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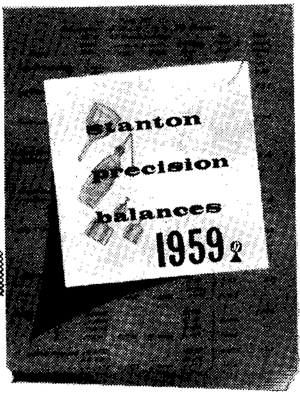

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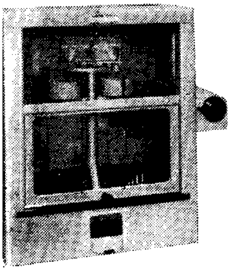

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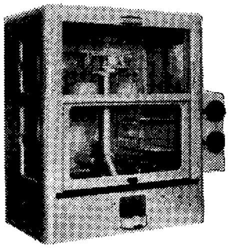

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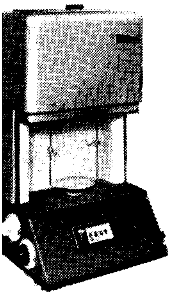

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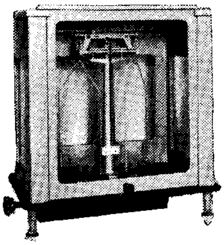

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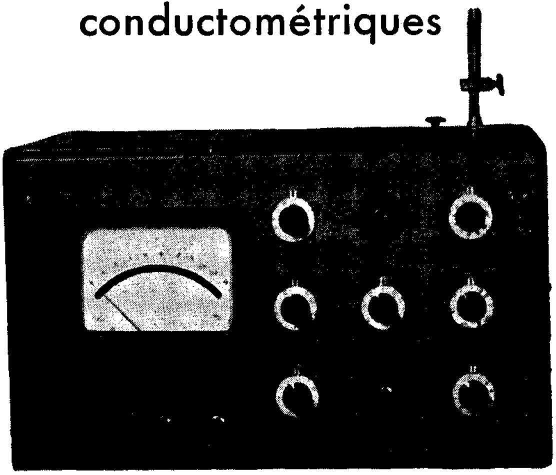

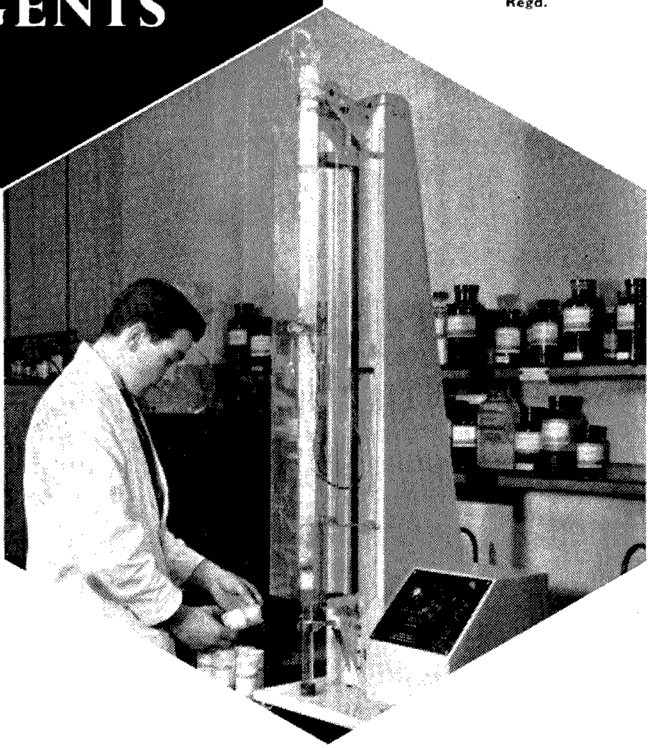

Zone melting apparatus manufactured by Baird & Tatlock (London) Ltd., in use in the H. & W. Chemical Laboratories for the preparation of P.V.S. Benzoic acid.

CHELATING PROPERTIES OF N,N,N',N'-TETRAKIS-(PHOSPHONOMETHYL)-1,2-CYCLOHEXANEDIAMINE*

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INTRODUCTION

Since the announcement about eleven years ago by SCHWARZENBACH and his co-workers[1] of a new volumetric method for determining the hardness of water by titration with ethylenediaminetetraacetic acid (EDTA or ENTA), the applications of chelate chemistry to analytical problems have been exceedingly numerous. The versatility of chelating agents as analytical reagents has resulted in considerable research in connection with the synthesis of new and different compounds. Many of the substances investigated contain carboxy groups and coordinate with the metal ion through oxygen atoms. It was considered to be of interest to investigate the possibility of a chelating agent containing some group other than the carboxy group which would still permit oxygen-to-metal bonds.

For many years various arsonic acids have been developed and used analytically[2]. The periodic relations between arsenic and phosphorus lead one to believe that phosphonic acids should be investigated for their analytical applications.

This work was a study of the preparation of a phosphonic acid chelating agent, N,N,N',N'-tetrakis-(phosphonomethyl)-1,2-cyclohexanediamine, and of some of its properties. A trivial name for the compound is cyclohexanediaminetetramethylphosphonic acid, or simply abbreviated to CDTMP.

PREPARATION

One of the general methods for the preparation of EDTA and related compounds involves the condensation of an amine with a halo acid, generally a chloro acid, in alkaline solution[3-5]. This procedure is quite versatile and nearly any kind of acid group can be attached to almost any amine. BERSWORTH[6] used this method to prepare N,N,N',N'-tetrakis-(phosphonomethyl)-ethylenediamine.

In this work, chloromethylphosphonic acid was reacted with 1,2-cyclohexanediamine in alkaline solution to prepare the desired compound.

Chloromethylphosphonic acid

Chloromethylphosphonic acid was prepared by causing phosphorus(III) chloride to

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* Abstracted from a dissertation submitted by ROGER E. YERICK to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

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*** Contribution No. 648. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

react with paraformaldehyde[7]. A two-step reaction was used, according to the following procedure.

20 g of paraformaldehyde were placed in a 500-ml two-necked reaction flask, fitted with standard taper joints. A reflux condenser and an addition funnel were put in place. A magnetic stirrer was used to provide the necessary agitation. 90 ml (142 g) of phosphorus(III) chloride were placed in the addition funnel. About 15 ml of this were added rapidly to the paraformaldehyde. After a few minutes a rather vigorous reaction occurred, during which considerable heat was evolved and most of the paraformaldehyde went into solution. When this reaction had subsided completely, stirring was begun and the remainder of the phosphorus(III) chloride was added at the rate of about 5 ml/min. When the addition was complete, the mixture was allowed to stir for an additional 10 min.

The mixture was sealed in a glass tube of about 400-ml capacity that had been constructed from medium-wall borosilicate glass tubing. The sealed tube was placed inside a piece of steel pipe that had been threaded at each end and fitted with pipe caps. This assembly was put into an oven which had been brought to a temperature of 240°–250°. During the first 2 h of heating, the pipe was removed from the oven at 30-min intervals and shaken briefly in order to thoroughly mix the contents of the sealed tube. The total heating period was 12 h.

At the end of the heating period, the sealed tube was allowed to cool to room temperature and its contents removed. At this stage, the product was dark brown or black in color. The crude product was fractionated and the portion of the distillate boiling between 93° and 98° at 17 mm of Hg pressure was collected. This fraction was chloromethylphosphonic dichloride.

Hydrolysis of the dichloride to yield the acid was accomplished by slowly adding the dichloride to a 50% excess of water with constant stirring. The water was removed by vacuum evaporation, never allowing the temperature of the mixture to exceed 30°. The resulting chloromethylphosphonic acid was a hygroscopic solid that crystallized in the form of long needles. It was stored in a vacuum desiccator containing phosphorus(V) oxide. The product, as isolated at this point, was satisfactory for the synthesis of CDTMP. It was possible to further purify it, if desired, by redissolving in water, treating with charcoal until a water-white filtrate was obtained and again removing the excess water by vacuum evaporation.

N,N,N′,N′-tetrakis-(phosphonomethyl)-1,2-cyclohexanediamine

CDTMP was prepared by reacting chloromethylphosphonic acid with 1,2-cyclohexanediamine in an alkaline solution. The diamine used was obtained in the form of the sulfate salt from Geigy Industrial Chemicals, New York, N.Y. The procedure developed was the following.

An amount of the diamine weighing 106 g was dissolved in approximately 500 ml of 15% (w/v) aqueous sodium hydroxide. This was extracted with 600 ml of ethyl ether in four portions of 200 ml, 200 ml, 100 ml, and 100 ml. The ether was removed by distillation to leave the free diamine, which was a pale yellow, oily liquid. Approximately 275 g of chloromethylphosphonic acid (the mole ratio of acid to diamine should be slightly more than 4:1) were dissolved in 600 ml of water. Sodium hydroxide pellets were added slowly and with constant stirring until a pH of 10–11 was obtained. Then the solution was saturated with sodium carbonate.

The free diamine was placed in a three-necked reaction flask of 3 l capacity which had been fitted with a reflux condenser and 75 ml of water were added. The pH was adjusted to 10–11 with sodium hydroxide and the solution heated to boiling. The chloromethylphosphonic acid solution was added at the rate of about 20 ml/min by means of an addition funnel. When all the acid had been added, the heat was adjusted to give moderate refluxing and the reaction was allowed to proceed for about 90 h.

At the end of the reflux period, the reaction mixture was allowed to cool and concentrated hydrochloric acid was added until the pH was lowered to about 6.5; the solution was filtered and the filtrate evaporated on a steam bath until a thick syrup was obtained. Approximately 250 ml of water were added and the mixture was heated and stirred for 10 min. It was filtered to remove any solids present and the residue was discarded.

To the filtrate was added an equal volume of ethyl alcohol. Two liquid phases resulted, the lower one containing the desired product. The mixture was stirred and the upper phase decanted. Another volume of alcohol was added and this procedure repeated. Successive portions of alcohol were added, followed by stirring and decantation until the lower phase had become jelly-like in character. Then another volume of alcohol was added and the mixture was stirred until it had the consistency of putty.

This solid was dissolved in as little water as possible without heating and was treated with decolorizing charcoal until a water-white filtrate was obtained. The alcohol-precipitation procedure was repeated, and the product was tested for the presence of chloride. If this test proved to be positive, the dissolution-precipitation procedure was repeated a third time. Generally, this served to remove all the chloride and presumably the other inorganic materials that were present in the original reaction mixture.

The product, as obtained at this stage, was a mixture of various partially-neutralized forms of CDTMP. In order to obtain completely the octasodium salt, the product was once again dissolved in a minimum amount of water and about 1 g of sodium hydroxide was added for every 10 g of product. After precipitation again by means of ethyl alcohol, the material was washed with about 1 l of the absolute ethyl alcohol and transferred to a crystallizing dish and placed in a vacuum desiccator containing phosphorus(V) oxide. The material was a white, rather hygroscopic solid; the yield was approximately 45%.

The octasodium salt was analyzed for sodium and phosphorus. Sodium: theoretical = 27.62%, found = 27.72%; phosphorus: theoretical = 18.59%, found = 18.66%.

IONIZATION CONSTANTS OF CDTMP

Aqueous titrations of the octasodium salt of CDTMP with acid resulted in a titration curve with two breaks. The first of these occurred at two moles of acid added per mole of salt initially present and the second at six moles of acid per mole of salt. A sample titration curve is given in Fig. 1. Although the titrations were done using samples of the octasodium salt, the explanation is perhaps more straightforward when approached from the standpoint of the free acid. However, it was impossible to isolate this in a form other than a thick syrup. The information obtained, though, lends itself to the following interpretation.

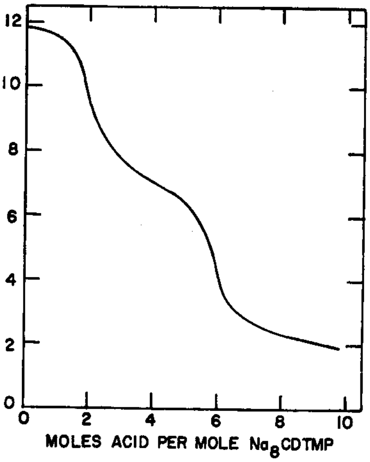

Fig. 1. Aqueous titration of the octasodium salt of CDTMP.

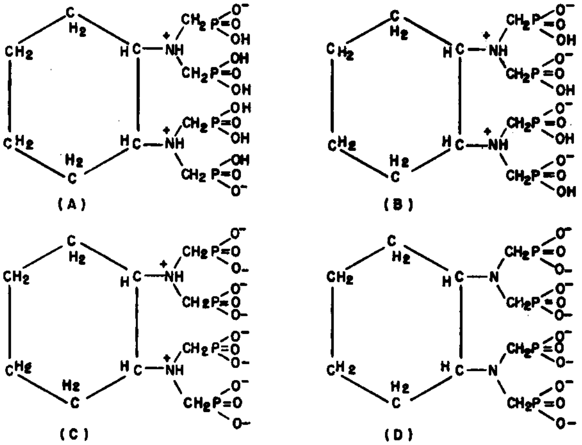

Fig. 2. Ionic species of CDTMP.

A double-dipolar structure, as indicated by (A) of Fig. 2 represents the free acid in solution. The first break in the titration curve represents the consumption of two moles of base per mole of acid, and the species present at this point is indicated by (B) of Fig. 2. Here, the two most acidic protons have been removed. These were originally on the phosphonic acid groups that contained two protons each, as shown in (A). This gives rise to a weak buffer region, and the removal of the protons remaining on the phosphonic acid groups is represented by only one break since they are about of the same acid strength. Hence, the species present at the second break in the titration curve is shown in (C) of Fig. 2. The two protons attached to the nitrogens are too weakly acidic in character to give a break in the titration curve, and the completely neutralized compound is represented by (D) of Fig. 2.

The method used for the determination of the eight ionization constants of the acid form of CDTMP was an extension of a procedure first suggested by SCHWARZENBACH, WILLI AND BACH[8]. In this study it was necessary to determine eight ionization constants from a titration curve possessing only two breaks.

The mathematical treatment connected with the determination of the ionization constants required that each point on the aqueous titration curve be expressed as a function of the total concentration of CDTMP in the solution, C_s, the hydrogen-ion concentration, the moles of base added per mole of CDTMP, the eight ionization constants of CDTMP, and the various ionic species of CDTMP present in the solution. However, it was possible to make use of certain simplifications in specific areas of the titration curve. An examination of the titration curve for CDTMP showed that the first break occurred at $b = 2$ and the second break at $b = 6$, where b represents the number of moles of base added per mole of CDTMP initially present. This meant that the several ionization constants could be grouped in the following ways for purposes of calculation. Only the first two ionization constants, K_1 and K_2, were considered up to the first break. In the region between the two breaks, only K_3, K_4, K_5, and K_6 were taken into account. After the second break, all except K_7 and K_8 were neglected.

For purposes of calculation, the various ionic species were represented as $[H_8R]$, $[H_7R^-]$, $[H_6R^{-2}]$, $[H_5R^{-3}]$, $[H_4R^{-4}]$, $[H_3R^{-5}]$, $[H_2R^{-6}]$, $[HR^{-7}]$, and $[R^{-8}]$. For purposes of simplification, later references to these species will omit the usual indication of the sign and magnitude of the charge on the ions.

In the region of the titration curve between $b = 0$ and $b = 2$, the data obtained was used to calculate the values of the first two ionization constants, K_1 and K_2. The expression derived for their calculation was this:

$$g + (g-1)\frac{K_1}{[H]} + (g-2)\frac{K_1K_2}{[H]^2} = 0 \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\text{where } g = \left(b + \frac{[H]}{C_s} - \frac{[OH]}{C_s}\right).$$

The only unknown terms were the two ionization constants; hence, two sets of values of C_s, b, and pH permitted the solution of two simultaneous equations for the individual values of K_1 and K_2.

Data taken from the region of the titration curve between the two breaks (*i.e.*, between $b = 2$ and $b = 6$) were used to determine the numerical values of K_3, K_4, K_5, and K_6. The final equation derived was as follows:

$$(g-2) + (g-3)\frac{K_3}{[H]} + (g-4)\frac{K_3K_4}{[H]^2} + (g-5)\frac{K_3K_4K_5}{[H]^3} + (g-6)\frac{K_3K_4K_5K_6}{[H]^4} = 0 \quad (2)$$

$$\text{where } g = \left(b + \frac{[H]}{C_s} - \frac{[OH]}{C_s}\right).$$

Four sets of values of C_s, b, and pH were required to give the necessary number of simultaneous equations.

Values of K_7 and K_8 were obtained from data derived from that part of the titration curve bounded by $b = 6$ and $b = 8$. The expression used was this:

$$(g-6) + (g-7)\frac{K_7}{[\mathrm{H}]} + (g-8)\frac{K_7K_8}{[\mathrm{H}]^2} = 0 \quad \ldots\ldots\ldots\ldots \quad (3)$$

$$\text{and again, } g = \left(b + \frac{[\mathrm{H}]}{C_s} - \frac{[\mathrm{OH}]}{C_s}\right).$$

Two solutions of the octasodium salt of CDTMP were prepared and sufficient perchloric acid was added to each to effectively give the acid form of the compound. The ionic strength was maintained at 0.1 by the use of sodium perchlorate and the temperature was kept at 25°. The solutions were titrated with sodium hydroxide. A Beckman, Model G, pH meter equipped with a calomel and Type E glass electrode was used to measure the pH. The concentrations of the solutions were determined by inspection of the titration curves. Knowing the normality of the sodium hydroxide and the volume of base required between the two breaks (which represented the titration of four protons), the amount of CDTMP present was calculated. Also from this, the amount of sodium hydroxide required to titrate the excess perchloric acid present was determined. In all the calculations, the decrease in C_s caused by the increase in total volume during the course of the titration was considered.

The results of the titrations and calculations are expressed in Tables I, II, and III.

It was of interest to determine just how well the experimentally obtained values of the ionization constants fitted with the potentiometric titration curve. Therefore, using the experimental values of $K_1 \ldots K_8$ in conjunction with eqns. (1), (2), and (3), various values of b were calculated for given values of pH. Table IV gives the results of these calculations, and a graphic comparison is shown in Fig. 3.

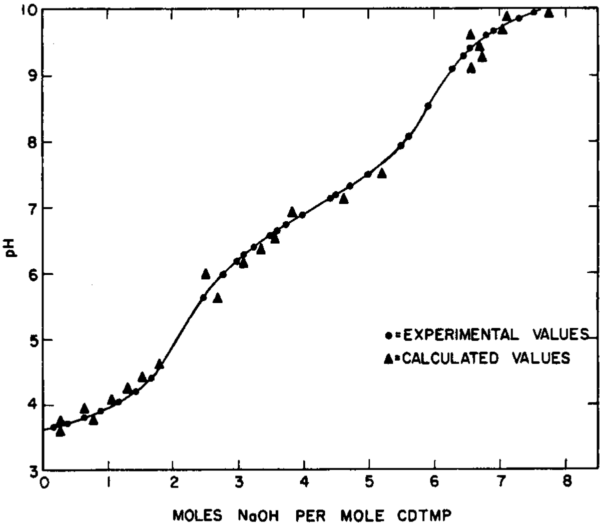

Fig. 3. Titration of CDTMP with sodium hydroxide.

TABLE I

APPARENT IONIZATION CONSTANTS OF CDTMP
CALCULATION OF K_1 AND K_2

b	*pH*	$K_1 \cdot 10^3$	$K_2 \cdot 10^4$
	CDTMP Solution I		
0.120	3.66	3.52	1.46
0.899	3.90		
0.380	3.72	3.91	1.92
1.160	4.02		
1.420	4.19	4.63	2.76
1.835	4.60		
0.639	3.81	4.29	2.58
1.679	4.41		
	CDTMP Solution II		
0.213	3.76	3.91	1.95
1.019	4.08		
0.747	3.96	4.78	2.91
1.509	4.45		
1.291	4.26	3.61	1.58
1.726	4.47		
1.400	4.35	3.84	1.63
1.888	5.02		

Average $K_1 = 4.07 \cdot 10^{-3}$; p$K_1 = 2.40$
Average $K_2 = 2.10 \cdot 10^{-4}$; p$K_2 = 3.70$

TABLE II

APPARENT IONIZATION CONSTANTS OF CDTMP. CALCULATION OF K_3, K_4, K_5 AND K_6

b	*pH*	$K_3 \cdot 10^6$	$K_4 \cdot 10^7$	$K_5 \cdot 10^7$	$K_6 \cdot 10^8$
		CDTMP Solution I			
2.460	5.65	4.37	3.16	0.82	1.65
2.964	6.20				
3.469	6.60				
3.974	6.90				
2.763	6.00	4.56	3.28	0.94	1.81
3.217	6.41				
4.426	7.03				
4.983	7.50				
3.066	6.29	4.79	3.61	1.28	2.27
3.571	6.67				
4.478	7.18				
5.493	7.96				
3.721	6.74	4.91	3.88	1.52	2.50
4.731	7.32				
5.595	8.07				
5.901	8.55				

(Contd. on p. 307)

TABLE II (Continued)

b	*pH*	$K_3\cdot10^6$	$K_4\cdot10^7$	$K_5\cdot10^7$	$K_6\cdot10^8$
		CDTMP Solution II			
2.216	5.56				
2.761	6.17	4.86	3.52	1.28	2.07
3.086	6.42				
3.625	6.77				
2.432	5.83				
2.870	6.27	5.19	4.19	1.73	2.83
3.305	6.58				
3.995	6.97				
2.542	5.96				
3.195	6.52	4.23	3.02	0.65	1.70
4.259	7.10				
4.894	7.45				
3.467	6.68				
4.417	7.18	4.57	3.31	0.96	1.91
5.209	7.67				
5.580	7.99				

Average $K_3 = 4.68\cdot10^{-6}$; pK_3 = 5.32
Average $K_4 = 3.47\cdot10^{-7}$; pK_4 = 6.46
Average $K_5 = 1.15\cdot10^{-7}$; pK_5 = 6.97
Average $K_6 = 2.09\cdot10^{-8}$; pK_6 = 7.69

TABLE III

APPARENT IONIZATION CONSTANTS OF CDTMP
CALCULATION OF K_7 AND K_8

b	*pH*	$K_7\cdot10^{10}$	$K_8\cdot10^{11}$
	CDTMP Solution I		
6.258	9.10	3.98	1.38
6.767	9.60		
6.565	9.42	3.72	1.09
7.532	9.99		
6.869	9.67	3.53	0.71
7.787	10.06		
6.461	9.33	4.57	1.93
7.277	9.89		
	CDTMP Solution II		
6.454	9.33	4.79	2.17
7.095	9.80		
6.668	9.52	4.01	1.65
7.735	10.07		
6.134	8.80	3.62	0.91
6.508	9.38		
6.775	9.60	3.89	1.02
7.468	9.98		

Average $K_7 = 4.02\cdot10^{-10}$; pK_7 = 9.39
Average $K_8 = 1.36\cdot10^{-11}$; pK_8 = 10.89

Attempts were made to fit the experimental curve in Fig. 3 by using only three constants, *i.e.*, $K_1' = (K_1K_2)^{\frac{1}{2}}$, $K_2' = (K_3K_4K_5K_6)^{\frac{1}{4}}$, and $K_3' = (K_7K_8)^{\frac{1}{2}}$. However, in this case, the agreement between the calculated and experimental curves was very poor.

STABILITIES OF CDTMP CHELATES

Potentiometric methods

Qualitative studies indicated that CDTMP reacted with numerous metal ions in a manner not unlike the common chelating agents. However, it was also found that most of the complexes formed were too weak to be of significant analytical use.

The nature of the complexes was investigated by the method of continuous variations[9,10]. Not all the chelates were subjected to this study, because it was felt that those studied were representative. In all cases it was found that a 1:1 chelate between the metal ion and CDTMP was formed.

TABLE IV

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF b

b, *exptl.*	*pH*	b, *calc.*
0.120	3.66	0.260
0.380	3.72	0.213
0.639	3.81	0.771
0.899	3.90	0.640
1.160	4.02	1.072
1.420	4.19	1.331
1.679	4.41	1.515
1.835	4.60	1.792
2.460	5.65	2.674
2.763	6.00	2.501
2.964	6.20	3.079
3.066	6.29	2.802[a]
3.217	6.41	3.329
3.469	6.60	3.560
3.571	6.67	3.702[a]
3.721	6.74	3.863[a]
3.974	6.90	3.782
4.426	7.03	4.638
4.478	7.18	4.263[a]
4.731	7.32	4.488[a]
5.493	7.96	5.714[a]
5.595	8.07	5.266[a]
5.901	8.55	6.399[a]
6.258	9.10	6.537
6.461	9.33	6.737
6.565	9.42	6.681
6.767	9.60	6.502
6.869	9.67	6.993
7.277	9.89	7.105
7.532	9.99	7.722
7.787	10.06	7.519

[a] Not plotted in Fig. 3.

The stabilities of most of the metal chelates were measured by a potentiometric procedure resulting from an extension of a method used by CARINI AND MARTELL[11]. The stability constants of the cobalt(II), nickel(II), and iron(III) chelates were determined by spectrophotometric methods.

The potentiometric determination of the chelate stabilities involved the titration of CDTMP in the presence of about a 20-fold excess of the metal ion being studied. The ionic strength was adjusted to 0.1 with sodium perchlorate and the temperature was maintained at 25°. From a knowledge of the equilibria involved, it was possible to derive an expression in which the only unknown was K_m, which represented the stability constant of the metal–CDTMP complex under investigation. The final form of the equation developed was this:

$$K_m\,[M]\,(4C_s—E) = E\,(\frac{[H]^8}{L_1}+\frac{[H]^7}{L_2}+\frac{[H]^6}{L_3}+\frac{[H]^5}{L_4}+\frac{[H]^4}{L_5}+\frac{[H]^3}{L_6}+\frac{[H]^2}{L_7}+\frac{[H]}{K_8}+$$

$$+1)+C_s(\frac{4[H]^8}{L_1}+\frac{3[H]^7}{L_2}+\frac{2[H]^6}{L_3}+\frac{[H]^5}{L_4}-\frac{[H]^3}{L_6}-\frac{2[H]^2}{L_7}-\frac{3[H]}{K_8}-4)\quad\ldots\ldots\quad(4)$$

where $E = (b—4)C_s + [H] — [OH]$,
b = moles sodium hydroxide per mole of CDTMP present,
C_s = total concentration of CDTMP present,
$L_1 = K_1K_2K_3K_4K_5K_6K_7K_8$,
$L_2 = K_2K_3K_4K_5K_6K_7K_8$,
$L_3 = K_3K_4K_5K_6K_7K_8$,
$L_4 = K_4K_5K_6K_7K_8$,
$L_5 = K_5K_6K_7K_8$,
$L_6 = K_6K_7K_8$,
$L_7 = K_7K_8$, and
the K's are the individual ionization constants of CDTMP.

The results of the titrations are presented in Figs. 4 and 5. The calculated values of the stability constant for the CDTMP–magnesium complex are given in Table V. A summary of the stability constants determined by the potentiometric method are given in Table VI.

Spectrophotometric methods

The stability constants of CDTMP chelates with cobalt(II) and nickel(II) could not be determined by the potentiometric method because of hydrolysis of the metal ions during the course of the titration. Instead, a spectrophotometric procedure was employed. In this study the pH was adjusted to approximately 11. Thus, all of the CDTMP was considered to be in the completely ionized form, and the only species considered was $[R^{-8}]$. This aided in the calculations, and as long as an excess of CDTMP

TABLE V

STABILITY OF CDTMP–MAGNESIUM COMPLEX

b	pH	$K_m \cdot 10^{-6}$	b	pH	$K_m \cdot 10^{-6}$
6.084	6.59	1.01	7.054	6.78	2.10
6.192	6.60	1.14	7.162	6.82	2.88
6.300	6.62	1.79	7.269	6.85	3.18
6.408	6.64	1.32	7.377	6.89	2.83
6.515	6.67	2.08	7.485	6.95	2.96
6.622	6.69	2.41	7.593	7.03	1.27
6.731	6.72	1.92	7.700	7.14	3.71
6.838	6.74	3.26	7.862	7.34	4.51
6.946	6.76	2.69	7.970	7.57	4.83

Average $K_m = 2.55 \pm 0.87 \cdot 10^6$, $t = 25°$, $\mu = 0.1$.

was present in the solution, no hydrolysis of the metal ion was encountered. The basic working equation derived was this:

$$A_t = (\varepsilon_2)\ (a)\ [\mathrm{R}] + \frac{(\mathrm{M}_t)\ (a)\ (\varepsilon_2) + (\mathrm{M}_t)\ (a)\ (\varepsilon_3)\ (K_m)\ [\mathrm{R}]}{1 + K_m[\mathrm{R}]} \quad (5)$$

where A_t = total measured absorbance,
a = cell length,
ε_1 = molar absorptivity of M, the metal,
ε_2 = molar absorptivity of R, the reagent,
ε_3 = molar absorptivity of MR, the chelate,
K_m = stability constant of the chelate, and
M_t = total metal concentration.

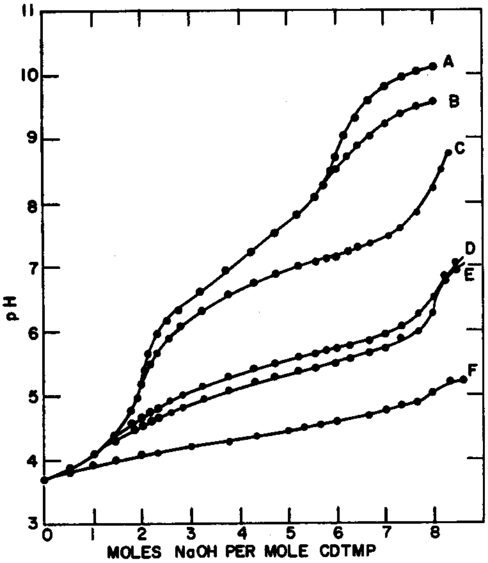

Fig. 4. Titration curves of CDTMP: curve A, CDTMP; curve B, CDTMP + barium; curve C, CDTMP + calcium; curve D, CDTMP + manganese(II); curve E, CDTMP + cadmium; curve F, CDTMP + copper(II).

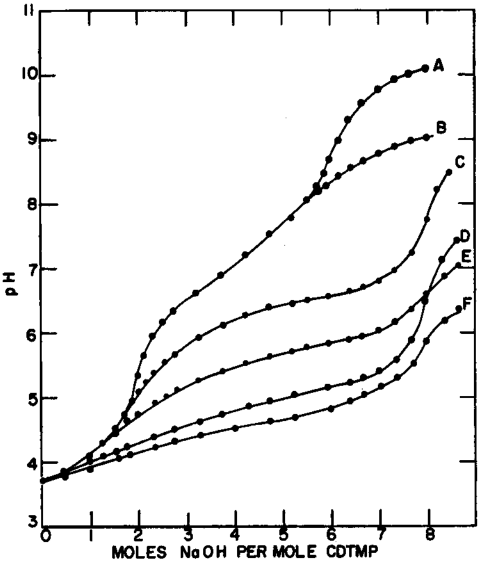

Fig. 5. Titration curves of CDTMP: curve A, CDTMP; curve B, CDTMP + strontium; curve C, CDTMP + magnesium; curve D, CDTMP + zinc; curve E, CDTMP + lead; curve F, CDTMP + mercury(II).

Under the conditions chosen for this study, there was no appreciable absorbance due to CDTMP itself; hence, the ε_2 term was neglected. The value of ε_1 was determined from measurements made on a solution containing only the metal ion in question. By the use of a series of successive approximations, it was possible to replace [R] by R_t, the total amount of R originally added. Thus, the only unknowns were the values of K_m and ε_3, and the solution of two simultaneous equations was necessary. The data taken and the results of the calculations for chelates of cobalt(II) and nickel(II) are presented in Tables VII and VIII.

The stability constant of the iron(III)-CDTMP chelate was determined spectrophotometrically by consideration of equilibria in acid solution. If an aqueous solution of CDTMP is adjusted to a pH of about 1.5, then for all practical purposes all of the

TABLE VI

STABILITY OF CDTMP–METAL COMPLEXES[a]

Metal	*Average K_m*
Magnesium	$2.55 \pm 0.87 \cdot 10^6$
Calcium	$3.12 \pm 0.91 \cdot 10^5$
Strontium	$5.27 \pm 1.09 \cdot 10^3$
Barium	$7.49 \pm 1.93 \cdot 10^2$
Zinc	$1.31 \pm 0.37 \cdot 10^9$
Cadmium	$1.15 \pm 0.35 \cdot 10^8$
Mercury(II)	$3.26 \pm 1.05 \cdot 10^9$
Lead	$9.75 \pm 2.14 \cdot 10^7$
Manganese(II)	$3.09 \pm 1.02 \cdot 10^8$
Copper(II)	$5.37 \pm 0.99 \cdot 10^9$

[a] $t = 25°, \mu = 0.1$.

CDTMP may be considered to be in the form of the acid, H_8R. This makes possible some simplifications in the equilibria involved.

In an acid solution, the reaction between iron(III) and CDTMP was expressed as follows:

$$Fe^{+3} + H_8R \rightleftharpoons FeH_{(8-n)}R^{-(n-3)} + nH^+ \quad \ldots\ldots\ldots\ldots\ldots \text{(a)}$$

It was necessary to devise some means of establishing the value of n and also of measuring the amount of iron(III) chelate present. This was done by first assuming the following reaction:

$$Fe^{+3} + H_8R \rightleftharpoons FeR^{-5} + 8H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(b)}$$

TABLE VII

STABILITY OF CDTMP–COBALT(II) COMPLEX

Solution No.	$M_t \cdot 10^3$	$R_t \cdot 10^3$	*pH*	A_t	ε_3	$K_m \cdot 10^{-3}$
1	1.86	3.72	11.08	0.497	64.2	1.27
2	1.86	4.65	11.13	0.501		
3	1.86	5.58	11.05	0.508	61.8	2.38
4	1.86	6.51	11.13	0.513		
5	1.86	7.44	11.21	0.520	58.2	4.35
6	1.86	8.37	11.07	0.524		
7	1.86	9.30	11.02	0.528	67.4	0.76
8	1.86	10.23	11.08	0.533		
9	1.86	11.16	11.23	0.548	65.5	0.97
10	1.86	12.09	11.16	0.554		
11	1.86	13.02	11.03	0.560	63.9	1.46
12	1.86	13.95	11.14	0.566		
13	1.86	14.88	11.09	0.569	59.8	3.18
14	1.86	15.81	11.17	0.573		

Average $K_m = 2.05 \pm 0.67 \cdot 10^3$, $t = 25°$, $\mu = 0.1$.

TABLE VIII

STABILITY OF CDTMP–NICKEL(II) COMPLEX

Solution No.	$M_t \cdot 10^3$	$R_t \cdot 10^3$	*pH*	A_t	ε_3	$K_m \cdot 10^{-3}$
1	1.86	3.72	11.22	0.636	79.8	7.47
2	1.86	4.65	11.28	0.640		
3	1.86	5.58	11.31	0.643	76.2	10.02
4	1.86	6.51	11.25	0.648		
5	1.86	7.44	11.06	0.654	79.1	7.19
6	1.86	8.37	11.13	0.657		
7	1.86	9.30	11.04	0.662	83.7	4.93
8	1.86	10.23	11.15	0.666		
9	1.86	11.16	11.22	0.669	72.3	12.18
10	1.86	12.09	11.07	0.671		
11	1.86	13.02	11.18	0.674	78.6	7.84
12	1.86	13.95	11.26	0.677		
13	1.86	14.88	11.01	0.679	73.5	11.76
14	1.86	15.81	11.14	0.681		

Average $K_m = 8.77 \pm 2.17 \cdot 10^3$, $t = 25°$, $\mu = 0.1$.

Insofar as spectrophotometric measurements were concerned, it was possible to derive this relationship (assuming a cell length of 1 cm):

$$A_t = \varepsilon_2\,[H_8R] + \frac{Fe_t(\varepsilon_1[H]^8 + \varepsilon_3 K_f[H_8R])}{[H]^8 + K_f[H_8R]} \quad \dots\dots\dots\dots\dots \quad (6)$$

where $K_f = \dfrac{[FeR^{-5}]\,[H^+]^8}{[Fe^{+3}]\,\,[H_8R]}$,

A_t = total measured absorbance,
ε_1 = molar absorptivity of Fe, the metal,
ε_2 = molar absorptivity of H_8R, the reagent, and
ε_3 = molar absorptivity of FeR, the chelate.

The only unknowns were K_f and ε_3, because H_8R was established, as before, by successive approximations.

Using equation (6) as a starting point, it was possible to calculate a value for K_f by measuring the absorbances of a series of solutions at constant pH containing a varying iron(III) : CDTMP ratio. Also, it was possible to write an expression for the total absorbance in terms of the unknown power of [H] as indicated by reaction (a):

$$A_t = \varepsilon_2[H_8R] + \frac{Fe_t\varepsilon_1[H]^n + Fe_t\varepsilon_3 K_f[H_8R]}{[H]^n + K_f[H_8R]} \quad \dots\dots\dots\dots\dots \quad (7)$$

Data were obtained for eqn. (7) by measuring the absorbances of a series of solutions containing a constant iron(III) : CDTMP ratio but varying pH. Then assuming the first value obtained for K_f, the value of n was determined. This value of n was used to calculate a new value for K_f. Repeating this process until constant values for n and K_f were obtained gave the desired results.

As a result of the calculations, it was found that

$$n = 6.13 \pm 0.67 \text{ and}$$
$$K_f = 6.44 \pm 1.95 \cdot 10^{-10}.$$

Accordingly, the reaction between iron(III) and CDTMP in acid solution was assumed to be the following:

$$Fe^{+3} + H_8R \rightleftharpoons FeH_2R^{-3} + 6H^+ \quad \ldots\ldots\ldots\ldots \quad (c)$$

The value for K_f applies to the equilibrium described in reaction (c). A more usual form for expressing the formation of the complex is given by this reaction:

$$Fe^{+3} + H_2R^{-6} \rightleftharpoons FeH_2R^{-3} \quad \ldots\ldots\ldots\ldots\ldots \quad (d)$$

The equilibrium constant for this reaction was obtained by dividing K_f by the product $K_1K_2K_3K_4K_5K_6$, where $K_1 \ldots K_6$ were the values of the individual ionization constants for CDTMP as previously determined. When this was done, the value for K_m for the iron(III)-CDTMP chelate was given as:

$$K_m = \frac{6.44 \pm 1.95 \cdot 10^{-10}}{3.09 \cdot 10^{-33}} = 2.06 \pm 0.63 \cdot 10^{23}.$$

TABLE IX

TITRATION OF IRON(III) WITH CDTMP IN PRESENCE OF VARIOUS CATIONS

Metal added	*Ratio metal : Fe(III)*	*Fe(III) found*[a] *mg*	*Error mg*
Mg	50:1	30.3	0.1
Ca	50:1	29.7	—0.5
Sr	50:1	30.5	0.3
Ba	50:1	29.8	—0.4
Al	50:1	29.9	—0.3
Zn	50:1	29.6	—0.6
Cd	50:1	30.4	0.2
Hg(II)	50:1	30.6	0.4
Cu(II)	50:1	29.9	—0.3
Co(II)	2:1	30.0	—0.2
Ti(IV)	50:1	30.7	0.5
Cr(III)	2:1	30.5	0.3
Be	50:1	29.7	—0.5
Mn(II)	50:1	30.8	0.6
Ni(II)	50:1	29.9	—0.3
V(IV)	5:1	29.8	—0.4
Zr	5:1	Interferes	
Th	3:1	Interferes	
Bi	2:1	Interferes	

[a] Fe(III) taken = 30.2 mg.

ANALYTICAL STUDIES WITH CDTMP

The metal chelates of CDTMP studied did not have the desired stabilities to allow the metals to be titrated with CDTMP using the common indicators. The single exception was iron(III), which could be titrated in acid solution.

Titration of iron(III)

It was possible to titrate iron(III) with CDTMP in a solution the pH of which was about 1.5. Sulfosalicylic acid was used as the indicator, and it was also found that the end-point was enhanced somewhat by the addition of a blue dye. At best, the end-point was poor and considerable practice was required to obtain reproducible results. The procedure developed for the titration of iron(III) was the following.

The sample to be titrated should be contained in a total volume of about 50 ml. The pH was adjusted between 1.0 and 1.5, and 0.5 ml (ten drops) of a 0.1*M* solution of sulfosalicylic acid was added, followed by five drops of a 0.1% solution of indigo carmine or naphthol blue-black. The titration was carried out until no "flashes" of green were evident upon the addition of CDTMP. Table IX summarizes the titration of iron(III) in the presence of various cations. The significant interferences were thorium, zirconium, and bismuth. In each case a precipitate was formed during the course of the titration. Evidently this was some type of phosphonate of the metal in question. Of the common anions studied, only fluoride and phosphate interfered, and these prevented the formation of the iron(III)-sulfosalicylic acid complex. On the other hand, nitrate, sulfate, perchlorate, acetate, formate, bromate, chloride, and iodide caused no interference with the titration.

SUMMARY

The octasodium salt of N,N,N′,N′-tetrakis-(phosphonomethyl)-1,2-cyclohexanediamine, Na_8-CDTMP, can be prepared in 45% yield from chloromethylphosphonic acid and 1,2-cyclohexanediamine. The titration curve resulting from the titration of the acid, CDTMP, with sodium hydroxide at 25° and $\mu = 0.1$ was used to estimate the eight pK values for the free acid. The stability constants of metal chelates of CDTMP were measured at 25° and $\mu = 0.1$ potentiometrically.

RÉSUMÉ

Le sel de sodium du N,N,N′,N′-tétrakis-(phosphonométhyl)-diamino-1,2-cyclohexane a été préparé à partir de l'acide chlorométhylphosphonique et du diamino-1,2-cyclohexane. On a déterminé les constantes de dissociation et les constantes de stabilité des chélates de ce composé avec divers métaux.

ZUSAMMENFASSUNG

Es wird die Herstellung des Natriumsalzes des N,N,N′,N′-Tetrakis-(methylphosphin)-1,2-diaminocyclohexans aus Chlormethylphosphinsäure und 1,2-Diaminocyclohexan beschrieben. Ferner wurden die Dissociationskonstanten der freien Säure sowie die Stabilitätskonstanten einer Reihe Metall-Chelate bestimmt.

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HIGH PRECISION TITRIMETRY*

I. AN EXAMINATION OF THE ATTAINABLE PRECISION

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Many excellent and meticulous examinations of factors influencing the precision of titrimetric operations have appeared in the past[1], though these are mainly 30 or more years old. In the present paper the accumulated observations of many years are offered in the form of a critical reassessment of the mechanical precision of normal titrimetric operations, an investigation of the maximum attainable mechanical precision, and some suggestions for improving replicability. It was hoped to establish whether or not there existed an ultimate limit to the precision, and therefore accuracy, of analytical processes, beyond which increase in mechanical precision of measurement brought no improvement in the chemical accuracy. The relevance of this to the chemical determination of atomic weights will be appreciated.

The accuracy and precision of routine volumetry and gravimetry are of the same order, roughly 0.1 to 0.5%. An increase of half an order is perhaps a little easier to achieve gravimetrically than volumetrically, but further increase calls for considerable refinement in both techniques, the advantage lying with volumetric or weight titrimetric methods. Protest must be maintained against the practice of reporting results to an excessive degree of accuracy. Though the precision (reproducibility) of the results, and the degree of fineness of measurement, may be good, the accuracy is often more apparent than real. Endeavours to improve or investigate the accuracy of a method by systematic examination of the factors involved often result initially in an apparent reduction in accuracy owing to removal of a previously compensating error. Attempts to improve the accuracy to the limits of mechanical precision of measurement are often defeated by physico-chemical limitations such as adsorption, equilibrium lability, non-stoichiometry, purity of materials and etc.

It is instructive to consider the mechanical limitations of the measurements. This inquiry relates not to routine work, but to titrimetric investigations into quantitativeness of reactions, and other problems which demand the highest degree of precision which the skill of the operator and the available instruments will allow.

INSTRUMENTS

Burettes

Normally the severest limitation is set by the burette, and more attention has properly been paid to improving precision in burettes than in other vessels. The

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ordinary burette cannot be read to better than ± 0.2%, but the best types with very fine ring graduations and well-made taps give setting errors of less than 0.005 ml (with very thin graduation lines) and reading errors of 0.01 ml, giving, with care and practice, a precision of 0.04%.

Many aids have been proposed for facilitation of reading and minimisation of parallax[2-5]; the card with a black line on it and a small piece of mirror held behind the burette are simple and good. The increased precision of sausage and bulb burettes (*e.g.*, B.S. 846) or EISSNER's double burette[6] is useful. The tap is often the weakest point, requiring lubrication and not being susceptible of minute manipulation. Most taps require initial seating by grinding with fine abrasive, and all should be reground from time to time.

Although lubrication is objectionable, pure white petroleum jelly has been found to be the least objectionable lubricant, and if the tap is manipulated gently, relubrication is needed only when the burette is cleaned. Silicone greases should be avoided because they spread rapidly over the internal surface of the burette, and are extremely difficult to remove. Lubrication by the titrant is applicable to needle valves in weight burettes[7], but not readily to volume burettes.

Delicacy of manipulation can be enhanced by extending one wing of the tap. A piece of stout, but light wire (aluminium tubing is excellent), glass tube, or shaped wood is attached to the tap, wired and sealed with sealing wax as shown in Fig. 1. Attachment of a plastic protractor card facilitates resetting to given delivery speeds. With a properly ground jet tip, very lightly waxed, extremely small drops can be formed, removed by touching the inside wall of the titration vessel or by a glass rod, and washed down.

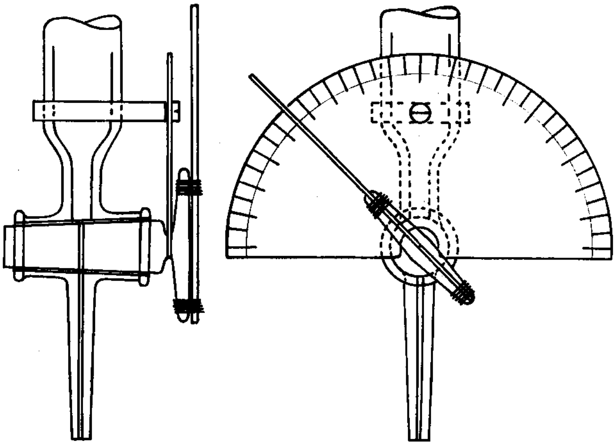

Fig. 1. Extension of burette tap wing, and attachment of a setting card by means of a Terry clip.

Drainage corrections

Variability of drainage errors due to the nature, vapour pressure and surface tension of the solution is of a second order of importance. With a perfectly clean burette and grease-free solutions, the error can be made remarkably uniform, thus permitting the application of a predetermined correction. The correction is much more dependent on delivery time than on drainage time. Drainage does not start immediately the outflow ceases; liquid builds up some 3–4 mm above the meniscus. This delay period becomes longer, and drainage becomes less, the slower the speed of delivery.

For a particular 50-ml burette, whose drainages are shown in Fig. 2, these factors became uniform at a delivery time of 6 min or longer, and a mathematical expression for drainage correction became possible:

$$\text{Drainage (ml)} = 0.2 \log_{10} \frac{\text{drainage time (min)}}{4[\text{delivery time (min)} - 3]}$$

Below 6 min, the relationship between delivery and delay times was no longer linear. The resemblance to the figures of LINDNER AND HASLWANTER[8] might suggest the universal application of the above expression, but the likeness must be ascribed to the accident of similar characteristics in the burettes used.

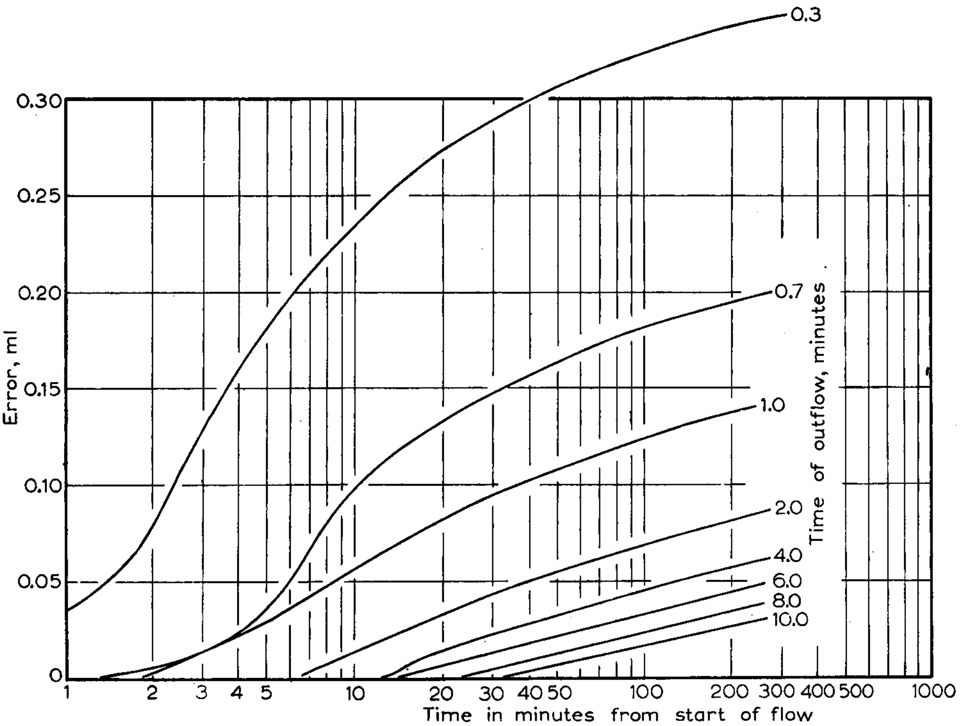

Fig. 2. Drainage of a 50-ml burette after various times of outflow.

With titrations of short duration, as in visual indicator or rapid electrometric working, no correction is necessary if the delivery speed is less than 8 ml per min, and the titration is completed within the delay period (the denominator of the above expression). With long titrations, as in careful plotting of potentiometric curves, when results have to be co-ordinated with rapid titrations, as in a study of indicator errors or quantitativeness of reactions, a correction corresponding to delivery speed and total time of titration may be taken from a drainage graph and either subtracted from the value for rapid titration, or, more properly, added to the figure for slow titration. If a burette is always used at the same delivery speed, a single, readily constructed drainage curve will suffice.

Since the delivery time at which uniformity begins is about three times as long as the "free delivery" time, on which standards institutions base their calibrations, recalibration at the new delivery time is necessary.

Errors due to inadequate rinsing are connected with drainage. Strongly held water films are not quickly replaced by the rinsing solution, and simple emptying by inversion leaves surprisingly large volumes of liquid behind. Large errors are incurred by the common practice of quickly rinsing a burette (or pipette) three times with 10–15 ml of solution and rapidly emptying between. Adequate drainage of 2–3 min between rinsings is important, and for the most accurate working the burette should be filled with solution after rinsing, allowed to stand 20–30 min, drained and refilled before commencing work. Table I shows the effect of this error in bromate–hydrazine titrations.

TABLE I

TITRATION OF 0.025M HYDRAZINE SULPHATE WITH 0.01667M POTASSIUM BROMATE

The titration was carried out in a solution 1.0M in hydrochloric acid and 0.1M in potassium bromide, using rosaniline hydrochloride as indicator. Theoretical end-point 24.52 ml.

Burette rinsed quickly 3 times without drainage	*Burette rinsed 3 times with intervening drainage*	*Burette rinsed 4 times with intervening drainage, and conditioned with solution*
24.63	24.55	24.52
24.65	24.52	24.52
24.70	24.54	24.515
24.58	24.56	24.52

The use of grease- and dust-free distilled water is a valuable aid in the reduction of errors. An automatic, self-cleaning, all-glass still, free of lubricated joints is used in this laboratory, the distillate filtered through porosity 3 sintered silica, stored in preconditioned bottles, and dispensed from a tapless apparatus. Moulds, algae and bacteria are also excluded by this method. A surface allowed to dry becomes greasy quickly, and a burette left empty overnight requires cleaning every 2 to 3 days. Slow alteration of the glass surface due to cleaning with such reagents as chromic acid demands that cleaning should be kept to a minimum. Frequency and duration of cleaning can be reduced by wet storage. A burette left completely filled with distilled water and covered with an inverted tube will remain clean when in daily use for 3 weeks or more, and if simply stored will remain clean for 3 or 4 months. Errors due to evaporation from a burette covered with an empty tube are small. Under very dry conditions, for dilute solutions at 20° evaporation is 0.002 ml/h for a full 50 ml burette, decreasing to about one twentieth of this as the burette is emptied. With ethanolic solutions[9], the loss from a covered burette is 0.03 ml/h when full, and 0.001 ml/h when nearly empty.

Pipettes

Pipettes are really precision instruments as the figures in Table II show. The above remarks on incomplete rinsing of burettes apply equally well to pipettes, thorough drainage between each of four rinsings being required.

TABLE II

WEIGHT OF WATER IN g DELIVERED BY PIPETTES AT 20°

Nominal volume, ml	*2*	*5*	*10*	*20*	*25*	*50*	*100*
Method (a)	1.983	4.993	9.984	19.964	25.008	49.892	99.771
	1.982	4.993	9.982	19.961	25.003	49.895	99.768
	1.981	4.995	9.985	19.963	25.005	49.892	99.773
Maximum scatter	0.002	0.002	0.003	0.003	0.005	0.003	0.005
Method (b)	1.9993	4.9955	9.9891	19.9777	24.9880	49.9226	99.8024
	1.9998	4.9953	9.9893	19.9776	24.9882	49.9229	99.8030
	1.9993	4.9956	9.9889	19.9780	24.9881	49.9220	99.8027
	1.9997	4.9954	9.9890	19.9778	24.9879	49.9224	99.8025
Maximum scatter	0.0005	0.0003	0.0004	0.0004	0.0003	0.0009	0.0006
Method (c)					24.9880		
					24.9881		
					24.9882		
					24.9880		
Maximum scatter					0.0002		

In method (a) student-type (class 'B') pipettes were held vertically by hand, suction applied by mouth, adjustment to the calibration mark made with the pipette tip, after wiping, touching the outer glass surface of a vessel, and delivery with the tip touching the inner surface of the receiving vessel, a timed interval of 15 sec being allowed after visible outflow ceased. The pipette was then withdrawn and the vessel weighed.

In method (b) standard class 'A' pipettes were used, clamped vertically, fitted with reading cards, and suction applied from a vacuum line *via* a two-way tap, whose other way was open to the air. After wiping the jet, adjustment to the calibration mark was made with the jet touching a glass surface. Free delivery was allowed with the jet touching the inner surface of the receiving vessel and a timed interval of 15 sec given after visible outflow ceased. The vessel was withdrawn from the pipette and weighed.

In method (c) the pipette was enclosed in a wide glass tubing water jacket connected to a thermostat tank, and water at the standard temperature circulated. Otherwise the method was similar to (b).

Many methods of using pipettes have been proposed from time to time, and a number of calibrations of a single pipette by a selection of these methods is shown in Table III. In methods 2, 4 and 6, the slight uncertainty of determining the point at which outflow ceases, together with the rapid drainage at this point, causes a considerable scatter of the results. The duration of the touch in 2, 3, 4 and 5 is open to various interpretations — about 1 sec was used — and gives variable errors.

TABLE III

WEIGHT OF WATER DELIVERED BY A NOMINAL 25 ml CLASS A PIPETTE OF OUTFLOW TIME 32 sec BY VARIOUS METHODS

Method	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
	24.866	24.884	24.982	24.890	24.972	24.919	24.986	24.9880	24.9880
	24.902	24.908	24.962	24.922	24.961	24.930	24.984	24.9882	24.9881
	24.872	24.924	24.970	24.913	24.985	24.941	24.989	24.9881	24.9882
	24.884	24.916	24.976	24.935	24.982	24.934	24.988	24.9879	24.9880
Mean	24.881	24.908	24.970	24.915	24.975	24.931	24.987	24.9881	24.9881
Maximum scatter	0.036	0.040	0.020	0.045	0.024	0.022	0.005	0.0003	0.0002

Method 1. Free outflow without touching wall of vessel.
2. Free outflow without touching wall of vessel during outflow, but touch wall once as soon as outflow ceases.
3. As in 2, but wait 15 sec before touching wall.
4. As in 2, but touch liquid surface instead of wall.
5. As in 4, but wait 15 sec before touching liquid.
6. Free outflow touching wall of vessel. No drainage allowed after outflow ceases.
7. Method (a) of Table II.
8. Method (b) of Table II.
9. Method (c) of Table II.

Storage of pipettes completely immersed in water in covered cylinders increases the intervals between cleaning, but manually manipulated pipettes do get dirty rather quickly. Mechanical handling as in Methods (b) and (c) above allows their use for 3 to 4 weeks between cleaning, despite the presence of a lubricated tap in the air line.

Flasks

The principal limitation resides in the diameter of the neck, which must be large enough to permit good mixing, but narrow enough to minimise setting errors. With the greatest care the setting error may be as little as 0.03 ml on a 1-l flask and 0.01 ml on a 100-ml flask, but is normally much higher than this, being usually 0.02 to 0.04% with care, or slightly better than the burette.

PROCEDURES

Weighing

For ordinary work, weighing errors are negligible, reagent purity not justifying further refinement, though a vacuum correction accounts for roughly 1 mg/ml of material. However, when a 1-g sample is weighed to 4 places the error is 0.02%, the same as the burette error. Weighing errors can be made very small with extreme care and adequate balances and weights.

Application of corrections

Measurements so made still require correction for temperature, pressure and humidity. Such corrections are well-known and fully worked out for dilute aqueous solutions, but are seldom applied. This omission is made on the grounds that if conditions are uniform the corrections cancel out, and this is often justified, though caution is necessary. Fully to correct a series of determinations for all sources of known errors of measurement is very troublesome. With electrometric titrations of some duration, conducted while room temperature is rising, temperature corrections become very complicated. With non-aqueous solutions, the corrections are seldom known.

Many errors are negligible compared with the burette errors, though their cumulative effect may have significance; such factors as, *e.g.*, pressure variation requiring a correction of 0.002% per cm, which are normally ignored, call for correction in the most precise work. These corrections, and the calibration of weights and vessels are themselves subject to errors, and the sigmoid may easily assume alarming proportions unless extreme care is taken.

Weight titrimetric methods

Many corrections are eliminated by the use of weight titrimetric methods. It is surprising that these are not more used for precise work in these days of rapid weighing balances.

Preparation of solutions by weight instead of by volume eliminates errors due to thermal expansion of glass and solution. In weight titrations, errors of drainage, reading and temperature change are eliminated. Only the usual vacuum weighing correction is required.

Weight titrimetry introduces one error of its own; adsorption of moisture on the glass surfaces. This, unfortunately, is an indeterminate and often considerable error. A second disadvantage is that a large set of accurate weights is needed.

The titrations may be carried out in two ways.

(1) Direct titration by visual indicator or electrometric methods to the end-point and weighing the burette before and after.

(2) Titration to near the end-point, when the burette is re-weighed, and the titration finished volumetrically using a suitably diluted solution prepared volumetrically.

The second method is often more convenient in plotting titration curves, but there is little to choose between them in precision and accuracy.

By this method the precision in routine working can readily be enhanced one order, from 0.2 to 0.02%, or twice the best precision of careful volumetric work. With very great care, the precision can be brought up to just better than 0.01%.

Further to increase precision presents rapidly mounting difficulties, not the least being the detection of the end-point and reagent purity. At about this stage precision of measurement begins to exceed the precision of the process. Two suggestions are offered, one for ready improvement of the precision of normal volumetric processes, the other[7] to push the precision of titrimetric measurements to the limit.

The pipette-dilution method

Table II illustrates the high precision attainable with an ordinary pipette. With care, a reproducibility of 0.001 ml is attainable, and this may profitably be utilised. A pipette may be used to deliver (after the manner of a weight burette in method (2) above) the bulk of the titrant, to within 0.25 or 0.025 ml before the end-point, and the titration completed with a 10- or 100-fold dilution of the original solution. This has proved particularly useful in investigating the end-point region in potentiometric curves.

This is reaching the limit of most indicators, even sharpened by photoelectric detection, and most electrometric techniques. It is also on the limit of reagent purity. Further increase in precision of measurement does not improve the reproducibility of the results.

TABLE IV

TITRATION OF $0.1M$ FERROCYANIDE WITH $0.1M$ CERATE IN $1M$ SULPHURIC ACID, USING VICTORIA GREEN AS INDICATOR

Method	*Careful direct volumetric visual end-point*	*Pipette dilution visual end-point*	*Pipette dilution photoelectric end-point*
Readings	24.98	24.984	24.983
	24.98	24.982	24.985
	24.99	24.984	24.984
	24.98	24.988	24.984
Scatter	0.01	0.006	0.002
Precision	0.04%	0.024%	0.008%
Method	*Direct weight-volumetric visual end-point*	*Dilution weight-volumetric visual end-point*	*Dilution weight-volumetric photoelectric end-point*
Readings	24.9816	24.9831	24.9833
	24.9845	24.9892	24.9839
	24.9898	24.9860	24.9854
	24.9837	24.9838	24.9842
Scatter	0.0082	0.0061	0.0021
Precision	0.033%	0.024%	0.0085%

Table IV shows that the pipette-dilution method increases the precision of the results in titration with a colour indicator to a visual end-point by allowing a further decimal place to be read. This improvement is small because the limit of visual

References p. 323

discrimination of colour has been reached. With photoelectric detection of the end-point, the extra precision of measurement becomes effective, and there is an improvement in reproducibility of results. On increasing the mechanical precision another order by weight titration, weighing to four places, the reproducibility of the results, either by visual or photoelectric detection of the end-point, is in no way improved. In the direct titration, increase of mechanical precision by two full orders by weighing instead of reading a burette yields hardly any improvement in reproducibility. The results of weight titrations have been converted to volumes for direct comparison.

CONCLUSION

With a proper appreciation of the mechanical errors of titrimetric measurements and adequate care in manipulative technique to take account of these, the precision and accuracy of the results of titrimetric determinations can readily be made commensurate with the precision of discrimination of end-point and the limits of normal reagent purity. Increase of mechanical precision beyond this affords no increase in the precision of the results.

ACKNOWLEDGEMENTS

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SUMMARY

A re-examination and critical assessment of the mechanical precision of titrimetric processes, with particular reference to the drainage errors of burettes, has been made and some manipulative improvements suggested.

The pipette-dilution method offers a useful improvement in the precision of volumetric methods, but further increase in mechanical precision affords little or no improvement in accuracy of determination.

RÉSUMÉ

La précision mécanique des méthodes titrimétriques est soumise à un nouvel examen critique, en particulier en vue des erreurs dues à l'écoulement des burettes. On constate que la précision des méthodes volumétriques peut être augmentée en se servant de pipettes et de solutions diluées pour la fin du titrage.

ZUSAMMENFASSUNG

Die mechanische Genauigkeit der titrimetrischen Verfahren wird aufs Neue kritisch untersucht, und zwar unter besonderer Berücksichtigung der Ausflussfehler der Büretten. Er wurde festgestellt, dass man durch Verwendung von Pipetten und von verdünnten Lösungen am Ende der Bestimmung, die Genauigkeit der volumetrischen Methoden erhöhen kann.

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THE CHELOMETRIC DETERMINATION OF CHROMIUM, COBALT(III) AND COPPER WITH A METALFLUORECHROMIC INDICATOR

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The successful application of calcein as a metalfluorechromic indicator for the determination of cobalt and iron[1] indicated that similar success would be attained with other highly colored EDTA–metal complexes. For this reason a study was initiated on the determination of chromium, cobalt(III) and copper. These elements form highly colored complexes with EDTA which cause considerable difficulty in their determination.

The determination of chromium is always conducted as a back titration because of the slow reaction between EDTA and chromium[2]. The titration using visual indicators is limited to relatively small amounts of chromium.

The titration of trivalent cobalt is seldom used due to the intense color of the EDTA–cobalt(III) complex. The determination of small amounts has been carried out by a back titration of an excess of EDTA using thorium as a titrant and xylenol orange as an indicator[3]. The cobalt(III)–EDTA complex is formed in ammoniacal solution by oxidation with hydrogen peroxide. The solution is subsequently acidified (pH = 2) and back titrated with thorium. The back titration of cobalt(III) in ammoniacal solution presents an additional difficulty in that most of the indicators used in ammoniacal solutions are sensitive to oxidizing agents.

The preliminary experiments were confined to ascertaining if calcein would function in ammoniacal solution in the presence of hydrogen peroxide. Several titrations of an EDTA solution at pH of 9.5 were conducted in the presence of hydrogen peroxide. The values obtained could not be distinguished from those in the absence of hydrogen peroxide.

PROCEDURES

Cobalt

A cobalt solution is adjusted to a pH of 9.5 with ammonium chloride–ammonium hydroxide buffer and somewhat more than the equivalent amount of EDTA is added. The volume is adjusted to approximately 150 ml, one drop of calcein (0.1% in 0.001*N* NaOH) is added and the solution back titrated under ultraviolet illumination with a standard copper solution. The equivalence point is characterized by the quenching of the brilliant green fluorescence of the indicator.

Chromium

To a slightly acidic solution of chromium add somewhat more than the equivalent amount of EDTA. Adjust the pH to 4.5 with sodium acetate–acetic acid buffer and dilute to approximately 150 ml with distilled water. Boil the solution for about 15 min, add one drop of calcein indicator and back titrate with a standard copper solution under ultraviolet illumination. The end-point is characterized by the quenching of the fluorescence of the free indicator.

Copper

Add somewhat more than the equivalent amount of EDTA to a copper solution which is buffered at a pH between 4.5 and 9.5. Dilute to approximately 150 ml, add one drop of calcein and back titrate with a standard copper solution to the quenching of the fluorescence of the free indicator.

DISCUSSION

The back titrations with standard copper solution are most conveniently carried out with ultraviolet light as the sole source of illumination. A convenient apparatus for this titration has been previously described[1]. The fluorescent radiation of the indicator before the end-point provides adequate illumination of the buret tip so as to make dropwise addition of the titrant feasible.

The titration of relatively large amounts of cobalt, chromium and copper by the methods described above are presented in Table I. It is apparent that the color of the EDTA-metal complexes does not interfere in the titration.

The possibility of determining the end-point in the presence of large amounts of copper is particularly advantageous. If an unusually large excess of EDTA is inadvertently added to a sample prior to a back titration with standard copper, the EDTA-copper complex formed during the back titration does not interfere with the titration.

TABLE I

DETERMINATION OF COBALT, CHROMIUM AND COPPER USING CALCEIN

Sample No.	*mg Co added*	*mg Co found*	*Sample No.*	*mg Cr added*	*mg Cr found*	*Sample No.*	*mg Cu added*	*mg Cu found*
1	21.25	21.20	12	20.00	19.97	23	47.65	47.61
2	21.25	21.23	13	20.00	19.89	24	47.65	47.60
3	42.50	42.47	14	20.00	19.99	25	47.65	47.64
4	42.50	42.52	15	20.00	19.97	26	47.65	47.66
5	42.50	42.56	16	40.00	39.98	27	47.65	47.63
6	42.50	42.52	17	40.00	39.87	28	47.65	47.67
7	63.75	63.88	18	40.00	40.06	29	47.65	47.67
8	63.75	63.79	19	40.00	40.03	30	47.65	47.65
9	63.75	63.70	20	40.00	39.97	31	57.18	57.16
10	63.75	63.86	21	40.00	40.12	32	57.18	57.21
11	63.75	63.70	22	40.00	39.95	33	57.18	57.20

SUMMARY

Calcein has been applied as a metalfluorechromic indicator for the back titration of relatively large amounts of cobalt(III), chromium(III) and copper(II). The fluorescent end-point is not impaired by the presence of the highly colored EDTA complexes with these ions. Calcein is suitable as an indicator which is not sensitive to oxidation in alkaline solutions.

RÉSUMÉ

La calcéine est proposée comme indicateur de fluorescence pour le titrage indirect de relativement fortes teneurs de cobalt, de chrome et de cuivre.

ZUSAMMENFASSUNG

Calcein wird als Fluoreszenz-Indikator für die indirekte Titration relativ grosser Mengen von Kobalt, Chrom und Kupfer vorgeschlagen.

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THE IODIMETRIC DETERMINATION OF THE REDUCING CAPACITY OF ALUMINIUM ALKYLS

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INTRODUCTION

Aluminium alkyls are used as catalysts in various chemical reactions. An important characteristic of this catalyst is its reducing capacity. This analytical method was developed to enable rapid and accurate determination of the total empirical reducing capacity of such a catalyst in concentration units of normality.

The procedure does not differentiate between aluminium alkyls, aluminium alkoxides, or aluminium hydrides.

OUTLINE OF METHOD

When aluminium alkyl comes into contact with an oxidizing agent, air, or water, a vigorous reaction results with the aluminium generally forming an inorganic salt or oxide and the alkyl usually going to a hydrocarbon or a halide. If this reaction goes to completion, one mole of triethyl aluminium will give up three electrons. However, depending on the strength and concentration of the oxidizing agent, diverse side reactions can take place. By careful control of the reaction conditions, the side reactions can be kept to a minimum.

To determine the reducing capacity of aluminium alkyl, an aliquot of the sample is added to a solution of iodine and potassium iodide in benzene.

The reactions taking place are as follows:

$$1.\ Al(C_2H_5)_3 + 3I_2 \rightarrow AlI_3 + 3C_2H_5I$$

$$2.\ I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Apparatus

The glass bomb used for sampling the aluminium trialkyl is shown in Fig. 1.

Reagents

Standard iodine solution. Dissolve 51 g of resublimed iodine in 1 l of benzene. Standardize against standard sodium thiosulfate.

Benzene. Dry over $Mg(ClO_4)_2$ for at least 1 day.

Standard sodium thiosulfate solution, 0.2*N*. Dissolve 31.6 of reagent-grade sodium thiosulfate in 1 l of boiled and cooled, deionised water. Standardize against 0.1*N* potassium iodate solution. (Use any standard text book procedure.)

Potassium iodide. Dry, reagent grade.

Glacial acetic acid. Reagent grade, dry.

Nitrogen. Pass over Drierite, heated copper turning, and Drierite again to eliminate water and oxygen.

Reference p. 329

Sampling

Flush sample bomb with dry, oxygen-free nitrogen. Attach the bomb to the sample source, avoiding contamination with air or moisture. Open all valves and allow a suitable sample to flow into the bomb. Close all valves, beginning with the one on the sample source.

Preparation of apparatus

All the equipment used should be ***thoroughly cleaned and dried.*** All stopcocks and joints should be greased with Apiezon grease or high vacuum silicone grease. After assembling the apparatus, flush the entire assembly with dry, oxygen-free nitrogen for 10 to 15 min to remove moisture and air. Close all stopcocks.

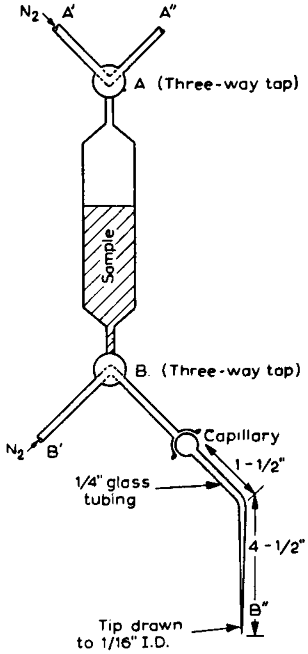

Fig. 1. Sample bomb.

Recommended procedure

Note: Use dry, oxygen-free nitrogen in all cases.

1. Prepare reaction beaker as follows: To a 100 ml, tall-form beaker add 25 ml of standard iodine solution plus 2 g of potassium iodide. Place a cover glass over the top of the beaker. The cover glass is made with three small holes to allow (a) the capillary inlet, (b) nitrogen inlet, and (c) burette inlet for titration. Flush with nitrogen to remove any dissolved oxygen and to form an inert blanket over the reaction vessel. Stir contents of beaker at a suitable rate on a magnetic stirrer.

2. Weigh sample bomb and sample.

3. Affix capillary tip.

4. Adjust nitrogen pressure to 2.5 ψ.

5. Connect nitrogen to taps A and B.

6. Turn taps A and B to allow passage from A′ to A″ and B′ to B″, respectively. Sweep out all tubing, capillary, and tip with nitrogen (see Fig. 1).

7. Immerse capillary tip below surface of reaction solution.
8. Run in a suitable sample by opening taps A and B and displacing with nitrogen.
9. Reweigh sample bomb plus remaining sample.
10. Add 5 ml of glacial acetic acid to reaction vessel.
11. Titrate with standard thiosulfate in the normal fashion using starch as an indicator.

The time taken to complete an analysis is approximately 30 min.

Calculations

Calculate the normality of the alkyl catalyst by the following equation:

$$\frac{(V_1 \times N_1) - (V_2 \times N_2)}{V_3} = N_3$$

Wt. of sample =
(wt. sample bomb + sample) — (wt. sample bomb + remaining sample)
V_1 = Volume of benzene–iodine solution
N_1 = Normality of benzene–iodine solution
V_2 = Vol. of sodium thiosulfate
N_2 = Normality of sodium thiosulfate
V_3 = Vol. of triethyl aluminium sample = wt. sample ÷ density*
N_3 = Reducing strength of triethyl aluminium expressed as normality.

Blank

If desired, a blank determination may be carried out on the solvent used to slurry the alkyl and the analytical results corrected in the normal way.

Precision

The following short term precision data have been obtained:

	Normality
	0.0625
	0.0626
	0.0627
	0.0625
	0.0628
	0.0629
	0.0629
	0.0630
	0.0632
Avg. =	0.0628
2σ =	0.00048 (95% confidence)

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* The density is considered to be the same as that of the solvent for low concentration slurries normally encountered.

DISCUSSION

The aluminium alkyls react instantaneously with air and moisture; the delivery tip of the burette may therefore become clogged at times with reacted alkyl. This will necessitate periodically cleaning the delivery tip with a fine wire. To keep clogging to a minimum, it should be thoroughly dried after each analysis and especially before leaving overnight.

Since iodine is volatile, KI is added to the iodine–benzene system to prevent the loss of I_2 by binding it as the I_3^- complex. The addition of KI also greatly increases the solubility of I_2 in water and gives a better end-point to the titration.

Glacial acetic acid is added in excess to the reaction mixture to prevent undesirable side reactions. The formation of sulfate, which would give high results, is retarded in an acidic medium.

The reaction of the aluminium alkyl catalyst with iodine also appears to be subject to side reactions. This is largely overcome by using a fourfold excess of iodine in respect to the alkyl concentration.

Reasonably good precision was obtained in practice if the proper steps were taken to prevent contact with air. It was also found desirable to analyse samples within a few hours, otherwise traces of air leaked into the sample bomb.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to J. L. JONES and Mrs. J. ELLERBE for their help and suggestions in completing this project; also, to Esso Standard Oil Company for permission to publish this paper.

SUMMARY

A rapid method for the determination of the reducing strength of aluminium alkyls has been developed. The method depends on the reaction with iodine. Replicate analysis shows a reasonable degree of precision.

RÉSUMÉ

Une méthode iodimétrique rapide est proposée pour déterminer le pouvoir réducteur des alcoyl-aluminiums.

ZUSAMMENFASSUNG

Es wird eine jodometrische Schnellmethode zur Bestimmung der Stärke der Reduktionswirkung von Aluminiumalkylen beschrieben.

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DAS RUTIN ALS ANORGANISCH-ANALYTISCHES REAGENS

II. NACHWEIS VON VANADIUM(V) MIT RUTIN

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Als in unserer vorläufigen Mitteilung[1] gemeldet wurde, gibt das Rutin (Quercetin-3-rutinosid) mit verschiedenen Metallionen eine Farbreaktion, welche durch entsprechende Auswahl der Umstände für die einzelnen Metallionen weitgehend spezifisch gestaltet werden kann. In diesem Artikel möchten wir über die sehr einfache und empfindliche Nachweismethode von Vanadium(V) berichten.

Die Reaktion wurde von uns anfänglich an einer 40, später 18 μg/ml Vanadium(V) enthaltenden Lösung näher studiert. Die 10-mal grössere Konzentration der — mit verdünnter Schwefelsäure bereiteten — Stammlösung wurde permanganometrisch bestimmt.

Fügt man zu 1 ml NH_4VO_3 Lösung, 1 ml 0.5%-ige Rutinlösung in Methanol, dann 3 ml 82%-ige Phosphorsäurelösung, so erscheint eine wohl beobachtbare orangerote Farbe.

Die Empfindlichkeit der Farbreaktion lässt sich durch Ammoniumpersulfat erheblich erhöhen. Fügt man z.B. zu 1 ml der Lösung die zu untersuchen ist, 1 ml 10%-ige Ammoniumpersulfatlösung, 1 ml 0.5%-ige Rutinlösung in Methanol, dann 3 ml 82%-ige Phosphorsäurelösung, so sieht man die orangerote Farbreaktion auch noch in Gegenwart von 0.3 μg Vanadium(V) klar. Die Farbe ist von der schwach grünlichgelben Farbe der Blindprobe gut unterscheidbar.

Eine interessante Beobachtung, in Bezug auf die Geschwindigkeit der Reaktion besteht darin, dass mit frischer Lösung von Ammoniumpersulfat in Gegenwart von weniger als 10 μg Vanadium(V) die orangerote Farbe erst in einigen Minuten hervorkommt, mit einer 1-2 Monat alten Ammoniumpersulfatlösung erscheint sie aber auch bei ganz kleinen Vanadiummengen sofort. Die an der Hand liegende Vermutung, dass dabei eventuell Wasserstoffperoxyd eine Rolle spielt, hat sich als unrichtig erwiesen. Gibt man nämlich zu einer 18 μg/ml enthaltenden Vanadiumprobe sogar 1 ml 5%-iger H_2O_2 Lösung anstatt der Ammoniumpersulfatlösung, so erscheint die Orangefarbe auch nach 5 Minuten noch nicht.

Die Reaktion wird von den meisten Ionen nicht gestört, sie ist also weitgehend spezifisch. Bei dem Nachweis von 1 μg/ml Vanadium(V) stören selbst in 1000-facher (also 1 mg/ml) Konzentration die folgenden Ionen nicht: Li, Na, K, (NH_4), Mg, Ca, Sr, Zn, Cd, Hg(II), Al(III), La(III), Ce(III), Tl(I), Sn(II), Sn(IV), Th(IV), As(III), As(V), Sb(III), Sb(V), Mo(VI), W(VI), U(VI), Mn(II), Co(II), Ni(II), Cu(II), Cl^-, NO_3^-, SO_4^{-2}.

Bei der obigen Ausführung der Reaktion wirken aber mehr als 100 μg Fe(II), oder Fe(III), 15 μg Ti(IV), 40 μg Ce(IV) und 250 μg MnO_4^- Ionen störend. Mit der eigenen Farbe stört mehr als 180 μg Cr(III) auch.

Literatur S. 331

Die störende Wirkung von Fe(II) und Fe(III) ist leicht auszuschalten durch Zugabe von 2 ml 5%-igen Äthylendiamintetraessigsäures Natrium zur untersuchenden Lösung noch vor dem Rutin. In Gegenwart von Ti(IV) fügt man zur Lösung noch 2 ml 3%-ige NaF Lösung, dann verfährt man wie oben. Die störende Wirkung der Ce(IV) bzw. MnO_4^- Ionen ist am einfachsten so auszuschalten, dass man zur untersuchenden saueren Lösung 1–2 Tropfen H_2O_2 gibt, danach ist die Reaktion ohne Störung ausführbar. So stören, bei dem Nachweis von 1 µg/ml Vanadium(V), auch 1000-fache Mengen von den genannten Ionen nicht mehr.

Die Farbreaktion gründet sich nach unseren Erfahrungen auf der katalytischen Oxydation des Rutins durch das Vanadium(V).

DANK

Das Rutin wurde uns von Herrn Prof. Dr. R. BOGNÁR und V. SZABÓ zur Verfügung gestellt. Wir möchten dafür auch an dieser Stelle unseren besten Dank aussprechen.

ZUSAMMENFASSUNG

Es wurde eine einfache, schnell ausführbare, empfindliche und weitgehend spezifische Methode zum Nachweis von Vanadium(V) ausgearbeitet. Das Wesen der Methode besteht in einer Farbreaktion des Vanadiums mit dem Rutin in Gegenwart von Ammoniumperoxydisulfat in phosphorsäurem Medium.

Nachweisgrenze: 0.3 µg Vanadium(V) in 1 ml Lösung.

SUMMARY

A simple, sensitive and highly specific test is presented for the detection of vanadium(V). The test is based on the color reaction of vanadium(V) with rutin (quercetin-3-rutinoside) in the presence of ammoniumperoxydisulfate in phosphoric acid.

Sensitivity: 0.3 µg vanadium(V) in 1 ml solution.

RÉSUMÉ

Une réaction simple, sensible et spécifique est proposée pour l'identification du vanadium. On effectue cet essai au moyen de rutine en présence de persulfate d'ammonium et d'acide phosphorique. On obtient une coloration rouge orange.

LITERATUR

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Eingegangen den 15. September 1958

SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF COBALT, NICKEL AND COPPER WITH DITHIO-OXAMIDE

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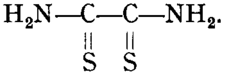
INTRODUCTION

Cobalt, nickel and copper are frequently used as alloying metals in steel, and copper and nickel are extensively used as alloying metals in aluminum.

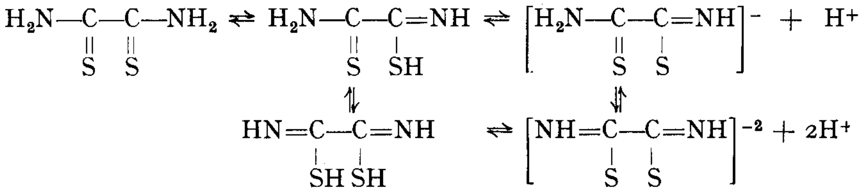
Since cobalt, nickel and copper are often found in the same substance, a method for the simultaneous determination of the three metals is of great practical importance. CHILTON[1] developed a simultaneous spectrophotometric method for cobalt, nickel and copper based upon the reactions of these ions with diethyldithiocarbamate and subsequent extraction of the complexes into carbon tetrachloride. This paper presents a simultaneous spectrophotometric method for the determination of cobalt, nickel and copper based upon the reactions of these ions with dithio-oxamide (rubeanic acid).

Dithio-oxamide or rubeanic acid has the following structure:



$$H_2N{-}\underset{\underset{S}{\|}}{C}{-}\underset{\underset{S}{\|}}{C}{-}NH_2.$$

In water–ethanol solutions, the following tautomerism and dissociation equilibria must be taken into account:



From a consideration of these equilibria, it is possible to increase the concentration of the dithio-oxamate anions considerably by suppressing or removing H^+ ions, *e.g.*, by addition of hydroxide ions.

RÂY[2] was the first to show that cobalt, nickel and copper can be precipitated quantitatively by dithio-oxamide from ammoniacal solution. Since then a number of investigators[3–13] have made studies primarily on the use of dithio-oxamide as a reagent for copper.

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APPARATUS

Spectrophotometers. Beckman spectrophotometers, Model DK-2 and Model DU, with 1-cm Corex cells were used.

pH Meter. A Beckman pH meter, Model G, was employed for all pH measurements. It was calibrated daily with Fisher Certified Standard Buffers.

REAGENTS

Standard cobalt solution. A solution containing 1 mg/ml cobalt was prepared by dissolving 2.03 g of cobalt chloride hexahydrate in doubly-distilled water. Twice distilled hydrochloric acid was added so that the final concentration, after dilution to 500 ml, was $1 M$. The solution was standardized electrolytically.

Standard nickel solution. A standard nickel solution containing 1 mg/ml nickel was prepared by dissolving 2.03 g nickel chloride hexahydrate in the above manner. The solution was standardized by the dimethylglyoxime gravimetric method.

Standard copper solution. A copper solution containing 1 mg/ml copper was prepared by dissolving 1.45 g of cupric chloride dihydrate in the above manner. The solution was standardized electrolytically.

Buffer solutions. A pH 9 buffer was prepared by dissolving 3.84 g of sodium borate decahydrate in 1 l of doubly-distilled water and a pH 4 buffer by dissolving 1.01 g of potassium acid phthalate in 100 ml of doubly-distilled water. All other buffers were prepared according to the directions given by BRITTON[14].

Dithio-oxamide solution. A $1.5 \cdot 10^{-3} M$ solution of dithio-oxamide was prepared by dissolving 45 mg in 250 ml of absolute ethanol.

Gum acacia solution. A 0.1% solution of gum acacia was prepared by dissolving 0.2 g in 200 ml of doubly-distilled water.

Doubly-distilled water. All water used in this work was distilled twice and finally run through a cation exchange resin, Amberlite IR-120. The resin column was 26 cm in length and had an internal diameter of 2 cm.

Other reagents. All other reagents were analytical grade and were used without further purification.

EXPERIMENTAL

Properties of the reagent

Dithio-oxamide is an orange-red solid which is soluble in ethanol forming an orange colored solution. The absorbance curve for a $1.2 \cdot 10^{-4} M$ solution is shown in Fig. 1.

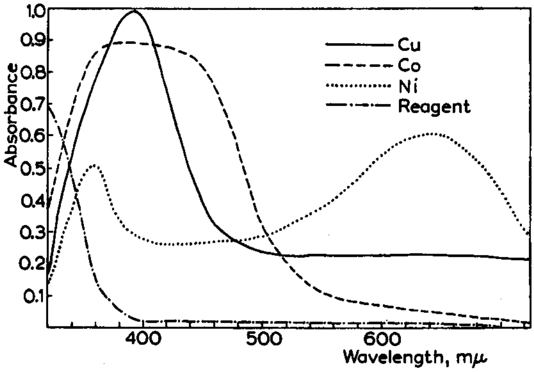


Fig. 1. Absorbance curves of 4.00 p.p.m. solutions of cobalt, nickel and copper; reagent curve, $1.2 \cdot 10^{-4} M$. All at pH 9.0 ± 0.3.

In order to cover the useful range of metal ion concentrations conveniently and to provide a sufficient excess of reagent, a $1.5 \cdot 10^{-3} M$ reagent solution was used.

The reagent solution is stable to light, hydrolysis, and oxygen and carbon dioxide of the air. Absorbance measurements on the reagent solution showed no significant change over a period of six weeks; measurements were not made over a longer period.

Properties of the complexes

Color. Cobalt, nickel and copper form water-insoluble complex salts with the reagent solution. The cobalt complex is yellow, the nickel complex blue and the copper complex olive green. A protective colloid such as gelatin or gum acacia keeps the complex in solution over the concentration range used. Gum acacia was used in this work in preference to gelatin because it is much more stable. Absorbance curves of 4.00 p.p.m. solutions of the complexes are shown in Fig. 1. The absorbances of the complexes were measured against a reagent blank. The nickel and copper complexes have a maximum at 640 mμ and 385 mμ, respectively, while the cobalt complex has a broad absorbance peak with the maximum occurring at approximately 370 mμ. At 440 mμ the absorbance of the cobalt complex is only about 3.5% less than at 370 mμ. Since the absorbances of the reagent, the nickel complex and the copper complex are all less at 440 mμ than at 370 mμ, the former is the most advantageous wavelength to use when simultaneous determinations are to be made.

Effect of pH. The effect of the hydrogen-ion concentration on the complexes is shown in Fig. 2. The absorbance curves were obtained by using 4.00 p.p.m. of the ion, 4 ml of a 0.1% gum acacia solution, 10 ml of a buffer solution of the desired pH and 3 ml of the reagent solution. The samples were diluted to 25 ml with distilled water and absorbance measurements made against a reagent blank. From the curves it is seen that the optimum pH for making simultaneous measurements is 9.0 ± 0.3.

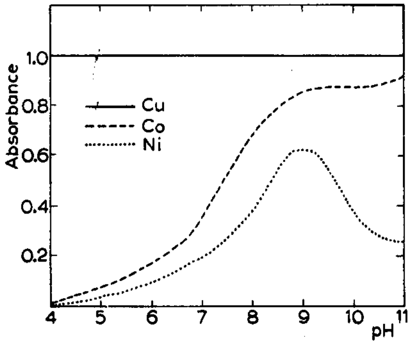


Fig. 2. Effect of pH on the cobalt, nickel and copper complexes.

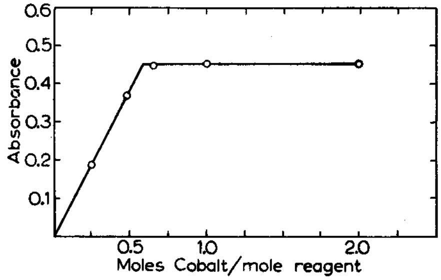


Fig. 3. Mole ratio method applied to cobalt complex.

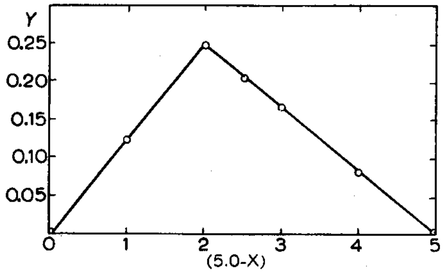


Fig. 4. Continuous variations method applied to cobalt complex.

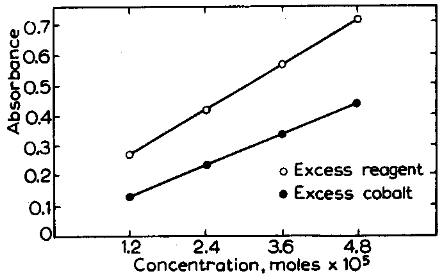
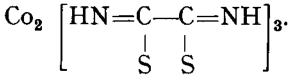


Fig. 5. Slope ratio method applied to cobalt complex.

Structure of the complexes in solution. The empirical formulas of the three complexes *in solution* were established by three independent methods: the mole ratio method of YOE AND JONES[15], the continuous variations method of JOB as modified by VOSBURG AND COOPER[16], and the slope ratio method of HARVEY AND MANNING[17]. The results of these three methods applied to the cobalt complex are shown in Figs. 3, 4 and 5. They indicate a ratio of 2 moles of cobalt to 3 moles of reagent. This corresponds to a salt of Co^{+3} and reagent having a formula



$$\mathrm{Co_2}\left[\mathrm{HN{=}\underset{\underset{S}{|}}{C}{-}\underset{\underset{S}{|}}{C}{=}NH}\right]_3.$$

Nickel and copper both combine in ratios of 1 mole ion to 1 mole reagent indicating that salts are formed by Ni^{+2} and Cu^{+2} reacting with the divalent dithio-oxamate anion.

Order of addition of reagents. For maximum sensitivity the solutions containing the metallic ion and protective colloid must be adjusted to the proper pH before the reagent solution is added.

Effect of temperature. Temperature studies made at 15°, 25°, and 35° showed each of the complexes to be independent of normal variations in laboratory temperature.

Adherence to Beer's law. A series of samples containing varying concentrations of the metallic ion, 4 ml gum acacia solution, 10 ml of pH 9 buffer and 3 ml of reagent solution was prepared and diluted to 25 ml with distilled water. The absorbances of these solutions were measured against a reagent blank at wavelengths of 640 mμ for the nickel complex, 385 mμ for the copper complex, and at wavelengths of 440 mμ and 370 mμ in the case of the cobalt complex. Fig. 6 shows that Beer's law is obeyed by the cobalt complex at both wavelengths over the range 0.16 p.p.m. to 4.00 p.p.m. The complexes of nickel and copper follow Beer's law over the same concentration range. Lower and higher concentrations were not investigated.

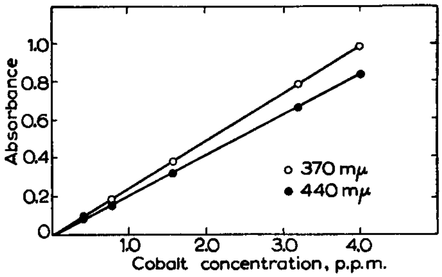


Fig. 6. Beer's law plot for cobalt complex.

Effect of diverse ions. The effect of foreign ions may be due to one of the following causes:

1. The foreign ion may react with the reagent.
2. The foreign ion may react with the ion to be determined.
3. The foreign ion may precipitate because of the pH of the solution.

The metal ions that react with dithio-oxamide in alkaline medium, exclusive of cobalt, nickel and copper, are palladium, silver, platinum, gold, mercury, and lead.

References p. 339

These ions interfere with the determination of cobalt, nickel and copper when present in ratios of 1:1 or more. An interference was arbitrarily chosen as a change in absorbance of 0.010 unit, corresponding to 0.2 p.p.m. Co, 0.3 p.p.m. Ni and 0.2 p.p.m. Cu.

The cyanide ion must be absent since it forms more stable complexes with the three ions than does dithio-oxamide. High concentrations of citrate and tartrate ions, *i.e.*, concentrations high enough to prevent the precipitation of iron and aluminum at pH 9, interfere in the determination of cobalt and nickel but not in the determination of copper.

Ions such as Fe^{+3}, Al^{+3}, Mn^{+2}, etc. which precipitate in alkaline solution must be absent or, if present, must either be removed or complexed to prevent their interference.

Sensitivity. The sensitivities of the color reactions as defined by SANDELL[18] are as follows:

for cobalt at 440 mμ, 0.0046 γ/cm^2;
for nickel at 640 mμ, 0.0068 γ/cm^2;
for copper at 385 mμ, 0.0037 γ/cm^2.

Practical sensitivities, *i.e.*, an absorbance of 0.005 unit are: 0.023 p.p.m. Co, 0.034 p.p.m. Ni and 0.019 p.p.m. Cu.

Simultaneous determination of cobalt, nickel and copper

Table I lists the values of the molar extinction coefficients of the complexes of cobalt, nickel and copper measured at wavelengths of 440 mμ, 640 mμ and 385 mμ, respectively. These values may be used to calculate equations for the determination of one or more components[19]. The equations derived from the above values are given in Table II.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF THE COBALT, NICKEL AND COPPER COMPLEXES

	385 mμ	*440 mμ*	*640 mμ*
ε_{Co}	12,950	12,500	618
ε_{Ni}	4,360	3,920	8,930
ε_{Cu}	15,800	6,060	4,010

Recommended procedure. The optimum conditions for the determination of cobalt, nickel and copper are those under which the absorbances of the complexes are the greatest, the most stable and the most reproducible. The results described up to this point show that these conditions are fulfilled by measuring the absorbance of a solution at 440 mμ, 640 mμ, and 385 mμ, against a reagent blank containing 2 ml reagent solution, which has been prepared as follows: the complexes are formed at a pH of 9.0 ± 0.3 in the presence of 4 ml of a 0.1% gum acacia solution by adding 3 ml of a $1.5 \cdot 10^{-3} M$ reagent solution. Dilute to 25 ml, mix and measure the absorbances at the indicated wavelengths. The molar concentrations of the ions are then calculated by using the spectrophotometric equations listed in Table II.

Interference of cobalt upon the determination of nickel. When solutions containing cobalt, nickel and copper were analysed by the above procedure, it was found that in some cases only one-half to one-third of the nickel added was recovered. This incomplete recovery was not encountered when samples containing only nickel and copper were analysed. However, when the complexes were developed individually and

TABLE II

SPECTROPHOTOMETRIC EQUATIONS USED

One of three ions present

$(\mathrm{Co}) \cdot 10^5 = 8.00\ A_{s440}$

$(\mathrm{Ni}) \cdot 10^5 = 11.2\ A_{s640}$

$(\mathrm{Cu}) \cdot 10^5 = 6.17\ A_{s385}$

Two of three ions present

$(\mathrm{Cu}) \cdot 10^5 = 10.4\ A_{s385} - 10.8\ A_{s440}$

$(\mathrm{Co}) \cdot 10^5 = 13.2\ A_{s440} - 5.06\ A_{s385}$

$(\mathrm{Cu}) \cdot 10^5 = 7.23\ A_{s385} - 3.53\ A_{s640}$

$(\mathrm{Ni}) \cdot 10^5 = 12.8\ A_{s640} - 3.24\ A_{s385}$

$(\mathrm{Co}) \cdot 10^5 = 8.17\ A_{s440} - 3.58\ A_{s640}$

$(\mathrm{Ni}) \cdot 10^5 = 11.4\ A_{s640} - 0.57\ A_{s440}$

Three ions present

$(\mathrm{Co}) \cdot 10^5 = 12.1\ A_{s440} - 3.76\ A_{s385} - 3.46\ A_{s640}$

$(\mathrm{Ni}) \cdot 10^5 = 11.6\ A_{s640} - 4.08\ A_{s440} - 4.50\ A_{s385}$

$(\mathrm{Cu}) \cdot 10^5 = 10.8\ A_{s385} - 11.0\ A_{s440} - 0.30\ A_{s640}$

then mixed before making measurements, the results were good. This phenomenon suggested that when the nickel complex was formed in the presence of cobalt, there was a shift in the absorbance peak of the nickel complex. It was further observed visually that when the concentration of nickel to cobalt was large (*ca.* 4 to 8) the effect appeared to be less pronounced. In order to determine this ratio precisely, the following experiment was performed: solutions were prepared which contained 0.40 p.p.m. cobalt and concentrations of nickel varying from 1.00 p.p.m. to 4.00 p.p.m. A blank was used which contained 0.40 p.p.m. cobalt. Since the absorbance due to the cobalt complex was subtracted in each case by the blank, the absorbances observed at each wavelength were those of the nickel complex. The results of this experiment are shown in Fig. 7. When the ratio of nickel to cobalt is 7 or greater, there is no shift in the nickel complex absorbance peak.

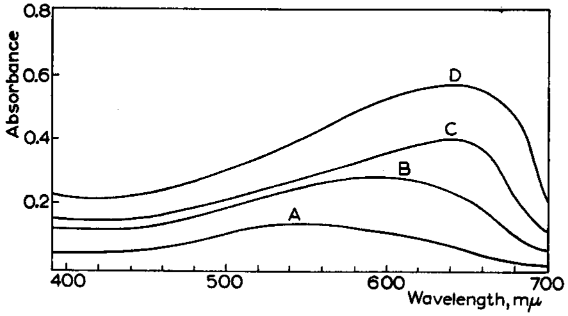


Fig. 7. Effect of 0.40 p.p.m. cobalt on (A) 1.00 p.p.m. nickel, (B) 2.00 p.p.m. nickel, (C) 3.00 p.p.m. nickel and (D) 4.00 p.p.m. nickel.

Analysis of synthetic samples and NBS standard samples

A series of synthetic samples and three National Bureau of Standards samples were analyzed by the procedure finally adopted. Each sample had the indicated ion concentration, 4 ml of a 0.1% gum acacia solution, 3 drops of a 0.1% thymolphthalein solution and was adjusted to a pH 9.0 ± 0.3 with ammonium hydroxide and hydrochloric acid until the blue color of the indicator just turned colorless. Three ml of a $1.5 \cdot 10^{-3} M$ reagent solution was added. The samples were diluted to the mark in 25

TABLE III

ANALYSIS OF SYNTHETIC SAMPLES

Sample	*Added (p.p.m.)*	*Found (p.p.m.)*
1	Ni 0.40	0.39
	Cu 2.40	2.47
2	Co 0.80	0.69
	Cu 2.00	2.06
3	Ni 1.00	1.14
	Cu 2.00	2.06
4	Co 0.40	0.44
	Ni 3.00	3.07
	Cu 2.00	1.85
5	Co 0.40	0.39
	Ni 3.50	3.66
	Cu 1.50	1.30
6	Co 0.40	0.31
	Ni 4.00	4.07
	Cu 1.00	0.98

TABLE IV

ANALYSIS OF NATIONAL BUREAU OF STANDARDS SAMPLES

Material	*NBS Value %*		*% Ni* *Found*	*% Cu*
Al alloy	Ni 0.41			
85a	Cu 2.48		0.42	2.42
			0.33	2.52
			0.39	2.38
			0.41	2.47
		av.	0.39	2.45
Al–Si alloy	Ni 0.59		0.54	0.28
87	Cu 0.30		0.58	0.30
			0.58	0.31
			0.60	0.30
		av.	0.58	0.30
Ferro-silicon	Ni 0.115		0.100	0.039
alloy 58	Cu 0.04		0.106	0.031
			0.107	0.032
			0.107	0.037
		av.	0.105	0.035

ml volumetric flasks, mixed and the absorbances measured at the respective wavelengths against a reagent blank which contained 2 ml of reagent solution. The results are given in Tables III and IV.

In order to prevent the precipitation of the hydrated oxides of aluminum and iron when the NBS samples 85a, 87 and 58 were analysed, the aluminum was complexed with 5 ml of a 5% sodium fluoride solution in the case of aluminum alloys 85a and 87 and the iron in the ferro-silicon alloy, 58, was extracted by diethyl ether from a 20% hydrochloric acid solution.

SUMMARY

The cobalt, nickel and copper complexes of dithio-oxamide have been characterized in terms of color, effect of pH, structure *in solution*, order of addition of reagents, adherence to Beer's law and sensitivity. The reactivity of the reagent to other ions has been reported.

A method for the simultaneous spectrophotometric determination of cobalt, nickel and copper has been developed. The results of the application of this procedure to synthetic samples and to several National Bureau of Standards Samples are given.

RÉSUMÉ

Les complexes du cobalt, du nickel et du cuivre avec la dithioxamide ont été examinés. Une méthode spectrophotométrique de dosages simultanés de ces trois éléments est proposée.

ZUSAMMENFASSUNG

Es werden die Komplexe von Kobalt, Nickel und Kupfer mit Dithiooxamid beschrieben und über eine spektrophotometrische Methode zur gleichzeitigen Bestimmung dieser drei Elemente berichtet.

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DETERMINATION OF MICROGRAM AMOUNTS OF COBALT IN SODIUM METAL*

2-NITROSO-1-NAPHTHOL SPECTROPHOTOMETRIC METHOD

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The valuable properties of pure sodium as coolant in certain types of atomic energy reactors are well known. After a calculated long-term operational period, the reactor must be shut down and the fuel rods exchanged. During the operational period the sodium and its impurities are subjected to irradiation and a "cooling" or "decay" period is foreseen at the shutdown. One of the many possible elements present in the sodium which could enforce an unusually long cooling period is cobalt, because of the likely presence of a long-lived cobalt isotope. Calculations show that not more than 2 p.p.m. of cobalt are permissible in the sodium, in order to prevent an uneconomically long cooling period before the irradiated sodium can be safely transported and handled.

Several colorimetric methods for analyzing small amounts of cobalt were examined. The reagent, 2-nitroso-1-naphthol, appeared to be the most applicable and it is this reagent which is used. A technique similar to that employed by ALMOND[1] for determining cobalt in soils was developed. The cobalt forms a complex with the reagent at a pH of 4 to 8.5. Other impurities such as ferric iron, copper and nickel cause no interference since the ferric iron does not complex at this pH and the copper and nickel complexes present in small amounts, are removed by washing.

APPARATUS AND REAGENTS

Apparatus

Spectrophotometer. Beckman spectrophotometer, Model DU, supplied with 5-cm cells.

pH Meter. Beckman pH meter, Model H was used.

Separatory funnels. Ultramax type with teflon valves to contain the carbon tetrachloride. 250-ml and 125-ml capacities.

Reagents

Reagent solution. Prepare 0.01% solution of 2-nitroso-1-naphthol by adding 2 drops of 1*N* sodium hydroxide and a small amount of water to 0.01 g of 2-nitroso-1-naphthol. Stir until in solution and dilute to a 100-ml volume.

Standard cobalt solutions. Dissolve 4.954 g of $Co(NO_3)_2{\cdot}6H_2O$ in H_2O and dilute to 1 l. Fume 100 ml with 1 ml H_2SO_4 and dilute to 1 l. Make subsequent dilutions from the sulfate solution. Standardize by direct ignition or by the 1-nitroso-2-naphthol gravimetric method.

Borate buffer[1]. Dissolve 19 g of $Na_2B_4O_7{\cdot}10H_2O$ in 800 ml of H_2O, add 10 ml of concentrated NH_4OH, and dilute to 1 l.

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* This report is based on studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

EXPERIMENTAL RESULTS

Effect of chloride

Preliminary studies were made using 25 g of sodium chloride, dissolved in 100 ml of water, to simulate a 10-g sample of sodium metal converted to the chloride. It was quickly noted that 6 μg of cobalt could not be extracted from an aqueous solution of low chloride content. In a 100-ml volume, it is requisite to have a minimum of 3 g of sodium chloride for complete cobalt recovery (Fig. 1).

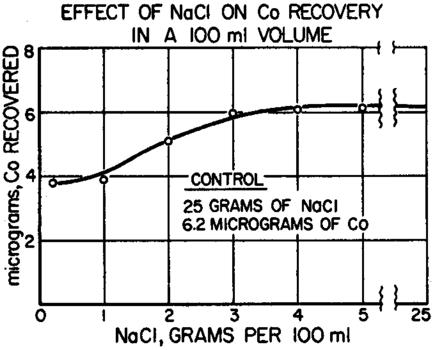

Fig. 1.

Removal of excess reagent

A brief study showed that 5 ml of the reagent (0.01%) was optimum, for the conditions used. The excess reagent present can be effectively removed by shaking the carbon tetrachloride extract with 4% sodium hydroxide containing a few drops of 10% potassium cyanide. This is shown by a low absorbance reading at 410 mμ, characteristic for this reagent.

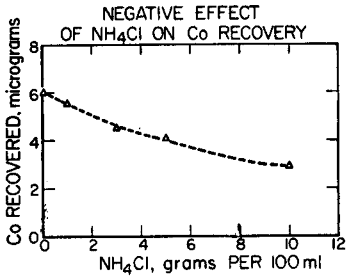

Fig. 2.

Effect of alkali metal ions

Potassium, lithium and sodium ions have no effect on the formation of the cobalt complex.

Ammonium ions of the order of gram quantities have an adverse effect on the formation of the cobalt complex with the 2-nitroso-1-naphthol (Fig. 2) despite the favorable presence of sodium chloride.

Effect of other metal ions

The amounts of the various foreign metals in commercial sodium metal are such that no interference occurs.

Ferric iron does not form a complex with the reagent at the 6.5 pH used; citrate is added to prevent hydrolytic precipitation of the iron.

The copper and nickel form complexes with the reagent but are removed in the same step which removes the excess reagent. Should larger amounts than normally present in sodium metal of these two ions exist, their removal can be effected by an additional washing step, in which the complexes in the carbon tetrachloride are shaken with hydrochloric acid[2]. Proportionally larger amounts of the reagent, 2-nitroso-1-naphthol are also required, so that these ions can be completely complexed and thus prevent possible incomplete formation of the cobalt complex.

PROCEDURE

Quickly weigh a portion (about 10 g) of the sodium metal to be analyzed and transfer the sodium metal into a Vycor test tube. Maintain a rapid flow of nitrogen over the surface of the sodium. Add water dropwise to the sodium, allowing time for the reaction to subside between additions. After the metal has completely reacted, wash the sodium hydroxide into a 250-ml beaker and then neutralize with hydrochloric acid. Add 1 ml of 10% ammonium citrate to the resulting salt solution and adjust the pH to 6.5 with borate buffer. Transfer the solution to a 250-ml separatory funnel, and add 5 ml of 0.01% 2-nitroso-1-naphthol. Extract the colored complexes by shaking 3 min with exactly 20 ml of carbon tetrachloride. Drain the carbon tetrachloride layer into a 125-ml separatory funnel which contains 10 ml of a 4% sodium hydroxide solution and 1 drop of 10% potassium cyanide solution. Shake for 15 sec. This step removes interfering complexes and excess reagent. Shake the carbon tetrachloride layer with 10 ml of 1% sodium chloride to remove small amounts of sodium hydroxide which might damage spectrophotometer cells. Filter the carbon tetrachloride through cotton into a small flask. Carry a reagent blank through the procedure.

Transfer the sample and the blank to 5.0-cm cells and measure the absorbance using carbon tetrachloride as reference at 535 mμ. Correct the sample for the blank reading and obtain the amount of cobalt present from the standard curve.

Standard curve

Prepare a series of samples containing known amounts of cobalt (0 to 10 μg) Adjust the volume to 100 ml, and add 25 g of sodium chloride (to simulate a 10-g sample of sodium). These are carried through the same procedure as given for the analysis of the sodium starting with the addition of 1 ml of 10% ammonium citrate. Correct the absorbances obtained for reagent blank, and plot on linear graph paper *versus* the μg of cobalt. A straight line is obtained. (The molar absorption coefficient is 11,780.)

DISCUSSION

Several reagents for determining μg amounts of cobalt were studied. Of these, the most favorable were tetraphenylarsonium chloride–thiocyanate, diethyldithiocarbamate and 2-nitroso-1-naphthol. The determination of cobalt as tetraphenylarsonium cobaltothiocyanate was not sufficiently sensitive, having a working range of approximately 20 to 100 μg when a range of 1 to 10 μg was desired for determining cobalt in sodium. The molar absorption coefficient for this reagent was found to be 1,800.

Diethyldithiocarbamate had been used by CHILTON[3,4] whereby copper, nickel, and cobalt were determined simultaneously. This reagent was quite sensitive for cobalt, having a molar absorption coefficient of 14,000. However, attempts to apply this method to determining cobalt in sodium were unsuccessful.

2-Nitroso-1-naphthol is also a very sensitive reagent for determining cobalt. The molar absorption coefficient was found to be 11,780.

Using 2-nitroso-1-naphthol as the reagent for determining cobalt, μg amounts of cobalt could be successfully extracted from 25 g of sodium chloride dissolved in 100 ml of water.

When experimentally extracting the small amounts of cobalt from a 100-ml volume of water, it was found necessary to have a minimum of 3 g of sodium chloride present (Fig. 1). The sodium chloride apparently furnishes the requisite chloride ion to complete extraction of the cobalt.

Using a 10-g sample of sodium, 0.1 p.p.m. of cobalt can be determined. The optical density for 1 μg of cobalt in 20 ml of carbon tetrachloride, corrected for a reagent blank, is 0.05 when measured in a 5-cm spectrophotometer cell. The standard deviation was found to be 5% of the value.

SUMMARY

A colorimetric method, with 2-nitroso-1-naphthol, is outlined for determining cobalt in sodium metal, which is used as a coolant in nuclear reactors. The sodium metal is reacted with water, neutralized with hydrochloric acid, and the cobalt content determined; the cobalt nitrosonaphtholate is extracted with carbon tetrachloride and the absorbance is measured at 535 mμ. Chloride ion is requisite for the extraction of the cobalt complex in dilute solutions. Lithium and potassium as well as sodium have no effect. Ammonium ions have an adverse effect. As little as 0.1 p.p.m. cobalt can be determined in sodium metal. In order to determine cobalt in the fractional p.p.m. range, 10 g of sample are used. The molar extinction coefficient is 11,780.

RÉSUMÉ

Une méthode colorimétrique est proposée pour le dosage du cabalt dans le sodium métallique, utilisé dans les réacteurs nucléaires. Le nitrosonaphtolate de cobalt est extrait au moyen de tétrachlorure de carbone. On mesure l'absorption à 535 mμ.

ZUSAMMENFASSUNG

Es wird eine colorimetrische Methode zur Bestimmung von Kobalt in Natrium-Metall, das als Kühlmittel in Kern-Reaktoren verwendet wird, beschrieben. Das Kobalt wird als Kobalt-nitrosonaphtholat mit Tetrachlorkohlenstoff extrahiert und die Absorption der Lösung bei 535 mμ gemessen.

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THE COULOMETRIC DETERMINATION OF SULFUR IN SILICON-IRON

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INTRODUCTION

Within the last few years there has been an increasing demand for a better method for the control analysis of sulfur in ferrous materials (especially silicon-iron) where the sulfur content is in the range of 0.0001 to 0.002 % by weight.

There are three methods that may be used for routine control purposes[1] given below:

(1) *Gravimetric method.* Conversion of sulfur to sulfate, precipitation as barium sulfate.

(2) *Evolution of sulfur as H_2S,* absorbing as an insoluble sulfide in an alkaline solution, followed by titrating with iodine in an acid solution.

(3) *Combustion method.* Burning the material in oxygen and (a) absorbing the oxides of the sulfur followed by titration with a standard alkaline solution, (b) absorbing the oxide sulfur gases into an acid iodine–iodide solution held at a constant iodine concentration by titrating with a standard iodate solution.

The first two methods are obviously unsatisfactory; the gravimetric procedure is time-consuming and unsuitable for such low percentages of sulfur, and the evolution technique is limited to materials containing no constituents that form acid-insoluble sulfides. Consequently, the combustion process (although empirical) has become predominant for routine sulfur analysis. Commercial apparatus is available for rapid sulfur analysis by the combustion technique. However, the minimum amount of sulfur that can be determined is 0.001% with a reproducible precision of ± 0.001%. Nevertheless, the rapidity of the combustion process in converting the sulfur in metals to SO_2 indicated that a method for the determination of smaller amounts of sulfur should be a refinement of existing technique rather than an entirely new attack upon the problem. The method described in this report is an adaption of the conventional combustion process to a coulometric titration technique sensitive enough to determine sulfur at the 0.0001% level.

CHEMISTRY

Two methods of determining the amount of sulfur (as SO_2) obtained by the combustion of the sample were used with equal success. In both cases, the number of coulombs of electricity necessary to oxidize sulfite ion to sulfate ion was an exact measure of the SO_2 obtained by the combustion process. Both methods are outlined below.

Direct method

The gases from the combustion tube were passed through distilled water to absorb the SO_2 as H_2SO_3[2]. This solution was added to an acid KBr solution containing a small amount of KI in a specially constructed cell with provisions for the generation of Br_2 (and I_2)[3] by electrolysis at constant current. The reactions in the cell are the following:

(a) At the generator anode:

$$2Br^- = Br_2 + 2e \quad (1)$$

$$2I^- = I_2 + 2e \quad (2)$$

(b) In the solution:

$$Br_2 + 2I^- = I_2 + 2Br^- \quad (1)$$

$$SO_3^{-2} + H_2O + I_2 = SO_4^{-2} + 2I^- + 2H^+ \quad (2)$$

There also may be the reaction:

$$SO_3^{-2} + H_2O + Br_2 = SO_4^{-2} + 2Br^- + 2H^+ \quad (3)$$

but the large amount of KI relative to the SO_3^{-2} concentration makes this improbable. In order to determine when the oxidation of SO_3^{-2} to SO_4^{-2} was complete, the cell contained two indicator electrodes, with a potential impressed across them such that a very small current flow was obtained, the reactions being:

In the absence of I_2

$$2H^+ + 2e = H_2 \text{ (cathode)}$$

$$2I^- = I_2 + 2e \quad \text{(anode)}$$

The reaction at the indicator cathode becomes

$$I_2 + 2e = 2I^-$$

with the first excess of I_2. This results in a large increase in the indicator current which indicates the completion of the titration.

Indirect method

In this case the gases from the combustion furnace were passed through an aqueous solution of potassium ferricyanide, the sulfite apparently being oxidized to sulfate with the corresponding reduction of ferricyanide to ferrocyanide. This solution was titrated in the same cell by electrolytically generated Br_2. The end-point was determined by the increase in the indicator current at the first excess of Br_2. The reactions taking place are:

$$2Br^- \rightarrow Br_2 + 2e \text{ (generator anode)} \quad (1)$$

$$Br_2 + 2Fe(CN)_6^{-4} \rightarrow 2Br^- + 2Fe(CN)_6^{-3} \text{ (in soln.)} \quad (2)$$

$$2Br^- \rightarrow Br_2 + 2e \text{ (indicator anode)} \quad (3)$$

$$2H^+ + 2e \rightarrow H_2 \text{ (indicator cathode before excess } Br_2\text{)} \quad (4)$$

$$Br_2 + 2e = 2Br^- \text{ (with excess } Br_2\text{)} \quad (5)$$

EXPERIMENTAL EQUIPMENT

The combustion unit was a commercial induction model manufactured for use in routine sulfur analysis of iron and steel. The O_2 purifying train preceding the combustion unit was set up exactly as specified by the manufacturer. Fig. 1 is a schematic illustration of the gas absorption vessel and titration cell and Fig. 2 is a photograph of this assembly. The gases from the combustion furnace were passed into the absorption cell in the same manner as they were passed into a conventional titration cell.

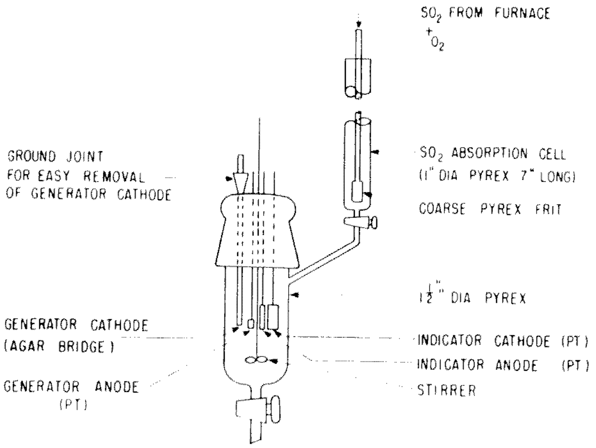

Fig. 1. Schematic illustration of low sulfur titration cell.

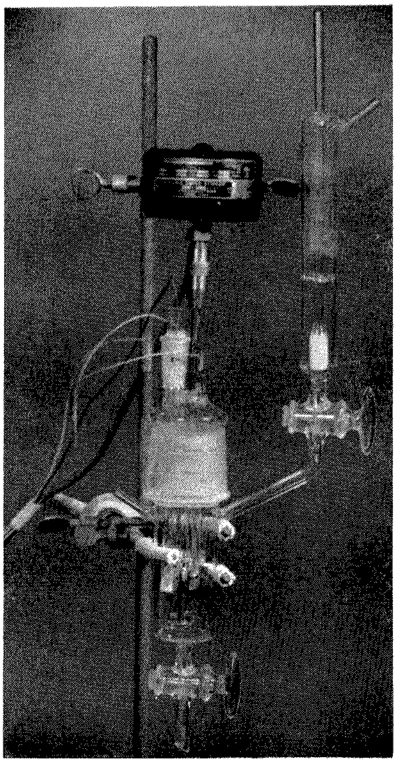

Fig. 2. The absorption and titration cell.

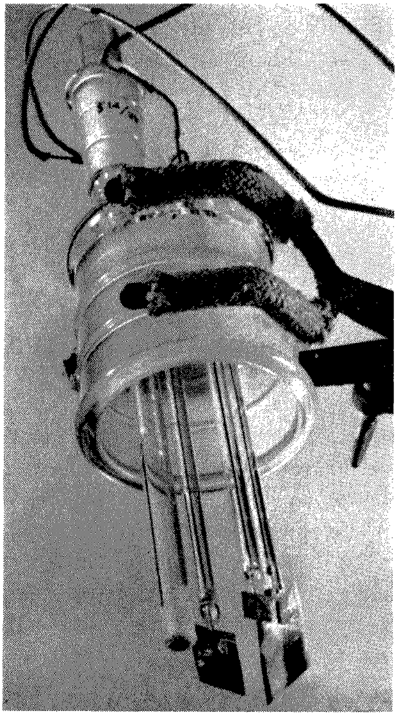

Fig. 3. The generator and indicator electrodes

References p. 352

The generator anode and both indicator electrodes were made of platinum sheet, spot-welded to platinum wire sealed into pyrex tubing. The relative positions of the electrodes are shown in Fig. 3.

The absorption cell and titration cell were fitted with suitable side arms (shown in Fig. 2) so that all the necessary solutions for collecting gases, titrating, and rinsing

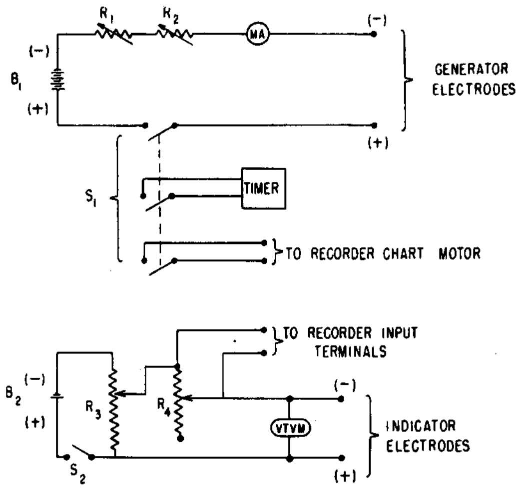

Fig. 4. Wiring diagram.

B_1: 45 V, dry cell; B_2: 1.5 V, dry cell; R_1: 2000 KΩ variable; R_2: 20 KΩ variable; R_3: 100 Ω variable; R_4: 2 KΩ variable; MA: 0.05 to 100 mA, d.c., multiple range; VTVM: vacuum tube volt meter, 1.2 V; S_1: 3 SPST switches, ganged to operate together; S_2: SPST switch; Timer: accurate to 0.01 minute; Recorder: 10 mV, L & N speedomax.

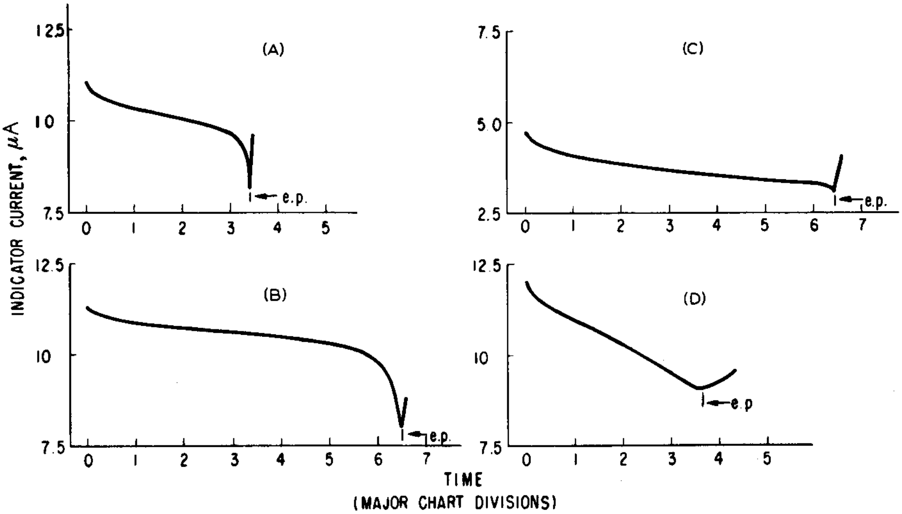

Fig. 5. Indicator current *vs.* time curves showing end-point sensitivity as a function of generator current; (A) Sample No. 8, Table II, 5 mA, gen. current; (B) Sample No. 3, Table IV, 2 mA, gen. current; (C) Sample No. 4, Table IV, 2 mA, gen. current; (D) Sample No. 16, Table III, 0.2 mA, gen. current.

could be admitted from reservoir bottles, controlled by means of air pressure. The KBr acid solution and the KI solutions were dispensed from automatic leveling burets. The titrating cell was constructed to hold 125 ml of solution with the stirrer operating. The absorption cell was constructed to hold 20 ml of solution with the O_2 flow set at 0.5 to 1 liter per minute.

The power supply and wiring is shown in Fig. 4. By using a 45-V dry cell as a current source for the generator electrodes, the stability of the circuit was more than adequate to obtain results in the range of precision desired. The indicator current was recorded by a Leeds and Northrup "Speedomax" 10 mV potentiometer recorder (Fig. 5). However, the chart speed of the instrument was not constant enough to use it to determine the time required for each titration. An electric timer, accurate to 0.01 min connected in the generator circuit was necessary for this data.

EXPERIMENTAL PROCEDURE

The experimental manipulation of burning the sample, collecting the SO_3 from the combustion process and titrating the collected sample was carried out in the same manner for all the materials investigated, except where differences were intentionally introduced in order to investigate the obvious variables of the method.

The oxygen flow rate was held at 0.8 l/min. 1 g of reagent-grade tin was used as a flux throughout the investigation. All samples were burned for a minimum of 5 min and a maximum of 7 min. The volume of gas-collecting solution was 20 ml in all cases. Loose fitting crucible lids, supplied by a manufacturer of crucibles for carbon and sulfur analyses, were employed. These lids were pre-fired by burning a charge of low-sulfur iron in the same manner as the experimental samples were burned. Unlike the crucibles, they were not severely damaged during the combustion process and could be used several times before it was necessary to discard them.

The generator current was adjusted to the desired value prior to running a series of determinations by filling the cell with the same solution that was used in the actual titrations, and adjusting the variable resistors R_1 and R_2. It was not necessary to change these resistance settings for subsequent determinations at the same generator current.

Immediately following combustion the absorption solution was drained into the titration cell (Fig. 1), which contained 80 ml of the acid solution containing KBr and/or KI, the stirrer turned on, and the titration carried out without unnecessary delay.

In order to facilitate rapid titration of the sample after collecting the SO_3, the recorder was turned on during the combustion period, the timer was set at zero, the indicator electrode potential was set at 0.2 V by means of R_4 (see Fig. 4) and S_2 was closed. Therefore, after the collecting solution was drained into the cell and the stirrer started, closing switch S_1 began the titration and simultaneously started the recorder chart and timer. The total time necessary for the titration was obtained by observing the recording of the indicator current and manually stopping the timer at the end-point.

The calculation of the per cent sulfur was made using the equation below:

$$\%S = \frac{(0.09618 \cdot 10^{-3})\ (i)\ (t)\ (100)}{W}$$

where: i = generator current in mA,
t = titration time in min,
W = sample weight in g.

The figure $0.09618 \cdot 10^{-3}$ is the weight (in g) of the sulfur contained in the SO_3^{-2} that is oxidized to SO_4^{-2} when one mA is passed for 1 min, calculated from Faraday's Law (96,500 coulombs necessary to oxidize, or reduce, 1 g-equivalent).

Experiments were conducted using four different sample materials, as follows;

(a) H-6435, a 3-1/4% Si-Fe alloy containing less than 0.001 % S.
(b) National Bureau of Standards Sample No. 36a, a Cr-Mo steel containing 0.018 % S.
(c) National Bureau of Standards Sample No. 132a, a Mo-W steel containing 0.006 % S.
(d) National Bureau of Standards Sample No. 125a, a 3.32% Si-Fe containing 0.013 % S.

The majority of the experiments were conducted using an aqueous solution containing 1 g/l of potassium ferricyanide to absorb the SO_3. The absorption solution was drained into a solution that was 2*M* in HCl and 0.1*M* in KBr.

A few experiments were conducted using distilled water to absorb the SO_3. In order to obtain a good end-point it was necessary to add 5 ml of an iodide solution (20 mg KI/l H_2O) to the HCl–KBr solution before titrating.

Crucibles obtained from two manufacturers were used, designated as type "A" and type "B" in this report. Type "A" is a mullite ceramic, and Type "B" a zirconia ceramic. Both types are manufactured for routine sulfur and carbon analysis by combustion methods. Experiments were conducted using each type in the "as-received" condition and after a pre-ignition firing in air at 1550° for 16 h.

In addition, titrations at different generator currents were made on two materials as well as variations in the sample weights to investigate the effect of these variables on the results obtained.

RESULTS AND CONCLUSIONS

Tables I through IV contain results of the experiments described. The letters R or I following the crucible type designation indicate the crucibles were used in the "as-received" condition or the pre-ignited condition respectively. Except for 3 samples (indicated in Table IV) the gas absorbent was the ferricyanide solution already described.

TABLE I

NBS STANDARD NO. 132a[a]

(Mo-W Steel)

Sample No.	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	1.000	A-R	2.0	0.0037
2	1.500	A-I	2.0	0.0038
3	1.500	A-R	2.0	0.0040
4	1.000	A-I	2.0	0.0033
5	1.000	A-R	2.0	0.0034
6	1.000	A-I	2.0	0.0035
7	1.500	A-I	2.0	0.0038
8	1.000	B-I	2.0	0.0044
9	1.000	B-R	2.0	0.0056
10	1.250	B-I	2.0	0.0059
11	1.250	B-R	2.0	0.0060

[a] NBS average value 0.006 % S.

The results tabulated in Table I show the difference in results obtained using both crucible types on a standard material containing less than 0.01 % S but greater than 0.001 % S. Comparison of the results of samples 1 through 7 with samples 8–11 indicate that the zirconia crucibles contain an impurity that results in an error of between 0.001 and 0.002 % S. Prefiring does not affect the results appreciably. Table I also indicates that the sample size taken for analysis can be varied from 1.0 g to 1.5 g without introducing significant error.

Table II is a tabulation of results obtained with a standard sample containing 0.018 % S (by conventional combustion methods). The average value for sulfur for all thirteen determinations (no results were discarded) is 0.017 %. The standard deviation is 0.001 %. The results indicate that the coulometric titration method could be used for materials containing up to 0.02 % S, although the method shows no advantages over the conventional combustion techniques presently employed for the determination of sulfur contents of this magnitude. The zirconia crucibles were used

TABLE II

NBS STANDARD NO. 36a[a]

(Cr-Mo Steel)

Sample No.	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	1.000	B-R	5.0	0.0159
2	1.000	B-R	5.0	0.0174
3	1.000	B-R	5.0	0.0184
4	1.000	B-R	10.0	0.0187
5	1.000	B-R	5.0	0.0159
6	1.000	B-R	5.0	0.0163
7	1.000	B-R	5.0	0.0160
8	1.000	B-R	5.0	0.0175
9	1.000	B-R	5.0	0.0163
10	1.000	B-R	10.0	0.0191
11	1.000	B-R	5.0	0.0166
12	1.000	B-R	5.0	0.0167
13	1.000	B-R	5.0	0.0184

[a] NBS average value 0.018 % S.

TABLE III

3.25 % SILICON IRON (LOW SULFUR)

Sample No.	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	1.000	A-R	0.5	0.00030
2	1.000	A-R	0.5	0.00040
3	1.000	A-R	1.0	0.00055
4	1.000	A-R	0.5	0.00065
5	1.500	A-R	0.5	0.00040
6	1.500	A-R	0.5	0.00033
7	1.000	A-I	0.5	0.00023
8	1.000	A-I	0.5	0.00033
9	1.500	A-I	0.5	0.00030
10	1.500	A-I	0.5	0.00036
11	1.500	A-I	0.2	0.00025
12	1.500	A-I	0.2	0.00015
13	1.500	A-I	0.2	0.00020
14	1.500	A-I	0.2	0.00013
15	1.500	A-I	0.2	0.00057
16	1.500	A-I	0.2	0.00048
17	1.500	A-I	0.2	0.00029
18	1.500	A-I	0.2	0.00033
19	1.500	A-I	0.2	0.00039
20	1.000	B-I	0.5	0.0023
21	1.000	B-I	0.5	0.0018
22	1.500	B-I	0.5	0.0020

for these samples because it was felt that the error caused by impurities was not large enough to be significant, and also because the supply of "Mullite" crucibles was limited and, therefore, reserved for the critical experiments on low sulfur silicon-iron samples.

Table III is a compilation of results using a silicon–iron alloy with a sulfur content below 0.001 %. Samples Nos. 1–19 were run using the "Mullite" crucibles, both in the "as-received" and the "pre-fired" condition. During the course of determining the sulfur content of these 19 samples, the generator current was varied from 0.2 mA to 1.0 mA, and the sample weights varied from 1.0 g to 1.5 g. Changes in sample weight, generator current, or prior treatment of the crucibles had no significant effect upon the amount of sulfur found. On the other hand, examination of the results of samples Nos. 20–22 shows that the zirconia crucibles, even after extended pre-firing are unsuitable for use for the determination of sulfur at this level and support the conclusions drawn after experiments using NBS Standard No. 132a (Table I).

The average value for sulfur, using the results of samples Nos. 1–19, discarding no results, is 0.00035 %. The standard deviation (σ), for all 19 determinations is 0.00014 % and the 3σ value is 0.00042 %.

Table IV shows the results of experiments using distilled water in place of the ferricyanide solution to absorb the gas from the combustion unit and indicates that this is a satisfactory technique, for low sulfur contents, as discussed above. However, the necessity of adding KI to the HCl–KBr solution in the titration cell, in order to obtain a sharp end-point makes the ferricyanide absorbing solution seem more convenient in actual practice.

TABLE IV[a]

Sample No.	*Sample material*	*Sample wt. (grams)*	*Crucible type*	*Generator current (milliamps)*	*% Sulfur found*
1	3.25 % Si-Fe	1.500	A-R	0.2	0.00040
2	3.25 % Si-Fe	1.500	A-R	0.2	0.00027
3	NBS No. 125a	1.500	A-R	2.0	0.0088
4	NBS No. 125a	1.500	A-R	2.0	0.0087

[a] Samples Nos. 1, 2 and 4: SO_2 collected in water, and end-point detected by indicator current due to excess I_2. Sample No. 3 run in same manner as those in Table I.

ACKNOWLEDGEMENTS

The authors would like to thank R. E. FRYXELL, of the Transformer Laboratories Department, General Electric Company, who supplied the low-sulfur silicon-iron and the mullite crucibles, and R. L. FULLMAN of the Research Laboratory Staff for assistance in the preparation of the manuscript.

SUMMARY

A coulometric method for the determination of sulfur in metallurgical products has been developed which meets the needs of production control of low sulfur contents. The method is rapid and more precise than the conventional combustion technique.

RÉSUMÉ

Une méthode coulométrique, rapide et précise, est proposée pour le dosage du soufre dans les produits métallurgiques.

ZUSAMMENFASSUNG

Es wird eine schnelle und genaue coulometrische Methode zur Bestimmung von Schwefel in metallurgischen Produkten beschrieben.

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A QUICK AND PRECISE HETEROMETRIC MICRODETERMINATION OF TRACES OF PALLADIUM IN METALS WITH NITRON

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INTRODUCTION

The reaction of palladium (II) with nitron in the presence of *large excesses of thiocyanate* has been studied previously[1]. In this investigation it was our intention to examine the reaction from the analytical point of view and to see if traces of palladium could be determined in *the presence of large excesses of foreign metals.* All the usual masking agents were tried out. It was very interesting to establish that the presence of very large excesses of trisodium citrate, disodium tartrate, pyro-, tripolyphosphate and disodium-EDTA had no influence on the results of the determination of palladium. The reaction, in the absence of bi- and polyvalent cations, proceeded with the same success at all pH values between 1–8. In most cases the amount of palladium present was less than 0.5%. In spite of this a complete titration took only 5–10 min, and the error found was generally between 0 and 1%. The *specificity* of the reaction is demonstrated by the fact that, amongst all the bi-, tri- and polyvalent metals, *palladium* is the *only* metal (with the exception of gold(III)) that gives an insoluble compound in the presence of the masking agents used. In all cases when nitron was used as titrant, only one compound, $Pd_2N_3\downarrow\downarrow$ (N = nitron) was obtained quantitatively at the end-point. The structures of the complexes of palladium, gold and platinum with nitron in thiocyanate solutions have been discussed elsewhere[1]. It was shown that this compound may be best presented as a salt, composed of cation and anion complexes

$$\left[\mathrm{N\!:\!Pd}\begin{matrix}\cdot\mathrm{N}\\ \cdot\mathrm{N}\end{matrix}\right]^{+2}\left[\mathrm{Pd(CNS)_4}\right]^{-2}\downarrow\downarrow.$$

References p. 357

EXPERIMENTAL

The same instrument and the same working conditions were used as in previous heterometric investigations[2]. The fundamental principles of heterometry have been presented before[3].

Reagents

All the chemicals used were either Baker AnalaR or chemically pure reagents.

Nitron (mol. wt. = 312.16). 0.7802 g nitron (Eastman Organic Chemicals, for chemical purposes) + 7 ml M CH_3COOH were dissolved in water and made up to 250 ml, giving a 0.01M solution. More dilute solutions were prepared from the standard solution. All solutions were kept in dark brown bottles. The dilute solutions were freshly prepared every few days.

Palladium chloride (Johnson Matthey). 1 g $PdCl_2$ + 56 ml M HCl were dissolved in water to give a volume of 562.8 ml (= 0.01M). More dilute solutions were prepared from the standard solution.

METHOD

General

20 ml aqueous solution containing ∼0.5 mg palladium and 2 ml M potassium thiocyanate and which may contain 99.5% of polyvalent cations, in addition to masking agents, are titrated heterometrically with 0.0015M – 0.002M nitron.

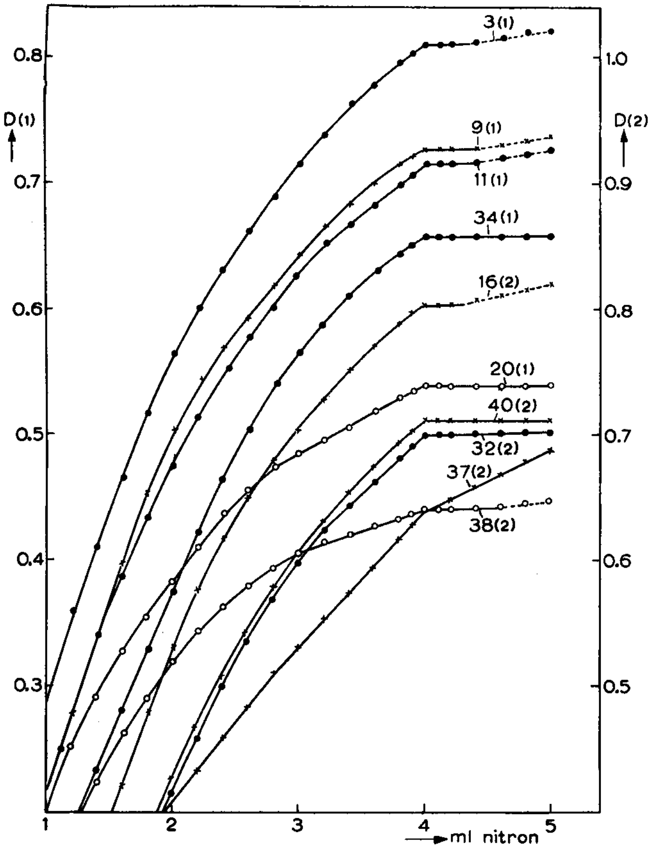

Fig. 1. Titrations of palladium chloride with nitron.

References p. 357

TABLE I

General composition: 4 ml 0.001M $PdCl_2$ + 2 ml M KCNS + a ml supplements + H_2O ad 20 ml + x ml 0.0015M nitron.
Temp. = 20°; content palladium = 0.4268 mg.

Expt. No.	*Supplements*	*% Pd*	*ml nitron at the end-point*	*Maximum density value*	*ml nitron at initial ppt.*	*% error*	*Titration time in min*	*Remarks*
1	3 ml M HCl		i 3.98 h	0.66	0.2	0.5	8	Beige ppt.
2	3 ml M CH_3COOH		i 4.00 h	0.67	0.2	0.0	7	Beige ppt.
3	1 ml M H_3PO_4		i 4.00 h	0.81	0.2	0.0	9	Beige ppt.
4	1 ml M CH_3COONa		i 4.00 h	0.78	0.2	0.0	7	Beige ppt.
5	2 ml 0.5M Na_2HPO_4		i 4.0 sh.h	0.74	0.2	0.0	7	Beige ppt.
6	8 ml 0.125M $Na_5P_3O_{10}$		i 4.02 sh.h	0.65	0.2	0.5	8	Beige ppt.
7	8 ml 0.125M $Na_4P_2O_7$		i 4.00 sh.h	0.67	0.2	0.0	12	Beige ppt.
8	4 ml M NH_4NO_3		i 4.00 h	0.60	0.4	0.0	5	Beige ppt.
9	3 ml M Na_3-citrate		i 3.99 h	0.73	0.2	0.3	7	Beige ppt.
10	3 ml M Na_2-tartrate		i 4.00 h	0.73	0.2	0.0	5	
11	10 ml 0.2M Na_2-EDTA		i 4.0 sh.h	0.72	0.2	0.0	6	Beige ppt.
12	3 ml 0.2M Na_4-EDTA			0.0	>5			
13	1 ml M NH_3			0.0	>5			Colourless solution
14	10 ml ethanol			0.0	>5			Yellow solution
15	2 ml 0.5M Na_2HPO_4 + 1 ml 0.2M KCN			0.0	>5			Colourless solution
16	2 ml 0.5M Na_2HPO_4 + 3 ml M Na_3-citrate		i 4.0 sh.h	0.80	0.2	0.0	9	Beige ppt.
17	1 ml M CH_3COONa + 2 ml M KF		i 4.00 h	0.70	0.2	0.0	8	Beige ppt.
18	2 ml M $Ca(NO_3)_2$	0.53	i 4.00 h	0.54	0.4	0.0	7	Beige ppt.
19	5 ml M Na_3-citrate + 4 ml M $Ca(NO_3)_2$	0.27	i 4.00 h	0.72	0.4	0.0	7	Beige ppt.; slight linear increase after the end-point
20	1 ml M $BaCl_2$	0.31	i 3.98 h	0.54	0.4	0.5	6	Beige ppt.
21	5 ml M Na_3-citrate + 2 ml M $BaCl_2$	0.15	i 3.98 h	0.76	0.4	0.5	6	Beige ppt.
22	2 ml M $MgCl_2$	0.87	i 3.97 h	0.54	0.4	0.8	7	Beige ppt.
23	5 ml M Na_3-citrate + 4 ml M $MgCl_2$	0.43	i 4.0 sh.h	0.79	0.2	0.0	8	Beige ppt.
24	3 ml M Na_3-citrate + 2 ml M $ZnSO_4$	0.33	i 4.0 sh.h	0.76	0.2	0.0	7	Beige ppt.
25	4 ml M Na_3-citrate + 3 ml M $MnCl_2$	0.26	i 4.00 h	0.75	0.2	0.0	7	Beige ppt.

i = intersection point; h = horizontal maximum density line; sh.h = short horizontal; in = increase.

TABLE I (Continued)

Expt. No.	*Supplements*	*% Pd*	*ml nitron at the end-point*	*Maximum density value*	*ml nitron at initial ppt.*	*% error*	*Titration time in min*	*Remarks*
26	1 ml M $Al(NO_3)_3$	1.6	i 4.00 h	0.71	0.6	0.0	7	Beige ppt.
27	4 ml M Na_3-citrate + 2 ml M $FeCl_3$	0.38	i 4.0 sh.h	0.76	0.2	0.0	8	Beige ppt.
28	3 ml M Na_3-citrate + 2 ml M $Cr(NO_3)_3$	0.41	i 3.98 sh.h	0.43	0.4	0.5	9	The colour of the solution is intense green-blue
29	3 ml M Na_3-citrate + 2 ml M $Co(NO_3)_2$	0.36	i 4.00 h	0.73	0.2	0.0	7	Carmine solution
30	5 ml M Na_3-citrate + 4 ml M $Ni(NO_3)_2$	0.18	i 4.00 h	0.74	0.2	0.0	7	Beige ppt.
31	10 ml 0.2M Na_2-EDTA + 2 ml 0.2M $UO_2(NO_3)_2$	0.45	i 4.00 h	0.67	0.2	0.0	5	Yellow solution; regular ppt.
32	3 ml M Na_3-citrate + 5 ml 0.2M $UO_2(NO_3)_2$	0.18	i 4.00 h	0.70	0.2	0.0	6	Beige ppt.
33	3 ml M Na_3-citrate + 2 ml 0.4M $SbCl_3$	0.44	i 4.01 h	0.65	0.4	0.3	7	Beige ppt.
34	3 ml M Na_3-citrate + 0.5 ml M $Bi(NO_3)_3$	0.41	i 4.00 h	0.66	0.2	0.0	7	Beige ppt.
35	8 ml 0.125M $Na_5P_3O_{10}$ + 0.5 ml M $Cd(NO_3)_2$	0.38	i 4.02 sh.h	0.76	0.2	0.5	6	Beige ppt.
36	8 ml 0.125M $Na_5P_3O_{10}$ + 5 ml 0.1M $Pb(NO_3)_2$	0.41	i 3.99 h	0.71	0.4	0.3	7	Beige ppt.
37	3 ml M Na_3-citrate + 2 ml 0.2M $Hg(NO_3)_2$	0.53	i 4.00	0.64	0.2	0.0	7	Beige ppt; linear increase after the end-point
38	3 ml M Na_3-citrate + 2 ml M $CuSO_4$	0.34	i 4.00 h(in)	0.64	0.2	0.0	8	Beige ppt.
39	8 ml 0.125M $Na_5P_3O_{10}$ + 5 ml 0.1M $TlNO_3$	0.42	i 4.0 sh.h	0.72	0.2	0.0	10	Beige ppt.
40	3 ml M Na_3-citrate + 5 ml 0.1M $Th(NO_3)_4$	0.37	i 4.00	0.71	0.4	0.0	7	
41	3 ml M Na_3-citrate + 1 ml 0.2M $ZrO(NO_3)_2$	2.3	i 4.0 sh.h	0.75	0.4	0.0	11	Beige ppt.
42	3 ml M Na_3-citrate + 5 ml 0.2M $Ce(NO_3)_3$	0.30	i 4.0 sh.h	0.76	0.2	0.0	5	Beige ppt.

i = intersection point; h = horizontal maximum density line; sh.h = short horizontal; in = increase.

Remarks

1. In the absence of polyvalent cations the titration may be carried out at pH's 1–8 with or without masking agents.

2. 3 to 5 ml *M* Na_3-citrate must be added if the following cations are present: Ca^{+2}, Ba^{+2}, Mg^{+2}, Mn^{+2}, Zn^{+2}, Co^{+2}, Ni^{+2}, UO_2^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, Sb^{+3}, Bi^{+3}, Hg^{+2}, Cu^{+2}, Th^{+4}, Ce^{+3} and ZrO^{+2}.

3. Solid $Na_5P_3O_{10}$ (or $K_5P_3O_{10}$) as powder (equal to $\sim$ 1 ml *M* solution) must be added when Cd^{+2}, Pb^{+2} or Tl^{+} are present.

4. The nitrate content of the solution being analysed may be as high as 8 ml *N* NO_3^-.

RESULTS

Table I shows the compositions and the results of a selection of heterometric titrations, which were carried out with the purpose of studying the sensitivity and the precision of the determination of palladium in the presence of various supplements including polyvalent metal salts. Contracted courses of a few titrations are given in Fig. 1. (The same numeration is used in the table and in the figure). The amount of the foreign metal present, as cited in the table, was generally approximately equal to the maximum amount that could be present without causing interferences in the results. In some cases (Expts. 18, 20 and 22) the maximum density value was much lower than usual although the usual end-point was still obtained. When these titrations were carried out in the presence of excesses of sodium citrate, normal maximum density values were obtained. The detrimental effect of the foreign metal was not observed then, although this metal content was doubled (compare Expts. 19, 21 and 23). Generally the maximum density value showed only small fluctuations in the experiments. This indicates that the variation in the pH between pH$\sim$1 and pH$\sim$9, as well as the presence of large amounts of cations, had no influence on the reaction measured (Expts. 1–11). In the presence of Na_4-EDTA, KCN or NH_3 — even when the last mentioned was dilute — the reaction studied did not take place (Expts. 12–15). Only a few foreign cations could be present without the necessity of using masking agents at all. They were: Ca^{+2}, Ba^{+2} and Mg^{+2}. Under our working conditions the solution being analysed could contain as much as 4 ml *M* NH_4NO_3 without interferences being observed (Expt. 8). In individual cases the nitrate content was even doubled! (Expt. 30).

The various masking agents used and their amounts in the individual cases can be seen in Table I. We found that an excess of trisodium citrate (at pH$\sim$7) was more successful than other complexing agents in the presence of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, UO_2^{+2}, Sb^{+3}, Bi^{+3}, Cu^{+2}, Hg^{+2}, Th^{+4}, Ce^{+3}, and $(ZrO)^{+2}$. In all cases the molar ratio of [citrate] : [cation] was higher than 1 : 1. Yet, even in the presence of citrate only restricted amounts of Al^{+3} could be present without harm.

By doubling the amount of Al^{+3} low density values were obtained and the end-points were no longer clear. In the presence of $(UO_2)^{+2}$, both Na_2-EDTA and Na_3-citrate could be used successfully as masking agents, but citrate is to be preferred since greater amounts of uranium could be masked (Expts. 31 and 32). In the presence of Cd^{+2}, Pb^{+2} and Tl^{+} tripolyphosphate must be used (Expts. 35, 36 and 39).

SUMMARY

A heterometric study was made of the reaction between palladium chloride and nitron in thiocyanate solutions in the presence of excesses of various masking agents.

A method is presented for the heterometric determination of $\sim$ 0.5 mg palladium in 20 ml aqueous solution with nitron, which can be carried out within 5–10 min. The solution to be analysed may in general contain $\sim$ 99.5% of the following foreign metals as cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, UO_2^{+2}, Cu^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}, Tl^{+}, Sb^{+3},Bi^{+3}, Th^{+4}, Ce^{+3} and ZrO^{+2}.

The error is between 0 and 1%.

RÉSUMÉ

Les auteurs ont effectué une étude hétérométrique de la réaction entre le palladium et le nitron, en solution thiocyanique et en présence de divers réactifs de masquage en excès. Une méthode de dosage est proposée.

ZUSAMMENFASSUNG

Es wurde eine heterometrische Untersuchung der Reaktion zwischen Palladiumchlorid und Nitron in thiocyanathaltiger Lösung und in Gegenwart eines Überschusses verschiedener Maskierungsmittel durchgeführt; eine Bestimmungsmethode für Palladium wird beschrieben.

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SOLUBILIZATION CHROMATOGRAPHY

III. ETHERS, CARBOXYLIC ACIDS, AND HYDROCARBONS

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In previous papers of this series, solubilization chromatography was applied to the separation of alcohols[1], phenols[1], and ketones[2]; and the general principles of the method were discussed. In the present paper, probably the last of the series, solubilization chromatography is applied to ethers, fatty acids, and hydrocarbons; also some experiments with a special resin of low capacity are described which throw further light on the nature of attraction between the resin and the organic solutes.

EXPERIMENTAL

Materials

All ethers, acids, and hydrocarbons used in this study were of the best grade commercially available. No further purification was required.

The resins used in these studies included: the strong-acid cation exchanger, Dowex-50; the strong-base anion exchanger, Dowex-1; the resinous adsorbent with a phenolic matrix and mixed polar functional groups, Duolite S-30; the "snake-cage" resin made from Dowex-1 and acrylic acid, Retardion 11A8[3]; polystyrene crosslinked with divinylbenzene; and a Dowex-50 resin of approximately one-half normal capacity.

The ratio of the interstitial volume to the bed volume, V/V_B, was determined for several of the resins used[4], and found to be: 0.333 for Dowex-50-X4, Lot No. 4177-40; 0.402 for Dowex-1-X4, Lot No. 1241; 0.371 for Dowex-50W-X8, Lot No. L·3937-40, capacity (Q) = 1.99 meq/g.

Eluents were prepared by dilution of reagent-grade glacial acetic acid and absolute ethanol.

Elutions

The samples were introduced onto the resin bed as previously reported[5]. The flow rate of eluent was 0.4 to 0.5 cm/min, unless otherwise specified. Fractions of approximately 5.0 ml were automatically collected with the aid of a constant-volume collecting device[6].

Analysis

Fractions containing acetic acid were analyzed by mixing them with 5.0 ml of 0.02M sodium dichromate in concentrated sulfuric acid, diluting with 25 ml of distilled water, and measuring spectrophotometrically the resultant Cr(III)[7]. All the solutes studied in this paper reduce dichromate.

Since the substituted benzenes and naphthalenes studied absorb light in the ultraviolet (225 to 289 mμ) region[8], the ethanolic eluates of these solutes were analyzed by ultraviolet absorption spectroscopy.

RESULTS AND DISCUSSION

Elution variables

Since the effects of such elution variables as choice of resin, particle size of resin, flow rate of eluent, sample size, etc. have been clearly established for both salting-out[5] and solubilization chromatography[1], no further study of these variables was made.

Dowex-50-X4 and Dowex-1-X4 were the resins primarily used. The low percentage of crosslinking was used to permit rapid diffusion of the large molecules encountered in this investigation.

One ml of feed solution was used in each elution. The solution contained 0.20 mmole of solute in an aqueous solution of the organic constituent of the eluent, concentrated enough to cause complete dissolution. Small volumes of feed solutions more concentrated in the organic constituent than the eluent itself were shown to cause insignificant change in the position of the elution maxima[1].

Acetic acid was chosen as the eluent for the ethers and acids because the spectrophotometric determination of the chromic ion produced by the reduction of dichromate is the most convenient method available for the determination of small amounts of these compounds in effluent fractions; and acetic acid is one of the few organic compounds not oxidized by dichromate. Ethanol was employed as an eluent for the hydrocarbons.

With each series of solutes studied, the elution variables just mentioned were kept constant at their optimum values while the most important variable, the concentration of the eluent solution, was varied. Values of the distribution ratio, C, were calculated by the equation[6]

$$U^* = CV + V \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where U^* is the volume of effluent collected from the point of addition of the sample to the peak of the elution graph and C is the distribution ratio of the solute (the total quantity of compound in the resin of any plate divided by the quantity in the solution of the same plate). The interstitial volume of the column is represented by V.

Ethers

Table I shows the distribution ratios, as calculated by equation (1), for the ethers

TABLE I

ELUTION DATA OF ETHERS ON DOWEX-50-X4, HYDROGEN FORM, 200-400 MESH

[HAc]	*0.0*	*1.0*	*2.0*	*4.0*	*6.0*	*Negative slope of plot of log C vs. M*	*Extent of linearity of plot of log C vs. M*
Diisopropyl ether	3.51	3.11	2.88	2.13	1.30	0.043	0–$2M$
Di-*n*-propyl ether	4.94	4.16	3.37	2.08	1.65	0.083	0–$6M$
Ethyl *n*-butyl ether	5.25	4.19	3.60	2.48	1.69	0.083	0–$6M$
Di-*n*-butyl ether	12.5	9.36	6.81	3.90	1.83	0.127	0–$4M$
Anisole	15.2	11.6	9.09	5.36	3.08	0.116	0–$6M$
Diphenyl ether	—	—	54.6	19.2	6.65	0.226	2–$6M$
Diisoamyl ether	—	—	—	—	2.28	—	—
Di-*n*-amyl ether	—	—	—	—	3.03	—	—

with eluents 0 to $6M$ in acetic acid and the results obtained by plotting log C *vs.* M. These results indicate the following:

1. Because of their greater solubility in aqueous solvents, branched-chain compounds are eluted before (have lower distribution ratios than) their straight-chain isomers.
2. The elution behavior of di-*n*-propyl ether and ethyl *n*-butyl ether is very similar, as is to be expected from their similar solubility characteristics.
3. Contrary to the results of salting-out chromatography[5], but similar to the previously published results of solubilization chromatography[1,2], some of the plots of log C *vs.* M are linear for only a limited region. At large molarities of acetic acid, the graphs tend to curve downward and converge. These results indicate that the change in solubility with molarity of acetic acid for these solutes is probably also nonlinear. This was shown to be true for two alcohols[1].
4. Similar to the earlier results of salting-out chromatography[5] and solubilization chromatography[1,2], the slopes of these plots (solubilization constants) are seen to increase as the ethers become less soluble in aqueous solutions.
5. Values of the distribution ratios of diisoamyl and di-*n*-amyl ethers, for eluents less concentrated than $6M$ acetic acid, could not be determined because of unsatisfactory elution graphs. With $4M$ acetic acid, both ethers gave elution graphs which rose to peaks immediately after the effluent volume equalled the interstitial volume, and then tailed for a large volume of effluent. This is probably due to the fact that most of these very large ether molecules are excluded from the resin by virtue of their size and eluted right after the interstitial volume. The molecules which do diffuse inside the resin are trapped there and cause the considerable tailing. Similar behavior was exhibited by di-*n*-hexyl ether in $6M$ acetic acid.

When introduced onto the resin bed with $6M$, $4M$ and $2M$ acetic acid eluents, diphenyl ether was precipitated as a white solid on the brown column of Dowex-50.

The precipitate redissolved and the band disappeared as the elution took place. The first two eluents gave completely satisfactory elution graphs; the latter yielded a very flat, severely spread peak. These results are probably due to the rates of redissolving in the various eluents used.

The elution data in Table I were used to plan[6,9] the separation of a synthetic mixture of 0.20 mmole of each of five ethers (Fig. 1). The calculated positions for the ether peaks and the actual U^* values were within experimental error. Di-*n*-propyl ether could have been included in the separation instead of ethyl *n*-butyl ether, but under the given elution conditions, it would have overlapped the peak of diisopropyl ether.

The elution behavior of diisoamyl ether, di-*n*-amyl ether, and di-*n*-hexyl ether was studied on Dowex-50-X2, Duolite S-30, and Retardion 11A8 in an attempt to get elution data which could be used to effect the separation of these compounds. None of these resins gave satisfactory results with eluents of a useful concentration range. It would have been possible to get symmetrical elution graphs for these compounds by use of extremely concentrated solutions of acetic acid. However, with these eluents the resin would show no selectivity among the three solutes. In effecting separations by solubilization chromatography, it is always necessary to find an eluent-resin combination which gives good selectivity and elution peaks which are both symmetrical and narrow. As is seen here, this is not always possible.

Carboxylic acids

Aqueous acetic acid and Dowex-50-X4, hydrogen form, were chosen for the study of the solubilization chromatography of the naturally occurring fatty acids. This system obviated any ion-exchange reactions between the acids and the resin phase.

Fig. 2 shows the separation of approximately 0.20 mmole of each of five acids and the plots of log C *vs.* M from which the conditions for the separation were chosen. Table II contains a summary of the elution data shown in the figure.

It is seen that with the acids, plots of log C *vs.* M of acetic acid are linear over the entire concentration range studied. There seems to be no way of predicting linearity or nonlinearity for a given compound.

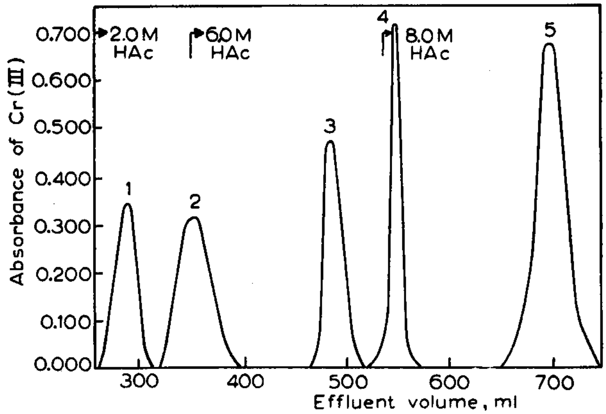

Fig. 1. The separation of a five-component ether mixture. 102.0 cm × 2.28 cm² Dowex-50-X4, 200-400 mesh, hydrogen form, 0.28 cm/min. Aqueous acetic acid eluent changed at 350 ml and 550 ml. 1. diisopropyl ether; 2. ethyl *n*-butyl ether; 3. di-*n*-butyl ether; 4. anisole; 5. diphenyl ether.

TABLE II

ELUTION DATA OF ACIDS ON DOWEX-50-X4, HYDROGEN FORM, 200-400 MESH

[HAc]	C 0.0	2.0	4.0	6.0	Negative slope of plot of log C vs. M	Extent of linearity of plot of log C vs. M
Butyric acid	2.17	1.81	1.45	1.24	0.041	0–6*M*
n-Caproic acid	4.99	3.35	2.01	1.40	0.092	0–6*M*
n-Caprylic acid	18.0	7.74	3.29	1.43	0.184	0–6*M*
n-Capric acid	—[a]	24.4	6.22	1.63	0.294	2–6*M*

[a] Too large to be accurately determined.

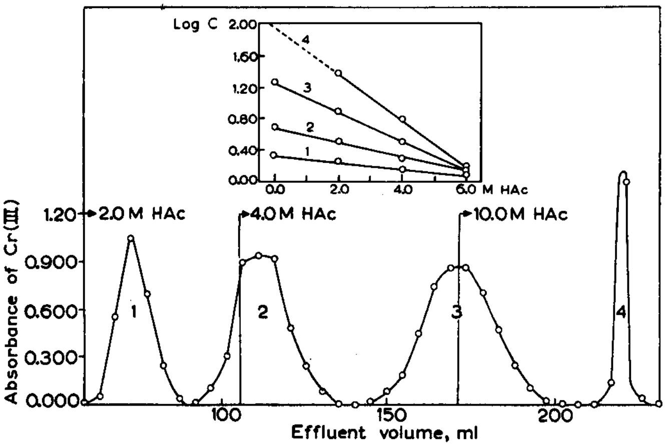

Fig. 2. Plots of log *C* *vs.* *M* for four acids and the separation of a four-component acid mixture planned from these data. 19.0 cm × 3.90 cm^2 Dowex-50-X4, 200-400 mesh, hydrogen form, 0.28 cm/min. Aqueous acetic acid changed at 105 ml and 170 ml. 1. butyric acid; 2. *n*-caproic acid; 3. *n*-caprylic acid; 4. *n*-capric acid.

From the length of the column used, it is obvious that this series was the easiest to separate of those studied in this and past work. This is because the constituents differed from each other by two carbon atoms, and had correspondingly large differences in their relative solubilities in aqueous solutions of acetic acid.

The twelve-carbon member, lauric acid, was precipitated when introduced onto a bed of resin equilibrated with even 6*M* acid. Some of the compound then appeared in the effluent immediately after the interstitial volume, but most of it was irreversibly sorbed and did not move from the top of the bed even after a large volume of effluent had passed. For this reason the study was stopped with *n*-capric acid.

Hydrocarbons

Because of the partially successful application of reversed-phase partition chromatography to the separation of methyl-substituted benzenes and naphthalenes with aqueous solutions of ethanol as the mobile phase, these eluents were initially tried in an attempt to improve these separations by use of solubilization chromatography.

However, solutions as concentrated as 50% ethanol by volume proved unsuccessful with Dowex-1-X4, Dowex-50-X4, and crosslinked polystyrene as the solid phase. In each case, severe tailing of the elution graphs occurred.

Acetic acid proved a satisfactory eluent for these hydrocarbons in that symmetrical elutions were in general obtained with Dowex-1 and Dowex-50. The use of crosslinked polystyrene again resulted in elution graphs with severe spread. This is due to the fact that polystyrene does not swell in aqueous solutions of acetic acid and adsorption rather than true absorption is the factor controlling equilibrium. Tailing is characteristic of adsorption phenomena. There is no obvious explanation why acetic acid should prove a much superior eluent than ethanol for the hydrocarbons when they were shown[2] to effect ketone elutions in a very similar manner.

A study was made of the effect of concentration of acetic acid on the elution behavior of these various benzene and naphthalene derivatives. Table III shows the results for Dowex-50-X4 and Dowex-1-X4 in terms of values of C. These data show, as was found for the alcohols[1], that Dowex-1 is a much stronger absorbent for organic solutes than is Dowex-50 because of its more hydrocarbon nature.

Toluene was visibly precipitated on the column equilibrated with 1.0M acetic acid and the elution graph spread severely. The same results were found for *m*-xylene with 2.0M acetic acid, mesitylene with 4.0M acetic acid, and durene with 6.0M acetic acid.

TABLE III

ELUTION DATA OF HYDROCARBONS ON DOWEX-50-X4, HYDROGEN FORM, AND DOWEX-1-X4, ACETATE FORM, 200-400 MESH

	Dowex-50-X4 *C*					*Dowex-1-X4* *C*	
[HAc]	*1.0*	*2.0*	*4.0*	*6.0*	*8.0*	*6.0*	*8.0*
Benzene	6.62	5.69	4.21	2.69		4.55	
Toluene	10.2	8.21	5.36	3.00		5.53	
m-Xylene		14.2	7.76	3.75		7.41	
Mesitylene			13.0	5.12		9.66	
Naphthalene					2.92	15.8	7.48
β-Methylnaphthalene					3.37	22.4	9.40
1,4-Dimethylnaphthalene					4.21	30.2	11.0

The plots of log C *vs.* M for the benzenes on Dowex-50-X4 begin to curve downward and converge at 4.0M acetic acid.

The elution data of Table III were sufficient to calculate[5,8] the conditions for the separation of 0.20 mmole of each of the seven solutes studied. Fig. 3 shows the conditions used and results obtained for this separation. The calculated positions of the peaks were 305, 359, 462, 542, 774, 860 and 952 ml, as compared with actual U^* values of 294, 354, 464, 549, 770, 869, and 956 ml.

The final two components were not completely separated by use of the given conditions because of the severe spread of the elution peaks. A complete separation of these two peaks could not be accomplished on a convenient-sized column of Dowex-1-X4.

References p. 365

Dowex–1–X4 was chosen in preference to Dowex–50–X4 for this separation because of the greater selectivity exhibited by the former resin for the compounds studied. An elution similar to that shown in Fig. 3 would require a column of Dowex–50–X4 well in excess of 100 cm.

Low-capacity resins

To test the usefulness of low-capacity resins in solubilization chromatography, several alcohols were eluted with acetic acid from a Dowex–50–X8 resin of less than one-half normal exchange capacity. Table IV compares the results of these elutions with those for the same alcohols on a Dowex–50–X8 resin of usual capacity and similar column dimension.

It is seen that although the low-capacity resin exhibits great selectivity among the three solutes studied, the severe spread of the elution peaks more than offsets this beneficial effect. It appears that resins of low capacity are useless for the chromatography of organic compounds of high molecular weight.

Theory of the process

Solubilization chromatography is a partition chromatography on ion-exchange resins. It differs from usual partition chromatography in that the two "phases" between which the solute is partitioned consist of the same solvent, and interactions between the "solid support" and the solute are important. Such interactions include (1) ion-dipole attractions of the functional group of the resin and/or its counter ion for the solute, and (2) London dispersion forces between the solute and the hydrocarbon part of the resin.

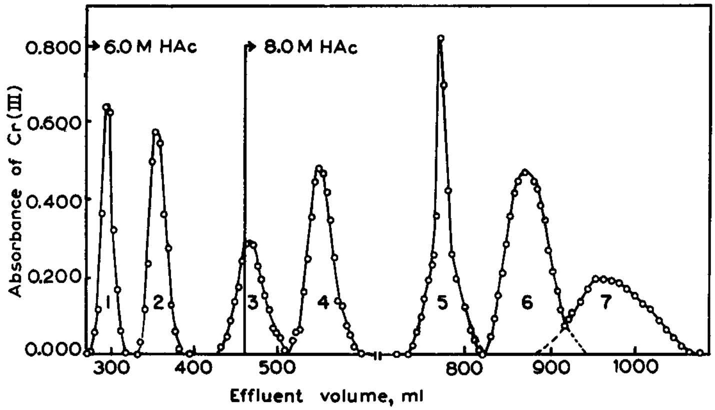

Fig. 3. Separation of a seven-component hydrocarbon mixture. 60 cm × 2.28 cm² Dowex–1–X4, 200–400 mesh, acetate form, 0.28 cm/min. Aqueous acetic acid eluent changed at 460 ml. 1. benzene; 2. toluene; 3. *m*-xylene; 4. mesitylene; 5. naphthalene; 6. *β*-methylnaphthalene; 7. 1,4-dimethylnaphthalene.

Consider a mixture of Dowex–50–X8, hydrogen form, 2.0*M* acetic acid, and a very small quantity of *n*-octyl alcohol. Both acetic acid and water molecules will be uni-

TABLE IV

EFFECT OF RESIN CAPACITY ON ELUTION BEHAVIOR

Resin	*Dowex-50W-X8* *Q = 1.99 meq/g* *lot No. L3937-40* *bed = 8.3 cm × 3.9 cm²*		*Dowex-50-X8* *Q = 5.2 meq/g* *lot No. 4226-28* *bed = 21.1 cm × 3.9 cm²*	
Eluent	8.0M $HC_2H_3O_2$		6.0M $HC_2H_3O_2$	
	C	U_T	C	U_T
n-Amyl alcohol	4.57	91.6 ml	1.43	53.5 ml
n-Hexyl alcohol	7.66	193.2	1.46	70.4
n-Octyl alcohol	a	a	1.85	101.2

[a] Irreversibly adsorbed on column.
U_T = Total volume of eluent used to elute the solute completely.

formly absorbed throughout the interior of the resin particles (REICHENBERG AND WALL[10] consider the simplest explanation to be that the resin absorbs water which in turn dissolves the acetic acid). The functional groups and counter ions of the resin will no doubt be almost exclusively solvated by water molecules rather than acetic acid molecules because of the greater number and greater polarity of the former. Since this leaves less free water inside the resin in which acetic acid can dissolve, the resinate ions can be said to salt-out acetic acid from the resin phase. Also, the small chain length of acetic acid molecules indicates that little van der Waals interactions will obtain between the benzene rings of the matrix and the acetic acid molecules. Hence the molarity of acetic acid inside the resin will be lower than the molarity outside the resin[10]. Even though this is true, the small amount of octyl alcohol will go almost completely inside the resin due primarily to the strong van der Waals interactions with the resin matrix.

The separations achieved by solubilization chromatography are based on the fact that solutes are differentially dissolved from the resin phase into the outside phase. Hence, the greatest separation among a group of constituents is obtained by use of an eluent containing a small amount of acetic acid since the compounds will have the greatest relative solubility differences in such an eluent. However, the eluent must contain enough acetic acid to give narrow elution graphs.

The results cited above with low-capacity resins indicate that van der Waals forces are much more important than polar interactions between a solute molecule and the resin. The resins of low capacity have a more hydrocarbon nature than the normal resins and hence exert a greater van der Waals attraction for the organic solutes. The fewer functional groups also mean that the resin can less effectively salt the solute out of the resin phase, a factor which would also tend to increase C values. If the ion-dipole attractions were important, the C values would decrease with diminishing capacity.

Since low-capacity resins contain much less internal water than do normal resins, slower diffusion rates and tailing are to be expected. Crosslinked polystyrene contains no functional groups and cannot swell at all in aqueous solvents. In this case only surface adsorption, and not true absorption, can occur. Hence, the tailing observed with the hydrocarbons on polystyrene would be characteristic of such an adsorption phenomenon.

ACKNOWLEDGEMENT

The authors express their gratitude to The Dow Chemical Company for financial support of this investigation and for supplying the resins used in the work.

SUMMARY

Synthetic mixtures of aliphatic and aromatic ethers, saturated fatty acids, and substituted benzenes and naphthalenes were separated by elution through columns of ion-exchange resins with aqueous solutions of acetic acid as eluent. An attempt was made to use a resin of low capacity for the separation of such mixtures, and the results of this attempt are used to help elucidate the theory of solubilization chromatography.

RÉUMÉS

Des mélanges d'éthers aliphatiques et aromatiques, d'acides gras saturés, de benzènes et de naphtalènes substitués ont été séparés par élution au moyen d'acide acétique sur des colonnes de résines d'échange d'ions.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Trennung von Gemischen von aliphatischen und aromatischen Aethern, gesättigten Fettsäuren und substituierten Benzolen und Naphthalinen mit Hilfe von Jonenaustauschern und Eluation mit verd. Essigsäure.

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SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

APPLICATION OF THE METHOD TO THE ANALYSIS OF LEACH SOLUTIONS AND MONAZITE

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The thiocyanate method for the spectrophotometric determination of uranium, as developed by CURRAH AND BEAMISH[1], is fairly sensitive and is free from cation interferences. The major difficulties encountered when using this method appear to be due to (i) the poor colour stability, (ii) the dependence of the colour intensity on the thiocyanate concentration over a wide range and (iii) interference from a large number of anions. In a recent paper NIETZEL AND DE SESA[2] briefly reviewed the various modifications that have been introduced into the method to make it applicable to the analysis of "relatively pure uranium samples" (*i.e.* samples containing only small amounts of certain impurities) and complex materials such as ores.

The present method is based upon the extraction of the uranyl thiocyanate complex with tributyl phosphate and its spectrophotometric determination in the organic layer. Though similar methods have previously been reported in the literature[3,4] no detailed study has been made of the various factors affecting the extraction and the interferences in the subsequent determination.

After this work was completed, a report was published by CLINCH AND GUY[5] on a similar procedure, where the interference due to a number of ions was eliminated by complexing them with ethylenediaminetetraacetic acid (EDTA) at pH 3.5–3.9. The conditions under which they worked, however, were such that reagent consumption was high (about 5 g ammonium thiocyanate per estimation) and a close check had to be kept on the pH. Moreover, for the determination of uranium in ores, including monazite, they found it necessary to carry out a preliminary separation of uranium, for which they used a cellulose column. From this point of view the method described in the present paper has some advantages which are discussed in the text below.

EXPERIMENTAL

Apparatus and reagents

All colour measurements were made with a Beckman Model DU spectrophotometer using 1 cm corex cells.

The extractions were carried out in 50 ml glass stoppered separating funnels.

Unless otherwise stated AnalaR grade chemicals were used for this work.

Tributyl phosphate–carbon tetrachloride mixture. 100 ml of tributyl phosphate (TBP) (B.D.H. Laboratory Reagent) were diluted to 1 l with carbon tetrachloride, washed thrice with 250 ml portions of 10% (w/v) sodium hydroxide and then with distilled water until the washings were free from alkali. The organic layer was separated, filtered and stored.

Ammonium thiocyanate. A 2.5*M* solution was prepared and filtered.

Ascorbic acid. 5 g of ascorbic acid was dissolved in 100 ml water.

Standard uranium solution. A solution containing about 5 g U_3O_8/l was prepared by dissolving the requisite amount of uranyl nitrate and the uranium content was then accurately determined gravimetrically.

Dilute solutions containing 0.10 mg U_3O_8/ml were made from the stock solution when required.

General procedure for extraction

Solutions of uranyl nitrate, ammonium thiocyanate and ascorbic acid (to reduce traces of iron) were carefully pipetted into a beaker and the volume made up to about 25 ml. The pH was adjusted to about 1.5 and the solution transferred to a separating funnel together with the rinsings. 25.0 ml of the solvent was pipetted into the separating funnel and the mixture shaken for 2 min. The two layers were allowed to settle and the organic layer was filtered through a plug of glass wool (previously washed with hydrochloric acid to remove traces of iron and dried) into a dry test tube where it was kept stoppered till required for colour measurement.

Choice of wavelength

5 ml uranyl nitrate solution (containing 0.50 mg U_3O_8) was extracted with 25.0 ml of TBP–CCl_4 after the addition of 2.5 ml ammonium thiocyanate and 2.0 ml ascorbic acid. The optical density of the organic layer was compared at wavelengths from 330 to 400 mμ against a blank obtained by extracting a solution prepared in the same manner, but without uranium.

The absorption spectrum is similar to that obtained by CLINCH AND GUY[5] and shows a maxima at 350 mμ.

Beer's law

A series of solutions containing 0.10 to 1.50 mg U_3O_8 were extracted as described above. The optical density measurements showed that Beer's law is obeyed at 350, 365, 380 and 400 mμ and probably at any other wavelength in this region. However, since the reproducibility of the data obtained at 365 mμ was better than at lower wavelengths, this wavelength was used for all subsequent work. The molecular extinction coefficient is 5100.

Optimum concentration range for estimation

A RINGBOM plot[6] was made from the calibration data obtained at 365 mμ and the optimum range of uranium concentration for a minimum spectrophotometric error was found to be 0.20 to 1.20 mg U_3O_8 in 25 ml of the extract.

Stability of the colour

The colour in the organic extract was stable for at least 24 hours.

Factors affecting uranium extraction

To find out the effect of various factors on uranium extraction, experiments were carried out under different conditions using 0.50 mg U_3O_8. The optical density of the extract corresponding to this amount of uranium in the calibration graph (uranium concentration *vs.* optical density at 365 mμ) was assumed to represent complete extraction and on that basis the percentage extraction was calculated in the following experiments.

(*a*) *Effect of TBP concentration in the organic phase.* The extraction was almost complete (Fig. 1) when the TBP concentration in the solvent was 8% (v/v). For all further work 10% (v/v) TBP in carbon tetrachloride was used.

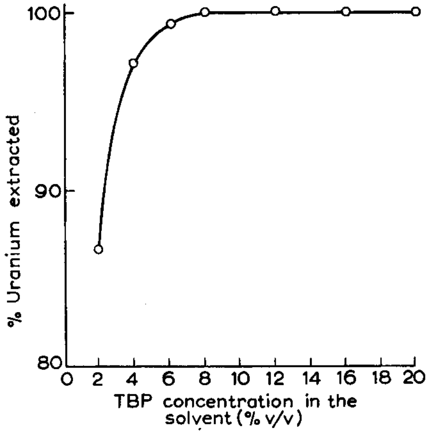

Fig. 1. Effect of TBP concentration on uranium extraction.

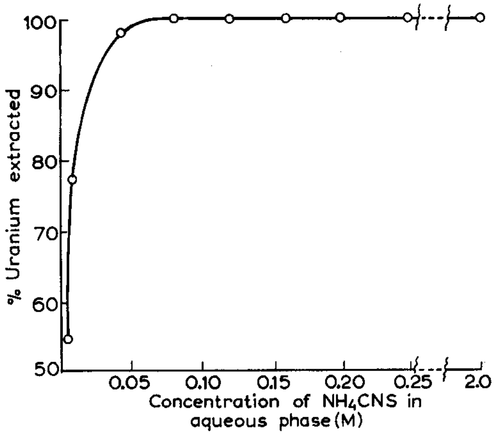

Fig. 2. Effect of thiocyanate concentration on uranium extraction.

(*b*) *Effect of thiocyanate concentration in the aqueous phase.* The extraction of uranium increased rapidly (Fig. 2) with thiocyanate concentration and reached a maximum value when the overall thiocyanate concentration was 0.1*M*. But for various reasons, which will be mentioned later, the concentration of thiocyanate was fixed at 0.25*M* (*i.e.* 2.5 ml of 2.5*M* solution) for all further work.

(*c*) *Effect of pH.* Extractions carried out after adjusting the aqueous solution to various pH values showed that there was a sharp fall in uranium extraction at pH 3.5, but between 2.5 and 0.5 there was no significant difference. From highly acidic solutions some HCNS was also extracted into the organic layer which affected the stability of the colour. Throughout this work, therefore, the pH of the aqueous solution was adjusted to roughly 1.5 before extraction.

(*d*) *Interferences.* The possible interference that a number of cations and anions might have on the uranium extraction and subsequent spectrophotometric determination was evaluated. The impurities were added separately to aliquots (0.5 mg U_3O_8) of standard uranium solution and carried through the extraction and estimation procedure. The error found was less than 2% when the following ions were added up to 200 mg: Na^+, K^+, Ca^{+2}, Mg^{+2}, Cd^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Al^{+3}, Cr^{+3}, La^{+3}, Ce^{+3}, Nd^{+3}, Zr^{+4}, Th^{+4} (all as chlorides or nitrates), Cl^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, tartrate and citrate (all as sodium salts). The effect of some other ions is given in Table I.

TABLE I

INTERFERENCES IN URANIUM DETERMINATIONS

Ion added	*Amount of ion giving 2% error (mg)*	*Remarks*
Co^{+2}	50	—
Pb^{+2}	20	Slight precipitate in aqueous phase
Hg^{+2}	50	Slight precipitate
Sn^{+2}	20	Turbidity in aqueous phase
Cu^{+2}	20	White precipitate of cuprous thiocyanate
Fe^{+3}	10	—
Ti^{+4}	5	0.5 g tartaric acid was also added. Otherwise less than 2 mg
V^{+5}	1	Positive error
Bi^{+3}	< 1	Positive error
Mo^{+6}	< 1	Positive error
F^-	5	Negative error
Oxalate	5	Negative error

Among the ions tested those of vanadium, bismuth, molybdenum, fluoride and oxalate proved to cause very serious interferences. Even though there was precipitate formation when some of the ions were added (Table I), the extracts were clear after filtering through the glass wool.

APPLICATION OF THE METHOD

Determination of uranium in leach solutions

On the basis of the observations described above, the method was tested for the determination of uranium in a synthetic solution (composition given below) and two leach solutions obtained by treating low-grade uranium ores with dilute sulphuric acid. The procedure was as follows.

Procedure. 2.0–5.0 ml of the leach solution was pipetted into a 50-ml beaker. 5.0 ml ascorbic acid and 2.5 ml ammonium thiocyanate were added and the solution diluted to about 25 ml. The pH was adjusted to about 1.5 and the extraction and spectrophotometric determination carried out as in the case of pure solutions. The results are summarised in Table II.

TABLE II

DETERMINATION OF URANIUM IN LEACH SOLUTIONS

Sample	*Uranium present g U_3O_8/l*	*Aliquot taken ml*	*Uranium determined by the present method*		
			No. of determinations made	*Mean value g U_3O_8/l*	*Standard deviation*
Synthetic solution[a]	0.211	2.0	9	0.210	0.004
Leach solution I	0.428	2.0	10	0.431	0.005
Leach solution II	0.084	5.0	8	0.083	0.001

[a] Composition (in g/l): U_3O_8 0.211, Fe^{+3} 10.0, Mn^{+2} 5.0, Cu^{+2}, Ni^{+2}, Al^{+3}, Ca^{+2}, Mg^{+2} 1.0 each, PO_4^{-3} 10.0, SO_4^{-2} 50.0. The pH was 1.0.

Determination of uranium in monazite concentrates

CLINCH AND GUY[5] determined uranium in a variety of ores, including monazite, but only after separation of uranium by the cellulose column method[7]. From the study of interferences reported above and the known composition of monazite concentrates it is evident that the present method can be applied without any preliminary separation. The following procedure was adopted and replicate analyses were carried out on a sample of monazite concentrate obtained from the Indian Rare Earths Ltd., Alwaye.

Procedure. 1.0 g of finely ground sand was mixed with about 3.0 ml concentrated sulphuric acid in a 50 ml beaker and heated for about 2 hours at a temperature just below the fuming stage. After cooling, the sulphates were extracted with ice-cold water, the solution transferred to a 50 ml volumetric flask and, after it had attained room temperature, made up to the mark. The solution was mixed occasionally and after 2 hours filtered through a dry Whatman No. 42 filter.

10 ml of the filtrate was carefully pipetted into a separating funnel, 2.5 ml thiocyanate, 5 ml ascorbic acid and about 10 ml water were added and the extraction and determination of uranium carried out.

Results:			
	U_3O_8 present	0.406%	(by cellulose column method[7])
	U_3O_8 found	0.403%	(mean of 10 determinations by present method)

Standard deviation: 0.014.

DISCUSSION

From the results reported it can be seen that extraction of the thiocyanate complex with TBP and subsequent spectrophotometric determination is a very convenient and rapid method for the determination of uranium in leach solutions, not containing vanadium, bismuth and molybdenum. The use of ascorbic acid, instead of EDTA for eliminating certain interferences offers an advantage in that the extraction of uranium is complete over a wide range of pH values of the aqueous phase; moreover, the reagent consumption is very much less and a lower concentration of TBP in the solvent can be used. Because of the acid conditions (pH 1.5 or less) employed there is no trouble due to precipitation of phosphates of uranium, thorium or hydrolysis of zirconium. The intensity of the colour is to a large extent independent of the thiocyanate concentration in the aqueous phase. Although, under the conditions employed, the extraction from pure uranium solutions is complete at a thiocyanate concentration of $0.1M$, a slightly higher concentration, *i.e.* $0.25M$, is generally employed to overcome the interference from anions such as SO_4^{-2} and PO_4^{-3}.

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SUMMARY

Uranyl thiocyanate complex is extracted from a slightly acid solution, using tributyl phosphate–carbon tetrachloride as solvent. The effect of various factors on the extraction of uranium and the interference of a number of cations and anions was studied. After extraction, uranium is determined spectrophotometrically in the organic solvent.

RÉSUMÉ

On propose une méthode de dosage spectrophotométrique de l'uranium. Elle est basée sur l'extraction du thiocyanate complexe au moyen du mélange phosphate de tributyle–tétrachlorure de carbone. L'influence d'un certain nombre de cations et d'anions a été examinée.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode zur Bestimmung von Uran beschrieben. Sie beruht auf der Extraktion des Uranyl-thiocyanat Komplexes mit einem Gemisch von Tributylphosphat und Tetrachlorkohlenstoff. Der Einfluss einer Anzahl Kationen und Anionen wird untersucht.

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OXIDATION OF HYDROXYLAMINE BY FERRICYANIDE IN PRESENCE OF ZINC SULFATE

A RAPID METHOD FOR ESTIMATING HYDROXYLAMINE AND HYDRAZINE IN A MIXTURE

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Both hydrazine and hydroxylamine are powerful reducing agents and their determination in presence of each other is usually a difficult problem. While hydrazine is almost always oxidized exclusively to nitrogen by various reagents, hydroxylamine tends to be converted non-stoichiometrically to several products such as N_2, N_2O, HNO_2, HNO_3 and other related compounds[1]. Nonetheless, under prescribed conditions, hydroxylamine is oxidized to nitrous oxide by cerium(IV)[2] and iron(III)[3], to nitric acid by bromate[4], and to nitrogen by ferricyanide[5]. The standard method of determining hydroxylamine is based on its conversion to nitric acid by an excess of potassium bromate in hydrochloric acid solution followed by an iodometric titration of the excess against thiosulfate[4]. Experience has shown that the bromate method requires considerable skill and rigid adherence to the prescribed conditions, especially in preventing the loss of free bromine which is formed during the reaction. Furman and

FLAGG[6] have suggested a useful modification of this procedure by adding an excess of standard arsenite solution to the unreacted bromate, and backtitrating with 0.1N bromate using methyl orange indicator. The results by this modification were found to be much better than by direct iodometry of the excess of bromate, but the method is still involved. Perhaps it might be preferable to use a bromate–bromide mixture in strongly hydrochloric acid or glacial acetic acid medium.

In the literature, two methods are described for the determination of hydrazine and hydroxylamine when present together. Potassium bromate in hydrochloric acid solution oxidizes hydrazine and hydroxylamine respectively to nitrogen and nitric acid. The excess of bromate is determined in one sample whereas in the second sample the volume of nitrogen evolved is measured[7]. According to LANG[8], hydrazine can be titrated in sulfuric acid solution with potassium iodate by the iodine cyanide procedure without oxidation of hydroxylamine, provided that not more than the equivalent of 0.07 g of $NH_2OH{\cdot}HCl$ are present. After the ICN is destroyed by just a sufficient quantity of sodium sulfite, the iodide ion is precipitated with silver nitrate. The hydroxylamine is then oxidized to nitrous oxide and water by boiling with an excess of ferric ammonium sulfate, and the iron(II) formed is titrated in presence of manganous sulfate catalyst with standard permanganate. While the former method necessitates a gasometric measurement, the latter is a lengthy procedure and is dangerous owing to the use of potassium cyanide.

SANT[5,9] developed a method of determining hydroxylamine, based on its conversion to nitrogen by an excess of ferricyanide in a weakly alkaline solution (pH 8–9). The analysis was completed by titrating the ferrocyanide formed with ceric sulfate or the unused ferricyanide iodometrically. In strongly alkaline medium the reaction is non-stoichiometric. Recently it has been shown that hot standard solutions of ferricyanide can be titrated directly with hydrazine sulfate[10] or sodium nitrite[11] in presence of zinc sulfate. Zinc sulfate raises the oxidation potential of the ferricyanide ion through the removal of ferrocyanide ion as sparingly soluble zinc potassium ferrocyanide. The complete decolorization of the solution indicates the end-point.

Preliminary experiments in these Laboratories revealed that the above ferricyanide procedures for hydrazine and nitrite could be extended to determine hydroxylamine. However, in presence of zinc sulfate, hydroxylamine is oxidized to nitric acid instead of to nitrogen as when ferricyanide is used in a weakly alkaline medium. Ferricyanide in strongly alkaline solutions or in presence of zinc sulfate always converts hydrazine to nitrogen so that oxidation of a sample containing both hydrazine and hydroxylamine by ferricyanide under different conditions should give a measure of the quantity of each reductant present. Ferricyanide in strongly alkaline medium does not convert hydroxylamine quantitatively to nitrogen but no data exist on the reaction between hydrazine and ferricyanide in weakly alkaline medium. A series of experiments showed that hydrazine is oxidized quantitatively to nitrogen by excess of ferricyanide in borax–boric acid buffer solution (pH 8–9). The analysis was completed by titrating both the ferrocyanide formed against standard ceric sulfate[12] and the unused ferricyanide iodometrically against standard thiosulfate[13]. These observations were used in the present work.

The present paper reports a simple method of determining milligram amounts of hydroxylamine by direct titration of alkaline ferricyanide in presence of zinc sulfate and a rapid procedure for the analysis of hydroxylamine and hydrazine when present together.

EXPERIMENTAL

An aqueous solution of hydroxylamine sulfate was prepared from a pure sample supplied by the Commercial Solvents Corporation. Its hydroxylamine content was checked by titrating the acid part and also by the ferricyanide method[5,9]. All other chemicals used were of reagent grade.

Procedure

Determination of hydroxylamine. To a measured volume of standard potassium ferricyanide solution, 2–3 g of crystalline zinc sulfate and a sufficient quantity of sodium or potassium hydroxide to maintain the total alkalinity at 0.5–1.0*N* were added and the mixture was heated to boiling. The hydroxylamine sulfate solution was added from a buret gradually till the precipitate was clear white and the supernatant liquid colorless. The reaction corresponds to the oxidation of hydroxylamine to nitric acid and water:

$$2K_3Fe(CN)_6 + 2KOH \rightarrow 2K_4Fe(CN)_6 + H_2O + [O]$$
$$2K_4Fe(CN)_6 + 3ZnSO_4 \rightarrow Zn_3K_2[Fe(CN)_6]_2 + 3K_2SO_4$$
$$NH_2OH + 3[O] \rightarrow HNO_3 + H_2O$$

Thus 1 ml of 1*N* $K_3Fe(CN)_6$ is equivalent to 5.505 mg NH_2OH. A typical set of results is given in Table I.

TABLE I

ESTIMATION OF HYDROXYLAMINE

NH_2OH (mg)		*Difference (mg)*
Calculated	*Found*	
1.114	1.101	0.013
2.228	2.203	0.025
4.456	4.407	0.049
8.912	8.818	0.094
13.368	13.224	0.144

Determination of hydroxylamine in presence of hydrazine. Measured quantities of hydroxylamine and hydrazine sulfates were mixed and the solution diluted to 250 ml. Oxidation was effected by ferricyanide as follows:

(*a*) An aliquot portion of the mixture was treated with a known excess of ferricyanide solution followed by 25–30 ml of borax–boric acid buffer solution (pH 8–9). After 15–30 min, the solution was diluted to a suitable volume. In aliquots of this solution either the unused ferricyanide was titrated iodometrically or the ferrocyanide formed was titrated with standard ceric sulfate.

(*b*) A known volume of ferricyanide was titrated hot in presence of zinc sulfate and at a total alkalinity of 0.5–0.8*N* with the mixed solution of hydrazine and hydroxylamine sulfates. The end-point was shown by the appearance of a clear white precipitate.

In the two methods (*a*) and (*b*), the reactions taking place are:

$$(a)\quad N_2H_4 + 4K_3Fe(CN)_6 + 4KOH \rightarrow N_2 + 4K_4Fe(CN)_6 + 4H_2O \quad . \; . \; . \; . \qquad (1)$$

$$2NH_2OH + 2K_3Fe(CN)_6 + 2KOH \rightarrow N_2 + 2K_4Fe(CN)_6 + 4H_2O \quad . \; . \; . \qquad (2)$$

$$(b)\quad N_2H_4 + 4K_3Fe(CN)_6 + 4KOH + 6ZnSO_4 \rightarrow N_2 + 2Zn_3K_2[Fe(CN)_6]_2 + 6K_2SO_4 + 4H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (3)$$

$$NH_2OH + 6K_3Fe(CN)_6 + 6KOH + 9ZnSO_4 \rightarrow HNO_3 + 3Zn_3K_2[Fe(CN)_6]_2 + 9K_2SO_4 + 4H_2O \quad . \; . \; . \; . \; . \qquad (4)$$

Let V_1 and V_2 be the volumes of ferricyanide consumed by the same quantity of the mixture in methods (*a*) and (*b*) respectively. If x ml of ferricyanide are consumed by hydrazine, then $(V_1 - x)$ ml will have been consumed by hydroxylamine in (*a*) and $(V_2 - x)$ ml in (*b*). Whereas the equivalent weight of hydroxylamine in (*a*) is the same as the molecular weight, it is one-sixth in (*b*). Therefore

$$(V_1 - x) = \frac{(V_2 - x)}{6}$$

From this the values of x, $(V_1 - x)$, and $(V_2 - x)$ can be obtained. The quantity of hydrazine equivalent to x ml of ferricyanide can be calculated from the relation 1 ml of 1*N* $K_3Fe(CN)_6 = 8.012$ mg hydrazine and the hydroxylamine equivalent of $(V_2 - x)$ ml of ferricyanide from the relation 1 ml of 1*N* $K_3Fe(CN)_6 = 5.505$ mg hydroxylamine.

RESULTS

A representative set of data is shown in Table II. The results are the average values of duplicate experiments.

TABLE II

ESTIMATION OF HYDRAZINE AND HYDROXYLAMINE IN A MIXTURE

Expt. No.	*N_2H_4 (mg)*			*NH_2OH (mg)*		
	Calcd.	*Found*	*Diff.*	*Calcd.*	*Found*	*Diff.*
1.	3.174	3.186	0.012	0.9635	0.9545	0.009
2.	1.440	1.450	0.010	1.927	1.909	0.018
3.	6.348	6.362	0.014	1.927	1.909	0.018
4.	1.440	1.450	0.010	3.854	3.820	0.034
5.	2.880	2.900	0.020	3.854	3.818	0.036
6.	2.880	2.900	0.020	7.708	7.640	0.068

DISCUSSION

The reaction between ferricyanide and hydroxylamine in presence of zinc sulfate was shown to be quantitative at an alkalinity of 0.5–1.0*N*. At lower alkalinity the reaction is slow, whereas in too alkaline a solution zinc ions tend to go into solution and interfere with reaction (4). This difficulty can be obviated by using larger quantities

References p. 375

of zinc sulfate. The amount of zinc sulfate is not critical provided that more than 2 g are present during each titration.

When hydroxylamine is oxidized to nitric acid, a good conversion factor is obtained so that the method is suitable for the determination of small amounts of hydroxylamine. Potassium bromate also effects this oxidation completely, but the present ferricyanide method is simpler and much less time-consuming. The availability of very pure potassium ferricyanide and its large equivalent weight (about 12 times that of potassium bromate) are also important.

In contrast to the bromate and the iodine cyanide methods for analyzing a mixture of hydrazine and hydroxylamine, the ferricyanide procedure described is not exacting and it can be completed within 45 minutes. The error rarely exceeds 2% which may be acceptable considering the difficulties involved in such an analysis.

ACKNOWLEDGEMENTS

The author is indebted to Boyd Professor PHILIP W. WEST for research facilities and interest in the work. The gratis sample of hydroxylamine sulfate by the Commercial Solvents Corporation, New York, is gratefully acknowledged.

SUMMARY

The direct titration of alkaline ferricyanide in presence of zinc sulfate with hydroxylamine sulfate has been studied. A clear white precipitate of zinc potassium ferrocyanide indicates the end-point. Hydroxylamine is oxidized to nitric acid and water, and milligram quantities of hydroxylamine can be determined. In the absence of zinc sulfate and in weakly alkaline medium, hydrazine and hydroxylamine are converted to nitrogen, while in presence of zinc sulfate hydrazine is oxidized to nitrogen. By ferricyanide oxidation of a mixed sample under different conditions, hydrazine and hydroxylamine when present together can be determined rapidly.

RÉSUMÉ

L'auteur décrit une méthode simple pour le microdosage de l'hydroxylamine, au moyen de ferricyanure, en présence de sulfate de zinc. Il propose également une méthode rapide pour le dosage de l'hydrazine et de l'hydroxylamine, en présence l'une de l'autre, par le ferricyanure de potassium, avec et sans sulfate de zinc.

ZUSAMMENFASSUNG

Es wird eine einfache Mikromethode beschrieben zur Bestimmung von Hydroxylamin mit Alkaliferricyanid in Gegenwart von Zinksulfat. Unter Einhaltung bestimmter Bedingungen können auch Hydroxylamin und Hydrazin nebeneinander mit Alkaliferricyanid bestimmt werden.

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THE APPARENT SOLUBILITY PRODUCT OF CEROUS FLUORIDE

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The present work grew out of an as yet unsuccessful attempt to determine fluoride ion coulogravimetrically with electrolytically generated cerous ion. Although cerous ion could be generated with 100% current efficiency from an acid solution of a ceric salt, in the presence of fluoride ion no visible precipitate was noted. Two causes are possible for this lack of precipitate: (a) the high solubility of cerous fluoride in acid solution and (b) the slow formation of precipitate under these conditions. The former possibility is the subject of the present paper.

No experimental data are available on the solubility product of cerous fluoride[1] although KURY[2] has calculated this constant from thermodynamic data. The apparent solubility product has now been determined by two independent methods and the values obtained checked fairly closely. However, these values are some 700 times larger than the calculated value. The solubility of cerous fluoride in solutions of varying acidity has also been determined.

REAGENTS AND APPARATUS

The reagents used were all of "analytical grade". The tracer employed was an acid solution of cerium-144(III) chloride and was obtained from Oak Ridge National Laboratory. Conductivity water was prepared by distillation in all-glass apparatus after the addition of a few crystals of potassium permanganate. The freshly distilled water was then passed through a Crystalab Deeminizer deionizing column. The water thus prepared was stored in polyethylene bottles and was used for the preparation of all solutions employed in the conductometric measurements. Due to the absorption of carbon dioxide, the conductivity of the water increased rapidly but within 8 min showed no further change, even after 24 h. All runs were made with equilibrium water having a specific conductance of $4.5 \cdot 10^{-6}$ mho.

Conductance measurements were made with a standard Wheatstone Bridge circuit; earphones were used as the null-detecting device and the 1000-cycle a.c. was obtained from a Jackson Model No. 652 audio frequency oscillator. The constant of the cell was 0.05398. Radioactive counting was by a Tracerlab TGC-5A Geiger tube and an Atom-lab Model A-65 scaler. All samples were mounted on polystyrene planchettes.

A Burrel Model BB Wrist Action Shaker was used to bring the solid cerous fluoride into equilibrium with its medium. All pH measurements were made on a Beckman Model H2 glass-electrode pH Meter.

EXPERIMENTAL PROCEDURES

Radioactive cerous fluoride was prepared by adding three drops of cerium-144(III) chloride to 20 ml of a 0.1*N* solution of cerous sulfate (G. Frederick Smith Chemical Co., Columbus, Ohio). This solution was then added dropwise with constant stirring to 20 ml of 0.1*N* sodium fluoride. The precipitate was allowed to stand for 30 min before filtration. It was then washed and dried at 110° for 3 h.

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A 200-mg sample of active cerous fluoride was placed in a 25-ml volumetric flask and water was added to bring to the mark. The flask was shaken and maintained at 25° ± 0.05° for 18 h to allow the cerous fluoride to come to equilibrium with the medium. At the end of this period, the mixture was filtered and an aliquot of the filtered solution was pipetted into a planchette and evaporated to dryness under a Fisher Radiator.

The solubility of cerous fluoride in solutions of varying acidity was determined as above except that perchloric acid solutions of known pH replaced the distilled water. Perchloric acid was chosen as it does not complex with cerous ion[3].

For conductometric measurements, 20 ml of approximately $0.1N$ cerous sulfate solution was added dropwise with constant stirring to an equal volume of $0.1N$ sodium fluoride. The precipitate was allowed to settle and the supernatant liquid was decanted. After washing with six 5-ml portions of conductivity water, 200-mg portions of the dried salt were placed in each of six polyethylene bottles containing 20 ml of conductivity water. The bottles were shaken and thermostatted as before. The mixture was filtered through a fine filter paper and the filtrate was used to rinse the cell before conductance measurements were made.

RESULTS

Solubility product measurements

The apparent solubility product of cerous fluoride was determined by radiometric and conductometric methods to be $8.1 \pm 1.1 \cdot 10^{-16}$ and $1.1 \pm 0.5 \cdot 10^{-15}$ respectively. These values are somewhat larger than the value of $1.4 \pm 0.2 \cdot 10^{-18}$ reported by KURY.

For conductometric measurements, the equivalent conductance was assumed to be equal to the equivalent conductance at infinite dilution. The ionic conductance of fluoride ion is reported to be 46.6 mhos/equivalent at 18° and can be corrected for temperature by use of the following equation:

$$\lambda_{t'} = \lambda_t(1 + c(t' - t))$$

where c is 0.0238, t' is the desired temperature, and t is 18°[4]. Since no information is available on the equivalent ionic conductance of cerous ion, the value for the lanthanum ion was used. The ionic radii of the lanthanum and cerous ions are similar, 1.15 and 1.18 Å respectively[5]. Ions having the same charge and similar ionic radii are known to have similar mobilities and equivalent ionic conductances[6].

Uncertainties in the conductance method are (a) the nature of the ions formed, (b) the values of the ionic conductances, and (c) the extent of salt hydrolysis. Complexing of cerous ion by fluoride to form the species CeF^{+2} has been proposed by KURY, HUGUS AND LATIMER[7]. The formation of a cerium–fluorine complex would increase the solubility product. However, the value obtained after correction for complex formation is still well within the limits of experimental error. Calculations of the solubility product based on the assumption that salt hydrolysis had taken place gave values which were much greater than any experimental value obtained. This suggests that salt hydrolysis must also be very small.

Variation of solubility with acidity

The radiometric method was used to study the effect of hydrogen-ion concentration on the solubility of cerous fluoride. The results in Fig. 1 show that the solubility decreases very gradually with a decrease in pH from 5 to 2 and then increases rapidly as the pH is further reduced from 2 to 0. Three factors should be considered in explaining these results, the effect of (a) a strong acid on the solution of the salt of a weak acid, (b) increased ionic strength in the more acid solutions, and (c) the deviation from Debye-Hückel behavior when the solution can no longer be considered dilute. The decrease in solubility between pH 5 and 2 may be explained as the deviation from the Debye-Hückel equation. Between pH 2 and 0 the first and second factors seem to predominate. Calculations employing the ionization constant of hydrogen fluoride indicate that a simple explanation as proposed in part (a) above is not of itself adequate.

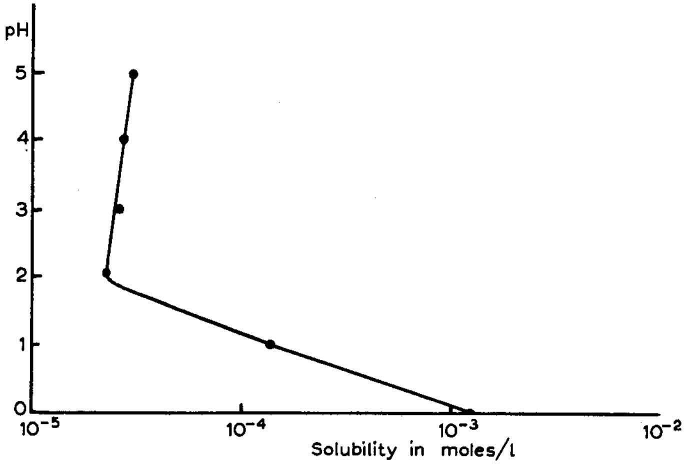

Fig. 1. pH–solubility relationship for cerous fluoride.

ACKNOWLEDGEMENT

The authors are indebted to the U.S. Atomic Energy Commission for partial support of this work.

SUMMARY

The apparent solubility product of cerous fluoride has been determined to be $8.1 \pm 1.1 \cdot 10^{-16}$ and $1.1 \pm 0.5 \cdot 10^{-15}$ by radiometric and conductometric methods respectively. Hydrolysis of cerous fluoride is thought to be negligible. The effect of hydrogen-ion concentration on the solubility of cerous fluoride has been measured in solutions of perchloric acid of varying acidity. The solubility was found to decrease slightly as the pH decreased from 5 to 2 and then to increase rapidly as the pH further decreased from 2 to 0.

RÉSUMÉ

Le produit de solubilité apparent du fluorure de cérium(III) a été déterminé par des méthodes radiométriques et conductométriques. L'influence du pH sur la solubilité de ce sel a été examinée.

References p. 379

ZUSAMMENFASSUNG

Es wird über die Bestimmung des wahrscheinlichen Löslichkeitsproduktes des Cer(III)-fluorids mit Hilfe von radiometrischen- und konduktometrischen Methoden berichtet und der Einfluss des pH auf die Löslichkeit dieser Verbindung untersucht.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

III. A COMPARATIVE STUDY OF 2-MERCAPTOBENZOTHIAZOLE AND 2-MERCAPTOBENZIMIDAZOLE AS ANALYTICAL REAGENTS

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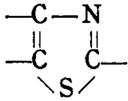
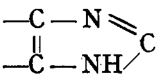
Spectrophotometric determinations of palladium with bismuthiols have already been discussed[1]. The palladium–bismuthiol complexes do not show any sharp peaks of maximum absorption, though density measurements at 400–410 mμ with bismuthiol I and 410–430 mμ with bismuthiol II establish their adherence to Beer's law at palladium concentrations of 0.8 to 8.0 μg/ml and 0.4 to 8.0 μg/ml respectively. Bismuthiol II complex, with the metal to reagent ratio of 1:2, is more stable ($K = 2.8 \cdot 10^{-12}$) compared to bismuthiol I complex ($K = 3.2 \cdot 10^{-5}$), where the metal to reagent ratio is 1:1.

The reagents, 2-mercaptobenzothiazole[2,3],  and 2-mercaptobenzimidazole[3–5],  having the same reactive mercapto groups as the bismuthiols, behave likewise in their reactions with palladium and are more akin to bismuthiol II. The red coloured complexes of the reagents with palladium give yellow to orange coloured systems while in solution of 10% alcohol or acetone. The reagents and the colour systems show high absorption in the ultraviolet region and less high in the visible, where they have no sharp peak of maximum absorption. The colour intensity of the complexes has, therefore, been measured at those regions of maximum absorption, where the reagents have minimum absorption.

The wave length used for the measurements of optical density of the systems at the optimum pH range of 3 to 6.5 is 380 mμ and at this wave length Beer's law has been found to hold good at palladium concentrations of 0.4–6.0 μg/ml. The corresponding optimum range, evaluated according to RINGBOM's method[6], is 1.6–4.0 μg/ml and the per cent relative analytical error, according to AYRES[7], per 1% absolute photometric error is 3.0. The respective sensitivities in μg of palladium per cm^2 for 2-mercaptobenzothiazole and 2-mercaptobenzimidazole are 0.06 and 0.07 (practical); 0.011 and 0.013 at 380 mμ (SANDELL[8]).

The colour systems are stable for over 24 h and are unaffected by excess reagent and by variations of temperature from 20° to 30°. Complexone III, which has no influence on the colour reaction or on the intensity of the colour, masks the interfering effects of a large number of ions. The presence of more than 10% of alcohol or acetone reduces the intensity, and the ions of gold, platinum, copper, chromium, mercury, silver, thallium, uranium, vanadate and cyanide interfere with the determination of palladium.

Job's method of continuous variation indicates that in solution the complexes contain palladium and the reagent in ratios of 1:2 with dissociation constants in the order of 10^{-12}.

EXPERIMENTAL

Apparatus and solution

The reagents, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole, were prepared and crystallised according to described methods[2,4,5]. A 0.2% aqueous solution of 2-mercaptobenzimidazole and a 0.2% solution of 2-mercaptobenzothiazole in dilute aqueous alkali were prepared and used as colour-forming reagents.

Solutions of palladium, of other cations and anions, and of complexone III and the organic solvents were the same as stated in previous communications[1]. Equimolecular and non-equimolecular solutions of palladium and the reagents were prepared for the study of the composition and the dissociation constants of the complexes.

The Unicam SP 600 spectrophotometer with 1 cm cell and the Cambridge pH indicator were the same as used previously.

Colour reaction

Both the reagents react instantaneously with palladium to produce red precipitates which are less soluble in water but dissolve easily in presence of ethyl alcohol or acetone. Thus stable colour systems were made by the addition of either of the said solvents (preferably ethyl alcohol due to its comparatively low volatility) to the extent of only 10% (v/v) of the total volume. An excess of the organic solvents usually reduces the colour intensity. Complexone III, which masks the influences of other ions, does not affect the colour reaction if only 50 mg of it is present in a total volume of 25 ml.

Fig. 1 represents the absorbance curves of the colour systems (I) of palladium complex against the reagent solutions, (II) of the palladium complex against water and (III) of reagent solution against water. The curves indicate that the optical densities of the reagents decrease sharply from 360 mμ and are almost negligible after 380 mμ, while the palladium complexes exhibit practically the same absorption between 380 and 390 mμ, and hence all measurements were made at 380 mμ.

For the density measurements, the colour systems with 2-mercaptobenzothiazole and 2-mercaptobenzimidazole were maintained at pH 4.2 and 3.6 respectively and contained, besides palladium, 2 ml of the reagent and 2.5 ml of ethyl alcohol in a total volume of 25 ml.

Effect of reagent, pH, time and temperature

The absorption study at 380 mµ of a number of solutions each with 4 µg of palladium per ml and with different quantities of any of the reagents (1 to 10 ml) and maintained at a pH of 5.0 (for 2-mercaptobenzothiazole) or 4.2 (for 2-mercaptobenzimidazole) reveals that the presence of an excess of the reagent has no adverse effect.

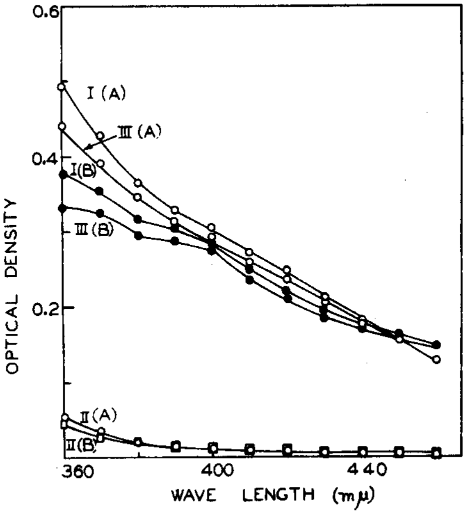


Fig. 1. Absorption regions of the colour systems. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole; I 4 µg of Pd per ml, II without Pd, III corrected values.

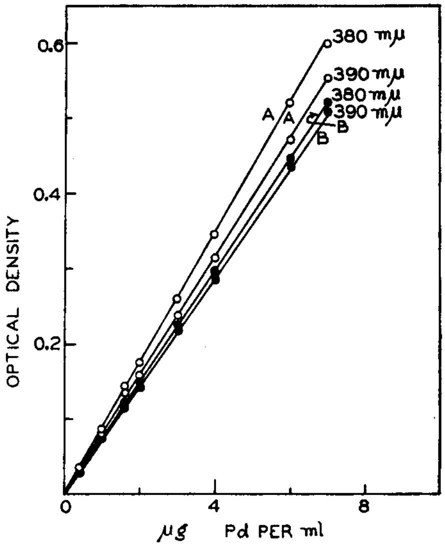


Fig. 2. Study of Beer's law. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

Similar studies with a number of coloured systems each adjusted to a definite pH show that the colour intensity as measured against a reagent blank remains practically unchanged for 24 h over the pH range of 3 to 6.5. It even remains unaffected when the temperature of the systems is varied between 20° and 30°, but at 35° a deviation of only 1% is observed.

Beer's law and sensitivity

The colour systems with 0.4 to 6.0 µg of palladium per ml were found to obey Beer's law as, when the optical densities at 380 and 390 mµ were plotted against the respective concentrations of palladium, straight lines which pass through the origin were obtained (Fig. 2).

With 2-mercaptobenzothiazole, the optical densities for 4 µg of palladium per ml are 0.345 and 0.312 respectively at 380 mµ and 390 mµ and the sensitivity of the colour reaction is 0.066 µg of palladium per cm^2 (practical); being 0.011 µg and 0.013 µg of palladium per cm^2 at 380 mµ and 390 mµ respectively (SANDELL).

With 2-mercaptobenzimidazole, for the same amount of palladium per ml, the optical densities are 0.296 and 0.287 at 380 mµ and 390 mµ respectively and the sensitivity of the colour reaction is 0.07 µg of palladium per cm^2; sensitivity values according to SANDELL are 0.013 µg and 0.014 µg of palladium per cm^2 at 380 mµ and 390 mµ respectively.

For Beer's law, optical density was measured against a reagent blank and the systems at pH 5.0 contained, in a total volume of 25 ml, 0.4 to 10.0 μg of palladium per ml, 4 ml of the reagent and 2.5 ml of ethyl alcohol.

Evaluation of optimum range of Beer's law and the accuracy in photometric analysis

The optimum concentration range and the accuracy of the photometric analysis are evaluated on plotting 'per cent absorption' as the ordinate against 'log concentration' as the abscissa (Fig. 3). Accuracy is greatest where the curve has its steepest slope. Thus the suitable range with the minimum error is in the region of 1.6 to 4.0 μg of palladium per ml, when the measurements are made at 380 mμ.

Per cent relative error per 1% absolute photometric error

The per cent relative error ((dc/c × 100) per 1% photometric error has been calculated and plotted against the transmission. Thus it is found that the measurements of the optical density of the systems can be made with the minimum error at 30.1% transmission with 2-mercaptobenzothiazole and at 35.8% transmission with 2-mer-

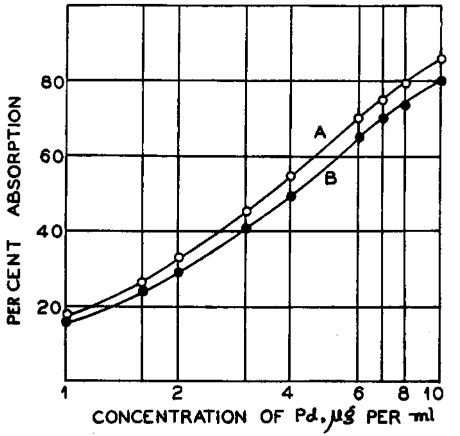


Fig. 3. Evaluation of optimum range of Beer's law. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

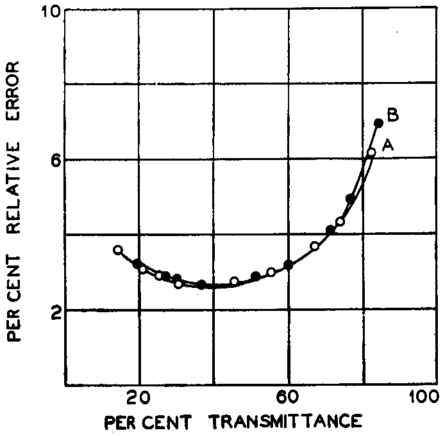


Fig. 4. Evaluation of relative error. (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

TABLE I

EVALUATION OF THE RELATIVE ERROR IN THE SYSTEM WITH 2-MERCAPTOBENZOTHIAZOLE

Concn. of Pd *μg/ml*	*Transmission*	$\frac{dc}{c}$ × *100 (% relative error per 1% photometric error)*
1.0	82.0	6.2
1.6	73.3	4.4
2.0	66.9	3.7
3.0	54.9	3.0
4.0	45.2	2.8
6.0	30.1	2.7
7.0	25.1	2.9
8.0	20.8	3.1
10.0	14.1	3.6

captobenzimidazole (Fig. 4). Tables I and II show the variation of the analytical error with the transmission.

TABLE II

EVALUATION OF THE RELATIVE ERROR IN THE SYSTEM WITH 2-MERCAPTOBENZIMIDAZOLE

Concn. of Pd µg/ml	*Transmission*	$\frac{dc}{c}$ × *100 (% relative error per 1% photometric error)*
1.0	84.1	6.9
1.6	76.4	4.9
2.0	71.1	4.1
3.0	59.7	3.2
4.0	50.6	2.9
6.0	35.8	2.7
7.0	30.1	2.8
8.0	26.3	2.9
10.0	19.3	3.2

TABLE III

INTERFERING EFFECT OF DIVERSE IONS

palladium taken, 100 µg

Ions	*Maximum amount tolerated µg*	*Ion/Pd ratio at maximum tolerance limit*	*Ions*	*Maximum amount tolerated µg*	*Ion/Pd ratio at maximum tolerance limit*
Ca^{+2}	200	50.0	Fe^{+3}	80	20.0
Ba^{+2}	200	50.0	Cl^{-}	250	62.5
Sr^{+2}	200	50.0	F^{-}	400	100.0
Mg^{+2}	200	50.0	Br^{-}	200	50.0
Co^{+2}	40	10.0	I^{-}	200	50.0
Mn^{+2}	100	25.0	NO_3^{-}	250	62.5
Ni^{+2}	40	10.0	NO_2^{-}	200	50.0
Zn^{+2}	100	25.0	SO_4^{-2}	200	50.0
Al^{+3}	100	25.0	$S_2O_3^{-2}$	200	50.0
Be^{+2}	50	12.5	PO_4^{-3}	200	50.0
Th^{+4}	120	30.0	AsO_4^{-3}	160	40.0
Zr^{+4}	140	35.0	AsO_3^{-3}	160	40.0
TiO_2^{+2}	50	12.5	BO_3^{-3}	200	50.0
Pb^{+2}	100	25.0	MoO_4^{-2}	100	25.0
Cd^{+2}	100	25.0	WO_4^{-2}	100	25.0
Bi^{+3}	100	25.0	Acetate	200	50.0
Sn^{+4}	40	10.0	Formate	250	62.5
Ru^{+3}	8	2.0	Oxalate	200	50.0
Os^{+4}	8	2.0	Benzoate	160	40.0
Ir^{+4}	8	2.0	Salicylate	160	40.0
Rh^{+3}	2	0.5	Citrate	200	50.0
Sb^{+3}	50	12.5	Tartrate	200	50.0

Procedure

On the basis of the results of the experiments, the following procedure is recommended.

Add to the palladium solution in succession 2 ml of the reagent solution and 2.5 ml of ethyl alcohol, and adjust its pH in such a way that on dilution with water to 25 ml, it remains between 3 and 6.5. After thorough mixing at 20°–25°, place the solution in a 1 cm cell and measure its optical density at 380 mμ. Similarly, prepare a reagent blank and measure its optical density.

Effect of diverse ions

The interfering effect of the ions was studied by means of the colour intensity produced on the addition of the solution of ion to the solution of palladium (100 μg) taken in a 25 ml-flask with 2.5 ml of 1% complexone III solution, 2 ml of the reagent and 2.5 ml of ethyl alcohol. After the adjustment of its pH, the solution was diluted to 25 ml as suggested above and its optical density in a 1-cm cell, at 20°–25°, was measured at 380 mμ against a reagent blank. An ion is considered to interfere if the absorbance differs by more than 0.005 from the value obtained in its absence. Tolerance limits for the ions are summarised in Table III. The ions of gold, platinum, copper, silver, mercury, thallium, chromium, uranium, vanadate and cyanide interfere.

Composition and dissociation constant of the palladium complex in solution

The composition and the dissociation constant of the complexes in solution at 20°–25° were ascertained in the same way as described in a previous paper[1]. For composition, equimolecular solutions of palladium and the reagent were taken in

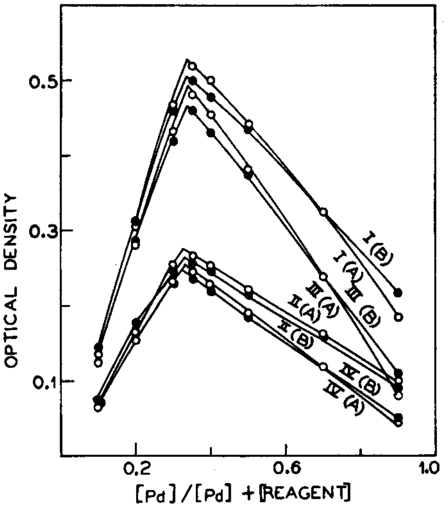


Fig. 5. Mixtures of equimolecular solutions. I 1.88 · $10^{-4}M$, II 0.94 · $10^{-4}M$, III and IV corrected values; (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

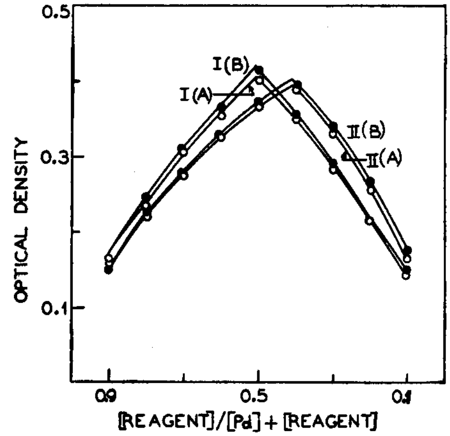


Fig. 6. Mixtures of non-equimolecular solutions. I 0.94 · $10^{-4}M$ Pd and 1.88 · $10^{-4}M$ reagent, II 0.94 · $10^{-4}M$ Pd and 2.82 · $10^{-4}M$ reagent; (A) 2-Mercaptobenzothiazole; (B) 2-Mercaptobenzimidazole.

different ratios to a constant volume of 20 ml which was then made up to 25 ml with a further addition of 2.5 ml of ethyl alcohol and the same amount of water. The curves in Fig. 5 show that the complexes are formed in the solution when the ratio of palladium to reagent is 1:2.

From the absorption data (Fig. 6) of the mixtures of non-equimolecular solutions at 20°–25°, the dissociation constant '*K*' of both complexes has been calculated on the basis of the values of *x*, *p* and *c*, the values of *m* and *n* being 1 and 2 respectively (Table IV).

TABLE IV

Curve	*Concn. of Pd* $\times 10^4 M$	*Concn. of reagent* $\times 10^4 M$	x	p	$K \times 10^{12}$
I	0.94	1.88	0.51	2	2.4
II	0.94	2.82	0.41	3	0.4

K (mean) $= 1.4 \cdot 10^{-12}$

SUMMARY

As spectrophotometric reagents for palladium, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole behave more or less in the same way. Colour systems formed by them, at a pH region of 3.0 to 6.5, obey Beer's law at 380 mμ with palladium concentrations of 0.4 to 6.0 μg per ml and the optimum range with the minimum error is from 1.6 to 4.0 μg of palladium per ml at 30.1% and 35.8% transmission with 2-mercaptobenzothiazole and 2-mercaptobenzimidazole respectively. By applying Job's method it was found that in solution the ratio of metal to reagent in the complexes is 1:2, and that the dissociation constants of the complexes are of the order of 10^{-12}

RÉSUMÉ

Le 2-mercaptobenzothiazole et le 2-mercaptobenzimidazole ont été examinés comme réactifs spectrophotométriques du palladium. La loi de Beer est obéie à 380 mμ pour des concentrations en palladium allant de 0.4 à 6.0 μg/ml.

ZUSAMMENFASSUNG

Es wurde die Anwendungsmöglichkeit von 2-Mercaptobenzothiazol und 2-Mercaptobenzimidazol als Reagenzien zur spektrophotometrischen Bestimmung von Palladium untersucht. Bei 380 mμ gilt das Beer'sche Gesetz für einen Konzentrationsbereich von 0.4 bis 6.0 μg Pd/ml.

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AMPEROMETRIC ESTIMATION OF PALLADIUM

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As early as 1897 SALOMON[1] first proposed the principle of amperometric titration, which in later years has been studied by many other investigators. Because of their sensitive and specific or selective reactions, organic reagents have of late been utilised by several workers as titrants. KOLTHOFF AND LANGER[2] suggested the use of α-nitroso-β-naphthol for the titration of palladium. Of the reagents dimethylglyoxime, salicylaldoxime, oxine and mercaptobenzothiazole, TOMICEK and his co-workers[3] found dimethylglyoxime and mercaptobenzothiazole to be sensitive as well as selective in their reactions with palladium, while WILSON AND WILSON[4] preferred 1,2,3-benzotriazole for its determination.

Mercapto compounds, such as bismuthiol I, bismuthiol II, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole, as reagents for the spectrophotometric determination of palladium have already been described in previous communications[5]. This paper records the findings of the work on the application of the said reagents for the amperometric estimation of that element. Constancy of the diffusion currents in sodium acetate–acetic acid buffer, of palladium and of the reagents enabled us to determine the former element amperometrically.

At an applied potential of —0.3 V (S.C.E.), bismuthiol I was found to be a reliable reagent for the estimation of only 1.2 to 2.5 mg of palladium, whereas with bismuthiol II and 2-mercaptobenzimidazole an applied potential of —0.5 V gives highly satisfactory results with 1.2 to 6.0 mg of the same element. 2-Mercaptobenzothiazole gives a positive error of about 5% when the amount of palladium is 6.0 mg. Further, from the above study it has been observed that the metal forms a 1:1 complex with bismuthiol I, while with the other reagents it forms a 1:2 complex.

EXPERIMENTAL

Apparatus

The amperometric set, consisting of a students' type potentiometer with a range of 0 to 1.6 V of Leeds and Northrup Co., a galvanometer, a micro-ammeter (0 to 30 μA), a titration cell and a saturated calomel electrode, was assembled according to the circuit diagram of LINGANE[6]. The potentiometer was calibrated against a galvanometer used as a null-point detector. The currents were measured at 30° ± 1° with a micro-ammeter whose oscillations were damped with a condenser of 250 μF capacity. The titration cell was connected with a saturated calomel electrode by an agar–potassium chloride bridge.

Solutions

A molar solution of palladium was prepared by proper dilution of a standard palladium chloride solution.

Molar solutions of bismuthiol I (A), bismuthiol II (B), 2-mercaptobenzothiazole (C) and 2-mercaptobenzimidazole (D) were obtained by dissolving separately weighed amounts of the reagents in 50% (v/v) ethyl alcohol.

A sodium acetate–acetic acid buffer solution was prepared by mixing 27.2 g of sodium acetate trihydrate in 11.6 ml of glacial acetic acid (sp.gr. 1.05) and then by diluting the mixture with water to 100 ml.

A 0.2% (w/v) gelatin solution in water and a 15% pyrogallol solution in 50% (v/v) aqueous caustic potash solution were the other solutions used.

Capillary

The characteristics of the capillary used were: m = 1.083 mg/sec, t = 6.0 sec (open circuit in distilled water) and h = 44.9 cm.

Measurements of diffusion currents of palladium and the reagents

A 20 ml portion of the solution of palladium was placed in the titration cell and 5 ml of the sodium acetate–acetic acid buffer solution and 1 ml of the gelatin solution were added. Oxygen-free nitrogen gas of high purity (British Oxygen Co., London) was passed through the alkaline pyrogallol solution and was then bubbled through the solution in the titration cell for 15 min. A few minutes later when the current due to a potential of 0.0 V (S.C.E.) became steady, the mean current which flowed through the micro-ammeter was measured. Afterwards, the steady current for the solution at —0.1 V (S.C.E.) was recorded. Then the voltage was slowly increased to —1.6 V (S.C.E.) and the corresponding steady current was measured. In the same way, diffusion currents for the reagents were measured with 20 ml portions of each solution and the results obtained were plotted in Fig. 1. From the figure, the diffusion currents for palladium and reagents against S.C.E. are: palladium, —0.3 to —0.8 V; bismuthiol I, 0.0 to —0.3 V; bismuthiol II, 0.0 to —0.8 V; 2-mercaptobenzothiazole, —0.4 to —0.6 V; and 2-mercaptobenzimidazole, —0.2 to —0.7 V.

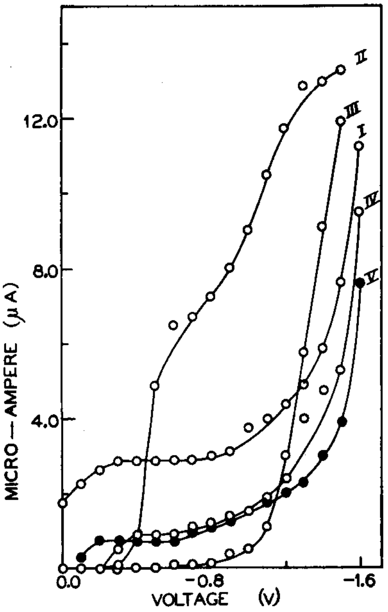

Fig. 1. Diffusion curve. I Palladium (8.762·10⁻⁴M), II Bismuthiol I (5.318·10⁻²M), III Bismuthiol II (2.769·10⁻³M), IV 2-Mercaptobenzothiazole (2.663 · 10⁻³M), V 2-Mercaptobenzimidazole (2.8 · 10⁻³M).

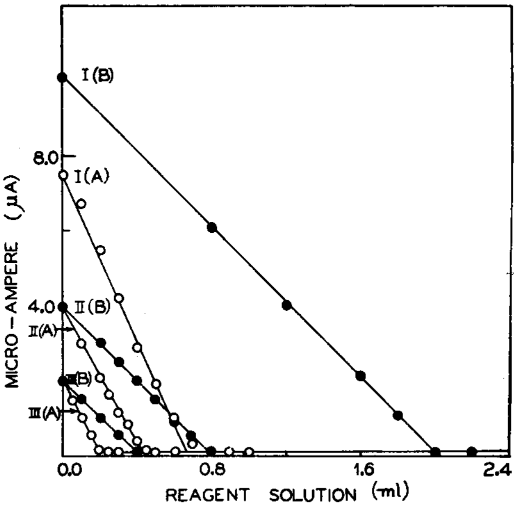

Fig. 2. (A) Bismuthiol I (5.318 · 10⁻²M,) (B) Bismuthiol II (5.6 · 10⁻²M).

Estimation of palladium

An aliquot quantity of the palladium solution was placed in the titration cell along with 5 ml of sodium acetate–acetic acid buffer and 1 ml of gelatin solution. After the addition of water to dilute it to 26 ml, oxygen-free nitrogen gas was passed through the solution for about 15 min. Then when the solution was ready for titration, the tip of a microburette containing the reagent solution was introduced through a hole in the stopper of the titration cell. The circuit was then closed with an applied potential of —0.3 V (S.C.E.) when titrating with bismuthiol I, but with the other reagents as titrants the applied potential was adjusted to —0.5 V (S.C.E.).

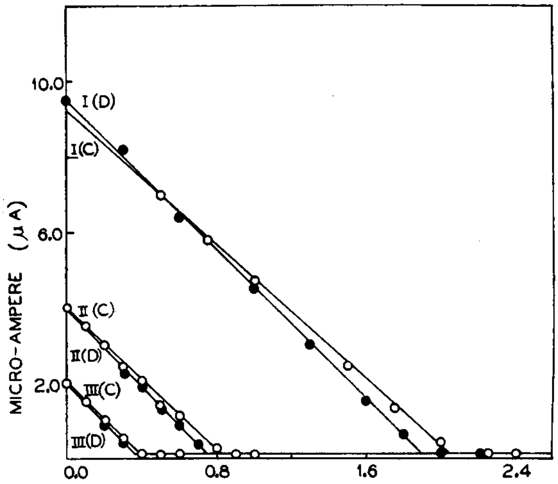

FIG.3.

Fig. 3. (C) 2-Mercaptobenzothiazole ($5.371 \cdot 10^{-2}M$), (D) 2-Mercaptobenzimidazole ($6.327 \cdot 10^{-2}M$).

When the current became steady, a small quantity of the titrant was run into the cell and after the passage of nitrogen through the solution for one minute, the steady current was measured. On plotting the currents against the volumes of the titrant, the equivalence point was extrapolated. The results are represented in Figs. 2 and 3 and tabulated in Table I.

TABLE I

Curve	*Pd taken mg*	*Pd found (mg)* A	B	C	*Pd taken mg*	*Pd found mg D*
I	6.00	3.80	5.97	6.31	6.50	6.40
II	2.40	2.44	2.39	2.41	2.60	2.55
III	1.20	1.14	1.19	1.20	1.30	1.28

SUMMARY

In sodium acetate–acetic acid buffer the diffusion currents of palladium and of the reagents bismuthiol I, bismuthiol II, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole remain constant respectively at potentials (*vs.* S.C.E.) of —0.3 to —0.8 V, 0.0 to —0.3 V, 0.0 to —0.8 V, —0.4 to —0.6 V and —0.2 to —0.7 V respectively. Bismuthiol I, at an applied potential of —0.3 V,

References p. 389

is effective for the estimation of 1.2 to 2.5 mg of palladium, whereas bismuthiol II and 2-mercaptobenzimidazole give highly satisfactory results with 1.2 to 6.0 mg of palladium at a potential of —0.5 V. 2-Mercaptobenzothiazole at the latter potential gives an error of about 5% when the concentration of palladium is about 6.0 mg.

RÉSUMÉ

Les auteurs ont effectué une étude en vue d'un dosage ampérométrique du palladium. Les réactifs examinés sont: bismuthiol I, bismuthiol II, 2-mercaptobenzothiazole et 2-mercaptobenzimidazole.

ZUSAMMENFASSUNG

Es wurden die Möglichkeiten einer amperometrischen Bestimmung von Palladium mit Hilfe von Wismutthiol I, Wismutthiol II, 2-Mercaptobenzothiazol und 2-Mercaptobenzimidazol untersucht.

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THE EFFECT OF THE ELECTRONIC STRUCTURE OF THE CATION UPON FLUORESCENCE IN METAL-8-HYDROXYQUINOLINE COMPLEXES

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INTRODUCTION AND THEORETICAL SECTION

Compounds of 8-hydroxyquinoline (oxine) have been prepared with metals in lower valency states in these laboratories[1] in connection with biochemical researches with metallic valency states. The complexes obtained with Mo, V, Fe, Cu, Au and Ti valencies, although distinctly coloured, were non-fluorescent in u.v. light. It is well known that some cations *e.g.* Al^{+3}, Zn^{+2}, Mg^{+2}, Ca^{+2}, Li^{+} etc. will form oxinates which fluoresce brightly in u.v. light, and the fluorescent properties of metallo-oxinates were therefore studied to determine whether a relationship existed between the electronic structure of the cation, and the ability of the complex to fluoresce.

Differences in the fluorescent and phosphorescent lifetimes of some metal-dibenzoylmethane complexes were explained by YUSTER AND WEISSMAN[2] on the basis of varying degrees of interaction between the optical electrons responsible for fluorescence in the complex and the field of the metal ion. This perturbation effect of the ionic field depended considerably upon the protection afforded to the optical electrons by the shells in the ion itself, as complete electron shells afforded more protection than empty shells against perturbation and dissipation of fluorescence. The incomplete 4f shell of the Gd^{+3} ion greatly reduced the luminescent life of the Gd complex owing to the large degree of perturbation caused by the unhomogeneous field of the paramagnetic ion. The non-fluorescence of the Yb^{+3} complex was suggested to be due to the removal of an electron from the 4f^{13} to the 5d or 6s or 6p shell resulting in an "internal quenching" effect.

If the considerations of YUSTER AND WEISSMAN are applied to 8-hydroxyquinoline complexes, it would be expected that the oxinates which fluoresced most readily would be those derived from cations containing the most stable electron groupings, *i.e.* where shells are either full or empty, and that incomplete shells or a transitional nature in the metal ion would reduce or destroy the fluorescence of the oxine complex. In the main this was found to be correct; of the metals which form, or would be expected on account of their electronic structure to form, fluorescent oxinates are shown in Table I.

Oxine compounds of the other metallic elements not listed in Table I were examined with the exception of Tc, Rh, Pm(II), Eu, Ho, Re, Os, Ir, Po and the "uranide" elements, and were found to be non-fluorescent in u.v. light. Those listed which were not examined would be expected on account of their electronic structures to yield non-fluorescent oxinates.

TABLE I

FLUORESCENT METALLO-8-HYDROXYQUINOLATES

Group	*Sub group A*	*Sub group B*
I	Li, Na, K, Rb, Cs, Fr[a]	Ag
II	Be, Mg, Ca, Sr, Ba, Ra[a]	Zn, Cd
III	Al, Sc, Y, La ... (Gd) ... Lu, Ac[a]	Ga, In
IV	Zr, Hf[a], Th	Ge, (Sn), ((Pb))
V	(Nb), Ta, Pa[a]	none
VI	none	none
Uranides	Cm[a]	
VII VIII	none	none

[a] Speculated from electronic structure of ion.
( ) Weak fluorescence.
(( )) Very weak fluorescence.

The alkali metals and Ag, and the alkaline-earth metals, Zn and Cd lose s electrons to form ions of one stable valency in which the remaining electron shells are full. In contrast Cu, Au, and Hg show transitional properties and each possesses two valencies which are relatively stable to one another; a perturbation or internal quenching effect may therefore occur with the optical electrons of their complexes which are consequently non-fluorescent. The behaviour of cations in Group IIIA provides evidence for the weakening of the fluorescent properties of oxinates by the presence of an incomplete 4f shell between La^{+3} and Lu^{+3}. Gd^{+3}, in which the 4f shell is half full (a condition which is regarded as having some stability), gives the weakest fluorescence in the Group. Other members of the rare-earth series in which the 4f shell contains <7, or >7 and <14 electrons yield non-fluorescent oxine complexes[3]. Actinium oxinate would be expected to fluoresce as the electronic groupings in Ac are similar to those in Lu but with 18 electrons added to complete the 5d, 6s and 6p shells. In Group IIIB, Ga and In each possess one stable cation, as ions of the lower valencies are very unstable, but with Tl both the uni- and trivalent cations are reasonably stable giving a transitional character to the metal, and non-fluorescent oxine complexes are formed with both valencies.

The metals in Group IVA show regular behaviour as regards fluorescence. The transitional nature of Ti with its moderately stable tri- and tetravalent states appears to preclude fluorescence in both oxinates derived from these valencies. Zr and Th, which possess only the cationic state M^{+4}, in which the remaining electron shells are full, form fluorescent oxinates, and it is predicted that Hf^{+4}, which like Zr^{+4} is formed by loss of d and s electrons leaving other shells full, will also form a luminescent oxine complex. Unfortunately no Hf material was available at the time this work was carried out.

Group IVB contains the anomalous case of Sn which forms fluorescent compounds with oxine in both Sn^{+2} and Sn^{+4} valency states. It may however be noted that in neither ion is there an incomplete electronic shell; moreover the fluorescence of the Sn compounds is feeble compared with that of the others listed in Table I. The same remarks also apply to Pb; here the fluorescence is very feeble and although the divalent cation is very stable, some stability exists in the Pb^{+4} condition.

In Group VA, as the valencies of less than 5 become increasingly unstable, any perturbing or quenching effects due to transitional character would be expected to become less and hence there is an increasing tendency for the oxinates to fluoresce on passing from V (all oxinates non-fluorescent) via Nb (oxinate of pentavalent state fluoresces feebly) to Ta (pentavalent state gives a moderately bright fluorescent complex). Pa which shows no sign of a valency other than 5, and whose electronic structure is similar to that of Ta but with an added 18 electrons to complete the 5d, 6s, and 6p shells, would be expected to give a fluorescent complex.

In Group VB it may be expected that Bi oxinate would show a feeble fluorescence as Bi^{+3} is the only stable cation in which remaining electron shells are full. However, it does not fluoresce and indeed in other cations which are formed by the loss of p, but not s, electrons from the same shell (*e.g.* Pb, Tl, Sb, Sn and possibly As) the fluorescent properties of the oxine complexes are either feeble or totally absent.

In Groups VI, VII, and VIII, oxinate fluorescence is notably lacking owing possibly to the internal quenching effect which incomplete d electron shells may exert in the highly transitional metals which comprise these Groups.

Of the "uranide elements" of Group VI, it might be expected that a weakly-fluorescent oxinate would be formed by Cm, as this metal has only one valency-state (3), and the electronic structure of the Cm^{+3} ion with its half-complete 5f shell resembles that of Gd^{+3}.

From the observations recorded above, it appears that the possession of fluorescent properties by a metal–8-hydroxyquinoline complex is dependent upon the formation of metal ions of only one stable valency in which the remaining electron shells are in a "symmetrically stable" state, *i.e.* empty, half-full or complete.

The fluorescence intensities, relative to a quinine sulphate standard, of a number of pure metal oxinates of the type $M(C_9H_6ON)_n$, where n = the valency of the metal ion, M, were examined by measuring the total fluorescent light emitted after irradiation of chloroform–ethanol solutions of the complexes with u.v. light. Concentrations of each complex from $\frac{M}{500}$ to $\frac{M}{10^6}$ were tested, and in dilute solutions $\left(\frac{M}{10^6} \text{ or } \frac{M}{10^5}\right)$ the fluorescent intensities of the compounds decreased in the series:

$$Al > Y > Sc, Zr, Mg, Sn > Be > Zn > Ag > Li > Na$$

The series was gradually broken up in solutions containing an increasing concentration of metal oxinate. Although these results do not provide much that is conclusive, it is interesting to note that as with the dibenzoylmethane complexes of YUSTER AND WEISSMAN[2], the Al compound exhibits the greatest degree of fluorescence, followed by Y and Sc. The weaker fluorescence of Ag may be due to some decomposition within the complex, and the relatively poor response of Li and Na is possibly because of a greater tendency to dissociate in the solvent.

The position of Sn in the series is anomalous, but a very pronounced quenching of the fluorescence of a Sn^{+2} oxinate solution takes place with increasing concentration. Thus the intensities at $\frac{M}{10^5}$, $\frac{M}{10^4}$ and $\frac{M}{10^3}$ are respectively 32%, 21% and 1% (based on the quinine sulphate standard). This is presumably due to the ready dissipation of the excitation energy in the molecules by collisions.

EXPERIMENTAL SECTION

Preparation of 8-hydroxyquinoline complexes

Most of the complexes were prepared in the standard way, using AnalaR materials, by mixing an aqueous-ethanolic solution of a suitable salt with an ethanolic solution of oxine, and precipitating the oxinates by the gradual addition of NH_4OH to the solution. The precipitates were filtered by suction, washed with water, ethanol, and ether and dried at the correct temperature. The preparation of oxine compounds which did not appear to have been previously reported, or which needed modified techniques are described below. Where necessary, the compositions of the compounds prepared were checked by C, H, N and, where appropriate, Cl analyses.

The alkali metals

Two methods were used for this group: (1) A "wet" method in which oxine was dissolved in a hot solution of the hydroxide; on cooling the precipitated complex was dried by suction filtration, dissolved in a minimum of warm ethanol and re-precipitated by the addition of an excess of ether. This precipitate was filtered off and washed with ether and dried at 90°. (2) A "dry" method where 1 part by weight of the anhydrous metal carbonate was added to 4–5 parts of molten oxine, and the temperature raised to boiling point. When the carbonate had dissolved according to the suggested reaction $M_2CO_3 + 2C_9H_7ON \rightarrow 2M(C_9H_6ON) + H_2O + CO_2$ the melt was cooled and powdered and dissolved in either hot 95% acetone (Li, Na, K) or hot ethanol (Rb, Cs). From the cooled solutions, after filtration (No. 41 filter paper), the oxinates were precipitated by adding an excess of ether. They were filtered by suction, washed with ether and dried.

The reaction between carbonates and molten oxine did not appear to be confined to the metals of Group IA, as the carbonates of Ag, Cu and Pb reacted in a similar way. Ca, Ba, and Bi carbonates in contrast appeared to remain unaffected by boiling oxine.

The Rb and Cs compounds, which do not appear to have been previously reported, were difficult to prepare by the "wet" method because they would not crystallise from the hydroxide solutions, due possibly to a higher degree of dissociation than with the K and Na complexes.

It would be expected that the power of the N atom of 8-hydroxyquinoline to co-ordinate with an alkali metal becomes less on passing from Li to Cs, and in conjunction with the weakly acidic H atom of the OH group it is not surprising that the Rb and Cs compounds approached the composition $MOH \cdot C_9H_7ON$ as indicated by the analyses below:

Found, for Rb: C 42.3, H 4.0, N 5.3. (Calc. for $RbOH \cdot C_9H_7ON$, C 43.7, H 3.2, N 5.6).
Found for Cs: C 35.6, H 2.8, N 4.6. (Calc. for $CsOH \cdot C_9H_7ON$, C 36.6, H 2.7, N 4.7).

The alkali metal oxinates were soluble in water (Li sparingly) and ethanol but insoluble in ether and chloroform. When the K, Rb, or Cs compounds were treated with a chloroform–acetone mixture (3:1) and warmed, a green or blue colour was produced at first and finally a purple solid was deposited. With K oxinate prepared by the "wet" method (and probably containing a little free alkali) the mixture boiled without any previous heating; the resulting purple solid was washed with ether and dried in vacuo over P_2O_5 in a desiccator. The purple compound contained Cl and was stable in air; it was however decomposed by warming, and also by water, which yielded an ink-blue solution. When the blue solution was boiled or the purple compound heated oxine vapour, but no chloroform, was evolved. The compound did not fluoresce in u.v. light and analyses showed that it was of variable composition. It is of interest to note that previous workers have observed a green or blue colour during the reaction of $CHCl_3$ and CCl_4 with hydroxyquinolines or β-naphthol respectively in caustic alkali solution[4,5].

The readiness to form this purple compound decreased from K *via* Na, where a slow reaction took place, to Li whose oxinate reacts only slightly. Oxinates prepared by the "wet" method reacted much more readily with chloroform than those produced by the "dry" method, owing possibly to the presence of a little free alkali in the former.

It was also noted that a blue-green colour was produced by the action of chloroform upon the oxine compounds of some alkaline earth metals and here again colour production decreased with decreasing basicity of the metal ion. The Ba compound gave considerable colour, at Ca it was slight, and no action appeared to take place with the Mg and Be complexes.

The action of carbon tetrachloride, methylene and ethylene dichlorides upon K oxinate was found to be slight; trichloroethylene and ethyl iodide were without effect.

Sc and Nb

The oxinates were prepared from Johnson-Matthey "specpure" Sc_2O_3 and B.D.H.

Nb_2O_5 respectively. Fusion with sodium bisulphate was necessary to obtain the elements in soluble form. After cooling, the melts were powdered and extracted with hot water. Sc was precipitated with ammonia, and the $Sc(OH)_3$ was filtered, washed and re-dissolved in warm dilute sulphuric acid. The Nb melt was hydrolysed during hot water treatment, and the precipitated Nb_2O_5 was filtered off and washed, and dissolved in warm concentrated sulphuric acid. The H_2SO_4 solution was cooled in ice water and diluted with acetone. The Sc and Nb oxine compounds were then prepared from these solutions in the standard way.

Sn

The oxine complexes of Sn do not seem to have been extensively studied. When solutions of $SnCl_2$ in HCl and oxine in ethanol were mixed, a yellow granular compound, which contained Cl, was precipitated. Analyses suggested that the compound was of variable composition.

When ethanol and water were added to the vessel in which this compound was precipitated, and the mixture heated, the precipitate dissolved. Addition of ammonia to the hot solution caused precipitation of a yellow solid, containing no Cl. Found: C 53.4, H 3.3, N 7.1. Calc. for $Sn(C_9H_6ON)_2$, C 53.2, H 3.0, N 6.9. This complex which, unlike the Cl-containing one, was easily soluble in chloroform was used in the measurement of fluorescence intensities (see below). Both compounds when decomposed with HCl formed solutions which readily reduced $HgCl_2$, due to the liberation of Sn^{+2} ions.

Compounds precipitated from solutions of $SnCl_4$ by oxine were also yellow and of variable composition. They would not dissolve in excess of hot aqueous ethanol or in chloroform and yielded non-reducing solutions when decomposed with HCl.

Ge

The only oxine complex of this metal which, to the author's knowledge, has been prepared is a molybdo-oxine compound to which the formula $(C_9H_7ON)_4H_4[Ge(Mo_{12}O_{40})]$ was assigned[6]. LEDERER reported the fluorescence of Ge spots on chromatograms developed with 8-hydroxyquinoline[7]. A yellow fluorescent powder was prepared by treating an ethanolic solution of $GeCl_4$ (prepared by boiling GeO_2 with 7–10*N* HCl and diluting the distillate with ethanol) with ethanolic oxine. Ammonia was added until the pH of the mixture was 4–5, and the volume of the solution reduced by boiling in a stream of CO_2 until on cooling in ice-water a granular precipitate separated out. This was filtered off and washed with water and ether and dried overnight in vacuo over P_2O_5. The yellow powder contained no Cl and was readily soluble in chloroform. When heated, decomposition began at about 110°, and was very marked at 150°. Analysis of the compound gave C 54.8, H 4.3, N 7.2. (Calc. for $(HO)_2Ge(C_9H_6ON)_2$, C 54.7, H 3.6, N 7.1).

Ta

SZYMANSKI AND ARCHIBALD[8] reported the preparation of an orange Ta-oxine compound, to which they assigned the formula $Ta(C_9H_6ON)_5 \cdot 5HCl$, by adding a solution of oxine in benzene to one of $TaCl_5$ in the same solvent. The author found

References p. 396

that this compound would not fluoresce in u.v. light, but if the solutions were mixed in the reverse order, a pale yellow precipitate was formed which fluoresced brightly in u.v. light. A fluorescent powder was also produced by passing oxine vapour, carried by dry CO_2, over heated $TaCl_5$ in a combustion tube.

An oxine compound of Ta, which appeared to be of constant composition, was prepared by fusing $TaCl_5$ (0.3 g) with oxine (6 g) and heating the mixture just to boiling point. The red liquid was cooled, and the resulting orange solid powdered and dissolved in the minimum quantity of warm ethanol. To this solution, after filtration, excess of ether was added and the mixture allowed to stand for about 30 min to let the precipitate flocculate. The latter was then filtered off and washed with ether, and dried over P_2O_5 in vacuo. The resulting yellow powder fluoresced greenish-yellow in u.v. light and was soluble in a mixture of chloroform and ethanol (9:1) giving a clear yellow solution. Analysis of the compound gave, on two independently prepared samples: C 58.8 H 4.7 N 7.7 Cl 18.9
58.8 4.7 8.0 20.2.

This compound could not be SZYMANSKI AND ARCHIBALD's complex which would have the composition C 50.0, H 3.2, N 6.4, and Cl 16.3. Recrystallisation of the orange powder, obtained by cooling the $TaCl_5$–oxine melt, from ethanol gave a red non-fluorescent compound of the composition C 60.8, H 4.7, N 7.7, Cl 9.45.

Comparison of fluorescence intensities

Stock solutions of the oxinates in chloroform–ethanol (1:1) were prepared by dissolving the correct weight of each complex in the solvent and diluting to volume. The strengths of the stock solutions were $\frac{M}{500}$ for Li, Na, Be, Zn, Al and Zr, $\frac{M}{1000}$ for Sn, $\frac{M}{4000}$ for Y, $\frac{M}{5000}$ for Ag and Mg and $\frac{M}{10^4}$ for Sc. Dilutions were made with

TABLE II

Oxinate of:	*Mol. wt.*	*% Fluorescence of solution* $\frac{M}{10^6}$	$\frac{M}{10^5}$
Al	459	18.6	128.2
Y	521	i.s.	51.5
Sc	622	,,	34.5
Zr	667	,,	34.5
Mg	312	,,	34.0
Sn^{+2}	406	,,	32.0
Be	297	,,	22.4
Zn	353.5	,,	10.6
Ag[a]	397[a]	,,	5.5
Li	151	,,	i.s.
Na	167	,,	,,

i.s. = insignificantly small *i.e.* where total fluorescence is <5%.
[a] $AgC_9H_6ON \cdot C_9H_7ON$.

the solvent as required. Measurements were made on the solutions using the fluorimeter attachment (SP 550) for the Unicam SP 500 Spectrophotometer (silica cells). Readings were taken using the red and blue photocells, first on the solvent and then on the oxinate solutions, and combining the differences to give total fluorescence. This was expressed as a percentage of the light emitted by the quinine sulphate standard (2.5 p.p.m. in 0.1*N* H_2SO_4) for which the instrument was set to read 100% fluorescence.

Chloroform–ethanol was used as the solvent because in pure chloroform the initial clear solution of Zn oxinate soon became turbid, and in which also the alkali metal compounds would not dissolve. The values of some relative fluorescence intensities (total) are given in Table II.

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SUMMARY

Experimental evidence suggests that the existence of only one stable cationic valency-state, in which the remaining electron shells are empty, half-full or complete are necessary conditions for the fluorescence of a metal–8-hydroxyquinoline complex in u.v. light. The preparations of hitherto unreported compounds of 8-hydroxyquinoline with Rb, Cs, Ge, Sn and Ta are described.

RÉSUMÉ

L'auteur a examiné les complexes métalliques de l'hydroxy-8-quinoléine et l'effet de la structure électronique du cation sur la fluorescence en lumière ultra-violette. La préparation de certains de ces composés est décrite.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass bei den Metall-Komplexen des 8-Oxychinolins die Elektronen-Konfiguration des Kations ausschlaggebend für das Auftreten von Fluoreszenz im U.V.-Licht ist. Die Darstellung einer Reihe von neuen Metallverbindungen des 8-Oxychinolins wird beschrieben.

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HALF-WAVE POTENTIALS OF METAL IONS IN ORGANIC HYDROXYACID SUPPORTING ELECTROLYTES. II

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INTRODUCTION

The first paper of this series[1] tabulated the polarographic characteristics of a number of metal ions in eight supporting electrolytes containing citrate, malonate, and tartrate ions. This paper presents similar data for ammoniacal solutions of the ammonium salts of these ions and for ammoniacal ammonium oxalate; to fill a gap in the literature, data are also included for a weakly acidic citrate medium. Data for a few metal ions in ammoniacal citrate, oxalate, and tartrate have been published by LINGANE[2] and MEITES[3], while isolated data in weakly acidic citrate media have been reported by HAMM, SHULL AND GRANT[4], HARRIS[5], HEYROVSKY[6] and KALOUSEK[6,7], LINGANE[2,8] and MEITES[8,9], NEUMAN, HAVILL AND FELDMAN[10], NORTON, STOENNER AND MEDALIA[11] and VANDENBOSCH[12], and a more complete study in such a medium has been described by DONO, MORINAGA AND NOMURA[13].

EXPERIMENTAL

The supporting electrolyte solutions were prepared by mixing the calculated amounts of reagent-grade ammonia and the appropriate acid. All pH values were measured with a Beckman Model G glass electrode pH meter, using saturated potassium hydrogen tartrate[14,15] as the reference standard.

The stock metal ion solutions were prepared from the best available salts. These were diluted so that the concentration of metal ion in the solution examined polarographically was always very nearly 1.0 mM, except in the case of thallous ion, whose concentration was always 0.2 mM. No maximum suppressor was used except as noted in the Tables.

All measurements were made at 25.00°, using the polarographic apparatus described in the second paragraph of the EXPERIMENTAL section of the preceding paper[1]. The solutions were deaerated with prepurified nitrogen; special care was taken to prevent the air-oxidation of such easily oxidizable species as those formed from iron(II), tin(II), and vanadium(IV). Drop times were generally between 2.5 and 4 sec.

Some of the data were secured with a silver - silver chloride - saturated potassium

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chloride reference electrode, but all half-wave potentials are referred to the saturated calomel electrode.

The symbols employed in the following Tables were defined in the preceding paper.

TABLE I

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIUM CITRATE, pH 6.1

Element and oxidation state	$E^{1/2}$, *V vs. S.C.E.*	*Oxidation state of product*	$E^{3/4}-E^{1/4}$, *mV*	*Notes**
Ag(I)	>0	0		Very i.-d., AgCl ppts.
As(III)	-1.45_6	—III	—152	I.-d., very large max.
As(V)	NR			
Bi(III)	-0.31_3	0	— 25	W.-d., very large max.
Cd(II)	—0.700	0	— 28	Very w.-d.
Co(II)	NR			
Cr(III)	—1.151	II(?)	—108	Abnormally small, not w.-d.
Cr(VI)	>0	III + VI		$i = 3/4 i_{total}$.
	—0.383	III	— 55	W.-d.
Cu(II)	—0.170	0	— 23	W.-d., small max. Reaction definitely does not produce Cu(I).[7]
Fe(II)	(—0.183)	III	+ 57	W.-d.
Fe(III)	—0.225	II	— 75	W.-d.
In(III)	NR			
Mn(II)	—1.615	0	— 52	I.-d.
Mo(VI)	—1.011		—130	Very w.-d. Wave height is close to expected value for $n = 3$.[9]
Ni(II)	NR			
Pb(II)	—0.542	0	— 27	W.-d., very small max.
Sb(III)	—0.771		— 54	Very w.-d., $i = 1/4\ i_{total}$.
	—1.120		—109	Very w.-d., $i = 3/7\ i_{total}$.
	—1.50	0		I.-d. Presumably 3 complexes in sluggish equilibrium.
Sb(V)	—1.564	0(?)	— 76	I.-d., wave height only about 2/3 of expected value for $n = 5$.
Sn(II)	(—0.406)	IV	+ 36	W.-d.
	—0.662	0	— 38	W.-d.
Sn(IV)	—1.0			Some indication of a very small wave.
Te(VI)	—1.237	—II	— 73	Very w.-d.
Tl(I)	—0.510	0	— 28	W.-d.
U(VI)	—0.415	IV + V	— 35	Max. at top of wave, min. at —0.9 V.
V(IV)	—0.44			Some indication of a very small wave.
	—1.485	II	—121	I.-d.
V(V)	>0	IV		W.-d., large max.
	-1.53_2	II	—190	I.-d.
W(VI)	-1.49_7	H_2(?)		Very i.-d., wave height corresponds to $n =$ *ca.* 5.
Yb(III)	NR			
Zn(II)	-1.37_3	0	—165	I.-d.

* i.-d. = ill-defined; w.-d. = well-defined.

TABLE II

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIA–0.1 *F* AMMONIUM CITRATE, pH 8.5

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}$—$E_{1/4}$, mV*	*Notes*
Ag(I)	>0	0		W.-d., large rounded max.
As(III)	—1.62$_9$	—III	— 57	Fairly w.-d., max.
As(V)	NR			
Bi(III)	—0.435	0	— 45	W.-d., rounded max. at 1.3 V.
Cd(II)	—0.706	0	— 42	Very w.-d.
Ce(IV)	>0	III		Very w.-d.
Co(II)	—1.38$_7$	0	— 82	Fairly w.-d.
	—1.7			Some indication of a small wave.
Cr(III)[a]	NR			
Cr(VI)	—0.235	III	— 75	Very w.-d. to *ca.* —0.9 V, then rises gradually.
	—1.8	0		Very i.-d.
Cu(II)	—0.165	I	— 58	Fairly i.-d.
	—0.340	0	— 58	Very w.-d.
Fe(II)	(—0.438)	III	+ 35	W.-d., max.
	—1.63	0		Very i.-d., height only about 1.5 times that of anodic wave.
Fe(III)	—0.457	II	— 58	Very w.-d., $i = 1/3\ i_{total}$.
	—0.935			W.-d., $i = 1/6\ i_{total}$.
	—1.61	0		I.-d., $i = 1/2\ i_{total}$.
In(III)	—1.34$_6$	?	—145	I.-d. and abnormally small.
Mn(II)	—1.62$_4$	0	— 71	I.-d.
Mo(VI)	—1.25$_7$	V	—122	Fairly w.-d., $i = 1/2\ i_{total}$.
	—1.70	IV		I.-d.
Ni(II)	—1.09$_3$		— 82	I.-d.
	—1.39$_5$	0	—106	Fairly w.-d. Probably two complexes in sluggish equilibrium.
Pb(II)	—0.522	0		W.-d., acute max.
Pb(II)[b]	—0.528	0	— 28	W.-d.
Sb(III)	—0.972	0	—114	Very w.-d.
	—1.79	—III		Very i.-d., max.
Sb(V)	NR			
Sn(II)	(—0.470)	IV	+ 13	W.-d. but oscillations are abnormally large near foot of wave.
	—0.752	0	— 57	Very w.-d. Curves change slightly with time; these data are for solutions aged to apparent equilibrium (*ca.* 30 min).
Sn(IV)	NR			
Te(VI)	—1.296	—II	— 73	Very w.-d.
Tl(I)	—0.447	0	— 58	W.-d.
U(VI)	—0.585	V	— 49	I.-d., max., wave height only about half expected value for $n = 1$.
	—1.065	IV	—132	Very w.-d., total wave height agrees with expected value for $n = 2$.
V(IV)	(—0.05)	V		Very i.-d.
	—1.48$_2$	II	—170	Fairly w.-d.

(Contd. on p. 400)

TABLE II (Continued)

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}—E_{1/4}$, mV*	*Notes*
V(V)	—0.268	IV	— 51	I.-d., large rounded min at *ca.* —0.75 V.
	—1.358	II	—101	W.-d.
W(VI)	—1.59	H_2(?)	— 53	I.-d., large max., wave height corresponds to *n* = *ca.* 12.
Yb(III)	NR			
Zn(II)[b]	—1.236	0	— 50	W.-d.

[a] Extensive precipitation from a 1 m*M* solution.

[b] With 0.002% Triton X-100.

TABLE III

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIA–0.1 *F* AMMONIUM MALONATE

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}—E_{1/4}$, mV*	*Notes*
Ag(I)	>0	0		Max. at ± 0.0 V is suppressed by 0.002% Triton X-100.
As(III)	—1.633	—III	— 82	I.-d., max. at —1.7 V is suppressed by 0.005% gelatin but not by 0.002% Triton X-100.
As(V)	NR			
Bi(III)[a]	NR			
Cd(II)	—0.676	0	— 28	W.-d.
Ce(IV)[a]	NR			Brownish-white ppt.
Co(II)	—1.217	0	— 49	W.-d.
Cr(III)[a]	NR			
Cr(VI)	—0.189[b]	III	— 68	Incompletely suppressed max. at —0.32 V is followed by long min. after which plateau assumes the normal shape.
	—1.701[c]	0	— 61	Max. at —1.71 V suppressed by gelatin.
Cu(II)[d]	—0.096	I	— 46	I.-d.
	—0.307	0	— 60	W.-d., max. at —0.54 V is suppressed by Triton.
Fe(II)	(—0.282)	III	+ 51	W.-d.
	—1.434	0	— 32	W.-d.
Fe(III)[a]	NR			
In(III)[a]	NR			
Mn(II)	—1.535	0	— 35	W.-d.
Mo(VI)[c]	—1.667	?	— 52	W.-d., max. at —1.80 V suppressed neither by gelatin nor by 0.002% Triton X-100. Wave height corresponds to *n* = *ca.* 3 without gelatin, *ca.* 8 with gelatin.
Ni(II)[b]	—0.983	0	— 75	W.-d., max. at —1.20 V is suppressed by Triton.
Pb(II)	—0.457	0	— 30	W.-d., some pptn. from a 1 m*M* solution.
Sb(III)	—0.670	0	—111	W.-d., small max. at —0.68 V is not suppressed by 0.002% Triton X-100.

(Contd. on p. 401)

TABLE III (Continued)

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}$—$E_{1/4}$, mV*	*Notes*
Sb(V)	NR			
Sn(IV)	NR			
Te(VI)[c]	—1.291	—II	—107	W.-d., max. at —1.34 V is suppressed by gelatin.
Tl(I)	—0.464	0	— 52	W.-d.
U(VI)	—0.509	V(?)	— 66	W.-d., some pptn. from a 1 m*M* solution.
V(IV)	(—0.249)	V	+ 36	I.-d.
	(—0.460)			Small anodic prewave.
	—1.324	II	— 82	I.-d.
V(V)	—0.39			Small cathodic prewave.
	—1.02$_7$	IV	—116	I.-d.
	—1.28$_6$	II	— 98	I.-d.
W(VI)[c]	—1.59$_0$	H_2(?)	— 83	I.-d., max. at —1.69 V not suppressed by gelatin. Wave height corresponds to n = *ca.* 15 without gelatin, *ca.* 10 with gelatin.
Yb(III)	—1.71$_9$	II	— 89	I.-d.
Zn(II)	—1.138	0	— 48	W.-d.

[a] Extensive precipitation from a 1 m*M* solution.
[b] With 0.002% Triton X-100.
[c] With 0.005% gelatin.
[d] With 0.005% Triton X-100.

TABLE IV

HALF-WAVE POTENTIALS IN 0.1 *F* AMMONIA–0.1 *F* AMMONIUM OXALATE

Element and oxidation state	*$E_{1/2}$, V vs. S.C.E.*	*Oxidation state of product*	*$E_{3/4}$—$E_{1/4}$, mV*	*Notes*
Ag(I)	>0	0		Very w.-d., large max. at —0.04 V is suppressed by 0.004% Triton X-100.
As(III)	—1.7	—III		Max., plateau has fairly large positive slope.
As(V)	NR			
Bi(III)[a]	—0.36			
Cd(II)	—0.705	0	— 57	Very w.-d.
Ce(IV)[a]	NR			Yellow precipitate.
Co(II)	—1.314	0	— 81	Very w.-d.
Cr(III)	—1.64	0		Small i.-d. irreversible wave, partial pptn.
Cr(VI)	—0.237	III	— 55	Very w.-d., small max.
	—1.7	0		Sharp max. followed by sharp min., then by plateau having positive slope.
Cr(VI)[b]	—0.284			Fairly i.-d.
	—1.15	III	—180	$i_2 = 2i_1$; total height same as that of first wave without Triton.
	—1.68	0		I.-d., max. and min, suppressed by Triton.
Cu(II)	—0.176	I	— 50	W.-d.
	—0.379	0	— 62	Very w.-d., small rounded max. at —0.7 V.
Cu(II)[b]	—0.172	I	— 50	W.-d.
	—0.407	0	— 95	Max. suppressed by Triton.

(Contd. on p. 402)

TABLE IV (Continued)

Element and oxidation state	$E_{1/2}$, *V vs. S.C.E.*	*Oxidation state of product*	$E_{3/4}-E_{1/4}$, *mV*	*Notes*
Fe(II)	(—0.287)	III	+ 57	W.-d.
	—1.518	0	— 50	W.-d., small rounded max. at —1.6 V.
Fe(II)[b]	(—0.286)	III	+ 59	W.-d.
	—1.560	0	— 68	W.-d., max. suppressed by Triton.
Fe(III)[a]	NR			
In(III)	—0.906	?	—117	Abnormally small wave, no pptn.
Mn(II)	—1.599	0	— 37	Fairly w.-d.
Mo(VI)	—1.66$_3$	?	— 53	Very i.-d.
Ni(II)	—1.073	0	— 97	Fairly w.-d.
Pb(II)	—0.532	0	— 25	Very w.-d.
Sb(III)	(—0.2)	V		Some indication of a very i.-d. anodic wave.
	—0.792		— 29	Presumably two complexes in sluggish equilibrium;
	—0.899	0	— 34	$i_3 = 1/4\ i_2$.
	—1.7	—III		Very i.-d., max.
Sb(III)[b]	(—0.2)	V		Some indication of a very i.-d. anodic wave.
	—0.800		— 30	Very w.-d.
	—0.926	0	— 61	Very w.-d., $i_3 = 1/2\ i_2$.
	—1.8	—III		Max. suppressed by Triton.
Sb(V)	NR			
Sb(II)	—1.12		— 47	Small prewave.
	—1.465	0	— 65	Fairly w.-d., small max.
Sn(II)[b]	—1.4			Prewave, height decreased 50% and max. suppressed by Triton.
	—1.540	0	—170	Very i.-d.
Sn(IV)	—1.510	0(?)	— 51	I.-d., $i = 1/4\ i_{total}$.
	—1.74$_8$		— 76	I.-d., total wave height is 3 times expected value for $n = 4$.
Te(IV)	—0.704	0	— 58	Very w.-d. to huge max. at —1.2 V, i.-d. thereafter.
Te(IV)[b]	—0.755	0	— 62	W.-d., max. reduced by Triton.
Te(VI)	—1.337	—II	— 71	Very w.-d., max. on rising portion of wave.
Te(VI)[b]	—1.408	—II	— 91	Very w.-d., max. suppressed by Triton.
Ti(III)[a]	NR			
Tl(I)	—0.473	0	— 59	Very w.-d.
U(VI)	—0.498	V	— 63	Very w.-d. to —1.0 V, oscillations irregular thereafter.
V(IV)	(—0.272)	V	+ 89	
	—0.99			Small cathodic prewave.
	—1.318	II	— 74	Very w.-d.
V(IV)[b]	(—0.214)	V	+ 69	
	—1.09			Small cathodic prewave.
	—1.403	II	— 86	Very w.-d.
W(VI)	—1.62$_6$	H_2(?)	— 54	Fairly i.-d., large max.
Yb(III)	NR			
Zn(II)	—1.229	0	— 25	Very w.-d., max.
Zn(II)[b]	—1.243	0	— 45	Very w.-d., max. suppressed by Triton.

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[a] Extensive precipitation from a 1 m*M* solution. [b] With 0.004% Triton X-100.

TABLE V

HALF-WAVE POTENTIALS IN 0.1 F AMMONIA–0.1 F AMMONIUM TARTRATE

Element and oxidation state	$E_{1/2}$, *V vs. S.C.E.*	$i_d/C\ m^{2/3}t^{1/6}$, *μA/mmole/l/mg$^{2/3}$sec$^{-1/2}$*	*Oxidation state of product*	$E_{3/4}—E_{1/4}$, *mV*	*Notes*
Ag(I)	>0				Max. at 0.0 V.
As(III)	—1.570	22.8	—III	— 71	Very i.-d., max. at —1.73 V nearly eliminated by 0.002% Triton X-100.
As(V)	NR				
Bi(III)	—0.543	4.23	0	— 66	Very w.-d.
Cd(II)	—0.727	3.40	0	— 36	Very w.-d.
Ce(IV)	—0.172	1.18	III	—172	Suggests two poorly separated waves.
	—1.015	1.74		—300	Possibly anomalous.
Co(II)[a]	—1.225	1.88	0	— 43	W.-d., small max. eliminated by Triton.
Cr(III)[b]	NR				
Cr(VI)	—0.244	6.23	III	— 43	Max. at —0.35 V, w.-d. to —1.3 V, i.-d. thereafter. Polarogram deformed by 0.005% Triton X-100.
Cu(II)[a]	—0.147	1.9	I	— 61	Fairly i.-d.
	—0.382	4.1	0	— 77	Max. at —0.57 V. eliminated by Triton, very w.-d.
Fe(II)	(—0.469)	—1.11	III	+118	Max. at —0.3 V, very w.-d., min. at 0.0 V.
	—1.418	+0.93	0	— 37	Very w.-d.
Fe(III)	—0.829	1.25	II	—144	I.-d.
	—1.416	3.94	0	— 28	Very w.-d.
In(III)	—1.156	1.28	?	—150	W.-d.
Mn(II)	—1.528	2.10	0	— 35	Very w.-d.
Mo(VI)	NR				
Ni(II)[a]	—0.960	3.16	0	— 52	Very w.-d., max. suppressed by Triton.
Os(VIII)	—0.259	1.5	VI	— 34	W.-d.
	—1.509	68	H_2	— 94	I.-d.
Pb(II)[a]	—0.541	2.67	0	— 26	Very w.-d., max. suppressed by Triton.
Ru(IV)	—1.577	17	H_2	— 74	
Sb(III)[a]	—0.952	3.74	0	—107	I.-d.
Sb(V)[c]	—1.715		?	— 64	I.-d.
Sn(II)[a]	(—0.534)	—2.54	IV	+ 42	Very w.-d.
	—0.769	+3.02	0	— 22	Very w.-d., max. suppressed by Triton.
Sn(IV)	NR				
Te(IV)	—0.705	6.39	0	— 74	W.-d. to huge max. at —1.26 V, i.-d. thereafter.
Te(VI)[a]	—1.513	10.1	—II	—123	I.-d., max. nearly suppressed by Triton.
Tl(I)	—0.468	2.21	0	— 57	Very w.-d.
U(VI)	—0.661	1.52	V	— 38	W.-d.
	—1.08	2.54	IV	—180	I.-d.
V(IV)	(—0.212)	—0.95	V	+ 68	Very i.-d.
	—1.576	1.17	III	— 92	Very i.-d.
V(V)	—0.26				Prewave with broad min. at —0.65 V.
	—0.979	1.58	IV	—190	Fairly w.-d.
	—1.58	3.2	III	—160	Very i.-d.

References p. 404

(Contd. on p. 404)

TABLE V (Continued)

Element and oxidation state	*$E^{1/2}$, V vs. S.C.E.*	*$i_d/C m^{2/3} t^{1/6}$, μA/mmole/l/mg$^{2/3}$sec$^{-1/2}$*	*Oxidation state of product*	*$E^{3/4}$—$E^{1/4}$, mV*	*Notes*
W(VI)	—1.627	20.3	H_2	— 33	I.-d.
Yb(III)	NR				
Zn(II)[a]	—1.204	3.32	0	— 40	W.-d., max. suppressed by Triton.

[a] With 0.001% Triton X-100.
[b] Apparently quantitative precipitation from a 1 m*M* solution.
[c] Partial precipitation from a 1 m*M* solution.

SUMMARY

Information is presented on the half-wave potentials, reversibilities, wave shapes, and probable electrode reaction products for the polarographic waves of most of the common heavy metal ions in 0.1 *F* ammonium citrate at pH 6 and in 0.1 *F* ammonium citrate, malonate, oxalate, and tartrate containing 0.1 *F* ammonia.

RÉSUMÉ

Les auteurs ont étudié le comportement polarographique de la plupart des ions métalliques courants en présence de différentes solutions de base.

ZUSAMMENFASSUNG

Es wird das polarographische Verhalten der am meisten vorkommenden Schwermetall-Ionen in ammoniakhaltigen Lösungen von Ammonium-citrat, -malonat, -oxalat und -tartrat beschrieben.

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CONTENTS