2$.

In a previous report the author has determined the value of log $\beta_2 = 20.4$, β_2 being the product of K_1 and K_2. By subtraction, the value of log K_1 is 11.6 for $PdOxSO_3$.

Conclusion

The method discussed here is one which should not be restricted to fluorescent materials. It might be used in any photometric titration in which the extent of complexation is dependent on the pH of the solution. Experimentally, the problem is to find workable combinations. As an example, the determination of K_1 for copper(II) runs into a pronounced decrease in fluorescence of the aluminum(III) complex as the pH decreases. An attempt to substitute gallium(III) for aluminum led to the discovery that the gallium(III) complex with $OxSO_3$ is more stable than the copper(II) complex. This is now under investigation.

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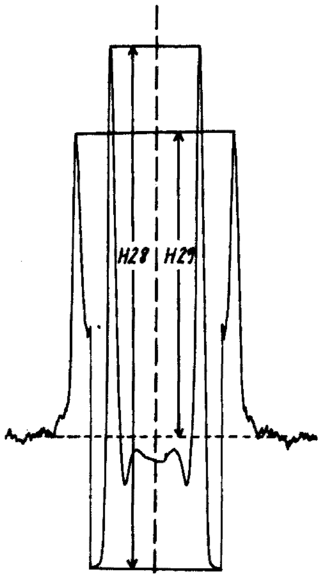
(Received 28th July 1970)

Anal. Chim. Acta, 53 (1971) 456–459

Improvements in the determination of nitrogen-15 in the low concentration range by emission spectroscopy

In the emission spectrographic determination of the abundance of nitrogen-15 in nitrogen gas samples, use is made of the fact that the ^{14}N–^{15}N band in the transition 2→0 is separated by about 0.6 nm from the ^{14}N–^{14}N band. The abundances of ^{14}N and ^{15}N can be determined from the heights of the peaks on the recording scan, but the ^{14}N–^{15}N band lies on the shoulder of the ^{14}N–^{14}N, hence a correction is necessary. Leichnam *et al.*[1] measured the peak heights from their corresponding base lines to the peak maxima (Fig. 1) and applied a correction factor (which was nearly constant



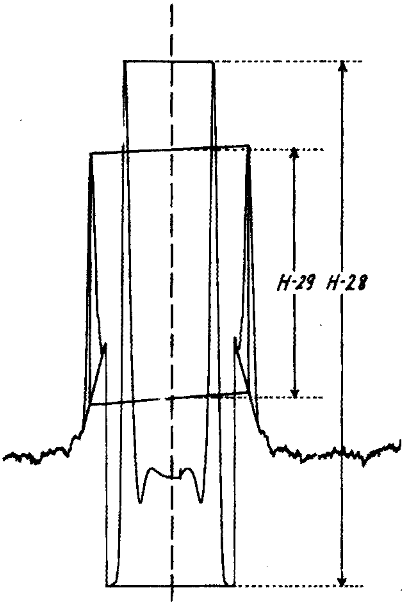


Fig. 1. Determination of peak heights with a correction curve.

Fig. 2. Determination of peak heights with graphical correction.

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for the limited range of enrichment investigated), when the nitrogen was prepared from ammonium chloride by the Rittenberg method. Faust, using a similar evaluation of peak height, constructed a calibration curve of peak height against the mass spectroscopic value for ^{15}N. Another possibility is to make a linear interpolation of the background under the ^{14}N–^{15}N peak, the height being measured as the vertical distance of the maximum to the estimated background (Fig. 2). However, when any of these methods are used in the determination of the ^{15}N content, deviations of ±10% and even more from the mass-spectrographic values sometimes occur in the range of natural ^{15}N abundance to 1% excess ^{15}N, the normal working range. These deviations were only observed, in agreement with H. Faust (private communication), when the nitrogen was prepared from nitrogen-containing material by the methods described by Faust[2] and by Goleb and Middelboe[3], *i.e.* the dried sample was heated in a sealed evacuated tube with a mixture of copper and calcium oxides (the dry Dumas method), so that gaseous nitrogen was released and other gases and vapours (*e.g.* CO_2, HCl, SO_3, H_2O, etc.) were absorbed by the oxides present.

However, measurements of a very pure nitrogen sample (Linde 99.99%) with the natural ^{15}N abundance, by means of the graphical correction (Fig. 2), gave a value of 0.354±0.004 at% which agrees with the mass spectrometric value of 0.360 at%. Nitrogen samples prepared by the Rittenberg method, in which the ammonium sulphate solution from a Kjeldahl digestion was oxidised with alkaline sodium hypobromite solution to yield a pure nitrogen gas, also gave results which lay within ±2% of the mass spectrometric values (Table I, column 3). These observations suggested that the errors mentioned above might be due to the presence of impurities in the nitrogen gas arising from the combusted sample and not completely removed from the gas phase by the CuO–CaO mixture. Experiments were therefore undertaken to determine the effect of increased activation of the Dumas mixture on the accuracy and precision of the ^{15}N determinations.

TABLE I

RESULTS OBTAINED (^{15}N at %) BY DIFFERENT METHODS OF PREPARATION OF THE NITROGEN SAMPLE FROM AMMONIUM SULPHATE

(Figures in brackets show the percentage deviation from the mass spectrometric values)

Dumas briquette (CuO–CaO mixed)	*Dumas chemical (CuO wire, $CaO+Al_2O_3$)*	*Rittenberg method*	*Mass spec.*
0.412 (+14.7)	0.361 (+0.6)	0.359 (0)	0.359
0.505 (+ 9.1)	0.470 (+1.5)	0.466 (+0.6)	0.463
0.610 (+ 6.6)	0.580 (+1.4)	0.576 (−0.9)	0.572
0.720 (+ 7.8)	0.658 (−1.5)	0.663 (−0.7)	0.668
0.797 (+ 3.2)	0.758 (−1.8)	—	0.772
0.851 (− 3.8)	0.881 (−0.4)	—	0.885
0.956 (− 3.0)	0.981 (−0.5)	—	0.986
1.043 (− 5.1)	1.080 (−1.7)	—	1.099
1.152 (− 1.6)	1.187 (+1.4)	—	1.171
1.243 (+ 3.3)	1.264 (−1.6)	—	1.285
1.365 (− 2.0)	1.394 (+0.1)	—	1.393

Optical equipment

Electrodeless quartz tubes containing nitrogen gas at a pressure of about 2 Torr were excited with a 100-Mc generator[4] operating at *ca.* 50 W. The light from the tube was focussed and resolved in a modified[5] Hilger-Watts quartz Spectrograph Model E 742 adapted with an RCA 1 P 28 photomultiplier tube. The signal was amplified with an extremely stable FET–d.c.-operational amplifier and recorded. An automatic wavelength scanner covered the range from 300.0 nm to 297.0 nm in both directions. The band heads $^{14}N-^{14}N$ at 297.7 nm and $^{14}N-^{15}N$ at 298.3 nm were used.

Description of the d.c. amplifier. The d.c. amplifier was of the current-sensitive operational type. The central part was a thick-film integrated d.c. amplifier with FET input ("Analog Devices" Type 149 C) with an open-loop gain of 10^5. The dynamic input impedance seen by the photomultiplier was 100 Ω shunted by 2.2 mF, and all the photomultiplier current i_{PH} flowed into the amplifier. The feedback branch consisted of $R_f = 10^7$ Ω and $C_f = 22$ nF. The total output voltage was $i_{PH} \cdot R_f$. The time dependence of the feedback loop (time constant of 0.22 sec) served to slow down the noise, without giving significant distortion of the recorded peak. With the help of helipot P (TC = 20 p.p.m.), the zero point of the set-up was adjusted. The output attenuator permitted adjustment of the output range. The resistor R_b protected the amplifier against external short circuit. The voltmeter served for coarse adjustment of the zero point and to recognize overloading of the amplifier (ranges: 1 V, 10 V).

All resistors were metal films (TC = 15 p.p.m.) except R_a and P.

Power supply stability: better than $1.4 \cdot 10^{-3}/°$

Output stability: *versus* temp. ±20 μV/° max

versus time ±70 μV/day max

Gain stability: ±30 p.p.m./° max

Saturation voltage: −10 V

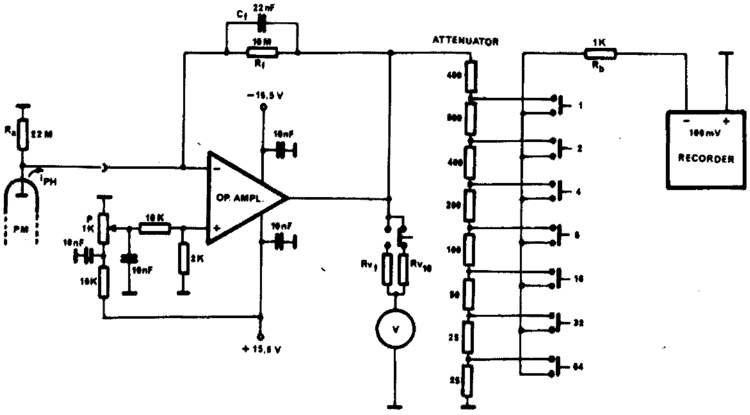

Fig. 3. Circuit diagram of the amplifier with attenuator.

Preparation and determination of the nitrogen sample

The electrodeless discharge tubes were prepared as described by Goleb and Middelboe[3]. The Dumas mixture recommended by these authors is a 1:1 mixture of copper oxide and calcium oxide, briquetted at a pressure of 10 kg cm^{-2}. The compressed mixture cannot, however, be degassed in high vacuum at temperatures above

600° because of decomposition of the copper oxide, so that calcium oxide is not activated completely. To overcome this difficulty, the reagents were added separately. To facilitate handling, calcium oxide was briquetted (with an equal quantity of alumina to improve mechanical stability) and added to the horizontal tube. Next a piece of copper oxide wire (Merck p.a.) was inserted a little apart from the calcium oxide. Finally, the sample was placed in the tube similarly separated in distance from the copper oxide. The tube was then evacuated and the lime was heated to about 1000° with a hand torch without heating the copper oxide above 600°. After the tube had been sealed, the contents were shaken and the normal combustion was done to release nitrogen gas.

The evaluation of the peak heights of the bands used was as shown in Fig. 2. The peak heights obtained were used directly for calculating the ^{15}N abundance as follows:

$$^{15}\mathrm{N}\ \mathrm{at}\% = 100\left(2\cdot\frac{^{14}\mathrm{N}\,^{14}\mathrm{N}}{^{14}\mathrm{N}\,^{15}\mathrm{N}}+1\right)^{-1}$$

Discussion of the results

In Table I the results of spectrophotometric determinations of ^{15}N in ammonium sulphate standards in the range of 0 to 1% excess ^{15}N prepared by different methods, are compared with mass spectrometric values. The values given are the mean of three measurements, each corresponding to a double scan. A comparison of the results in columns 2 and 4 shows that the nitrogen gas samples prepared by the improved Dumas method give values with a maximum deviation of ±2% from the mass spectrometric ones, while those shown in column 1 have a much greater variation.

TABLE II

RESULTS OF ^{15}N DETERMINATION BY EMISSION SPECTROSCOPY IN DIFFERENT SAMPLES WITH NATURAL ^{15}N ABUNDANCE

	Pure N 99.99%	*Dry air*	*Ammonium sulphate (Merck p.a.)*	*Glutamic acid (Merck p.a.)*	*Plant sample*
Mean value[a]	0.354	0.361	0.358	0.368	0.370
S.D.	0.004	0.007	0.004	0.005	0.005
Mass spec. value	0.360	0.363	0.359	0.365	0.366
S.D.	0.003	0.002	0.003	0.003	0.003

[a] These values are the mean of 10 separate recorder tracings, each being a double scan.

Table II, column 1, shows the results of analysis of pure nitrogen gas (Linde 99.99%) with natural nitrogen-15 abundance. The heights of the ^{14}N–^{15}N peaks were obtained by the linear interpolation of the ^{14}N–^{14}N background. The mean value is in excellent agreement with the mass spectroscopic value and the standard deviation of a single determination was ±1.2%. In order to check the influence of oxygen which is always present in varying amounts after the combustion of a nitrogenous compound with copper oxide, dry air samples were measured (column 2); the excellent agreement with the mass spectrographic determination, shows that oxygen has little or no effect on the results, confirming the work of Leichnam *et al.*[1]. Nitrogen from ammonium sulphate, glutamic acid and a plant sample was prepared by the modified Dumas method; excellent agreement with mass spectrometric values was obtained and the standard deviations for single determinations were ±1.2%, ±1.5% and ±1.5%, respectively. In all cases, the amount of total nitrogen in each discharge tube was about 5 μg. The mass spectrometric values show that the natural abundance of nitrogen-15 varies slightly depending on the origin of the sample.

Conclusion

The results show that the simple linear interpolation of the background ^{14}N–^{14}N band in the region of the ^{14}N–^{15}N peak is a satisfactory basis for the measurement of the size of the latter peak and with pure nitrogen, analyses for ^{15}N with a precision better than ±2% are possible in the region of natural to 1% excess ^{15}N. With proper activation of the Dumas chemicals, it is possible to obtain a sample of nitrogen from organic and inorganic nitrogenous material which is sufficiently free from impurities so that results with a precision of ±2% are possible on a routine basis from natural to 2% abundance.

The authors are indebted to Dr. G. B. Cook for valuable discussions and help in the preparation of the paper, to Mr. Fiedler for the mass spectrometric analyses.

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(Received 2nd September 1970)

Anal. Chim. Acta, 53 (1971) 459–463

Preparation of pellets from ion-exchange resins for direct analysis for metal ions by X-ray spectroscopy

Combined applications of ion-exchange materials and X-ray spectroscopy for elemental analysis have been in use for some time. Campbell *et al.*[1] have recently reviewed applications of ion-exchange resin-loaded papers in this field. Batch equilibration of an ion-exchange resin with a solution of the ion to be determined was reported by Miles *et al.*[2] for the analysis of titanium alloys. This technique is considerably faster than the use of membranes or papers impregnated with ion-exchange resins. Moreover, a homogeneous distribution of the sample on the resin is achieved. However, a high distribution coefficient of the ion of interest is required for quantitative removal of the ion from solution, especially if large concentrations of other ions are present. In this communication are reported the application of a chelating ion-exchange resin, Chelex 100, to the determination of barium ions in solutions containing 1 *M* sodium chloride, and a technique for the improvement of handling the treated resin. The ion-exchange resin Chelex 100 (Dowex A-1) contains iminodiacetic acid functional groups which are highly selective for divalent and polyvalent metal ions. Therefore, this resin offers a considerable advantage over less selective resins for removal of alkaline earth and transition metal ions from a solution of alkali metal salts. The sensitivity of previously reported analyses may be improved as a result of the greater selectivity and uptake of the metal ions by the chelating resins.

In previous applications of ion-exchange resins for preconcentration of ions and as a matrix for these ions during spectrographic analysis, the wet resin beads were essentially decanted into a sample holder[2].

Experimental

Apparatus. The ion-exchange resin pellets were analyzed with a Phillips-Norelco Universal vacuum-path X-ray spectrograph. Most of the work was done with a high-intensity chromium target X-ray tube, a lithium fluoride analyzing crystal and a flow-proportional counter. The X-ray path was evacuated to less than 200 μm. A few determinations were made with a tungsten target tube. The resin pellets were inserted into the center hole of an iron disk and placed in the circular windowed sample holders. Samples were rotated to minimize the effects of small variations in sample position in the iron disk.

Reagents. Stock solutions of metal salts were prepared and standardized by photometric titrations with EDTA. Chelex 100 (BioRad Laboratories) was used with no further treatment.

Procedure. Place *ca.* 0.75 g of 100–200 mesh Chelex 100 in a Teflon beaker containing 60 ml of distilled water. Adjust the pH to 11–12 with potassium hydroxide until no detectable drift in pH is observed over a 10-min period. Add an aliquot of the barium solution and stir for *ca.* 30 min. Filter the resin, wash and return to the beaker. Add distilled water, adjust the pH to 5–6 with hydrochloric acid, allowing for drift, and add an aliquot of 10 μmoles of lanthanum nitrate. Stir for 30 min, and filter and wash the resin. Dry the resin for 3 h at 80°.

Prepare pellets by placing the hot dried resin in a hot 0.5-in diameter stainless steel die similar to a standard KBr pellet die. Spread the beads evenly in the die and add sufficient molten paraffin to cover the resin. Insert the die piston and apply sufficient pressure by tightening a C-clamp so that the excess paraffin is forced out of the die through the 0.002-in clearance around the piston. Then chill the die and C-clamp in ice to solidify the paraffin. Remove the pellet from the die by pressing the piston out of the die using a bench vice. Mark the pellets and then store in recesses cut into aluminum strips to prevent accidental breakage or contamination.

The pellets were easily handled and no detrimental effect of the vacuum or radiation during analysis was observed. The irradiated pellets tended to darken somewhat, but successive reanalysis gave essentially identical results. The side of the pellet not irradiated may be labeled with a marking pen but a check for contamination from the ink is advisable. No unusual precautions were found necessary during the analytical procedure.

The procedure used for analysis was to count barium and lanthanum $L_{\alpha_{1,2}}$ lines and two background levels close to but unaffected by the intensity of these L lines. The background was subtracted from the peak counts and the ratio of barium to lanthanum counting rates computed. This procedure was found satisfactory except at the lower barium concentrations where differences between the counting rates at the background and barium emission wavelengths were computed by analyzing blank pellets.

The counting times needed to obtain a statistically significant analysis varied from 10 sec at high barium concentrations to 100 sec at the lowest concentration levels. In practice each peak and background was counted 5 times and the mean value used.

Results and discussion

A study of the feasibility of direct determination from calibration curves prepared from these resin pellets was made. The results showed that whereas direct analysis was possible, dilution of the sample caused the counting rate to decrease in a linear manner with an increase in the weight of resin used to prepare the pellet. The precision of direct analysis therefore depends greatly upon the reproducibility of the resin weight and pellet preparation procedures. Use of an internal standard eliminated the necessity of the tedious preparation of pellets of precisely known weight, density, etc. The criteria for the selection of an internal standard for X-ray spectrography and the use of lanthanum as an internal standard for barium have been discussed by Lewis and Goldberg[3].

TABLE I

BARIUM DETERMINATION IN THE ABSENCE AND PRESENCE OF CALCIUM AND STRONTIUM

Ba^{2+} taken (μmole)	*Ca^{2+} (μmole)*	*Sr^{2+} (μmole)*	*Ba^{2+} found[a] (μmole)*	*% Rel. error*	*Confidence interval[b]*
0.300	—	—	0.309	+3	±0.03
0.800	—	—	0.826	+3.3	±0.11
3.00	—	—	2.98	−0.67	±0.30
5.00	—	—	4.88	−2.4	±0.10
10.00	—	—	10.22	+2.2	±0.50
5.20	5.00	0.10	5.42	+4.2	
5.20	1.00	0.50	5.14	−1.2	
5.20	0.50	1.00	5.19	−0.2	
5.20	0.10	5.00	5.18	−0.4	

[a] Average of 4 runs.

[b] Based on $\mu = \bar{x} \pm ts/n^{\frac{1}{2}}$ at 90% level.

Table I shows the results of the analysis of several synthetic samples for barium content, in the absence and presence of various amounts of calcium and strontium. These results indicate the potential usefulness of chelating resin for sample matrices in X-ray analysis. The pellet prepared from these resins is a considerable improvement over loose resin beads.

We have found recently that Chelex 100 may be pressed into pellets without the addition of a binder. However, the quality of the pellet depends greatly upon the moisture content of the resin and more study is required to reproduce the quality of the pellet.

This work has been supported in part by Research Grant GA-001667 from the National Science Foundation.

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(Received 11th September 1970)

Detection of traces of transition metals by formation of peroxy compounds and sorption on a chelating resin

Formation of coloured peroxy compounds permits the detection of traces of some transition elements[1-3], but when extremely small concentrations are used, the colours are not distinct and are sometimes unstable.

However, if the reactions are carried out in presence of a little white coloured chelating resin, the peroxy compounds are adsorbed and concentrated on the resin and their colours are intensified; the sensitivity of the detection reactions is thus improved. Moreover, unstable peroxy compounds (*e.g.* of chromium and vanadium) are stabilized by sorption on chelating resins. Conventional ion-exchange resios (cationic or anionic) can also adsorb peroxy compounds, but they have no stabilizing action.

Experimental

Tests were made with Dowex A-1 resin which has a polystyrene matrix with iminodiacetic chelating groups[4]; the resin is in the form of white coloured small pearls (30–70 mesh).

Recommended procedure for analysis. To a cavity of a white porcelain spot plate, transfer 50 mg of the resin and 4–5 drops of the test solution; add one drop of each reagent successively to develop the colour. In dealing with extremely small concentrations, it is necessary to carry out a blank in another cavity of the spot plate, with an equal amount of resin, 4–5 drops of distilled water and the same

TABLE I

DETECTION REACTIONS OF TRANSITION METALS AS PEROXY COMPOUNDS AND THEIR SENSITIVITY IN PRESENCE OF DOWEX A-1 CHELATING RESIN (ON 4–5 DROPS OF TEST SOLUTION)

Element	*Reagents*[a]	*Initial form of the element*	*Probable form of peroxy compound*	*Ref.*	*Colour*	*Dilution limit*
Ti	H_2SO_4 30% H_2O_2 30%	TiO_2^{2+}	$TiO_2(SO_4)_2^{2-}$ or $Ti(H_2O_2)^{4+}$	5,6	Orange	$1:2 \cdot 10^6$
V	H_2SO_4 10% H_2O_2 1%	VO_3^-	VO_4^{6+}	7	Redbrown	$1:1 \cdot 10^6$
Cr	H_2SO_4 3% H_2O_2 3%	CrO_4^{2-}	CrO_8^{3-}	8	Blue	$1:1 \cdot 10^6$
Mo	NaOH 30% H_2O_2 30%	MoO_4^{2-}	$Mo_2O_{11}^{2-}$	9	Redbrown	$1:5 \cdot 10^5$
Ce	NH_4OH 20% H_2O_2 20%	Ce^{3+}	CeO_3^{3+}	10	Yellow	$1:3 \cdot 10^5$
U	Na_2CO_3 10% H_2O_2 30%	UO_2^{2+}	UO_6^{4-}	11, 12	Yellow	$1:5 \cdot 10^4$

[a] One drop of each is added.

reagents.

Table I shows the results obtained on diluted solutions of transition metals; reagents and dilution limits are also reported.

With smaller concentrations, if a large amount of test solution is available, a simple enrichment can be made by passing the solution, treated with the oxidizing reagents, through a chelating resin bed in a glass column; in this case, the colour of the peroxy compound appears at the top of the bed.

Observations

Peroxy compounds of niobium, tantalum and tungsten are not adsorbed in similar conditions, because the reagents regenerate the resin

Peroxy compounds of chromium and vanadium are quite stable when adsorbed on chelating resins: a sample of Dowex A-1 which adsorbed chromium–peroxy compounds from an acidic solution showed a blue colour two months after the adsorption.

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(Received 10th August 1970)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK REVIEWS

Progress in Nuclear Energy. Series IX. Analytical Chemistry. Vol. 10, Edited by D. C. Stewart and H. A. Elion, Pergamon Press, Oxford, 1970, viii + 474 pp., price £ 10.

This book is devoted to the remote analysis of radioactive materials, and it contains 14 chapters each of which has been written by a different author or group of authors. Several of the authors are well-known analytical chemists who have spent many years in this specialised sphere of analytical chemistry, particularly in the United States of America.

In the early chapters consideration is given to the problems of weighing, pipetting, sampling, dissolving, evaporating, etc. in the specialised facilities needed for the safe handling of radioactive materials, and some equipment which is suitable for these operations is described. Much of the remainder of the book is concentrated on instrumental techniques which are applicable to the analysis of radioactive samples, and there are separate chapters on electroanalysis, titrimetry, spectrography, atomic absorption and flame emission spectroscopy, gas analysis, ion exchange, solvent extraction, etc. The final two chapters deal with analytical chemistry in glove boxes, and the effects of radiation on common analytical reagents. A useful survey of shielded facilities available in different countries throughout the world is also included.

This book certainly achieves its objectives of presenting the problems facing the analytical chemist in the nuclear energy field, and of describing suitable solutions to these problems. Many photographs of apparatus are reproduced, and these are of help to the reader. The task of eliminating overlap completely would have been a very difficult one for the editors to achieve with so many different authors involved in the compilation of this book. In fact some overlap does occur, but this does not constitute a serious fault. Perhaps the worst feature is the fact that the literature references in many chapters stop at 1966, and only a few chapters contain references to work published in 1967. Therefore the reader will not find mention of any of the important developments that have taken place during the past 3 years or so.

This book constitutes an essential text for all analytical chemists working on the analysis of radioactive materials. Other analytical chemists will also find much useful information and sound advice within the 474 pages of text. The quality of the production is good, but this should be expected for a book with a selling price of £ 10.

G. W. C. Milner (Harwell)

L. Gascó Sanchez, *Teoría y Práctica de la Cromatografía en Fase Gaseosa*, Ediciones JEN, Madrid, 1969, xxiv + 549 pp., price Pts. 715.0.

This is the first major text in Spanish to cover both theoretical and practical aspects of gas chromatography, and thus fills a considerable gap in the Spanish literature.

The contents are divided into three parts. After a general discussion of chromatographic methods, and an introduction to gas chromatography, the basic theory of gas chromatography is discussed in detail. The second part is devoted to a description of column parameters and their effects on separations. This is followed by a section on apparatus, including columns, sampling, injection techniques and detectors. The third part deals with the applications of gas chromatography (qualitative and quantitative analysis, programming techniques, trace analysis, high-temperature gas chromatography, special techniques and preparative gas chromatography). The book ends with an interesting chapter on physico-chemical applications. Various appendices contain bibliographic data on applications, retention indices for various compounds on different columns, and commercial names of supports and liquid phases.

Well written and clearly laid out, with selected up-to-date references, this book is an excellent contribution to the Spanish scientific literature and should be welcomed by all interested in gas chromatography.

J. A. Rodriguez-Vazquez (Santiago de Compostela)

Richard A. Passwater, *Guide to Fluorescence Literature*, Vol. 2, Plenum Data Corporation, New York, 1970, vi + 369 pp., price $22.50.

The titles (in English), authors and journal references of all papers that appeared in 1964 through 1968 concerning fluorescence (including atomic fluorescence), phosphorescence and chemiluminescence, are listed. The papers are arranged in sections (organic analytical, inorganic analytical, theoretical, immunofluorescence, phosphors) with an addendum for papers omitted from the classified lists in Volumes 1 and 2. Within each section, the papers are arranged in annual sections, and listed alphabetically by the first author's surname.

As befits a book of this nature, there are extensive author and subject indexes (91 pp.). For anyone concerned with fluorescence, this book will save valuable time in literature searching and might bring to his attention papers that would otherwise remain unnoticed.

A. Townshend (Birmingham)

The Role of Nucleotides for the Function and Conformation of Enzymes, Edited by H. M. Kalckar, H. Klenow, A. Munch-Petersen, M. Ottesen and J. H. Thaysen, Scandinavian University Books, Munksgaard, Copenhagen, 1969, 335 pp., price Dan. Kr. 90,—.

This book contains the *Proceedings of the Alfred Benzon Symposium I*, held at *Copenhagen* in *September 1968*. The full text of 13 papers on various aspects of enzyme–nucleotide interaction and allosteric regulation of enzymes is given. Each paper is followed by a transcription of the discussions. The authors are distinguished biological scientists, but this is a highly specialized text and contains little of interest to analytical chemists.

A. Townshend (Birmingham)

PUBLICATIONS RECEIVED

P. Desnuelle, H. Neurath and M. Ottesen (Eds), *Structure–Function Relationships of Proteolytic Enzymes*, Proceedings of the International Symposium, Copenhagen, 1969, Munksgaard, Copenhagen, 1970, 309 pp., price Danish Kr. 110,00.

This volume contains the Proceedings of the Symposium held in Copenhagen in June 1969. It contains the 23 papers which were read at the symposium under the headings: *Pancreatic Proteases*, *Microbeal Proteases*, *Pepsin and Related Enzymes*, and *Sulfhydryl Proteases*. The plenary lecture by Professor E. Katchalski, entitled *A Synthetic Approach to the Study of Microenvironmental Effects on Enzyme Action*, is given in full.

G. J. Lutz, R. J. Boreni, R. S. Maddock and W. W. Meinke (Eds), *Activation Analysis: A Bibliography, Parts 1 and 2*, National Burea of Standards Technical Note 467, 264 pp., $8.50 per set.

G. J. Lutz (Ed.), *Determination of Light Elements in Metals: A Bibliography of Activation Analysis Papers*, National Bureau of Standards Technical Note 524, 1970, 41 pp., price $0.75.

M. Dub and R. W. Weiss, *Organometallic Compounds, Formula Index* (for the 2nd edition of Volumes I–III), Springer Verlag, Berlin, 1970, vii + 343 pp., clothbound DM 72.00.
n-*Pentane and Methane*–n-*Pentane*, NBS-NSRDS-NBS 32, June 1970, 73 pp., 70 cents.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK ANNOUNCEMENTS

NATIONAL BUREAU OF STANDARDS PUBLICATIONS

The following Technical Notes, Standards and Monographs have recently become available. They can be obtained, prepaid, from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151, U.S.A., quoting the relevant number. Foreign remittances must include an additional ¼ of the price to cover mailing costs.

S. H. Greenfeld, E. R. Warner and H. W. Reinhart, *Bibliographies on Fabric Flammability—Interior Furnishings*, NBS Tech. Note 498-1, June 1970, 24 pp., 30 cents.

G. J. Lutz, *Forensic Science: A Bibliography of Activation Analysis Papers*, NBS Tech. Note 519, March 1970, 47 pp., 50 cents.

G. J. Lutz, *Oceanography. A Bibliography of Selected Activation Analysis Literature*, NBS Tech. Note 534, June 1970, 36 pp., 50 cents.

G. J. Lutz, *Pollution Analysis: A Bibliography of the Literature of Activation Analysis*, NBS Tech. Note 532, June 1970, 23 pp., 45 cents.

A. D. Franklin and H. S. Bennett, *ARPA-NBS Program of Research on High-Temperature Materials and Laser Materials*, NBS Tech. Note 531, June 1970, 75 pp., 70 cents.

G. J. Lutz, *14-MeV Neutron Generators in Activation Analysis. A Bibliography*, NBS Tech. Note 533, June 1970, 91 pp., $1.00.

W. J. Hamer and H. J. DeWane, *Electrolytic Conductance and the Conductances of the Halogen Acids in Water*, NBS-NSRDS-NBS 33, May 1970, 37 pp., 50 cents.

V. M. Berry and B. H. Sage, *Phase Behavior in Binary and Multicomponent Systems at Elevated Pressures.* n-*Pentane and Methane*-n-*Pentane*, NBS-NSRDS-NBS 32, June 1970, 73 pp., 70 cents.

M. E. Stevens, *Automatic Indexing: A State-of-the-Art Report*, NBS Monograph 91 revised, February 1970, 290 pp., $2.25.

J. T. Hougen, *The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules*, NBS Monograph 115, June 1970, 52 pp., 55 cents.

W. G. Brombacher, *Survey of Micromanometers*, NBS Monograph 114, June 1970, 62 pp., 60 cents.

K. F. J. Heinrich, *Present State of the Classical Theory of Quantitative Electron Probe Microanalysis*, NBS Tech. Note 521, August 1970, 17 pp., 30 cents.

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PRINTED IN THE NETHERLANDS