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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 27, No. 5, November 1962

STUDIES ON THE EXTRACTION OF CHROMIUM(VI) BY KETONES

A study of the extraction of chromium(VI) from aqueous media by ketones was made. Extraction of chromium was found to be most efficient from aqueous hydrochloric acid solutions. A mechanism for the extraction of chromium(VI) from aqueous hydrochloric acid solutions by methyl isobutyl ketone is proposed involving the formation of a receptor in the organic phase, the exchange of the chloride ion of the receptor for the anionic chromium(VI) species of the aqueous phase, and the solvation of the extracted chromium species. The differences in the abilities of various ketones to extract chromium(VI) from aqueous hydrochloric acid solutions, and the differences in the extraction of chromium(VI) from various aqueous acids by methyl isobutyl ketone are attributed to the differences in the formation of receptors.

S. A. KATZ, W. M. MCNABB AND J. F. HAZEL, *Anal. Chim. Acta*, 27 (1962) 405–415

THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

PART III. NATURE AND PROPERTIES OF THE MERCURY COMPLEXES

The reactions of diphenylcarbazone or diphenylcarbazide with mercury(I) or mercury(II) are studied by qualitative analysis, extraction JOB's method. Only carbazone complexes are formed. Mercury(I) and (II) both form two complexes, a 1 : 1 and a 1 : 2 complex (cation : carbazone). The complexes formed are colloids in aqueous alcoholic solutions. Decomposition of these complexes, to form diphenylcarbodiazone, is accelerated by ultraviolet and visible light.

S. BALT AND E. VAN DALEN, *Anal. Chim. Acta*, 27 (1962) 416–421

THE SEPARATION OF COPPER, LEAD, CADMIUM AND ZINC FROM HIGH PURITY URANIUM METAL BY ION EXCHANGE ON CELLULOSE PHOSPHATE AND THEIR DETERMINATION BY SQUARE WAVE POLAROGRAPHY

A method has been developed for the determination of copper, lead, cadmium and zinc in high purity uranium metal. Conditions are described for the separation of these elements from uranium(VI) and iron(III) by ion-exchange on cellulose phosphate and for their determination by square wave polarography using orthophosphoric acid as base electrolyte.

The procedure has been shown to be applicable to metal containing less than 5 p.p.m. of each impurity and results are compared with those obtained by other methods.

G. C. GOODE AND M. C. CAMPBELL, *Anal. Chim. Acta*, 27 (1962) 422–428

THE POLAROGRAPHIC DETERMINATION OF THALLIUM

A polarographic method is described for the determination of thallium in sodium triphosphate supporting electrolyte. The incorporation of 0.1% camphor in the electrolyte displaces the cathodic steps of many interfering ions, *e.g.*, lead(II), copper(II), iron(III) and bismuth(III) to a more negative potential (≈ -1.0 V), well away from the thallium step which remains unaffected.

P. S. Shetty, P. R. Subbaraman and J. Gupta, *Anal. Chim. Acta*, 27 (1962) 429–433

A COLORIMETRIC METHOD FOR THE DETERMINATION OF CARBONYL GROUPS IN CELLULOSE

A method is suggested for the determination of carbonyl groups in cellulose based on the reaction with hydrazine. After washing with water, the cellulose hydrazone is dissolved in sulfuric acid and hydrolyzed. The liberated hydrazine is determined colorimetrically with *p*-dimethylaminobenzaldehyde. Possible interferences from carboxyl groups are discussed.

U. Albertsson and O. Samuelson, *Anal. Chim. Acta*, 27 (1962) 434–440

DETERMINATION OF NITRATE IN SEA WATER

Nitrate in sea water is determined by reduction to nitrite with zinc metal in ammoniacal solution in the presence of manganese(IV) as catalyst. The effects of hydrogen ion concentration, reduction temperature, reaction time and the order of reagent addition are discussed. The nascent nitrite diazotizes with sulfanilamide and is then coupled by N-1-naphthylethylenediamine in acid medium forming a diazo-dye which is measured spectrophotometrically.

T. J. Chow and M. S. Johnstone, *Anal. Chim. Acta*, 27 (1962) 441–446

DETERMINATION OF SMALL AMOUNTS OF URANIUM IN HAFNIUM, ZIRCONIUM AND ZIRCALOY-2

To meet specification requirements, selected methods for determining uranium have been examined and two satisfactory procedures have been developed for application to the analysis of reactor-grades of hafnium, zirconium and Zircaloy-2.

These procedures are based on extraction of uranyl ions from a solution of the sample with a tri-*n*-butyl phosphate–iso-octane mixture. Following this extraction, uranium over the range 10–150 p.p.m. is determined by a spectrophotometric method, using dibenzoylmethane. For smaller amounts of uranium, down to about 0.5 p.p.m., the determination is completed by square-wave polarography.

D. F. Wood and R. H. McKenna, *Anal. Chim. Acta*, 27 (1962) 446–453

STUDIES ON COORDINATION POLYMERS

PART I. COORDINATION POLYMERS OF 8,8′-DIHYDROXY-5,5′-BIQUINOLYL

Coordination polymers of 8,8′-dihydroxy-5,5′-biquinolyl(I) with Cu(II), Zn(II), Cd(II), Ni(II), Co(II) and Mn(II) were prepared and studied. The polymers were all powders, very insoluble in all the common organic solvents, apparently of low molecular weight and all began to decompose between 250–300°. The polymers of cobalt and nickel were amorphous, whereas the polymers of copper, zinc, cadmium and manganese were crystalline. Infrared studies confirmed the chelation reaction between metal and (I). As a spot test reagent, (I) gave instant color reactions with 14 common ions but the sensitivity of the reagent is not particularly impressive. The most interesting result is the detection of 2 μg of gallium.

E. W. BERG AND A. ALAM, *Anal. Chim. Acta*, 27 (1962) 454–459

SPECTROPHOTOMETRIC OR ABSORPTIOMETRIC DETERMINATION OF COPPER WITH 2,2′-DIAMINODIETHYLETHER-N,N,N′,N′-TETRAACETIC ACID

A spectrophotometric determination of copper with 2,2′-diaminodiethylether-N,N,N′,N′-tetraacetic acid is proposed. Maximum absorbance is obtained at 720 mμ at pH 2 (1–3) and 25–650 μg Cu/ml can be determined. The reaction is unaffected by temperature or time of standing, and very few ions interfere. A 1 : 1 copper–EEDTA complex is formed.

F. BERMEJO-MARTÍNEZ AND A. G. BLAS-PÉREZ, *Anal. Chim. Acta*, 27 (1962) 459–464

OBSERVATIONS IN ATOMIC ABSORPTION SPECTROSCOPY

Four features of atomic absorption have been studied. Results show that spectral slit width markedly affects sensitivity; an electrical discharge can be used for sample atomization; a flame adapter can be used to increase the sensitivity of noble metals, and the double-wavelength system is satisfactory under some conditions.

J. W. ROBINSON, *Anal. Chim. Acta*, 27 (1962) 465-469

DETERMINATION OF RHENIUM AND TECHNETIUM BY INFRARED SPECTROSCOPY

The determination of μg amounts of rhenium, as perrhenate, and technetium, as pertechnetate, by infrared spectroscopy is described. The species are precipitated with tetraphenylarsonium chloride in presence of potassium perchlorate as carrier; the precipitate is filtered, dried, and pressed with potassium bromide into a disc for examination. The tetraphenylarsonium complexes of perrhenate and pertechnetate show strong sharp bands at 10.94 and 11.09 μ respectively.

R. J. MAGEE AND M. AL-KAYSSI, *Anal. Chim. Acta*, 27 (1962) 469–473

DIFFERENTIAL THERMAL ANALYSIS OF DIVALENT METAL 8-HYDROXYQUINOLINE CHELATES

DTA curves were obtained for a number of anhydrous metal chelates derived from the important analytical reagent 8-hydroxyquinoline. The compounds were heated in an inert atmosphere to avoid interaction with oxygen or water vapor. The Cu, Pb, Zn, Ni and Co chelates melted without decomposition, under the conditions used, while the remainder of the compounds underwent partial decomposition upon melting. The order of increasing melting point is $Pb < Cu < Zn < Ni < Co < Ba < Mn < Cd < Sr < Mg < Ca$. The order of decreasing heat stability is $Ca > Mg > Sr > Cd > Mn > Ba > Co > Ni > Zn > Pb > Cu$.

R. G. Charles, *Anal. Chim. Acta*, 27 (1962) 474–479

THE DISTRIBUTION COEFFICIENT OF CUPFERRON

A spectrophotometric method for the determination of the distribution coefficient of cupferron, based on a colour reaction of cupferron with sodium pentacyanoammine ferrate(II), is described. A value of 142 was obtained above pH 3 for chloroform and aqueous solutions of perchloric and hydrochloric acid. At higher acidities lower values (120–135) were obtained. Some possible causes for this are briefly discussed.

D. M. Kemp, *Anal. Chim. Acta*, 27 (1962) 480–489

TITRIMETRIC DETERMINATION OF THIOCYANATES WITH SULFATOCERIC ACID

The direct oxidative titration of thiocyanate has been investigated in order to correlate the divergent views previously expressed. Sulfatoceric acid was used as the oxidant with iodine monochloride as a preoxidant and indicator. The low results at high acidities observed by previous investigators are attributed to loss of hydrogen sulfide and sulfur dioxide, which can be detected by infrared spectra. Cobalt(II), zinc(II), and mercury(II) were also determined by titrating the precipitated complex thiocyanates. Accurate and reproducible results were obtained in hydrochloric acid concentrations ranging from 1.7–4.5 *N*.

S. Singh and J. R. Siefker, *Anal. Chim. Acta*, 27 (1962) 489–492

ANALYTICAL STUDIES OF THE REACTION OF THALLIUM(III) WITH HYDRAZINE SULPHATE

(in German)

The reaction of thallium(III) with hydrazine sulphate has been studied. In solutions slightly acidified with sulphuric acid the reaction is rapid and quantitative; direct potentiometric titration of thallium(III) with hydrazine sulphate solutions is possible, as well as the reverse titration. The electrode system Pt–C is recommended.

Hydrazine sulphate may also be determined indirectly by oxidation with excess of thallium(III) which is then titrated compleximetrically.

A. Berka and A. I. Busev, *Anal. Chim. Acta*, 27 (1962) 493–497

ANALYTICAL APPLICATIONS OF THE REACTION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID

PART V. DETERMINATION OF SILVER

Silver is determined titrimetrically after precipitation from neutral or dilute nitric acid solution as silver hexacyanoferrate(III). The filtered precipitate is converted to silver hexacyanoferrate(II) and the hexacyanoferrate(III) ions released are eventually titrated with ascorbic acid.

L. Erdey, L. Koltai and G. Svehla, *Anal. Chim. Acta*, 27 (1962) 498–500

STUDIES ON THE EXTRACTION OF CHROMIUM(VI) BY KETONES

SIDNEY A. KATZ, WALLACE M. McNABB AND J. FRED HAZEL

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(Received April 4th, 1962)

Several investigators[1-3] have used methyl isobutyl ketone to extract chromium(VI) from aqueous hydrochloric acid solutions as a separation technique before the determination of chromium. However, no data have been reported concerning the process by which this extraction takes place. It is the object of these studies to investigate the mechanism of the extraction of chromium(VI) by ketones.

EXPERIMENTAL

Apparatus

Beckman Models DU and DB spectrophotometers were used for visible and ultraviolet spectra studies. Matched 1-cm absorption cells were used in both instruments.

Infrared spectra were obtained with a Perkin-Elmer Infracord.

Conductance measurements were made using a Serfass Conductance Bridge and a dip-type electrode.

Potentiometric titrations were carried out with the aid of a Leeds and Northrup pH Meter. Calomel and glass electrodes were used for acid–base titrations, and calomel and silver electrodes were used in the determination of chloride.

Extractions were performed in 60-ml conical separatory funnels.

Reagents

The organic solvents used as extractants were obtained from commercial sources and purified by distillation before use.

All inorganic compounds were reagent grade, and they were used without further purification.

Preliminary studies

Preliminary studies were carried out in which aqueous solutions, 0.001 M in potassium dichromate and 0.1 M in a second electrolyte, were shaken with an equal volume of organic solvent. The extraction of chromium(VI) was evaluated qualitatively by noting the transfer of the orange color to the organic phase. The results of this study are presented in Table I.

From the data presented in Table I, it is seen that chromium(VI) was extracted from aqueous hydrochloric acid solutions into alcohols, ethers, esters, and ketones. Although alcohols and ethers were able to extract chromium(VI), they rapidly

TABLE I

EXTRACTION OF CHROMIUM(VI) FROM AQUEOUS SOLUTIONS INTO ORGANIC SOLVENTS

Organic phase	*0.1 M* *HCl*	*0.1 M* H_2SO_4	*Aqueous phase* *water*	*0.1 M* *NaOH*	*0.1 M* Na_2CO_3
Benzene	no ext'n	no ext'n	no ext'n	no ext'n	no ext'n
n-Heptane	no ext'n	no ext'n	no ext'n	no ext'n	no ext'n
Carbon tetrachloride	no ext'n	no ext'n	no ext'n	no ext'n	no ext'n
Chloroform	no ext'n	no ext'n	no ext'n	no ext'n	no ext'n
Ether	ext'n red'n	red'n	no ext'n	no ext'n	no ext'n
Isoamyl alcohol	ext'n red'n	red'n	no ext'n	no ext'n	no ext'n
Ethyl acetate	ext'n	no ext'n	no ext'n	no ext'n	no ext'n
Methyl isobutyl ketone	ext'n	no ext'n	no ext'n	no ext'n	no ext'n

reduced it as shown by the appearance of the green chromic ion. Ketones and esters, on the other hand, appeared to extract chromium(VI) without reducing it.

Extraction studies

In order to study quantitatively the extraction of chromium(VI), a suitable method for its determination was needed. The classical method of adding a measured excess of standard ferrous ammonium sulfate and back-titrating to the diphenylamine sulfonate end-point with standard dichromate was chosen because it was found to be more rapid than polarographic or colorimetric methods.

Preliminary studies showed that solutions of hydrochloric acid more concentrated than 3 *M* gave low results. The low results were attributed to the reduction of small amounts of chromium(VI). For this reason, the extraction of chromium(VI) was studied in the 0–3 *M* hydrochloric acid concentration range.

A series of quantitative extraction studies was carried out by treating a fixed amount of chromium(VI) (1 mequiv.) with a measured amount of standard hydrochloric acid and diluting to a convenient volume. These aqueous solutions were extracted with equal volumes of ketone, and after separation of the phases, each phase was analyzed for chromium(VI). The results of this study are presented in

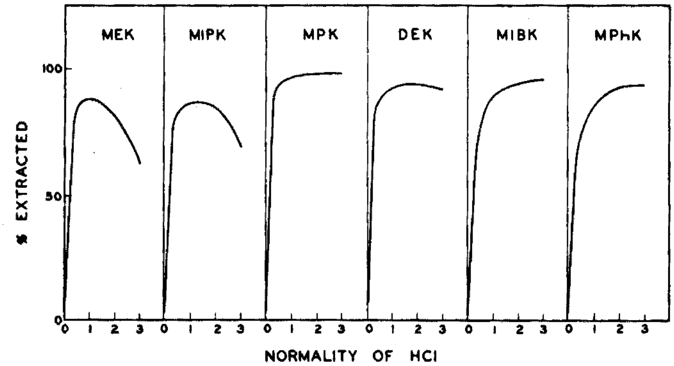


Fig. 1. Extraction of chromium(VI), from aqueous hydrochloric acid solutions with various ketones. MEK = methyl ethyl ketone, MIPK = methyl isopropyl ketone, MPK = methyl *n*-propyl ketone, DEK = diethyl ketone, MIBK = methyl isobutyl ketone, MPhK = methyl phenyl ketone.

Fig. 1. From these data, it is seen that the ketones differ in their ability to extract chromium(VI). The amount of chromium extracted from a given hydrochloric acid solution differs for each ketone.

The distribution coefficients for the extraction of chromium(VI) into each ketone from hydrochloric acid solutions of concentrations found to give the maximum extraction, were determined over the 0.005–0.250 *M* potassium dichromate concentration range. Measured volumes of a standard potassium dichromate solution were treated with measured volumes of standard hydrochloric acid and diluted to the desired volume with water in order to control the hydrochloric acid concentration. The aqueous solutions were extracted with equal volumes of the desired ketone, and aliquots of each phase were analyzed for chromium(VI). The results of this study are presented in Table II in which the distribution coefficient, K_D, is the ratio of the number of mequiv. of chromium(VI) per 10 ml aliquot of ketone phase to the number of mequiv. of chromium(VI) per 10 ml aliquot of aqueous phase. The distribution coefficients indicate that each ketone differs in its ability to extract chromium(VI).

TABLE II

DISTRIBUTION COEFFICIENTS FOR CHROMIUM(VI) PARTITIONING BETWEEN AQUEOUS HYDROCHLORIC ACID AND KETONES

Methyl ethyl ketone– 1.2 *M* HCl	Methyl isopropyl ketone– 1.5 *M* HCl	Methyl *n*-propyl ketone– 3.0 *M* HCl
253/16 = 15.8	290/0 = —	301/7 = 43.0
492/43 = 14.9	534/0 = —	591/11 = 53.6
755/59 = 12.8	812/0 = —	889/14 = 63.5
1016/90 = 11.3	1097/0 = —	1188/17 = 70.0
1291/121 = 10.7	1370/0 = —	1460/20 = 73.0
13.1	—	60.6
Diethyl ketone– 1.5 *M* HCl	**Methyl isobutyl ketone– 3.0 *M* HCl**	**Methyl phenyl ketone– 2.4 *M* HCl**
279/5 = 55.8	290/14 = 30.7	290/4 = 72.5
482/10 = 48.2	583/16 = 36.4	565/14 = 40.4
768/16 = 48.0	887/23 = 38.6	856/21 = 40.8
1059/23 = 46.1	1184/36 = 32.9	1180/29 = 40.7
1336/27 = 49.5	1456/51 = 28.5	1434/33 = 43.6
49.5	33.2	47.6

TABLE III

EFFECT OF VARIOUS CHROMATES ON THE EXTRACTION OF CHROMIUM(VI) FROM 3.00 *M* HCl BY METHYL ISOBUTYL KETONE

	$Na_2Cr_2O_7$	$K_2Cr_2O_7$	CrO_3
	421/12 = 35.1	286/8 = 35.7	388/11 = 35.3
	834/24 = 34.8	559/17 = 32.9	580/17 = 34.1
	1259/38 = 33.2	839/25 = 33.6	760/22 = 34.6
	1657/56 = 29.6	1125/33 = 34.1	1142/41 = 33.8
		1412/42 = 33.6	1510/53 = 34.5
mean	33.4	34.0	34.5

The process by which chromium(VI) is extracted from aqueous solutions of hydrochloric acid was studied in detail using only one of the previously mentioned ketones, methyl isobutyl ketone.

Effect of dichromate salts

A series of studies was made in which chromium(VI) from potassium dichromate, sodium dichromate, and chromic anhydride was extracted from 3.00 *M* hydrochloric acid into methyl isobutyl ketone. Distribution coefficients were determined for each system by analyzing aliquots of each phase. The results of this study are presented in Table III. The data indicate that K_D is independent of the source of chromium(VI). This suggests that only the anionic chromium(VI) is involved in the extraction.

Nature of extracted chromium

Attempts were made to isolate the chromium-containing species from the organic phase. A purple–black residue was obtained by stripping the extracted chromium from the ketone with water and evaporating the washings to dryness. This residue was dissolved in water, and the visible and ultraviolet spectra of the resulting solution were found to be identical to those of aqueous potassium dichromate and chromic anhydride. The infrared spectrum of this residue in a potassium bromide disc was recorded and compared to the spectra of potassium dichromate and chromic anhydride. An absorption band at 950 cm^{-1} was common to all spectra, and in the case of the residue, no bands characteristic of methyl isobutyl ketone were found.

Four different samples of the chromium-containing residue were analyzed in duplicate for both total and hexavalent chromium. The results of the analyses are presented in Table IV. Since the analyses showed no constant relationship, it was concluded that the residue did not represent a chemical compound but it probably was a mixture of trivalent and hexavalent chromium compounds. It is suggested that the chromium species stripped from the ketone was partially reduced during the evaporation process.

TABLE IV

ANALYSIS OF CHROMIUM-CONTAINING RESIDUE

Sample	*1*	*2*	*3*	*4*
Total Cr	41.4, 40.5	48.4, 48.5	35.6, 34.8	46.9, 47.0
Cr(VI)	25.7, 26.0	38.4, 40.0	13.9, 14.2	15.6, 15.8

TABLE V

ANALYSIS OF EXTRACT

Cr(VI) found (mmoles)	*H^+ 1st break (mequiv.)*	*H^+ 2nd break (mequiv.)*	*Cl^- (mequiv.)*
0.0000	0.522	—	0.516
0.037	0.882	0.974	0.776
0.095	0.776	0.926	0.508
0.152	1.158	1.360	0.760
0.203	1.140	1.404	0.520
0.251	1.239	1.559	0.500

In order to characterize the chromium-containing species stripped from the organic phase, a series of 3.00 *M* hydrochloric acid solutions containing varying amounts of chromium(VI) were extracted with equal volumes of methyl isobutyl ketone. The chromium was stripped from the ketone with water, and the washings were diluted to a convenient volume. Aliquots of the washings were analyzed for chromium(VI), chloride ion, and hydrogen ion, the latter two determinations being performed by potentiometric titrations. The results of this study are presented in Table V.

In Table V, it is seen that the hydrogen ion determinations indicated the presence of both strong and weak acids. No relationship was found to exist between the amount of chromium(VI) and strong acid stripped from the ketone. In the case of the weak acid function, it was found that there was one proton for every atom of chromium(VI). This indicates that the weak acid is $HCrO_4^-$. No relationship was found between the amounts of chloride ion and chromium(VI) stripped from the ketone. From these data, it is concluded that both hydrochloric acid and a chromic acid are the substances stripped from the organic phase.

Effect of variables

The process by which chromium(VI) is extracted from the aqueous phase into methyl isobutyl ketone was investigated in relation to the presence of chloride ion, hydrogen ion, and methyl isobutyl ketone.

The effect of chloride ion was studied by extracting 3.00 *N* sulfuric acid solutions

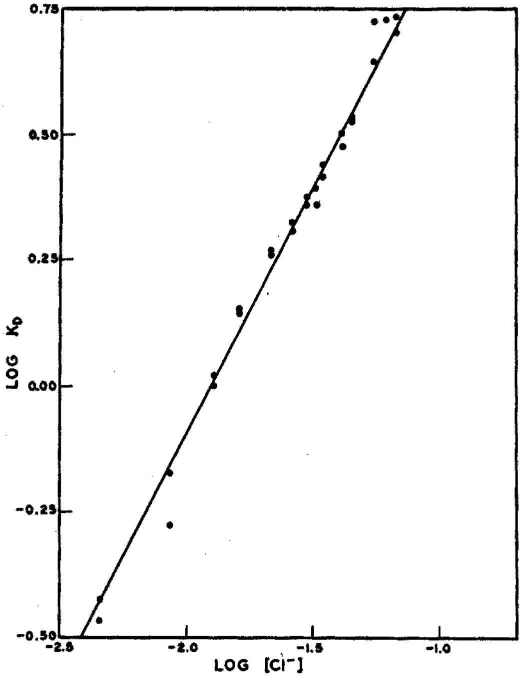


Fig. 2. Effect of chloride ion on the extraction of chromium(VI) from 3 *N* sulfuric acid with methyl isobutyl ketone.

containing a fixed amount of chromium(VI) and varying amounts of potassium chloride with equal volumes of methyl isobutyl ketone and analyzing aliquots of each phase for chromium(VI). In Fig. 2, a plot of log K_D against log [Cl$^-$] gave a straight line with a slope of 0.974 indicating that the extraction is dependent upon the first power of the chloride ion concentration.

The effect of chloride ion was further investigated by extracting 0.30 M solutions of hydrochloric acid containing a fixed amount of chromium(VI) and varying amounts of potassium chloride with equal volumes of methyl isobutyl ketone, and analyzing aliquots of each phase for chromium(VI). The results of this study are listed in Table VI. The data show that increasing chloride ion concentration has little effect

TABLE VI

EFFECT OF CHLORIDE ION ON THE EXTRACTION OF CHROMIUM(VI) FROM 0.30 M HCl BY METHYL ISOBUTYL KETONE

M KCl	K_D
0.0056	1.48
0.0111	1.45
0.0222	1.40
0.0333	1.48
0.0444	1.48
0.0555	1.51

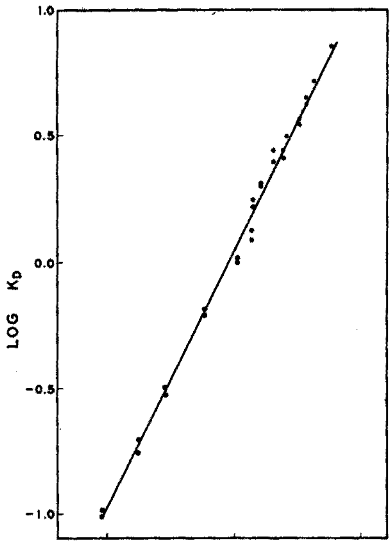


Fig. 3. Effect of hydrogen ion on the extraction of chromium(VI) from 3 M potassium chloride with methyl isobutyl ketone.

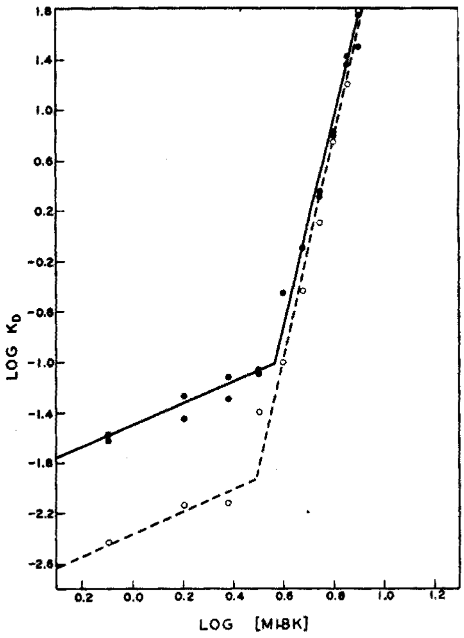


Fig. 4. Effect of methyl isobutyl ketone on the extraction of chromium(VI) from 3 M hydrochloric acid. ● benzene diluent. ○ carbon tetrachloride diluent.

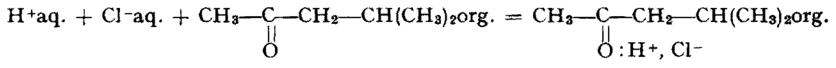
on K_D. A plot of log K_D against log $[Cl^-]$ gave a slope of 0.010 indicating that the extraction is independent of chloride ion. This apparent discrepancy is resolved by assuming that the extraction is dependent upon the first power of the hydrochloric acid concentration. In the presence of excess sulfuric acid, there are sufficient protons to form hydrochloric acid from the added potassium chloride. However, in 0.30 *M* hydrochloric acid, the added potassium chloride has little effect because there are no excess protons.

The effect of protons was studied by extracting 3.00 *M* potassium chloride solutions containing fixed amounts of chromium(VI) and varying amounts of sulfuric acid with an equal volume of methyl isobutyl ketone and analyzing aliquots of each phase for chromium(VI). The results of this study are given in Fig. 3 where a plot of log K_D against log $[H^+]$ gave a straight line with a slope of 2.10 indicating that the extraction is dependent upon the square of the hydrogen ion concentration.

The effect of ketone concentration was studied by extracting 3.00 *M* solutions of hydrochloric acid containing fixed amounts of chromium with equal volumes of inert organic solvents containing varying amounts of methyl isobutyl ketone, and analyzing aliquots of each phase for chromium(VI). Two inert solvents were used as diluents for the methyl isobutyl ketone, benzene and carbon tetrachloride. The results of this study are listed in Fig. 4. The plot of log K_D against log of the concentration of methyl isobutyl ketone indicates that the extraction depends on the first power of the ketone concentration at low ketone concentrations and the eighth power at higher ketone concentrations.

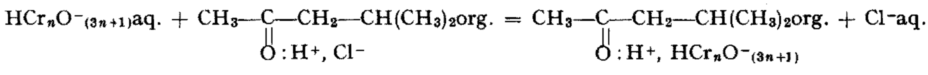
Mechanism of the extraction

The data in Fig. 2 and Table VI show that the extraction is dependent on the first power of the hydrochloric acid concentration. The data in Fig. 3 indicate a second power dependence on the hydrogen ion concentration; one of the protons in this case is the proton of the hydrochloric acid. The data in Fig. 4 show, at low concentrations of ketone, a first power dependence of the extraction on the concentration of methyl isobutyl ketone; at higher ketone concentrations, an eighth power dependence is indicated. From these data, the mechanism of the extraction of chromium(VI) from aqueous hydrochloric acid solutions into methyl isobutyl ketone is postulated as follows:

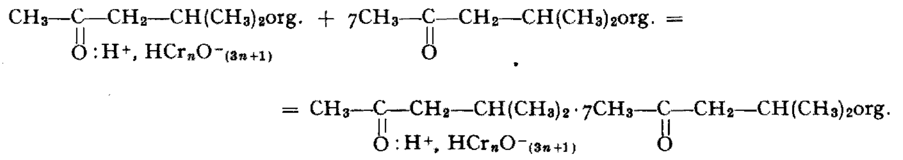


$$H^+\text{aq.} + Cl^-\text{aq.} + CH_3\text{—}\underset{\substack{\| \\ O}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\text{org.} = CH_3\text{—}\underset{\substack{\| \\ O:H^+,\ Cl^-}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\text{org.} \tag{1}$$

$$Cr_nO^{2-}_{(3n+1)}\text{aq.} + H^+\text{aq.} = HCr_nO^-_{(3n+1)}\text{aq.} \tag{2}$$



$$HCr_nO^-_{(3n+1)}\text{aq.} + CH_3\text{—}\underset{\substack{\| \\ O:H^+,\ Cl^-}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\text{org.} = CH_3\text{—}\underset{\substack{\| \\ O:H^+,\ HCr_nO^-_{(3n+1)}}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\text{org.} + Cl^-\text{aq.} \tag{3}$$



$$CH_3\text{—}\underset{\substack{\| \\ O:H^+,\ HCr_nO^-_{(3n+1)}}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\text{org.} + 7CH_3\text{—}\underset{\substack{\| \\ O}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\text{org.} =$$

$$= CH_3\text{—}\underset{\substack{\| \\ O:H^+,\ HCr_nO^-_{(3n+1)}}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\cdot 7CH_3\text{—}\underset{\substack{\| \\ O}}{C}\text{—}CH_2\text{—}CH(CH_3)_2\text{org.} \tag{4}$$

Equation (1) demonstrates the first power dependence on the hydrochloric acid concentration in the formation of a "receptor" in the organic phase. Equations (1) and (2) represent the second power dependence on the hydrogen ion concentration. One proton is involved in the formation of the "receptor", and the other proton is involved in the formation of the extractable chromium species. Equation (3) shows the first power dependence of the extraction at low ketone concentrations. The extractable chromium species is extracted by an ion-exchange mechanism with the chloride ion of the "receptor". Equation (4), taken with equation (3), explains the eighth power dependence of the extraction on the ketone concentration. The extractable chromium species first reacts with one ketone "receptor", and then seven more ketone molecules complete the solvation of the extracted chromium species.

Extraction into other ketones

In order to explain why each of the six ketones in Fig. 1 differed in its ability to extract chromium(VI), a series of studies was undertaken to determine the distribution of hydrochloric acid between water and these ketones. Aqueous hydrochloric acid solutions of known concentration were extracted with equal volumes of the desired ketone, and the acidities of the organic phases were measured. The results of this study are presented in Fig. 5 where the conductance of the organic phases was used as a measure of the number of receptors. In addition, the hydrogen ion concentration of the organic phases was determined by titration with standard base. These data are thought to be less reliable than the conductance measurements because of the difficulties encountered in separating the phases. Small amounts of the aqueous phases remained on the walls of the separatory funnel, and these small amounts added greatly to the apparent acidity of the organic phase. Because of these difficulties, the results of these determinations were not reproducible, and the quantities of hydro-

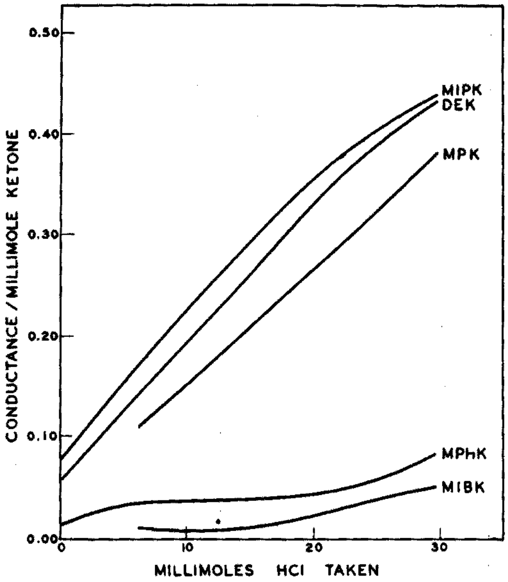
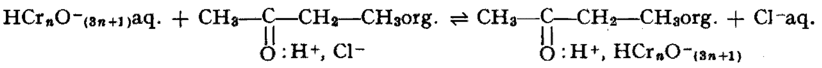


Fig. 5. Conductance of ketones after extracting various hydrochloric acid solutions.

chloric acid found in the organic phases ranged from 0.3 to 3.5 mequiv./mmole of ketone.

The data in Fig. 5 show that each ketone differs in its ability to extract hydrochloric acid. If the conductance measurements in Fig. 5 are considered to be a measure of the concentration of "receptors", postulates can be made concerning the extracting abilities of the various ketones. The distribution coefficients listed in Table II show that methyl *n*-propyl ketone is a better extractant than methyl isobutyl ketone when chromium is extracted from 3.00 *M* hydrochloric acid. The K_D values are 60.6 and 33.4, respectively. The conductance measurements in Fig. 5 suggest that methyl *n*-propyl ketone has a higher "receptor" concentration under these conditions. Similarly, methyl phenyl ketone is a better extractant than methyl isobutyl ketone.

Methyl ethyl ketone does not follow the trend of low K_D–low receptor concentration. The K_D value for this ketone is the lowest of all, 13.1, and it shows the highest "receptor" concentration. It is postulated that the extraction of $\mathrm{HCr}_n\mathrm{O}^-_{(3n+1)}$ into the organic phase is inhibited by the high chloride ion concentration of the organic phase. If the extraction is represented by the following equilibrium expression:



$$\mathrm{HCr}_n\mathrm{O}^-_{(3n+1)}\text{aq.} + \mathrm{CH_3{-}}\underset{\underset{\mathrm{O:H^+,\ Cl^-}}{\|}}{\mathrm{C}}\mathrm{{-}CH_2{-}CH_3}\text{org.} \rightleftharpoons \mathrm{CH_3{-}}\underset{\underset{\mathrm{O:H^+,\ HCr_nO^-_{(3n+1)}}}{\|}}{\mathrm{C}}\mathrm{{-}CH_2{-}CH_3}\text{org.} + \mathrm{Cl}^-\text{aq.}$$

it is seen that a high chloride ion concentration would oppose the extraction of chromium(VI) and thereby give a low K_D value.

Extraction from other acids

GOTO AND KAKITA[4] have studied the extraction of chromium(VI) from aqueous hydrochloric, nitric, sulfuric, and perchloric acid solutions by methyl isobutyl ketone.

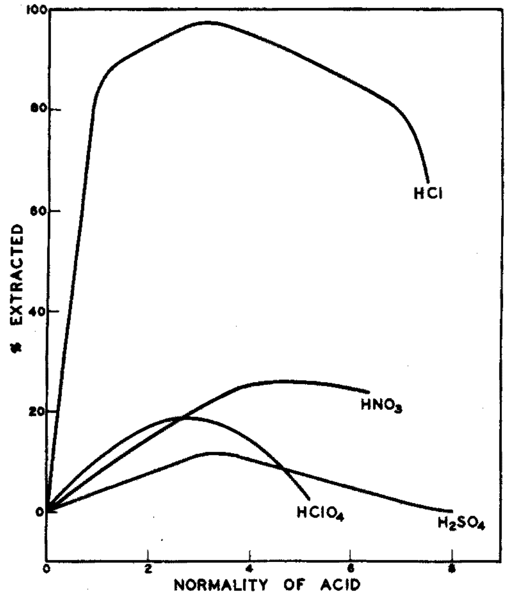


Fig. 6. Extraction of chromium(VI) from various acids by methyl isobutyl ketone.

It was found that the amount of chromium extracted increased to a maximum with increasing acid concentration and then decreased. Hydrochloric acid provided the best extraction medium, and the amount extracted decreased in proceeding from hydrochloric to perchloric to nitric to sulfuric acid.

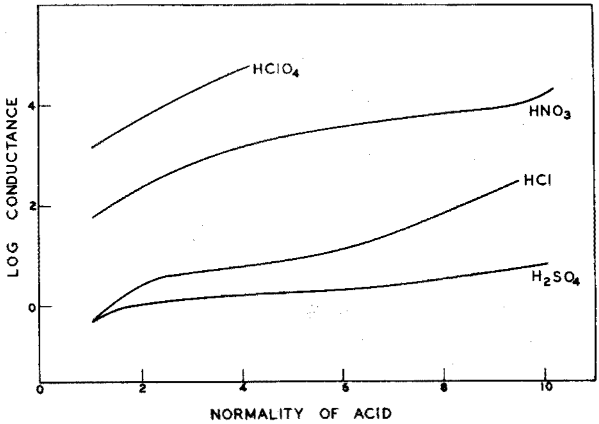


Fig. 7. Conductance of methyl isobutyl ketone after extraction of various acid solutions.

A similar series of studies was undertaken in the present investigation except that both phases were analyzed. A fixed amount of chromium(VI) was treated with a measured volume of standard acid and diluted to a convenient volume with water to control the acid concentration. The aqueous phase was extracted with an equal volume of methyl isobutyl ketone, and the chromium content of each phase was determined. The results of this study are presented in Fig. 6. It is seen that the amount of chromium extracted decreased in progressing from hydrochloric to nitric to perchloric to sulfuric acid.

In order to throw light on the difference in the extraction behavior of the different acids, conductance measurements were made on the ketone after extraction of these acids from water. The results are given in Fig. 7 where it is seen that the conductance of the ketone containing hydrochloric acid increases after extraction of aqueous solutions of the respective acids of the same normality. This indicates that sulfuric acid forms fewer "receptors" than hydrochloric acid, and the amount of chromium(VI) extracted from sulfuric acid is less than the amount of chromium extracted from hydrochloric acid of the same concentration. The conductance of ketone containing nitric or perchloric acid is two to three powers of ten greater than the conductance of ketone containing hydrochloric acid. In these cases, it is postulated that the high nitrate or perchlorate ion concentration of the ketone phase hinders the extraction of chromium(VI) in much the same way as the high chloride ion concentration of methyl ethyl ketone hinders the extraction of chromium(VI) from aqueous hydrochloric acid solutions.

CONCLUSIONS

From the data obtained in these studies, the extraction of chromium(VI) from aqueous hydrochloric acid solutions into methyl isobutyl ketone was found to involve the formation of an extractable species, possibly a monoprotic polychromate anion, the formation of a "receptor" in the organic phase, possibly a protonated ketone, the exchange on the extractable species in the aqueous phase for the anion of the ketone phase, and the solvation of the extracted species in the ketone phase. The ability of various ketones to extract chromium(VI) is attributed to their ability to form "receptors" with hydrochloric acid. The effects of various acids on the extraction of chromium also are explained by the formation of "receptors" with the ketone.

SUMMARY

A study of the extraction of chromium(VI) from aqueous media by ketones was made. Extraction of chromium was found to be most efficient from aqueous hydrochloric acid solutions. A mechanism for the extraction of chromium(VI) from aqueous hydrochloric acid solutions by methyl isobutyl ketone is proposed involving the formation of a receptor in the organic phase, the exchange of the chloride ion of the receptor for the anionic chromium(VI) species of the aqueous phase, and the solvation of the extracted chromium species. The differences in the abilities of various ketones to extract chromium(VI) from aqueous hydrochloric acid solutions, and the differences in the extraction of chromium(VI) from various aqueous acids by methyl isobutyl ketone are attributed to the differences in the formation of receptors.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du chrome(VI), en solution aqueuse, au moyen de diverses cétones. Un mécanisme est proposé pour l'extraction du chrome(VI), au moyen de méthylisobutylcétone, à partir de solutions dans l'acide chlorhydrique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Chrom-(VI) aus wässrigen Lösungen mit verschiedenen Ketonen. Ein Mechanismus für die Extraktion mit Methyl-isobutylketon wird diskutiert zur Erklärung des unterschiedlichen Verhaltens der einzelnen Ketone.

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THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

PART III*. NATURE AND PROPERTIES OF THE MERCURY COMPLEXES

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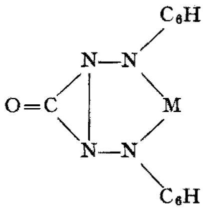
Diphenylcarbazide and diphenylcarbazone are sensitive reagents for mercury(I) and mercury(II), and it is possible to detect as little as 0.05 μg of mercury[1]. Cazeneuve[2] was the first to propose these reagents for the detection of mercury(II), chromium(VI) and copper(II). He assumed that the complexes formed are always carbazonates; before complex formation the carbazide would be oxidized. Feigl and Lederer[3] reported that the carbazide can also form metal complexes without a preceding oxidation, an opinion later supported by two Russian authors[4].

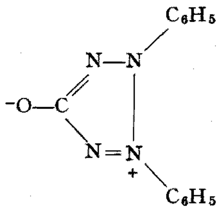
The composition of the complexes is another difficulty. Cazeneuve[5] gives for the mercury(II) complex the formula $Hg(HD)_2$ (in which H_2D is diphenylcarbazone); for the mercury(I) complex, formed in the reaction between mercury(II) and diphenylcarbazide, he gives the formula Hg_2D^2. Feigl and Lederer[3] and Fischer[6] give the same compositions for the carbazone compounds.

Korenman and Djatsjkowskaja[4] found by the method of continuous variations[7] that one carbazide molecule reacts with two mercury(II) or one mercury(I) ions. They conclude that a carbazide compound is formed only in the first reaction; the second reaction yields the mercury(I) compound Hg_2D, after oxidation of the carbazide by the mercury(II). Kemula *et al.*[8], using the same method, found a (1 : 1) compound for mercury(II) and diphenylcarbazone, if the pH exceeds 1.9; they regard the formula as $Hg(HD)^+$, a cation.

Bamberger[9] has postulated that in the carbazone complexes the reagent occurs in the enolic form, in contradiction to the ketonic form proposed by Cazeneuve[2,5]. Feigl and Lederer give another structure (I) but it is not probable that a compound with such ring tension could exist.



(I)



(II)

Korenman and Djatsjkowskaja favoured the structure given by Cazeneuve. It is known that solutions of the mercury complexes fade on standing because of a

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* Part II: *Anal. Chim. Acta*, 27 (1962) 188.

Anal. Chim. Acta, 27 (1962) 416–421

reaction in which diphenylcarbodiazone, the oxidation product of the carbazone, is formed[10]. This compound would occur in the betaine form (II), according to BAMBERGER *et al.*[11].

From this short summary it is clear that there is no agreement about the reactions in which the complexes are formed and about the composition of these complexes.

In this study, the method of continuous variation was used and the complexes were isolated and analysed; it was confirmed that in the reactions between mercury(I) or mercury(II) on the one hand and diphenylcarbazide or diphenylcarbazone on the other hand, only carbazone complexes are formed. In the case of the reaction with the carbazide, an oxidation-reduction reaction precedes complex formation.

The complexes proved to be neutral molecules, not cations; both mercury(I) and (II) form two complexes with the carbazone, a (1 : 1) and a (1 : 2) complex.

EXPERIMENTAL

All the chemicals used were of pro analysi grade. Mercury(II) solutions were made by dissolving HgO in twice-distilled water containing perchloric acid. For mercury(I) solutions, $Hg_2(NO_3)_2$ was used. These solutions were standardized with standard solutions of ammonium thiocyanate and of iodine respectively.

Sodium perchlorate solutions were made by neutralizing sodium hydroxide with perchloric acid.

Diphenylcarbazone was separated from the carbazide according to KRUMHOLZ AND KRUMHOLZ[12].

Diphenylcarbazide was freshly recrystallized from alcohol before the experiments. Its solutions were freed from oxygen (to avoid oxidation of the carbazide) by bubbling nitrogen through the solvents before dissolving the carbazide.

Diphenylcarbodiazone was prepared from the carbazone by oxidation with silver-(I)[10] or isoamylnitrite[11]. Both methods yielded a product exploding at about 160–165°.

Toluene was made methylthiophene-free by refluxing with a sodium–potassium alloy[13].

Extinction measurements were made with a Unicam SP 500 spectrophotometer, with 1.0-cm cuvettes. The pH was measured with a Philips PR 9400 pH-meter, with a glass electrode and a saturated calomel electrode; the latter was separated from the solutions measured by an ammonium nitrate bridge to prevent leakage of chloride ion.

RESULTS

General

A purple complex is formed when a solution of the carbazide or carbazone in aqueous alcohol (an alcoholic solution diluted with water) is mixed with mercury(I) or (II) salts in the same solvent at pH 2–4. The complexes with carbazone are formed immediately, but the carbazide reacts more slowly. In all four cases the complex solutions show the Tyndall effect; the same is true for the carbazide and carbazone solutions alone. The colloids flocculate on heating or on addition of an indifferent electrolyte.

Irradiation of the solutions by ultraviolet or visible light bleaches the complexes. Solutions kept in the dark decompose more slowly. A logarithmic plot of the extinction of a toluene solution of these complexes, kept in the dark, against time yields a straight line, which proves the decomposition to be a first order reaction, for both the mercury-

(I) and (II) complexes. The product formed in this reaction can be identified with diphenylcarbodiazone by the absorption spectra. Moreover, a mercury mirror is formed. Schematically the reaction is: complex → diphenylcarbodiazone + Hg.

The decomposition of the complexes is accelerated by shaking the toluene solutions with aqueous solutions of a mercury(I) or (II) salt. Shaking with water alone has no effect. The reaction involved must be an oxidation of diphenylcarbazone by the mercury ions. To eliminate these reactions as much as possible, the experiments were performed in darkened·glassware.

Nature of the complexes

The formulae of the formed complexes were studied in three ways: by isolation and analysis of the complexes, by JOB curves and by obtaining data on substitution of protons.

(*a*) *Isolation and analysis of the complexes*

Mercury(I) or mercury(II) nitrate solutions (about $2 \cdot 10^{-3} M$) at pH 3–4 were treated with equal volumes of reagent solutions ($6–8 \cdot 10^{-3}$ M), containing sodium nitrate as an indifferent electrolyte to flocculate the complexes. The medium was an alcohol-water mixture (20:80 v/v). The complexes were filtered, washed with 96% alcohol and water, and then treated on the filter with 2 N perchloric acid to redissolve the components; part of the carbazone formed remained on the filter and was identified as such.

In the perchlorate solutions tests were made for diphenylcarbazone, diphenylcarbazide, mercury(I) and mercury(II). Diphenylcarbazone was detected in basic solution by formation of the red anion when mercury(I) and (II) ions were made inactive by adding sodium chloride. Diphenylcarbazide was detected with chromium(VI) which reacts with the carbazide only[14]. Mercury(I) was detected with chloride ion, and mercury(II) with hydrogen sulphide after removal of mercury(I) as the chloride.

The results obtained for the complexes formed in the four possible reactions are summarized in Table I.

TABLE I

QUALITATIVE TESTS ON THE COMPLEXES

Reaction	*Test for:*			
	carbazide	*carbazone*	Hg^{2+}	Hg_2^{2+}
I Hg_2^{2+} + diphenylcarbazide	—	+	—	+
II Hg_2^{2+} + diphenylcarbazone	—	+	—	+
III Hg^{2+} + diphenylcarbazide	—	+	—	+
IV Hg^{2+} + diphenylcarbazone	—	+	+	—

In reaction (I) solutions of concentrations about 10^{-3} M formed a distinct mercury mirror; in less concentrated solutions the mirror was scarcely visible.

The results prove that in the reactions of mercury(I) and (II) ions with the carbazide, a carbazone complex is formed after oxidation of the carbazide by the metal ions.

(*b*) *Job curves*

The results obtained by JOB's method[7], showing the ratio of the reacting molecules, are summarized in Table II. The medium was an alcohol–water mixture (20 : 80 v/v) at pH 3.5. The extinctions, measured at 540 mμ, 560 mμ and 580 mμ, were taken as a measure of the concentration of the complex formed, because the extinction of the separate reacting species at these wavelengths is negligible under the conditions used. In the reactions of the carbazide, the extinction was measured 10 min after the reactants had been mixed, to obtain complete reaction.

TABLE II

RESULTS OF JOB CURVES

Reaction[a]	*Total concentration (cation + reagent) (M)*	*Cation: reagent at the maximum*
I	$8.9 \cdot 10^{-5}$	2 : 1
II	$2.7 \cdot 10^{-5}$	1 : 1
III	$5.1 \cdot 10^{-5}$	2 : 1
IV	$8.5 \cdot 10^{-5}$	1 : 1

[a] Numbered as in Table I.

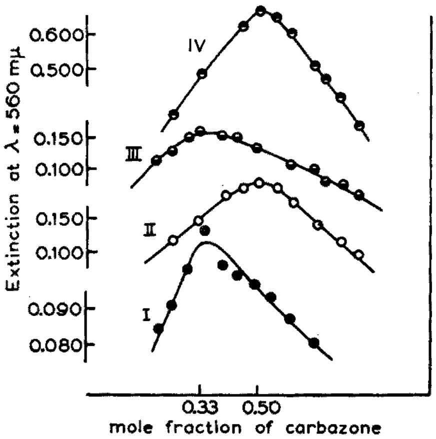

Fig. 1. Continuous variation plot for the systems: I Hg_2^{2+} + diphenylcarbazide, II Hg_2^{2+} + diphenylcarbazone, III Hg^{2+} + diphenylcarbazide, IV Hg^{2+} + diphenylcarbazone.

Fig. 1 gives the JOB curves at $\lambda = 560$ mμ. At the other wavelengths the curves were of the same shape. JOB curves in a two-phase system[15], water–toluene, at pH 3–4 give the same value, 1 : 1, for the carbazone complexes as those in aqueous alcoholic solutions. At lower pH values, however, the symmetry of the curves disappears (Fig. 2), indicating that a second complex which contains more carbazone is formed; this may be the 1 : 2 complex.

(*c*) *Number of protons substituted*

As a result of the complex formation the pH decreases. To determine the number of protons released from the carbazone, a known amount of mercury (I) or (II) was converted to the complex as follows. A solution of the carbazone in carbon tetrachloride was added to the neutral aqueous solution of the mercury salt and equilibration of the two-phase system was obtained by shaking. The acid content of the aqueous solution was determined by titration with standard barium hydroxide solution. For 0.087 mmole of mercury(II) taken, 0.167 mmole of hydrogen ion was found, and for 0.058 mmole of mercury(I), 0.102 mmole of hydrogen ion was found. Thus, one mercury cation replaces 2 protons. This result disagrees with the statement of KEMULA AND JANOWSKI[8]; we must conclude that the complexes are not cations.

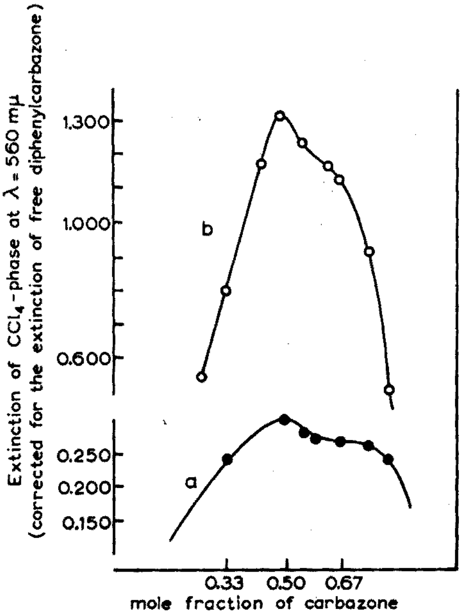

Fig. 2. Continuous variation plot for the systems: (a) Hg_2^{2+} + diphenylcarbazone in water–carbon tetrachloride. Total concentration = $3.4 \cdot 10^{-5}$ *M*; pH = 2.0; (b) Hg^{2+} + diphenylcarbazone in water–carbon tetrachloride. Total concentration = $3.7 \cdot 10^{-4}$ *M*; pH = 0.9.

This conclusion was confirmed in a different manner: mercury(I) or (II) diphenylcarbazone complex was precipitated from mercury(I) or (II) sulphate solutions, washed with water, and treated with 2 *N* perchloric acid. In the solution of the dissolved complex no sulphate ion was found, hence the complex did not contain a different anion. Separation of the complexes by means of extraction with carbon tetrachloride, followed by decomposition of the complexes by shaking with 2 *N* perchloric acid, yielded the same negative test for sulphate.

CONCLUSION

The following reactions are compatible with the experiments described above.

I $2Hg_2^{2+}$ + diphenylcarbazide $\rightarrow Hg_2D + 2Hg + 4H^+$
II Hg_2^{2+} + diphenylcarbazone $\rightleftarrows Hg_2D + 2H^+$
III $2Hg^{2+}$ + diphenylcarbazide $\rightarrow Hg_2D + 4H^+$
IV Hg^{2+} + diphenylcarbazone $\rightleftarrows HgD + 2H^+$
(H_2D = diphenylcarbazone)

According to the results obtained by isolation of the complexes diphenylcarbazide is not regenerated when the complexes formed in the reactions I and III are dissolved, which indicates that reactions I and III are irreversible. The carbazide does not form mercury complexes. Mercury(I) and (II) oxidize the carbazide to the carbazone, after which a carbazone complex is formed.

As the formulae for the 1 : 1 complexes are HgD and Hg_2D, it seems reasonable to assume for the second complexes the formulae $Hg(HD)_2$ and $Hg_2(HD)_2$. Evidence for these formulae will be given in a following article, in which the dissociation constants of the complexes, measured in the two-phase system water–toluene, will be discussed. In the reactions investigated four complexes are formed: two mercury(I) complexes, Hg_2D and $Hg_2(HD)_2$, and two mercury(II) complexes, HgD and $Hg(HD)_2$.

SUMMARY

The reactions of diphenylcarbazone or diphenylcarbazide with mercury(I) or mercury(II) are studied by qualitative analysis, extraction and Job's method. Only carbazone complexes are formed. Mercury(I) and (II) both form two complexes, a 1 : 1 and a 1 : 2 complex (cation : carbazone). The complexes formed are colloids in aqueous alcoholic solutions. Decomposition of these complexes, to form diphenylcarbodiazone, is accelerated by ultraviolet and visible light.

RÉSUMÉ

Les réactions de la diphénylcarbazone et de la diphénylcarbazide avec le mercure(I) et (II) ont été examinées par analyse qualitative, extraction et par la méthode de Job. Seuls se forment les complexes de la carbazone.

ZUSAMMENFASSUNG

Die Reaktionen von Diphenylcarbazon und Diphenylcarbazid mit Quecksilber-(I) und-(II) wurden mit Hilfe der qualitativen Analyse, Extraktion und der Methode von Job untersucht. Bei der Reaktion entstehen nur Carbazon-Komplexe, die bei Carbazid über eine Oxydation-Reduktionsreaktion als Zwischenstufe gebildet werden.

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THE SEPARATION OF COPPER, LEAD, CADMIUM AND ZINC FROM HIGH PURITY URANIUM METAL BY ION EXCHANGE ON CELLULOSE PHOSPHATE AND THEIR DETERMINATION BY SQUARE WAVE POLAROGRAPHY

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The production of uranium metal of very high purity has necessitated the development of analytical procedures for the determination of small amounts of impurities. Many of these are of metallurgical interest and often a full analysis is required. For this reason methods which allow the simultaneous determination of a number of elements are advantageous and spectrographic methods are usually employed[1,2]. Although these procedures are generally suitable for most metallic elements at very low levels, occasionally difficulties arise, *e.g.* in the determination of copper and zinc, and alternative procedures are required.

Square wave polarography[3], with its high resolution and sensitivity provides such an alternative and consideration has been given to the determination of copper, lead, cadmium and zinc in uranium by this technique.

A study of the polarographic literature indicated that many base electrolytes are available for this determination. Of these the most suitable appeared to be 1 *M* orthophosphoric acid, because no interference results from tin in the determination of lead, or from indium in the determination of cadmium in this electrolyte. MILNER AND SLEE[4] have investigated the reduction of a number of metal ions in 1 *M* orthophosphoric acid and have successfully used this base electrolyte in the direct analysis of a number of alloy and mineral systems. Other workers[5,6] have estimated copper, lead and zinc in the presence of large amounts of indium in this electrolyte.

Considerable interference from uranium(VI) in the determination of lead, and from iron(III) in the determination of copper would be expected, which necessitates separation of these ions before polarography. Although several conventional ion-exchange or solvent extraction procedures would be suitable for this separation, some attention has been given to the applicability of the ion-exchange material, cellulose phosphate, to this problem. The properties of this material have been studied by HEAD *et al.*[7] who showed that, in marked contrast to the behaviour of sulphonic acid cation exchangers, it possessed a very high affinity for certain ions including Th^{4+}, Ti^{4+}, Ce^{4+}, Fe^{3+}, ZrO^{2+} and UO_2^{2+} and that divalent cations were not adsorbed. The high capacity of cellulose phosphate for these ions, and its ability to adsorb from 1 *M* mineral acid solutions makes it an attractive material for analytical separations. So far, however, its applications have been almost entirely restricted to large scale separation and purification processes[8,9].

This paper describes work carried out on the separation of copper, lead, cadmium and zinc from uranium using this material and the development of a polarographic method for the determination of these elements in high purity metal at levels below 5 p.p.m.

EXPERIMENTAL

Polarography

Preliminary polarographic experiments with orthophosphoric acid solutions as base electrolyte showed that a considerable increase in sensitivity resulted on dilution of the acid. This effect is shown in Fig. 1 by square wave polarograms from solutions of zinc containing 1 μg per ml. A tenfold dilution of the 1 M orthophosphoric acid solution resulted in an 80 % increase in peak height, but results were not reproducible at this dilution. Using 0.5 M acid reproducible peaks were obtained which were 25 % higher than those obtained with 1 M acid, and this strength of electrolyte was adopted for subsequent work. The use of the dilute base electrolyte is also desirable because it reduces the blank arising from impurities present in the orthophosphoric acid.

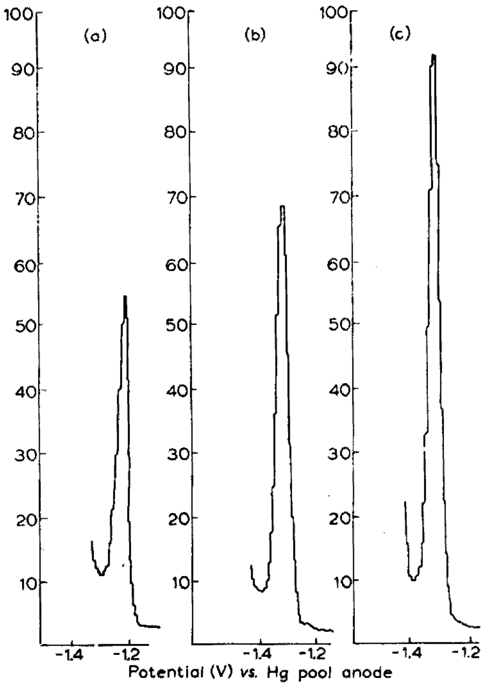

Fig. 1. Square wave polarogram of 1 μg Zn per ml at 1/16 maximum sensitivity. (a) 1 M H_3PO_4, (b) 0.5 M H_3PO_4, (c) 0.1 M H_3PO_4.

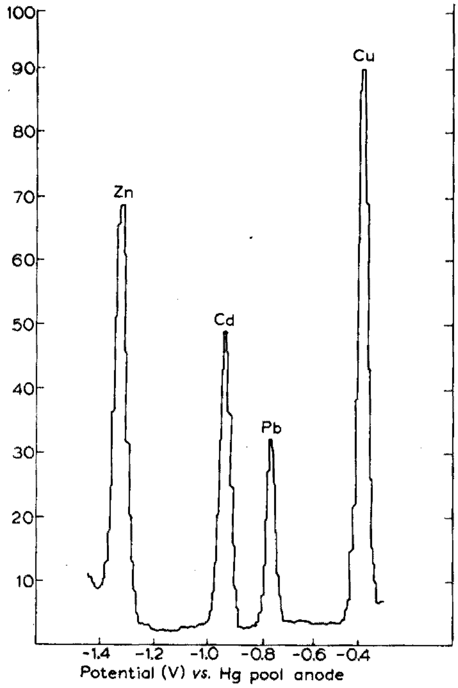

Fig. 2. Square wave polarogram of 1 μg Cu, Pb, Cd and Zn per ml in 0.5 M H_3PO_4 at 1/16 maximum sensitivity.

Fig. 2 shows the well-defined peaks obtained for 1 μg per ml solutions of copper, lead, cadmium and zinc in 0.5 *M* acid. Half-wave potentials recorded against the mercury pool anode were –0.35, –0.76, –0.94 and –1.36 V for Cu, Pb, Cd and Zn respectively. All polarographic measurements were made at 25 ± 1°.

Interferences

The irreversible two-electron reduction of uranium(VI) in orthophosphoric acid solutions reported by KUBOTA[10] was confirmed using a solution containing 5 μg of uranium(VI) per ml. The square wave polarogram in Fig. 3 shows that uranium(VI) causes serious interference with the copper and lead waves. In addition it was shown that interference with the copper wave resulted from the presence of microgram quantities of iron(III). An efficient separation of both these ions is therefore necessary before polarography.

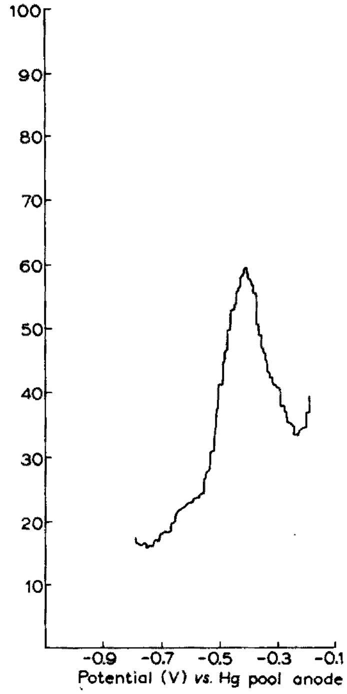

Fig. 3. Square wave polarogram of 5 μg U(VI) per ml in 0.5 *M* H_3PO_4 at 1/4 maximum sensitivity.

Interference from nickel in the zinc wave has also been reported[4]; this could be serious because these elements would not be separated in the procedure. Investigation showed however that negligible interference arises from nickel to zinc ratios of up to 20:1; such ratios would be unlikely to be exceeded in high purity uranium.

Separation of Cu, Pb, Cd and Zn from U and Fe using cellulose phosphate

Cellulose phosphate is available in a powdered form suitable for the preparation of columns and can be obtained in grades of varying capacity. Material of maximum capacity (Grade P70 with a capacity of 7.4 mequiv per g) was chosen. Preliminary experiments on the preparation of columns for analytical separations with this material were made and some difficulties were encountered owing to channelling and leakage of fine particles of cellulose phosphate into the effluent. Considerable improvement resulted if the glass surfaces were made water-repellent by suitable treatment with a solution of dimethyldichlorosilane in carbon tetrachloride, and if a sintered glass disc was used to support the solid.

The optimum hydrochloric acid concentration for the separation of uranium from copper, lead, cadmium and zinc was found to be 1 *M*. At lower concentration slight adsorption of cadmium and lead occurred and above 1 *M* the capacity for uranium was reduced considerably. Effluents after evaporation were found to contain small amounts of organic material probably from partial hydrolysis of the cellulose phosphate; if not destroyed by wet oxidation with nitric and perchloric acids these traces caused serious interference in polarographic measurements.

The removal of adsorbed uranium from the column requires a strong complexing medium, *e.g.* sodium carbonate solution, but columns treated in this way became gelatinous and unsuitable for further use. It was thus found necessary to prepare a new column for each separation.

Apparatus

Mervyn-Harwell Square Wave Polarograph and dropping mercury electrode assembly.

Ion-Exchange Columns 20 × 1.6 cm fitted with a sintered glass disc of porosity 2.

Reagents

All reagents used were AnalaR unless otherwise stated.

Concentrated hydrochloric, nitric and perchloric acids. Specially purified acids for foodstuffs analysis (supplied by British Drug Houses, Ltd.).

Grade P70 cellulose phosphate cation exchanger (supplied by H. Reeve Angel and Co., Ltd., 9 Bridewell Place, London, E.C.4). Wash the powder thoroughly with 1 *M* hydrochloric acid solution until a clear supernate is obtained, and prepare a slurry in 1 *M* hydrochloric acid for the preparation of columns.

Standard copper, lead, cadmium and zinc solution containing 100 μg per ml. Dissolve 0.1 g of "Spectrographically pure" metal in 20 ml of 8 *M* nitric acid and dilute to 1 l with water. Prepare working standards containing 10 μg per ml by suitable dilution.

Nitrogen containing less than 10 p.p.m. of oxygen.

Procedure

Cleaning and preparation of samples. Degrease the metal samples before analysis by treatment with a suitable solvent. Remove any surface oxide by warming with 8 *M* nitric acid (high purity acid is not required) until a bright surface is produced and then wash thoroughly with distilled water to remove traces of acid. Finally rinse with acetone and dry with compressed air, avoiding the use of heat.

Preparation of columns. Treat the inner surfaces of the ion-exchange columns with a 10 % (v/v) solution of dimethyldichlorosilane in carbon tetrachloride and remove the solvent by heating for 30 min at 100°. Prepare columns from 3 g of cellulose phosphate by allowing the slurry in 1 *M* hydrochloric acid to settle under gravity.

Method. Dissolve 0.5 g of uranium metal in 5 ml of 4 *M* hydrochloric acid and add hydrogen peroxide (100 vol) dropwise until a clear yellow solution is produced. Evaporate the solution to dryness and dissolve the residue in 2 ml of 1 *M* hydrochloric acid. Transfer the solution to an ion-exchange column and elute the impurities with 1 *M* hydrochloric acid using a flow rate not exceeding 1 ml per min. Collect 50 ml of the effluent and evaporate to a small volume, cool, add 4 ml of concentrated nitric acid and 1 ml of concentrated perchloric acid and evaporate to dryness. Dissolve the residue in 10 ml of 0.5 *M* orthophosphoric acid solution, transfer to a polarographic cell and deoxygenate the solution with oxygen-free nitrogen. Record the square wave polarogram at a suitable sensitivity scanning from −0.1 to −1.4 V *vs.* mercury pool anode, and determine the amounts of copper, lead, cadmium and zinc present by the standard addition technique.

Determine the reagent blank by repeating the procedure in the absence of uranium.

RESULTS

Analysis of synthetic mixtures

The efficiency of the separation procedure was evaluated by analysis of uranium solutions obtained from spectrographically pure U_3O_8 to which standard additions of each ion had been made.

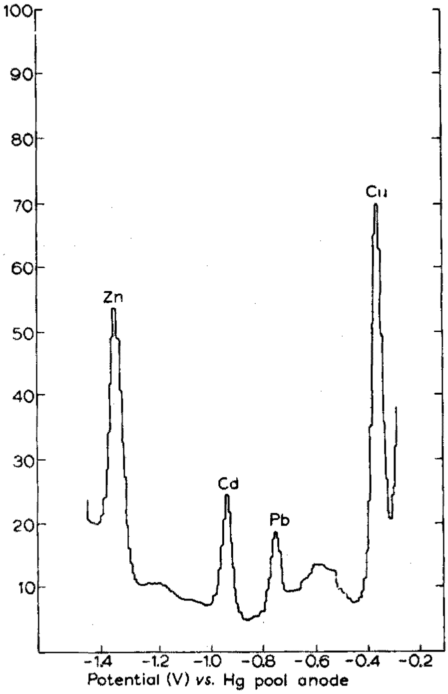

Fig. 4. Square wave polarogram of 2 μg Cu, Pb, Cd and Zn in 10 ml 0.5 *M* H_3PO_4 at 1/16 maximum sensitivity after separation from 0.5 g uranium.

Fig. 4 shows the square wave polarogram obtained after separation of 2 μg of copper, lead, cadmium and zinc from 0.5 g of uranium. The small peak obtained at

−0.6 V is probably due to a small amount of organic material remaining, but is insufficient to cause serious interference.

The results obtained using a number of synthetic mixtures are shown in Table I.

TABLE I

SEPARATION OF IMPURITIES FROM 0.5 g URANIUM

μg added				*μg found*			
Cu	*Pb*	*Cd*	*Zn*	*Cu*	*Pb*	*Cd*	*Zn*
10.0	20.0	10.0	10.0	10.0	19.9	9.9	9.4
10.0	10.0	10.0	10.0	11.0	9.2	9.7	9.0
10.0	10.0	10.0	10.0	10.3	9.2	9.7	8.9
10.0	10.0	10.0	10.0	10.6	9.8	9.6	9.2
5.0	5.0	5.0	5.0	4.6	5.0	4.9	5.9
4.0	4.0	4.0	4.0	3.8	4.6	3.9	3.6
4.0	4.0	4.0	4.0	3.3	4.2	3.9	3.3
2.0	2.0	2.0	2.0	2.2	2.1	1.9	1.8
2.0	2.0	2.0	2.0	2.2	1.7	1.9	1.6
1.0	0.5	0.5	1.0	0.8	0.7	0.6	1.0

Analysis of uranium metal

The impurities were determined in three samples of high purity natural uranium metal; the results obtained, together with some determined by other procedures are summarised in Table II.

TABLE II

ANALYSIS OF NATURAL URANIUM METAL

Sample	*Technique used*	*Cu (p.p.m.)*	*Pb (p.p.m.)*	*Cd (p.p.m.)*	*Zn (p.p.m.)*
I	Polarographic	4.8; 4.0	1.8; 1.7	< 0.5	2.3; 2.2
	Spectrographic	2^{a}	$< 10^{a}$	$< 2^{a}$	$< 5^{b}$
	Spectrophotometric	4.2^{c}	—	—	—
II	Polarographic	3.3; 2.2	4.8; 4.0	< 0.5	2.4; 2.2
	Spectrographic	4^{a}	$< 10^{a}$	$< 2^{a}$	$< 5^{b}$
	Spectrophotometric	3.2^{c}	—	—	—
III	Polarographic	3.2; 2.4	2.2; 2.8	< 0.5	2.2; 2.0
	Spectrographic	2^{a}	$< 10^{a}$	$< 2^{a}$	$< 5^{b}$
	Spectrophotometric	4.8^{c}	—	—	—

[a] Carrier distillation procedure[1].
[b] Atomic absorption spectroscopy[2].
[c] Spectrophotometric determination as 2,2′-diquinolyl complex extracted into amyl alcohol.

CONCLUSIONS

The method described has been shown to be applicable to the determination of copper, lead, cadmium and zinc in uranium metal containing less than 5 p.p.m. of each impurity and is more sensitive than spectrographic procedures for lead, cadmium and zinc. The total reagent blank has been minimised by the use of specially purified acids which are available for the analysis of foodstuffs, and is negligible in the case of cadmium and lead. The limit of detection for these elements is thus determined by the sensitivity of the square wave polarograph and has been estimated to be 0.25 μg. Reagent blanks for copper and zinc are somewhat higher giving a limit of about 0.5 μg. These blanks could almost certainly be reduced by further purification of reagents, *e.g.* by controlled potential electrolysis, but this has been unnecessary in the application.

ACKNOWLEDGEMENTS

We wish to thank Messrs. W. A. BETTISON, G. I. GOODFELLOW and K. A. EXELBY for carrying out the spectrographic and spectrophotometric determinations.

SUMMARY

A method has been developed for the determination of copper, lead, cadmium and zinc in high purity uranium metal. Conditions are described for the separation of these elements from uranium(VI) and iron(III) by ion-exchange on cellulose phosphate and for their determination by square wave polarography using orthophosphoric acid as base electrolyte.

The procedure has been shown to be applicable to metal containing less than 5 p.p.m. of each impurity and results are compared with those obtained by other methods.

RÉSUMÉ

Une méthode est décrite pour le dosage du cuivre, du plomb, du cadmium et du zinc dans un uranium de grande pureté. La séparation d'avec l'uranium(VI) et le fer(III) est effectuée au moyen d'un échangeur d'ions (phosphate de cellulose); le dosage se fait par polarographie à ondes carrées, en utilisant l'acide phosphorique comme électrolyte de base.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Kupfer, Blei, Cadmium und Zink in hochreinem Uranmetall. Nach Abtrennung dieser Elemente von Uran-(VI) und Eisen-(III) durch Ionenaustausch auf phosphorylierter Cellulose erfolgt ihre Bestimmung durch "square-wave" Polarographie.

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THE POLAROGRAPHIC DETERMINATION OF THALLIUM*

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Owing to the lack of specific and sensitive spectrophotometric methods, thallium at milligram or microgram levels is best determined polarographically. Although thallium is somewhat rare and not of commercial importance, its toxic nature calls for its determination in many biological samples. In aqueous solutions, thallium(I) gives a well-defined cathodic wave, and the $E_{\frac{1}{2}}$ does not shift significantly from about -0.5 V *vs.* S.C.E. even in presence of strong complexing agents. Electrolytes recommended for the polarographic determination of thallium are generally aimed at eliminating the interferences of lead and copper with which the element is commonly associated. Other likely contaminants are iron derived from the original sample or from the reagents and, less frequently, bismuth. We are not aware of a supporting electrolyte in which all these four interfering elements would give steps sufficiently more negative than -0.5 V. Large steps before the thallium step resulting from reduction of a major constituent create difficulty particularly in conventional D.C. polarography. In the alkaline tartrate medium recommended by WEINIG[1], iron(III), bismuth and lead give steps at considerably more negative potentials than thallium, but the step due to copper(II) occurs in advance of thallium(I) so that copper(II) interferes in large concentrations. In EDTA at pH 4, proposed by PŘIBIL AND ZABRANSKY[2], only the lead step occurs after thallium, iron(III) and copper(II) giving steps at more positive potentials, and the bismuth step lying very near to that of thallium.

It is known that interfering steps can sometimes be eliminated by the use of a surface-active agent. The phenomenon was termed 'electrochemical masking' by REILLEY[3] who observed that the interference of bismuth in the amperometric titration of lead with EDTA could be eliminated by adding either gelatin or Triton X-100, both of which suppressed the cathodic step of the bismuth–EDTA complex. A more recent example of electrochemical masking is the effect of gelatin and camphor on the reduction steps of metal–polyphosphate complexes[4,5]. In a sodium triphosphate base electrolyte, the cathodic steps of most metals other than thallium(I) and silver(I) were either practically obliterated by gelatin, or displaced to considerably more negative potentials by camphor. Advantage has been taken of this observation in working out a polarographic method for the determination of thallium in presence of many other elements normally associated with it.

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* Communication No. 502 from National Chemical Laboratory, India.

EXPERIMENTAL

Apparatus

Pen-Recording Tinsley Polarograph; Beckman H2 pH meter; H-type cell with S.C.E. as reference electrode. The capillary had $m = 1.515$ mg/sec, $t = 5.1$ sec/drop at -0.7 V in an aqueous solution which was 0.1 M with respect to sodium triphosphate as well as sodium perchlorate and 0.1% with respect to camphor. Measurements were made at 30 ± 0.5°. To prevent loss of camphor from the sample solution during the removal of oxygen, nitrogen gas was bubbled through a blank solution containing camphor before its entry into the H-cell which contained the sample solution.

Chemicals

Thallous nitrate (BDH) was used after testing its purity and determining thallium by the conventional gravimetric thallous chromate method. Sodium triphosphate (99% pure) was prepared from disodium phosphate and phosphoric acid by controlled baking followed by crystallisations from aqueous alcohol.

RESULTS

Thallium(I) gives a well-defined, one-electron cathodic wave from sodium triphosphate solution in the pH range 2 to 10. The $E_{\frac{1}{2}}$ (about -0.5 V *vs.* S.C.E.) does not change much either with pH or with the concentration of sodium triphosphate. Camphor and gelatin have no effect on the step. Copper(II), lead(II), bismuth(III) and iron(III) also give good steps[6], but their $E_{\frac{1}{2}}$ values become more negative with increasing pH; moreover, they are pushed to even more negative potentials (nearly to -1.0 V) by camphor, and suppressed by gelatin[5]. As a consequence, when a sodium triphosphate solution containing thallium(I) with the other ions is polarographed after the addition of a little camphor or gelatin, the resulting polarogram shows the thallium(I) step standing in virtual isolation from the others. The lead

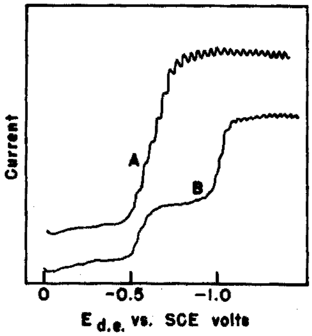

Fig. 1. Polarograms of 0.25 mM Tl^+ + 0.2 mM Pb^{2+} in 0.05 M $Na_5P_3O_{10}$, 0.2 M $NaClO_4$, pH 9.4. A, no surface-active agent; B, 0.01 % camphor.

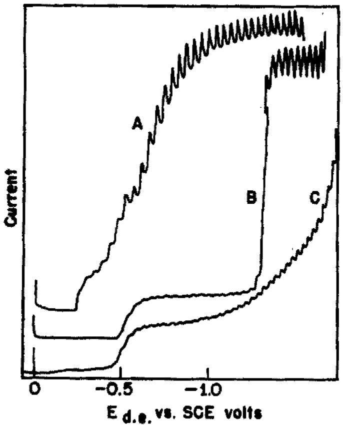

Fig. 2. Polarograms of a solution containing Tl^+, Cu^{2+}, Pb^{2+}, Bi^{3+}, Fe^{3+} each 1 mM, 0.1 M $Na_5P_3O_{10}$, 0.1 M $NaClO_4$, pH 7. A, no surface-active agent; B, 0.1% camphor; C, 0.1% gelatin.

and thallium(I) steps, which almost coincide (Fig. 1, line A) in many supporting electrolytes, show a complete separation (Fig. 1, line B) in presence of 0.01% camphor in the electrolyte by displacement of the lead step to a much more negative potential. The polarogram of a solution containing thallium, lead, copper, iron and bismuth shows a crowding of all the steps in the same region (Fig. 2, line A), but with the same solution containing 0.1% camphor the thallium step is completely isolated (Fig. 2, line B) from the other steps, which then occur around a potential of −1.3 V. Substantially the same result is obtained by substituting gelatin for camphor (Fig. 2, line C), but the rise of current from the reduction of the other ions is observed to begin at a less negative potential (−1.0 V), and is more drawn out and much less in height. Thus, though both camphor and gelatin may serve in the electrochemical masking of the interfering steps, camphor functions more effectively and elegantly.

Effect of pH and sodium triphosphate concentration

A slight negative shift in the $E_{\frac{1}{2}}$ of the thallium step with increasing pH and with increasing sodium triphosphate concentration is observable (Tables I and II). This may be due to a decrease in the dissociation of the thallium-triphosphate complex. From pH 4 to 8, the diffusion current diminishes by about 35%, which is reminiscent of the thallium(I) step obtained in sodium pyrophosphate[7].

TABLE I

EFFECT OF pH ON THALLIUM(I) WAVE

Electrolyte composition: 1.0 mM thallium(I), 0.1 M sodium triphosphate, 0.1% camphor, ionic strength adjusted to 1.6 with sodium perchlorate

pH	$E_{\frac{1}{2}}$ *vs. S.C.E. (V)*	i_d *(μA · 100)*
4	−0.461	387
6	−0.468	320
8	−0.510	245
10	−0.521	241

TABLE II

EFFECT OF SODIUM TRIPHOSPHATE CONCENTRATION ON THALLIUM(I) WAVE

Electrolyte composition: 0.5 mM thallium(I), 0.1% camphor, pH 7, ionic strength adjusted to 1.2 with sodium perchlorate

Sodium triphosphate (M)	$E_{\frac{1}{2}}$ *vs. S.C.E. (V)*	i_d *(μA · 100)*
0.01	−0.466	192
0.04	−0.474	144
0.06	−0.492	138
0.10	−0.505	122

Effect of camphor

0.01% camphor has no effect either on the $E_{\frac{1}{2}}$ or on the diffusion current of the thallium(I) step. Even 0.1% camphor has no effect on the $E_{\frac{1}{2}}$, but the diffusion current is reduced by nearly 7% though the linear relationship between the diffusion current and thallium concentration is still maintained in the investigated range of 0.05 m*M* to 2 m*M* (Table III).

TABLE III

i_d *vs.* THALLIUM CONCENTRATION

Electrolyte composition: thallous nitrate, 0.1 *M* $Na_5P_3O_{10}$, 0.1 *M* $NaClO_4$ and 0.1% camphor, pH 7

Tl^+ (mM)	i_d ($\mu A \cdot 100$)	i_d/c
0.05	12.0	240
0.10	24.2	244
0.20	48.0	240
0.50	122	244
1.00	242	242
1.50	356	237
2.00	482	241

Choice of pH

Since camphor is not effective[5] in displacing waves which rise at potentials less negative than −0.2 V *vs.* S.C.E., care should be taken to ensure that the steps of iron(III), bismuth(III) and copper(II) do not rise too early. This is accomplished by maintaining the pH above 4. Copper in high concentrations (4 m*M*) tends to interfere even at pH 5 by slightly augmenting the thallium diffusion current. On the other hand, bismuth tends to precipitate out above pH 8. A working pH of 7 is satisfactory.

Estimation of thallium in synthetic samples

Mixtures were prepared with the metals usually associated with thallium. To an aqueous solution containing a measured amount of thallium(I) and the other metallic ions (volume *ca.* 10 ml), about 1.2 g of sodium triphosphate hexahydrate, 0.3 g of sodium perchlorate and 2.5 ml of camphor solution (1% in aqueous alcohol) were added and stirred until dissolution was complete; the pH was then adjusted to 7 by careful addition of dilute sodium hydroxide or perchloric acid. Since the pH is not very critical, it is conveniently measured by a narrow range pH paper. The solution is then diluted to 25 ml and an aliquot is polarographed. The diffusion current at −0.7 V is measured and corrected for the residual current. Instead of the thallium being calculated from a diffusion current *vs.* concentration calibration curve, it is determined by the method of standard addition since the diffusion current of thallium(I) shows (Tables I and II) variation with pH, concentration of sodium triphosphate and concentration of camphor. Table IV indicates that thallium in $5 \cdot 10^{-5}$ *M* solutions is readily determined in presence of at least 400 times as much lead or iron, 200 times as much bismuth and 80 times as much copper.

Interferences by elements other than the four metals mentioned above have not been examined yet, but it is reasonable to expect that several other ions such as Cd(II), Ti(IV), Nb(V), Mo(VI) and U(VI) would not interfere since their steps in triphosphate at pH 7 either occur at potentials more negative than −1.0 V or are likely to be pushed to that region by camphor. The step due to silver, though not displaced by camphor, occurs in the neighbourhood of 0.0 V and therefore does not interfere in low concentrations; this is easily achieved on account of the low solubility of silver in sodium triphosphate solution at the working pH.

TABLE IV

DETERMINATION OF THALLIUM IN SYNTHETIC MIXTURES

No.	*Addition to electrolyte (mM)*	*Tl^+ taken (mM)*	*Tl^+ found (mM)*	*No.*	*Addition to electrolyte (mM)*	*Tl^+ taken (mM)*	*Tl^+ found (mM)*
1	Pb^{2+} 20	0.050	0.050	5	Pb^{2+} 2		
		0.238	0.235		Cu^{2+} 1	0.050	0.050
		0.455	0.454		Fe^{3+} 2		
					Bi^{3+} 2		
2	Fe^{3+} 20	0.050	0.050				
		0.238	0.239	6		0.099	0.100
		0.455	0.454		As in	0.196	0.200
					no. 5	0.385	0.383
3	Bi^{3+} 10	0.050	0.050			0.566	0.575
		0.238	0.232			0.741	0.750
		0.455	0.440			0.909	0.917
						1.07	1.07
4	Cu^{2+} 4	0.050	0.050			1.45	1.48
		0.238	0.233				
		0.495	0.481				

SUMMARY

A polarographic method is described for the determination of thallium in sodium triphosphate supporting electrolyte. The incorporation of 0.1% camphor in the electrolyte displaces the cathodic steps of many interfering ions, *e.g.*, lead(II), copper(II), iron(III) and bismuth(III) to a more negative potential (≏ −1.0 V), well away from the thallium step which remains unaffected.

RÉSUMÉ

Une méthode polarographique est décrite pour le dosage du thallium, en utilisant le phosphate trisodique comme électrolyte de base. Les sauts de plusieurs éléments gênants (Pb, Cu, Fe(III) et Bi) peuvent être déplacés par adjonction de camphre.

ZUSAMMENFASSUNG

Beschreibung einer polarographischen Methode zur Bestimmung von Thallium unter Verwendung von Trinatriumphosphat als Grundelektrolyt. Die durch Blei, Kupfer, Eisen-(III) und Wismut gebildeten Stufen können durch Zusatz von Kampher verschoben werden, wobei die Thalliumstufe unbeeinflusst bleibt.

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A COLORIMETRIC METHOD FOR THE DETERMINATION OF CARBONYL GROUPS IN CELLULOSE

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Most methods available for the determination of carbonyl groups in cellulose are non-stoichiometric. In our laboratory a method devised by GEIGER AND WISSLER[1], and slightly modified by WENNERBLOM[2], has been used for a number of years. The method is based upon the formation of a hydrazone with GIRARD's reagent P. In this way the cellulose is converted into an anion exchanger and from the determination of its exchange capacity the number of carbonyl groups can be calculated. The reproducibility is extremely good but, as pointed out in an earlier paper[3], the penetration of the large reagent molecules into the cellulose fibers is not complete.

Experiments with smaller molecules, such as hydrazine and dimethylhydrazine and subsequent determination of the anion-exchange capacity, have been carried out by the authors. Hydrazine gave values which were in good agreement with those obtained according to GEIGER AND WISSLER, whereas the results obtained with dimethylhydrazine were not reproducible. Methods based upon the determination of total nitrogen in the cellulose after the reaction with, for instance, hydroxylamine[2,4,5] can probably be useful if the carbonyl content is high compared with the nitrogen content in the untreated fibers. With the samples of hydrocellulose investigated in the present work (see ref.[4]) the nitrogen content is fairly high and no reliable results have been obtained using this technique.

Based upon this experience an attempt has been made to find an improved method for the determination of carbonyl groups in cellulose. The method proposed in the present work is based upon the reaction between cellulose and hydrazine. After washing, the cellulose is dissolved in sulfuric acid and the hydrazine present in the solution is determined colorimetrically. The proposed method gives values which are higher than those obtained by the method of GEIGER AND WISSLER and for cellulose samples subjected to mild hydrolysis the values are in good agreement with those expected from osmotic measurements.

EXPERIMENTAL

Solutions

0.5 *M* Hydrazine dihydrochloride containing 10 g/l of boric acid; the pH is adjusted to 9.0 with sodium hydroxide.

p-Dimethylaminobenzaldehyde: 16 g is dissolved in 800 ml of ethanol (99.5%) and 80 ml of concentrated hydrochloric acid is added.

Standard hydrazine sulfate solution (approx. 1 p.p.m.), approx. 1 *N* with respect to hydrochloric acid. The titer of a concentrated stock solution of hydrazine sulfate is controlled by potentiometric titration with sodium hydroxide.

Procedure

A sample of 20–40 mg of hydrocellulose (air dried, with known moisture content) is weighed and transferred into a small Erlenmeyer flask. About 15 ml of the hydrazine solution is added. After the reaction time (about 20 h at room temperature) the cellulose hydrazone is washed on a G3 glass filter with 200 ml water in 15-ml portions. Each portion should be in contact with the cellulose for 2–3 min.

The cellulose hydrazone is dissolved in 6 g of sulfuric acid (70% by weight) in a 50-ml Erlenmeyer flask. The flask is shaken to dissolve the sample and is then placed in the water bath at 35°. After 1 h (see Table II), the solution is diluted with about 10 ml of water and transferred quantitatively into a 100-ml volumetric flask. *p*-Dimethylaminobenzaldehyde solution (40 ml) is added by pipet. After filling to the mark with water and thermostatting at 20°, the absorbance is measured in a spectrophotometer at 458 mμ. A calibration curve is made using the standardized hydrazine solution. These determinations are carried out at the same acid concentration (about 1 *N*). A blank solution made from 40 ml of *p*-dimethylaminobenzaldehyde solution and 1 *N* hydrochloric acid is used as reference.

Note. The glass walls adsorb hydrazine from strong hydrazine solutions and the adsorbed hydrazine is removed by acid. To avoid any contamination the use of separate flasks for the condensation and the dissolution is recommended.

RESULTS AND DISCUSSION

The influence of the time of reaction and the pH during the condensation with hydrazine was studied using a sample of hydrolyzed cotton. The results in Fig. 1 show that the observed carbonyl content increases when the pH is increased from 7 to 9. At pH 10 the values are about the same as those obtained at pH 9. During

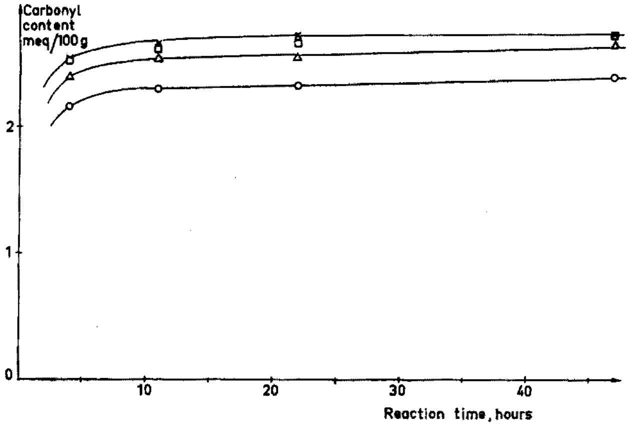

Fig. 1. Observed carbonyl content as a function of the time of reaction between hydrazine and cellulose. ○ pH 7; △ pH 8; × pH 9; □ pH 10.

the first period of the reaction the rate is fairly high, but then the reaction slows down. After 15 h, the observed carbonyl content increases only slightly.

The conditions during the washing step were studied in experiments carried out with varying amounts of water. As can be seen from the data given in Table I, no difference in carbonyl content can be observed when the amount of washing water is increased from 200 to 600 ml. The slight decrease observed with 800 ml of water can be ascribed to a loss of some short fibers.

TABLE I

WASHING OF THE CELLULOSE HYDRAZONE

Amount of washing water (ml)	*Carbonyl content (meq/100 g)*	
200	3.35	3.37
400	3.34	3.38
600	3.36	3.40
800	3.28	3.34

TABLE II

DISSOLUTION AND HYDROLYSIS OF THE CELLULOSE HYDRAZONE IN 70% SULFURIC ACID

Temperature (°)	*Time (h)*	*Observed carbonyl content (meq/100 g)*
35	1	2.39
35	2	2.34
35	3	2.33
35	4	2.33
45	1	2.37
45	2	2.32
45	3	2.23
45	4	2.20

The cellulose hydrazone can be dissolved and hydrolyzed in either hydrochloric or sulfuric acid. The differences observed between these two methods are insignificant. If this step is performed at room temperature a flocculation occurs on addition of the *p*-dimethylaminobenzaldehyde solution, hence the solution must be filtered before the spectrophotometric determination. This operation can be omitted if the sample is hydrolyzed at elevated temperature. As can be seen from Table II, the absorbance decreases significantly with time at 45°. At 35° this decrease is very small. With the cellulose samples used in the present work (cotton hydrocellulose), a clear solution is obtained when, after shaking with 70% sulfuric acid, the sample is kept at 35° for 1 h.

The conditions during the spectrophotometric determination of hydrazine are in most respects the same as those used by WATT AND CHRISP[6]. From their investigation it is seen that the acid concentration has a slight influence upon the absorbance. Variations in acid concentration (hydrochloric or sulfuric acids) of about 20% have no detectable effect upon the absorbance.

In the present work it was found that an addition of 50 mg of glucose has no influence upon the determination. Nor has cellulose dissolved in the acid any influence upon the blank test.

As is the case in other methods for the determination of carbonyl groups, the presence of carboxyl groups has to be taken into consideration. A possible interference would be an uptake of hydrazine by a cation-exchange mechanism. Experiments were carried out with a sample of mercerized and subsequently alkali-cooked (170°) cotton. The carboxyl content in the sample was 2.80 meq per 100 g of cellulose. After the reaction with hydrazine at pH 9.0 for 15 h, the sample was divided in several parts which were subjected to washing under various conditions. The results given in Table III show that washing with water gives the same results as washing with hydrochloric acid or with barium acetate. If hydrazine is taken up by the cellulose because of an ion-exchange mechanism, this part of the hydrazine is displaced during the washing with water.

TABLE III

WASHING OF ALKALI-COOKED COTTON AFTER THE REACTION WITH HYDRAZINE AT pH 9.0 FOR 15 h

Washing	*Apparent carbonyl content (meq/100 g)*	
200 ml H_2O	0.49	0.52
100 ml H_2O + 100 ml 0.004 N hydrochloric acid	0.47	0.48
100 ml H_2O + 100 ml 0.01 M barium acetate	0.49	0.51

TABLE IV

PRETREATMENT OF HYDROCELLULOSE WITH AN ALKALINE SALT SOLUTION (0.01 N NaOH CONTAINING 25 g OF NaCl PER LITER) FOR 30 h

Sample	*Carbonyl content without pretreatment (meq/100 g)*		*Carbonyl content after pretreatment (meq/100 g)*	
A	3.44	3.49	3.26	3.30
B	2.53	2.57	2.36	2.40

Another interference is the reaction of hydrazine with lactone groups (or other ester groups) to form a hydrazide. This reaction involves a more serious source of error. Experiments were carried out with the same sample of alkali-cooked cotton which, before the reaction with hydrazine, was treated with alkaline salt solution for 6 h at room temperature[8]. In two experiments the carbonyl content was found to be 0.18 and 0.20 meq per 100 g instead of 0.49 meq obtained without the pretreatment. This decrease can be explained by the saponification of ester groups during the pretreatment with alkaline salt solution, but it should be observed that with samples rich in carbonyl groups, a loss in carbonyl groups during this pretreatment may occur and introduce an error in the determination.

Experiments were carried out with a sample of hydrolyzed cotton, with and without a pretreatment with alkaline salt solution. In this experiment the time for the pretreatment was increased to 30 h. The results given in Table IV show that lower carbonyl contents were observed after the pretreatment with alkaline salt solution. The carboxyl contents in these samples are low and the decrease in the observed carbonyl content must be ascribed chiefly to a decrease in the carbonyl content during the pretreatment[7].

From the data given above, it may be concluded that carboxyl groups, if present in large amounts, can interfere seriously provided that these carboxyl groups are present as lactones or other esters[8]. Such samples should therefore be treated with alkaline salt solution to saponify the lactones before the reaction with hydrazine. It should, however, be remembered that a decrease in carbonyl content might occur (Table IV). With samples containing only small amounts of carboxyl groups or with samples containing carboxyl groups in their salt form, this pretreatment should be omitted. With samples containing large amounts of carboxyl groups as well as carbonyl groups it may be advisable to make determinations both with and without pretreatment to obtain a lower and an upper limit.

In an earlier paper[3] a comparison was made between the carbonyl content determined by the method of GEIGER AND WISSLER and the DP (determined osmotically) for mercerized cotton subjected to acid hydrolysis. It was found that the observed number of carbonyl groups per molecule was less than unity. The deviations from unity were larger for samples of a low DP. Even the sum of carbonyl and carboxyl groups was found to be less than unity. The results were explained by an incomplete penetration of GIRARD's reagent (acethydrazidepyridinium chloride). In the present work these experiments were repeated with a sample of native cotton (purified) subjected to acid hydrolysis. In addition, determinations of the carbonyl content by the proposed hydrazine method were carried out. The results given in Table V confirm that the carbonyl contents obtained by the method of GEIGER AND WISSLER correspond to less than one carbonyl group per molecule, the deviations from unity increasing for an increased time of hydrolysis. The values obtained by the proposed hydrazine method approach unity for the samples subjected to comparatively mild hydrolysis.

TABLE V

ACID HYDROLYSIS OF COTTON CELLULOSE FOR DIFFERENT PERIODS OF TIME AT 100°

Time of hydrolysis (h)	*Carbonyl groups*				$(DP)_n$		*Number of carbonyl groups per molecule of cellulose*	
	Geiger and Wissler (meq/100 g)		*Proposed method (meq/100 g)*				*Geiger and Wissler*	*Proposed method*
2	0.93	0.95	1.17	1.18	483	510	0.76	0.95
3.5	1.37	1.39	1.66	1.71	356		0.80	0.97
6	1.83	1.86	2.24	2.47	230	232	0.69	0.88
10	2.31	2.33	2.70	2.74	169	169	0.64	0.75
20	3.00	3.02	3.58	3.75	140	144	0.69	0.84

According to the generally accepted reaction scheme one carbonyl group is formed at each breakage of the cellulose chain during acid hydrolysis (see *e.g.*[3]). If the original sample contained carbonyl end groups the degraded samples should, therefore, contain one carbonyl group per molecule. The carbonyl content in the original cellulose is very low. Determinations by the proposed method indicate the presence of 0.08 meq per 100 g of cellulose. This value is, of course, rather uncertain. It is likely that a small amount of carboxyl end groups is also present in the original cellulose and that these carboxyl groups are not removed completely during acid hydrolysis. Determinations by the methods available at present are, however, very uncertain and no results from our attempts to determine the carboxyl content will, therefore, be included in this paper. It is unlikely that with hydrocellulose the proposed hydrazine method would give carbonyl values which are too high. The observation that in the least degraded samples the observed number of carbonyl end groups per molecule approaches unity indicates that the number of carboxyl end groups is small and that the reaction between the carbonyl end groups and hydrazine is complete.

With the most degraded samples the observed number of carbonyl groups is significantly lower than unity. No carboxyl groups are formed during acid hydrolysis and the number of carboxyl end groups in these samples must be very low. It may, therefore, be concluded that in these samples all carbonyl groups are not accessible to hydrazine. The values obtained by the hydrazine method are, however, higher than those obtained with GIRARD's reagent. This is explained by the smaller dimensions of the hydrazine molecule. It should be observed that in the last experiment the sample had lost its fiber structure almost completely.

The decrease in accessibility towards hydrazine and GIRARD's reagent can be compared with the accessibility of the cellulose towards acid[3,9]. The accessibility of the cotton cellulose towards acid is demonstrated in Fig. 2. It is seen that the rate of degradation decreases during the last part of the reaction, indicating that the accessibility of the cellulose chains to the attack of acid is lower than during the first part of the hydrolysis. The results indicate that some of the carbonyl groups formed during the last part of the hydrolysis are formed in areas which are not accessible to hydrazine. Another explanation of the fact that the observed number of carbonyl groups is less than unity might be that each hydrazine molecule reacts

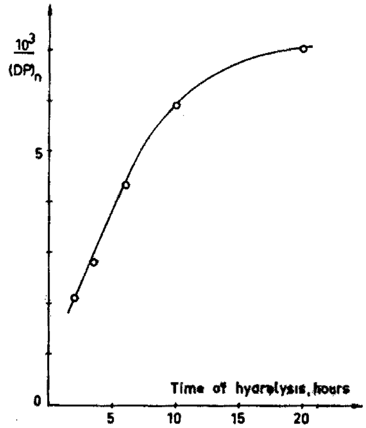

Fig. 2. Rate of degradation during acid hydrolysis illustrated by $1/(DP)_n$ *vs.* time of hydrolysis.

with more than one carbonyl group, *i.e.*, that azines may be formed. The excess of hydrazine used in these determinations is, however, so large that this type of reaction would seem less probable.

Summarizing the results presented above it can be said that the carbonyl values obtained by the proposed hydrazine method are higher than those obtained by GEIGER AND WISSLER's method. With samples of cellulose subjected to mild hydrolysis the reaction with carbonyl groups seems to be complete, whereas an incomplete reaction occurs with hydrocellulose powder.

ACKNOWLEDGEMENTS

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SUMMARY

A method is suggested for the determination of carbonyl groups in cellulose based on the reaction with hydrazine. After washing with water, the cellulose hydrazone is dissolved in sulfuric acid and hydrolyzed. The liberated hydrazine is determined colorimetrically with *p*-dimethylaminobenzaldehyde. Possible interferences from carboxyl groups are discussed.

RÉSUMÉ

Une méthode est proposée pour le dosage des groups carbonyles dans la cellulose, basée sur la réaction avec l'hydrazine. Après lavage à l'eau, l'hydrazone cellulosique est dissoute dans l'acide sulfurique et hydrolysée. L'hydrazine libérée est dosée colorimétriquement au moyen de *p*-diméthylaminobenzaldéhyde.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Carbonylgruppen in Cellulose durch Umsetzung mit Hydrazin. Nach Isolierung des Hydrazons wird dieses verseift und das frei gewordene Hydrazin mit *p*-Dimethylaminobenzaldehyd colorimetrisch bestimmt.

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DETERMINATION OF NITRATE IN SEA WATER*

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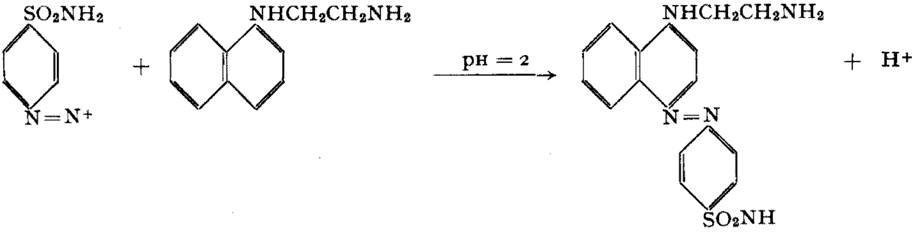
The biological importance of the nitrogen cycle in the ocean has long been recognized, but studies of the nitrate content of sea water are few owing to the lack of a simple and reliable analytical method. Attempts to develop a satisfactory technique have met with varying degrees of success. Early work by HARVEY[1] which involved the use of reduced strychnine lacked sufficient convenience and reliability. CHOW AND ROBINSON[2] developed a polarographic technique which provided sensitivity and precision, but which could not be performed on shipboard so that sea water samples had to be brought to the laboratory for analysis. They also discovered that the polyethylene bottles which were used to preserve frozen sea water samples introduced contaminants which masked the nitrate reduction polarographic wave.

MULLIN AND RILEY[3] developed the generally adopted technique involving the reduction of nitrate to nitrite with hydrazine followed by diazotization. The main disadvantage of this technique lies in the fact that the reduction must be carried out at a constant temperature for at least 8 h and a total reaction time of 20 h is required for the reduction to reach equilibrium. NELSON, KURTZ AND BRAY[4] used zinc to reduce nitrate to nitrite for the analysis of soil and plant samples. Their work was followed by MIDDLETON[5] and later by LAMBERT AND ZITOMER[6] who used the procedure to determine the nitrate content of fresh water. The present method was developed with emphasis on the determination of nitrate in sea water.

Nitrate is reduced to nitrite by zinc metal in a chilled, ammoniacal solution in the presence of manganese hydroxide.

$$NO_3^- + Zn + H_2O \xrightarrow[pH = 10,\ 0^\circ]{Mn(OH)_4} NO_2^- + Zn^{2+} + 2OH^- \qquad (1)$$

The nascent nitrite diazotizes the sulfanilamide in the solution in the usual way. At



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the end of the reduction, the excess zinc is removed, and the solution is acidified. With the addition of N-1-naphthylethylenediamine, the coupling reaction proceeds to form the diazo-dye[7].

EXPERIMENTAL

Recommended procedure

Pipette 50 ml of sea water sample into a 125-ml Erlenmeyer flask. Add 3 ml of 20% ammonia solution, 0.5 ml of 1% manganese(II) sulfate, 1 ml of 1% sulfanilamide and 0.1 g of zinc dust. Place the flask in an ice-bath and stir with a magnetic stirrer for 20 min. Adjust the stirring rate so that the zinc dust remains in suspension. At the end of the reduction, remove the excess zinc by vacuum filtration using a porosity M sintered glass funnel. Add 5 ml of 20% hydrochloric acid to the filtrate, followed by 1 ml of 0.1% N-1-naphthylethylenediamine. Maximum colour intensity develops within 15 min. Read the absorbancy of the solution at 543 mμ in a Beckman DU spectrophotometer with a 1-cm absorption cell. Determine a reagent blank by substituting nitrate-free distilled water for sea water.

DISCUSSION

Reduction temperature

In a series of controlled temperature experiments, it was observed that the reduction of nitrate was more efficient and reproducible at temperatures below 10°. This is in agreement with MIDDLETON's observation[5] that the reduction is more favourable at room temperature than at elevated temperature. It may be postulated that side reactions which compete with the nitrate–nitrite reaction are suppressed at low temperature. Since the reaction is temperature-dependent, it is recommended that the reduction be carried out in an ice-bath.

Reduction time

The time required for the reduction to reach equilibrium was examined. As shown

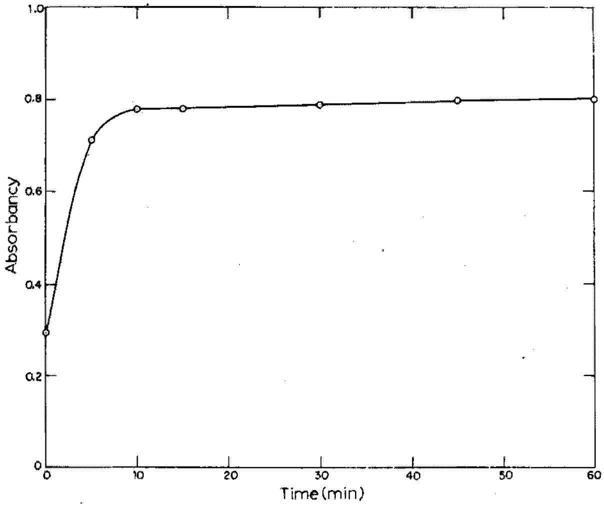

Fig. 1. Rate of nitrate reduction. 20 μg-at nitrate/l, 1-cm absorption cell.

in Fig. 1, the reduction took place as soon as the reagents were introduced and reached equilibrium after 15 min of stirring at 0°. No further increase in colour intensity was observed on prolonged stirring. To ensure complete reaction, a stirring time of 20–30 min is recommended.

Reagents

The order of introducing various reagents to the reaction flask was investigated. The sequence given in the procedure was found to yield maximum colour intensity. The effectiveness of the catalyst and the diazotizing reagent diminished when the sequence was changed. It is essential for the sulfanilamide to be in the solution during the reduction process. The nascent nitrite thus diazotizes the amine without being further reduced. The amount of ammonia added should be such that the pH of the solution is between 10 and 11. Various metallic ions were tried as the catalyst; the manganese ion proved to be most satisfactory.

Colour intensity

After reduction was complete and N-1-naphthylethylenediamine was added to the acidified solution, full colour intensity developed in about 15 min as shown in Fig. 2. However, 30 min were allowed for the chilled solution to reach the room temperature before the absorbancy was read. No appreciable colour fading was observed in 24 h when the solution was kept in the dark. The intensity deteriorated rapidly if trace amounts of zinc dust remained in the solution.

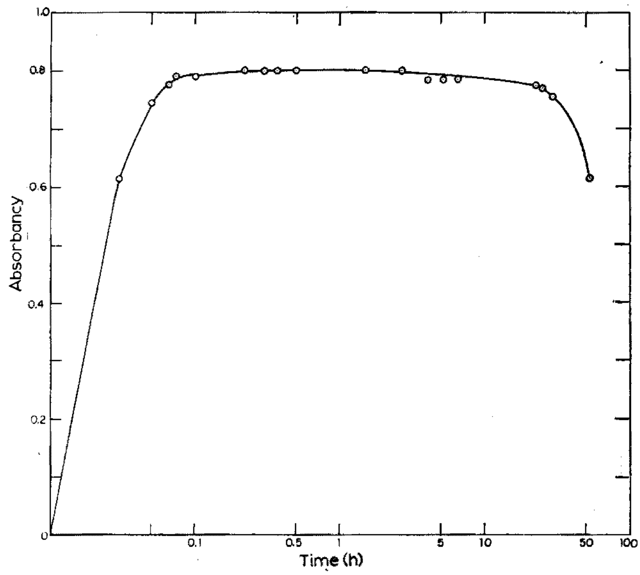

Fig. 2. Development and stability of the colour intensity. 20 μg-at nitrate/l, 1-cm absorption cell.

Reduction yield

After optimum conditions had been established for the nitrate reduction process, the reaction yield was determined (Fig. 3). By comparison of the slopes of the nitrate reduction lines with those of nitrite, the reduction yield was calculated to be 85–90%.

Calibration curve

A common practice of previous investigators has been the preparation of a synthetic sea water medium. Since most analytical grade chemicals contain trace quantities of nitrate, the reliability of the synthetic sea water is in question. In order to make the nitrate reduction independent of the chemical and physical conditions of the solutions being analysed, the standard addition method was used. The method was as follows: A series of standard solutions containing various known quantities of nitrate were

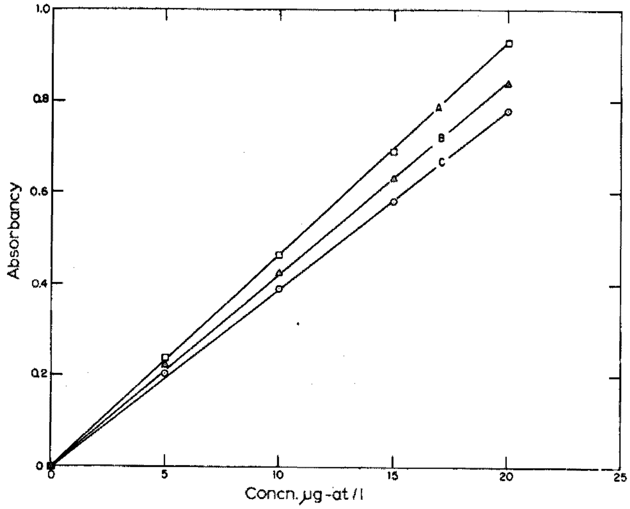

Fig. 3. Comparison of nitrate and nitrite standard curves. 1-cm absorption cell, line A: nitrite in distilled water, line B: nitrate reduction in distilled water, line C: nitrate reduction in sea water.

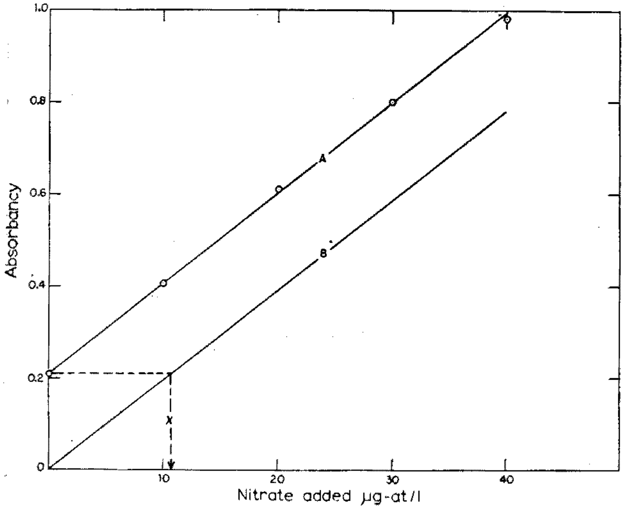

Fig. 4. Calibration curve by standard addition technique. 1-cm absorption cell.

added to equal volumes of the sea water sample to be analysed for nitrate. The nitrate reduction and diazotization were carried out as described in the procedure. The colour intensity of the resulting solutions was proportional to the nitrate in the standard plus that in the unknown. If any interfering substances existed in the solution, they would equally affect the colour intensity produced by the standard as well as by the unknown. The resulting colour intensities were plotted linearly against the concentrations of the standard solution which had been added to the unknown. The line intersecting the ordinate indicates the concentration of the nitrate in the unknown. An example is illustrated in Fig. 4. Since the graph in Fig. 4 is a straight line, $Y = a + b X$; the unknown nitrate concentration, X, is given by the ratio of Y to the slope of the line, when $a = 0$.

The present technique was applied to the analysis of sea water samples collected at various depths off the Peruvian coast during the STEP - I Expedition of the Scripps Institution of Oceanography. These results will be reported elsewhere.

STATISTICAL TEST

The statistical method of BENNETT AND FRANKLIN[8] was used to test the precision of the nitrate determination. A series of 23 consecutive duplicate analyses of sea water were selected for the test. These samples were deep waters obtained off the Peruvian coast having a nitrate concentration of from 24–50 μg-at/l. It is assumed without proof that these represent k populations with varying means, $\mu_1, \mu_2, \mu_3, \ldots \mu_k$, the values of which are unknown, and that each of the k populations has the same variance σ^2. An unbiased estimate of the variance may be obtained by:

$$s = \frac{\sum_{i=1}^{k} d_i^2}{2k} \qquad (3)$$

where d_i is the difference between duplicates in each analysis. Using eqn. (3) and the experimental data mentioned above, s^2 is calculated to be 0.685. Assuming that the observed means, $\bar{x}$, are normally distributed, 95% of the results will not differ from the true population mean by more than 2 standard deviations.

In stating the above assumption, the fact that s^2, the estimated variance, has the χ^2 distribution with k degrees of freedom has been neglected. Hence, s^2 may differ considerably from σ^2. In the case of χ^2 distribution, a large number of degrees of freedom is required in order to establish at the 95% confidence level that s^2 does not differ appreciably from σ^2. The cumbersome calculations with a large number of degrees of freedom can be avoided by rejecting all duplicate determinations that differ by greater than the mean difference plus or minus 2 standard deviations of the mean difference. With these criteria and within the range of the above data, if all duplicates which differ by 3.3 μg-at/l are rejected, the observed mean, $\bar{x}$, will not differ from the true mean, μ, by more than 1.7 μg-at/l. This value, however, exceeds the limit of reproducibility set by STRICKLAND AND PARSONS[9].

SUMMARY

Nitrate in sea water is determined by reduction to nitrite with zinc metal in ammoniacal solution in the presence of manganese(IV) as catalyst. The effects of hydrogen ion concentration, reduction temperature, reaction time and the order of reagent addition are discussed. The nascent nitrite diazotizes with sulfanilamide and is then coupled by N-1-naphthylethylenediamine in acid medium forming a diazo-dye which is measured spectrophotometrically.

RÉSUMÉ

Les auteurs ont mis au point une méthode pour le dosage des nitrates dans l'eau de mer. Elle est basée sur la réduction en nitrite, au moyen de zinc, en solution ammoniacale, en présence de manganèse(IV) comme catalyseur. Différents facteurs ont été étudiés. Le nitrite formé est déterminé spectrophotométriquement après diazotation et copulation.

ZUSAMMENFASSUNG

Zur Bestimmung von Nitraten in Meerwasser werden diese zu Nitrit reduziert, mit Sulfanilamid diazotiert und in einen Diazofarbstoff übergeführt, der spektrophotometrisch gemessen wird.

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DETERMINATION OF SMALL AMOUNTS OF URANIUM IN HAFNIUM, ZIRCONIUM AND ZIRCALOY-2

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Certain specifications for hafnium and zirconium include limiting concentrations of uranium. Initially, these specifications necessitated the provision of a satisfactory analytical procedure for determining up to 100 p.p.m. of uranium in hafnium, but subsequently, a procedure was required for determining less than 5 p.p.m. of uranium in hafnium, zirconium and Zircaloy-2.

Published methods for determining small amounts of uranium in hafnium and/or zirconium depend on the separation of uranium by liquid–liquid extraction[1,2] followed by a fluorometric determination, *i.e.* a procedure in which an aliquot of the uranium extract is fused with a fluoride flux and the resulting bead is caused to fluoresce in ultraviolet light. In this procedure, the fusion conditions must be critically controlled and trace amounts of numerous elements cause "quenching" of the fluorescence. Further, relatively expensive fluorometric equipment is required. An alternative method was, therefore, desirable.

For determining uranium in other materials, various spectrophotometric methods have been proposed; these include procedures based on the formation of complexes between uranium and thiocyanate[3], hydrogen peroxide[4], ferrocyanide[5] and dibenzoylmethane[6]. Of these, the dibenzoylmethane reaction is the most sensitive and has been applied by FRANCOIS[6] to the analysis of ores, following separation of uranium by extraction of the sample solution, containing added aluminium nitrate, with a tri-*n*-butyl phosphate–iso-octane mixture (TBP/IOM). Polarographic methods are also available for determining small amounts of uranium, again after a preliminary chemical separation[7,8].

From this available information, a combined extraction/spectrophotometric procedure, similar to that used by FRANCOIS, appeared to be suitable for the determination of uranium in hafnium, at the 20/100 p.p.m. level, and tests were made accordingly. With the subsequent introduction of a maximum specification limit of 5 p.p.m. of uranium in hafnium, zirconium and Zircaloy-2, the possibility of completing the determination by means of a square-wave polarograph was also investigated.

EXPERIMENTAL

(1) *Spectrophotometric determination of uranium ($<$100 p.p.m.) in hafnium*

A calibration graph was prepared, in the absence of hafnium, using colour development conditions similar to those recommended by FRANCOIS, but with uranium over a lower range, *viz.* 10 to 80 μg (equivalent to 20–160 p.p.m., calculated on a 0.5 g sample). In these initial tests, the TBP/IOM extraction was omitted. Optical densities were measured at 4100 Å using 4 cm cells, and a linear graph was obtained, with an optical density of 0.2, equivalent to 40 p.p.m. of uranium; the optical density of the reagent blank was 0.01.

Further tests indicated that extraction of the uranium (10 to 80 μg), with TBP/IOM, from a saturated aluminium nitrate solution, followed by development of the characteristic uranium–dibenzoylmethane colour, referred to earlier, was 99–100% efficient. The optical density of the reagent blank in this series of tests, was about 0.03.

Solutions containing 10 to 80 μg of uranium were next added to platinum dishes, each containing 0.5 g of hafnium, and the samples were dissolved in dilute hydrofluoric acid. Each solution was oxidised with concentrated nitric acid, evaporated to dryness on a boiling water bath to remove excess hydrofluoric acid (which had been shown to give rise to incomplete recovery of uranium), and the residue was dissolved in 1 drop of hydrofluoric acid and 5 ml of water. A saturated aluminium nitrate solution was added, and uranium was extracted and determined as before. Recoveries were identical with those obtained in similar tests in the absence of hafnium. (In the recommended method, the details are essentially those used in these preliminary experiments, although the method of dissolving the sample and subsequent oxidation are modified.)

Conditions for extraction and colour development

FRANCOIS states that "99% of the uranium is extracted when the pH of the aqueous phase is between 3 and 6". Tests under his recommended experimental conditions[6], however, showed that the extraction is actually made from a solution of about pH 1.5 and, as modified for application to the analysis of hafnium, the pH was about 1.0. This had no adverse effect on the recovery of uranium.

According to FRANCOIS, development of the uranium–dibenzoylmethane colour is complete within 1 h but, during the present investigation, tests indicated that complete colour development was obtained within 15 min.

Solutions containing 0.5 g of hafnium and 2.5 mg (equivalent to 0.5%) of each of the following metals, added separately, were carried through the proposed method and no interference was observed: chromium, copper, iron, lead, manganese, molybdenum, nickel, silicon, tin, titanium and tungsten.

Spectrophotometric method
(Uranium over the range 10–150 p.p.m. in hafnium)

Special reagents

Standard uranium solution. Dissolve 0.4219 g of $UO_2(NO_3)_2 \cdot 6H_2O$ in about 50 ml of nitric acid (1:4) and dilute to 1 l (1 ml = 0.2 mg U). Dilute 100 ml of this solution to 1 l (1 ml = 0.02 mg U).

Aluminium nitrate solution. Dissolve 900 g of $Al(NO_3)_3 \cdot 9H_2O$ in about 500 ml of hot water. Cool and dilute to 1 l.

m-*Cresol purple indicator solution.* Dissolve 0.1 g of the reagent in 50 ml of water containing 2.62 ml of sodium hydroxide (0.1 N) and dilute to 100 ml.

Tri-n-butyl phosphate solution (5%) *-TBP/IOM.* Dilute 5 ml of tri-*n*-butyl phosphate to 100 ml with iso-octane.

Dibenzoylmethane solution. Dissolve 1 g of the reagent in 100 ml of acetone.

Chromogenic reagent. To 17.5 ml of dibenzoylmethane solution, add 800 ml of acetone and 45 ml of pyridine, and dilute to 1 l with water.

Preparation of calibration graph

Add, separately, 0.5, 1.0, 2.0, 3.0, and 4.0 ml of the standard uranium solution (1 ml = 0.02 mg U, equivalent to 40 p.p.m. on 0.5 g sample) to five 30-ml beakers and dilute each solution to 5 ml. To each, and a blank (5 ml of water), add 1 drop of hydrofluoric acid (40% w/w) and 1 drop of *m*-cresol purple indicator solution, followed by ammonium hydroxide (sp. gr. 0.91) dropwise, until the colour of the solution changes from red to orange. Immediately, add 1 drop of hydrofluoric acid (40% w/w) and swirl to dissolve any precipitate which may have formed. Add 10 ml of the aluminium nitrate solution and transfer to a separating funnel (100 ml). Add 3.0 ml of TBP/IOM and shake for about 1 min. Allow the two layers to separate, then run off and discard the aqueous layer. Transfer the organic layer to a dry 10-ml measuring cylinder, pipette 2.0 ml into a 25-ml calibrated flask and dilute to the mark with chromogenic reagent. Mix well and allow to stand for about 15 min.

Determine the optical densities at a wavelength of 4100 Å using 4 cm cells. Use the chromogenic reagent as the reference solution.

Procedure

With each batch of samples, a reagent blank must be determined. To 0.5 g of the sample (for amounts of uranium above 150 p.p.m., use a smaller sample weight) in a platinum dish (100 ml), add 2 ml of water, 10 ml of methanol and about 2 ml of hydrofluoric acid (40% w/w), added dropwise. When the sample has dissolved, add a further 5 ml of methanol, oxidise with liquid bromine (about 0.5 ml) and evaporate to dryness on a boiling-water bath. Cool the residue, add 1 drop of hydrofluoric acid (40% w/w) and 5 ml of water; swirl to dissolve, add 1 drop of *m*-cresol purple indicator solution, and continue as described for preparation of the calibration graph.

Calculate the uranium content of the sample using the calibration graph.

Application

The method was successfully applied to several samples of reactor-grade hafnium, with and without additions of uranium; typical results are shown in Table I.

TABLE I

RECOVERY OF URANIUM FROM REACTOR-GRADE HAFNIUM

Sample no.	*Uranium (p.p.m.)*		
	Added	*Recovered*	
1	Nil	<10	<10
	40	45	40
	80	80	85
	160	165	165
2	Nil	<10	<10
	40	40	40
	80	80	75
	160	160	155

(2) *Polarographic determination of uranium (<5 p.p.m.) in hafnium, zirconium and Zircaloy-2*

(*a*) *Polarography*

Uranyl ions produce well-defined waves in a variety of supporting electrolytes[9,10]. Tests indicated that sufficient sensitivity could be obtained with a Mervyn-Harwell square-wave polarograph, to determine 0.25 to 2.5 µg of uranium in 2.0 ml of 0.25 *M* nitric acid as supporting electrolyte. Copper in the distilled water initially used in preparing the electrolyte produced a large wave at about -0.4 V, which distorted the uranium wave; this effect was avoided by passing the distilled water through a deioniser.

Polarograms were recorded on de-oxygenated solutions over a voltage range from -0.35 to -1.0 V (*vs.* mercury-pool anode) and well-defined waves, proportional to the amounts of uranium added, were obtained at -0.49 V. With 1/4 sensitivity, a wave height of about 90 mm was recorded with 2.0 µg uranium.

(*b*) *Extraction*

Solutions containing only uranium in the range 0.25 to 2.5 µg (0.5 to 5 p.p.m., calculated on a 0.5 g sample) were extracted with TBP/IOM as described previously. Uranium was back-extracted from the solvent with deionised water; the aqueous extracts were then evaporated to dryness with perchloric and nitric acids. Residues were dissolved in 2.0 ml of 0.25 *M* nitric acid and solutions were examined polarographically. In these tests, the uranium wave occurred at about −0.58 V, and this shift in half-wave potential was attributed to the presence of perchlorate in the residue. Recovery of uranium was about 98% and similar recoveries were obtained when uranium (0.25 to 2.5 μg) was extracted from solutions containing the equivalent of 0.5 g of hafnium; these hafnium solutions were prepared in precisely the same way as those used in the spectrophotometric method.

In tests using solutions containing 0.5 g of zirconium, sparingly soluble residues were obtained after evaporating the sample solution, but this difficulty was overcome by carefully controlling evaporation of the sample solution at 60–65° for about 4 h, and allowing the resulting residue to stand overnight at room temperature. To facilitate solution of the sample and reduce the time required for evaporation at 60–65°, samples were dissolved in a mixture of 2 ml of hydrofluoric acid and 10 ml of methanol, then oxidised with liquid bromine, instead of nitric acid. With these modifications to the procedure, the residue dissolved readily in 1 drop of hydrofluoric acid and 5 ml of water, and recoveries of uranium were about 98%.

Effect of other metals

Tests showed that solutions containing the equivalent of 2% tin, 0.2% chromium or iron, 0.1% nickel or 1% copper, separately added to 0.5 g samples of zirconium, caused no interference when carried through the entire procedure.

When more than 200 p.p.m. of molybdenum (as ammonium molybdate) was present, a small amount of molybdenum was extracted with the uranium, and this produced a wave which coalesced with the uranium wave. This interference, however, was avoided by incorporating a preliminary extraction of molybdenum(VI) with iso-amyl acetate, from 5–6 *N* hydrochloric acid[11].

Although some loss of uranium occurred using this modified procedure (uranium recoveries were consistently about 70%), satisfactory results could be obtained by reference to a standard examined under identical conditions. The molybdenum content of reactor-grades of hafnium, zirconium and Zircaloy-2, however, is usually less than 10 p.p.m. and its separation is therefore unnecessary.

Polarographic method

(*Uranium over the range 0.5–5 p.p.m. in hafnium, zirconium and Zircaloy-2*)

Special reagents (see also Spectrophotometric method)

Throughout, use water which has been distilled, then deionised. All reagents must be of a very high order of purity, *e.g.* hydrofluoric acid (40% w/w), transistor grade.

Standard uranium solution. Dilute 50 ml of the standard uranium solution (1 ml = 0.02 mg U) to 1 l (1 ml = 1 μg U).

Procedure

With each batch of samples, include a reagent blank and a control prepared by adding 2.0 ml of uranium solution (1 ml = 1 μg U, equivalent to 2 p.p.m. on a 0.5 g sample) to a duplicate of one of the samples.

Dissolve 0.5 g of the sample as described in the spectrophotometric procedure; do not add 2 ml of water to the control. After oxidation, evaporate the solution to dryness; in the examination of hafnium samples, solutions may be evaporated on a boiling water bath, but solutions containing zirconium must be evaporated on a water bath controlled at 60–65°, for at least 2 h. Residues from zirconium solutions must be left overnight, but those from hafnium solutions may be proceeded with immediately after evaporation. To the residue, add one drop of hydrofluoric acid (40% w/w) and 5 ml of water; swirl to dissolve. Add one drop of *m*-cresol purple indicator solution then ammonium hydroxide (sp. gr. 0.91) dropwise, until the colour of the solution changes from red to orange. Add one drop of hydrofluoric acid (40% w/w) and swirl to dissolve any precipitate which may have formed.

Using a minimum amount of water, transfer the solution to a dry 60-ml polythene bottle, then wash the platinum dish with two 5 ml portions of the aluminium nitrate solution; add these to the solution in the bottle. Add 3.0 ml of TBP/IOM and shake on a mechanical shaker for 10 min.

Transfer the solution to a dry 100-ml separating funnel and allow the layers to separate. Run off and discard the aqueous layer. Transfer the organic layer to a dry 10-ml measuring cylinder and pipette 2.0 ml into a dry 100-ml separating funnel (this ensures that no aqueous solution is removed with the 2-ml aliquot). Add 10 ml of water and shake for 1 min. Allow the layers to separate, then run off the aqueous layer into a platinum dish; wash down the stem of the funnel, and repeat the extraction with a further 5 ml of water. To the solution in the dish, add 1.5 ml of nitric acid (sp. gr. 1.42) and 1.5 ml of perchloric acid (sp. gr. 1.54), then evaporate to dryness under a radiant heater, *i.e.* until fumes of perchloric acid cease to be evolved.

Add 2.0 ml of 0.25 M nitric acid, warm the dish to dissolve the residue, and transfer the solution to a polarographic cell. Bubble argon through the solution for about 2 min, and prepare a polarogram at 25°.

Suitable conditions, using a Mervyn-Harwell square-wave polarograph are as follows:

Start potential	–	−0.35 V
Scan rate	–	3
Sensitivity	–	$^1/_2$ or $^1/_4$ (For uranium content greater than 5 p.p.m. use a lower sensitivity)

The half-wave potential of uranium occurs at about −0.58 V (*vs.* mercury-pool anode).

Measure the wave height and calculate the uranium content of the sample by reference to the wave height of the control.

Application

The proposed polarographic method was successfully applied to the analysis of reactor-grades of hafnium, zirconium and Zircaloy-2 (zirconium/1.5% Sn/0.12% Fe/0.1% Cr/0.05% Ni) with and without additions of uranium (Table II), and the uranium content of these materials was found to be in the range <0.5 to about 2 p.p.m.

The standard deviation was shown to be about 0.03 p.p.m. at the 1 p.p.m. uranium level.

Results obtained on samples of Zircaloy-2 using the proposed method were compared with those obtained by the fluorometric procedure; these are shown in Table III. It can be seen that at the higher levels of uranium, better reproducibility was obtained using the recommended polarographic method.

TABLE II

POLAROGRAPHIC DETERMINATION OF URANIUM IN HAFNIUM, ZIRCONIUM AND ZIRCALOY-2

Sample no.	*Nominal composition*	*Uranium (p.p.m.)*			
		Added	*Recovered*		
1	Hafnium	Nil	0.3		0.4
		1.0	1.3		1.3
		2.0	2.2		2.3
		4.0	4.4		4.2
2	Reactor-grade zirconium	Nil	0.2		0.2
		1.0	1.0		1.1
		2.0	2.1		2.1
		4.0	4.0		4.0
3	Zircaloy-2 (zirconium/1.5% Sn/0.12% Fe/0.1% Cr/0.05% Ni)	Nil	0.80	0.80	0.85
		1.0	1.8	1.9	1.7
		2.0	2.7	2.8	2.8
		4.0	4.6	4.7	4.6
4	Zircaloy-2	Nil	1.3		1.5
		1.0	2.5		2.3
		2.0	3.2		3.4
		4.0	5.3		5.4

TABLE III

URANIUM IN ZIRCALOY-2 BY POLAROGRAPHIC AND FLUOROMETRIC METHODS

Sample no.	*Uranium (p.p.m.)*								
	Fluorometric method					*Polarographic method*			
1	0.7	0.7		0.7	0.8	0.65	0.7	0.7	0.7
2	1.9	2.1	2.1	2.8	2.0	2.0	1.9	1.9	2.0
3	44	33	34	25	47	51	53	53	54

CONCLUSIONS

A procedure based on preliminary extraction of uranyl ions with tri-*n*-butyl phosphate–iso-octane mixture and spectrophotometric determination of uranium using dibenzoylmethane, has been shown to be suitable for determining uranium from about 10 to 150 p.p.m. in hafnium. This procedure should also be suitable for determining uranium above about 10 p.p.m., in zirconium-base and other metallurgical materials, provided that in the examination of zirconium-base samples the sample solution is evaporated under carefully controlled conditions to avoid the formation of sparingly soluble residues. Chromium, copper, iron, lead, manganese, nickel, silicon, tin, titanium and tungsten each up to at least 0.5% do not interfere.

For the determination of smaller amounts of uranium, down to about 0.5 p.p.m. in hafnium, zirconium and Zircaloy-2, a method based on the use of a square-wave polarograph following the TBP/IOM extraction is recommended. In applying this procedure to samples containing molybdenum, a preliminary separation of molybdenum is necessary; this leads to a reduction in the recovery of uranium, from 98% to about 70%, but provided that a control solution is carried through the entire procedure, a compensation can be made and satisfactory results obtained.

Tests have shown that the uranium content of reactor-grades of hafnium, zirconium and Zircaloy-2 is usually in the range <0.5 to 2 p.p.m.

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SUMMARY

To meet specification requirements, selected methods for determining uranium have been examined and two satisfactory procedures have been developed for application to the analysis of reactor-grades of hafnium, zirconium and Zircaloy-2.

These procedures are based on extraction of uranyl ions from a solution of the sample with a tri-*n*-butyl phosphate–iso-octane mixture. Following this extraction, uranium over the range 10–150 p.p.m. is determined by a spectrophotometric method, using dibenzoylmethane. For smaller amounts of uranium, down to about 0.5 p.p.m., the determination is completed by square-wave polarography.

RÉSUMÉ

Deux méthodes ont été mises au point pour le dosage de l'uranium, en faible teneur, dans l'hafnium, le zirconium et le Zircaloy-2. Elles sont basées sur l'extraction des ions uranyle dans un mélange tributyl-phosphate/isooctane. L'uranium est ensuite dosé spectrophotométriquement au moyen de dibenzoylméthane ou par polarographie à ondes carrées.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Bestimmung von kleinen Mengen Uran in Hafnium, Zirkonium und Zircaloy-2 durch Extraktion mit Tributylphosphat. Kleinere Mengen als 10 p.p.m. werden polarographisch, Mengen von 10–150 p.p.m. spektrophotometrisch mit Dibenzoylmethan bestimmt.

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with synthetic standards prepared from strontium-free calcium carbonate and orthophosphoric acid solution.

Reagents

Hydrochloric acid, concentrated, d. 1.16.

Calcium carbonate, strontium-free, dried to constant weight at 100°.

Strontium carbonate, dried to constant weight at 100°.

Orthophosphoric acid, d. 1.75, 90% H_3PO_4.

Whenever possible reagents should be of AnalaR quality and the use of redistilled or demineralised water is implied throughout.

Standards

Master standards: *Strontium, 1000 p.p.m.* Weigh 0.169 g of strontium carbonate into a beaker, cover with 10–20 ml of water and add concentrated hydrochloric acid dropwise until dissolved. Make up to 100 ml with water to give a master solution containing 1000 p.p.m. of strontium. Dilute this master solution as necessary to give working standard solutions.

Calcium, 1%. Weigh 4.994 g of calcium carbonate (strontium-free) into a beaker, cover with 10–20 ml of water and dissolve in just sufficient concentrated hydrochloric acid. Make up to 200 ml with water.

Orthophosphoric acid, 1.63%. Weigh 3.62 g of orthophosphoric acid (90% H_3PO_4) into a beaker and make up to 200 ml with water.

Working standards: *Blank solution*. Measure 10 ml of the 1% calcium solution into a 100-ml flask, and add 5 ml of concentrated hydrochloric acid and 10 ml of the 1.63% phosphoric acid solution. Make up to 100 ml with water.

1000 p.p.m. strontium with respect to calcium solution. Proceed as for the preparation of the blank solution above, but before making up to 100 ml add 10 ml of 10 p.p.m. strontium solution. Additional standards for use in constructing a calibration curve are prepared in a similar way.

Preparation of sample

Dissolve 25.8 mg of the sample in 0.5 ml of concentrated hydrochloric acid and 1 ml of water, heat if necessary and allow to cool. Make up to 10 ml with water.

Flame photometry

Adjust the flame photometer for optimum operating conditions at 4607.3 Å (for a full description of the flame photometer and detailed operating instructions see ref. [2]). Obtain duplicate readings for each sample solution in turn and repeat to obtain a total of eight readings. Calculate the mean and read the strontium to calcium ratio from the calibration curve (Fig. 5).

ACCURACY AND REPRODUCIBILITY

The accuracy of the method was assessed by analysing samples the strontium content of which had already been determined by the techniques of neutron activation, emission spectroscopy and X-ray fluorescence. As can be seen from Tables II and III no significant bias was evident. An additional check on accuracy was obtained by a purified product by three-fold recrystallization from dimethylformamide yielded light yellowish white needles decomposing above 310°. (Calculated for $C_{18}H_{12}O_2N_2$: C, 75.00%; H, 4.17%; N, 9.37%; Found: C, 74.35, 74.59%; H, 4.29, 4.17%; N, 9.34, 9.22%.)

Preparation of coordination polymers

An equimolar mixture of (I) and the appropriate metal acetate was refluxed in dimethylformamide in a nitrogen atmosphere at 130–140° for 5–6 h. The hot reaction mixture was then filtered and the precipitate was treated with boiling water and alcohol, washed with ethyl ether and dried under vacuum over boiling acetone (56°) for 12 h. The dried product was then kept in a desiccator until submitted for analysis.

Analysis of the polymers

Analyses of the polymers for carbon, hydrogen and nitrogen were made by Galbraith Laboratories, Inc., Knoxville 21, Tennessee. Analyses of the metal contents of the polymers were performed by usual EDTA titration with the exception of copper which was done by conventional iodometry. Results of the analyses are reported in Table I.

TABLE I

COMPOSITION OF POLYMERIC COMPOUNDS ON THE BASIS OF STRUCTURE (II)

Polymer	*Carbon%*		*Hydrogen%*		*Nitrogen%*		*Metal%*	
	calc.	*found*	*calc.*	*found*	*calc.*	*found*	*calc.*	*found*
Copper	61.79	60.67 60.68	2.86	2.98 3.17	8.01	7.69 7.80	18.17	18.16 18.11
Zinc	61.47	57.28 57.04	2.85	2.89 3.02	7.97	7.26 7.29	18.61	18.67 18.69
Cobalt	62.63	55.31 55.46	2.90	3.85 3.80	8.12	7.25 7.20	17.10	14.11 14.23
Nickel	62.66	55.58 55.38	2.90	3.70 3.61	8.12	7.33 7.12	17.03	13.13 13.17
Manganese	63.37	58.86 59.06	2.93	3.28 3.54	8.22	7.84 7.63	16.12	14.99 14.89
Cadmium	54.22	50.65 50.48	2.51	2.24 2.43	7.04	6.51 6.33	28.21	30.34 30.45

Thermal stability studies of the polymers

Thermal stability studies were made on all the polymers of (I) by heating samples in small pyrex test tubes at various temperatures in air. The tubes were removed at intervals, cooled in a desiccator over phosphorus pentoxide and infrared spectra recorded. Observations are summarized in Table II.

X-ray studies of the polymers

X-ray powder diffraction patterns of the polymer samples were recorded photographically with a cylindrical camera and also by using a diffractometer with a recorder. The instrument used was a Norelco X-ray Spectrograph of Philips Electronic Instruments.

TABLE II

THERMAL PROPERTIES OF POLYMERIC COMPOUNDS

Polymer	*Temp.(°) range in which polymer changes color*	*Color change*	*Approx. weight loss in 1 h at 300° in air (%)*
Copper	280–310	red brown to dark brown to black	15–16
Zinc	300–325	yellow to reddish yellow	3–4
Cobalt	250–300	light brown to dull brown to black	15–16
Nickel	250–300	brown to dull brown to black	10–11
Manganese	250–300	dull green to black	14–15
Cadmium	300–350	light yellow to dark yellow to brownish yellow	4–5

Spot Test Procedure

A 0.1% solution of (I) in dimethylformamide was used as reagent solution. To 1 drop of the test solution on a spot plate were added 2 drops of acetic acid–acetate buffer and 2 drops of the reagent solution. Results of the tests are shown in Table III.

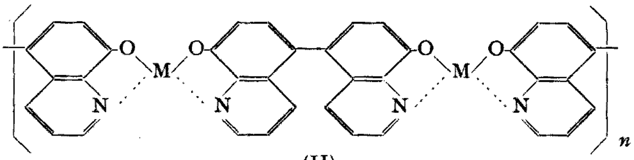
TABLE III

SPOT TEST OF METAL IONS WITH 8,8′-DIHYDROXY-5,5′-BIQUINOLYL

Metal ions	*Color of precipitate*	*Identification limit in μg*
Gold(III)	yellowish black	5
Aluminum(III)	yellow	10
Cobalt(II)	yellow	3
Cadmium(II)	yellow	10
Iron(II)	greenish black	20
Iron(III)	greenish black	20
Gallium(III)	yellow	2
Lead(II)	yellow	50
Manganese(II)	yellow	50
Mercury(II)	orange yellow	4
Zinc(II)	yellow	5
Copper(II)	brown-yellow	4
Uranyl(II)	brownish-yellow	5
Nickel(II)	yellow	3

DISCUSSION

Polymers of (I) with Cu(II), Zn(II), Co(II), Ni(II), Mn(II) and Cd(II) were formed by chelation. Presumably, polymerization of (I) with divalent metals would give polymers of the type represented below:



(II)

The infrared spectra of (I) and the various derived polymers were recorded on solid samples of the compound in potassium bromide discs. The spectra of these compounds show positive evidence for the chelation of (I) with metals and are all quite similar between 5 and 12 μ (2000–830 cm^{-1}) in general resembling one another more closely than they do the spectrum of (I). The strong absorption at about 1115 cm^{-1} (9 μ), which has been attributed to vibrations of the M-O-C$<$ bond of the chelates of 8-hydroxyquinoline by CHARLES *et al.*[4], was observed at about 1125 cm^{-1} in all the polymers of (I). The —C=N— vibration of the quinoline ring was found in the region 1580–1600 cm^{-1}. In the chelated species this band is displaced to 1565–1575 cm^{-1}.

The polymers precipitated almost immediately when the dimethylformamide solution of (I) was added to the appropriate metal acetate solution in dimethylformamide. All polymers obtained were powders, very insoluble in the common organic solvents, and most probably were of low molecular weight since their great insolubility would remove them from solution before a high degree of polymerization was reached. The insolubility of these compounds prevented a verification of molecular weights by the usual procedures.

TABLE IV

COMPOSITION OF POLYMERIC COMPOUNDS OF COBALT, NICKEL AND MANGANESE ON THE BASIS OF TWO WATER MOLECULES PER METAL ATOM

Polymer	*Carbon%*		*Hydrogen%*		*Nitrogen%*		*Metal%*	
	calc.	*found*	*calc.*	*found*	*calc.*	*found*	*calc.*	*found*
Cobalt	56.71	55.31 55.46	3.71	3.85 3.80	7.35	7.25 7.20	15.46	14.11 14.23
Nickel	56.75	55.58 55.38	3.71	3.70 3.61	7.36	7.33 7.12	15.41	13.13 13.17
Manganese	57.30	58.86 59.06	3.75	3.28 3.54	7.43	7.84 7.63	14.56	14.99 14.89

From the results in Table I it is evident that only in the case of the polymer of (I) with copper is the degree of polymerization comparatively large. Higher percentages of metal in the case of zinc and cadmium polymers of (I) show the degree of polymerization to be low in the resulting compound. In the case of the polymers of (I) with cobalt, nickel and manganese lower values in the elemental analyses than those calculated for a 1:1 compound show the polymerization coefficient[5] to be between 4 and 10.

Agreement between calculated and found analytical values for the 1:1 compounds can be greatly improved if it is presumed that there is water associated with the polymers. Such an association of water in coordination polymers of naphthazarine with cobalt has been reported by BAILS AND CALVIN[6]. In the case of nickel, cobalt and manganese polymers this is expected because of their strong affinity for water molecules and also their maximum coordination number six. Thus if 2 moles of water are considered to be associated per metal atom in the structure of these polymers, the elemental results are greatly improved for a 1:1 compound (Table IV).

From our study we believe that some monomers, dimers, etc. occur along with the polymer product. We arrived at this conclusion because simple monomers could not be made by controlling the metal-ligand ratio in the preparation. Thus the percentage calculated for a 1:1 compound or polymer is 18.17: that for a 1:2 compound, 9.97. Analyses showed that the product of the 1:1 preparation contained 18.16 and

18.11% copper and that of the 1 : 2 preparation 12.90 and 12.88% copper. Because of their high decomposition ranges (Table II), and high insolubility in common organic solvents, these compounds could not be purified by ordinary methods. This further complicates the analytical results.

X-ray examinations of the coordination polymers of (I) have shown that the polymers containing cobalt and nickel are amorphous, whereas copper-, zinc-, manganese- and cadmium-containing polymers are crystalline. Fig. 1 shows the X-ray powder photograph of the polymer of (I) with copper as an example.

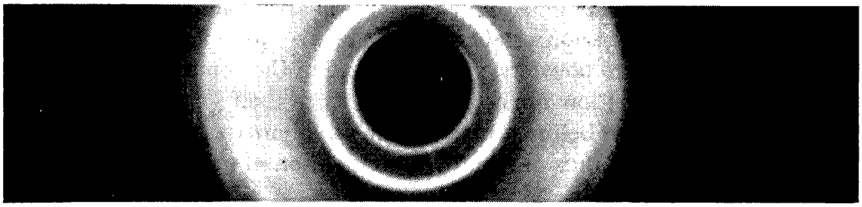


Fig. 1. Powder X-ray pattern of polymer of 8,8'-dihydroxy-5,5'-biquinolyl with copper.

Spot tests of metal ions with dimethylformamide solutions of (I) show a wide precipitation ability of the reagent in acetic acid–acetate buffer (Table III). Like 8-hydroxyquinoline this reagent is not specific. However, its selective action possibly could be enhanced by careful adjustment of the pH values and by judicious use of masking agents.

The thermal behaviour of these polymers is shown in Table II. It was expected that the coordination polymers would be thermally more stable than the organic reagent, but this property was not apparent in any of these polymers. From the data it appears that the coordination polymers of (I) begin to decompose between 250 and 300°. This has been verified from infrared spectra recorded before and after heating the samples.

An attempt was made to prepare a polymer of (I) with zinc(II) by a melt polymerization reaction with zinc acetylacetonate under vacuum at 220–230°, but the attempt was not successful. A yellow compound was obtained which contained 45.80% carbon, 3.21% hydrogen, 4.16% nitrogen and 23.48% zinc. The composition of the expected 1 : 1 compound is shown in Table I.

SUMMARY

Coordination polymers of 8,8'-dihydroxy-5,5'-biquinolyl(I) with Cu(II), Zn(II), Cd(II), Ni(II), Co(II) and Mn(II) were prepared and studied. The polymers were all powders, very insoluble in all the common organic solvents, apparently of low molecular weight and all began to decompose between 250–300°. The polymers of cobalt and nickel were amorphous, whereas the polymers of copper, zinc, cadmium and manganese were crystalline. Infrared.studies confirmed the chelation reaction between metal and (I). As a spot test reagent, (I) gave instant color reactions with 14 common ions but the sensitivity of the reagent is not particularly impressive. The most interesting result is the detection of 2 μg of gallium.

RÉSUMÉ

Les auteurs ont effectué une étude sur la préparation et les propriétés des complexes de la dihydroxy-8,8'-biquinolyle-5,5', avec le cuivre, le zinc, le cadmium, le nickel, le cobalt et le manganèse. Les réactions obtenues sont peu sensibles et peu sélectives. Le résultat le plus intéressant est la détection de 2 μg de gallium.

ZUSAMMENFASSUNG

Es werden die Herstellung und Eigenschaften der Koordinations-Polymeren von 8,8'-Dihydroxy-5,5'-dichinolyl mit Cu(II), Zn(II), Cd(II), Ni(II), Co(II) und Mn(II) beschrieben. Aehnlich dem 8-Hydroxychinolin ist das Reagenz wenig spezifisch. Als interessant wird der Nachweis von 2 μg Gallium angegeben.

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SPECTROPHOTOMETRIC OR ABSORPTIOMETRIC DETERMINATION OF COPPER WITH 2,2'-DIAMINODIETHYLETHER-N,N,N', N'-TETRA-ACETIC ACID*

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Many colorimetric reagents are available for the determination of copper but few of these are entirely satisfactory; the conventional reagents such as sodium diethyldithiocarbamate generally require an extraction process before the spectrophotometric measurement[1]. Recently, LINDLEY[2] has proposed a method in which hydrochloric acid is added and the chlorocuprate complex formed is measured at 950 mμ.

Polyaminopolycarboxylic acids have been recommended for the spectrophotometric determination of copper on several occasions. NIELSCH AND BOLTZ[3] suggested EDTA, the copper complex of which absorbs strongly at 700–750 mμ. This has been utilized for the determination of copper in aluminium alloys[4]; other elements present in such alloys do not interfere except for large amounts of iron, cobalt or nickel (which are not commonly found). A more sensitive method is possible with 1,2-diaminocyclohexanetetraacetic acid (DCTA); 10–540 μg copper per ml can be determined, the complex absorbing about twice as strongly as that of EDTA[5]. Similar sensitivity can be achieved with ethyleneglycol bis(β-aminoethylether)-tetraacetic acid (EGTA)[6].

In a preliminary study of the reactions of 2,2'-diaminodiethylether-N,N,N',N'-

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* Part XXXI of Analytical Applications of EDTA and Related Compounds.

tetraacetic acid (EEDTA) with several coloured ions[7], it was observed that the normal blue colour of aqueous copper solutions became much more intense in the presence of EEDTA. A detailed examination of the reaction has allowed the development of a new spectrophotometric determination of copper which has several advantages over previous procedures.

The polyaminopolycarboxylic acids have great advantages as colorimetric reagents; they act by deepening the colour of the ion and most interfering ions are simultaneously masked. Moreover, a large excess of reagent does not usually affect the absorbance of the solution.

Absorbance curve of the copper–EEDTA complex

The absorbance curve of the complex formed in aqueous solution was determined at different pH values. An aliquot of copper sulphate solution was transferred to a 25-ml volumetric flask, 2 ml of 5% EEDTA solution was added and the pH was adjusted to the required value by addition of hydrochloric acid or ammonium hydroxide using a Beckman model G pH meter. The solution was then diluted to volume (the final copper concentration was 324 μg Cu/ml) and the absorbance was measured against a similarly prepared blank in 1-cm Corex cells at 18° on a Beckman DU spectrophotometer.

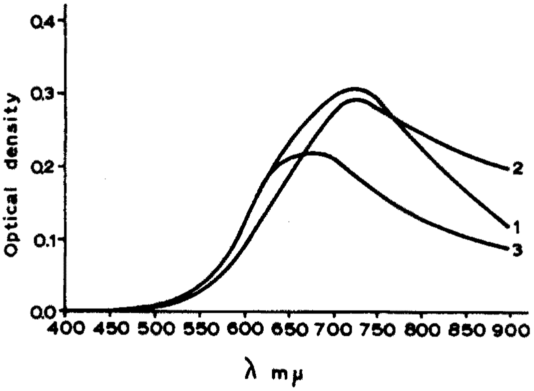

Fig. 1. Absorption curve of the copper–EEDTA complex. 1, pH 2.00; 2, pH 4.50; 3, pH 10.00.

The curves obtained are shown in Fig. 1. It can be seen that in alkaline medium, there is an absorbance band at about 680 mμ, which is displaced to higher wavelengths as the pH is decreased. Maximum absorbance is shown at about 720 mμ in acidic medium. Thus for an absorptiometric determination with a Spekker absorptiometer, a filter such as the Ilford No. 608, should be used.

Effects of pH, excess of reagent, temperature and time

The effect of pH on the absorbance of the copper–EEDTA complex was studied at a copper concentration of 210 μg/ml using a Spekker absorptiometer and 1-cm cells. Measurements were made against distilled water at 18°. The optical density remained steady at about 0.15 from pH 0.8 to 3.0 and then decreased slightly becoming constant again over the pH range 5.0 to 11.0. A pH value of 2 was chosen for all further measurements because it provided the maximum sensitivity.

The effect of excess of EEDTA reagent was examined under these conditions. With 210 μg of copper per ml, the optical density reached a maximum on addition of 0.9 ml of 5% EEDTA solution; further additions up to at least 4 ml did not affect the results. It is therefore clear that a large excess of reagent can be present.

To examine the effect of temperature, solutions of the complex were heated to 30°, 60°, and 90° as well as on a steam bath; after the solutions had cooled, they were adjusted to volume and the optical densities were measured. The temperature of formation of the complex or the period of heating had no effect on the measurements.

It was also shown that the complex was stable for at least 3 days at room temperature in diffuse light.

Study of the complex formed and compliance with Beer's law

The complex formed by copper(II) with EEDTA was examined by the molar ratio method[8] and by the method of continuous variations[9]. Both methods showed that a 1:1 complex was formed.

To check that the system obeyed Beer's law, solutions were prepared under the conditions mentioned below and the absorbances were measured spectrophotometrically and absorptiometrically. It can be seen from Fig. 2 that the law is obeyed up to 650 μg of copper(II) per ml.

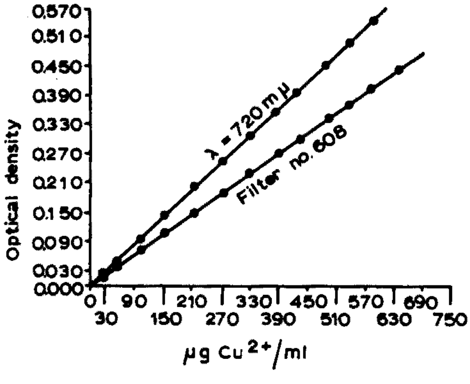

Fig. 2. Calibration curves for the proposed method.

Effect of diverse ions

To study the effects of various foreign ions, solutions containing 210 μg of copper(II) per ml were mixed with amounts of the required ion and taken through the procedure given below. Measurements were made 5 min after a homogeneous solution had been obtained. With regard to anions, negligible errors (*i.e.* less than ±2%) were obtained in presence of 1 ml of a saturated solution of sodium tetraborate, salicylate, or fluoride, or in presence of 100 mg of sodium sulphate, nitrate, chloride or bromide; 50 mg of sodium nitrite, arsenate or phosphate, 20 mg of sodium tungstate, and 10 mg of potassium dichromate, sodium molybdate or ammonium vanadate could be tolerated. Interfering anions are shown in Table I. Cations which did not interfere are listed in table II.

TABLE I

EFFECT OF ANIONS

Salt added	*Amount added*	*% Error*
Sodium tartrate	1 ml satd. soln.	−16
Sodium oxalate	,, ,, ,, ,,	−50
Sodium benzoate	,, ,, ,, ,,	− 8
Sodium acetate	40 mg	− 3
Sodium thiosulphate	10 mg	−40

EXPERIMENTAL

Apparatus

A Spekker absorptiometer, Hilger and Watts, Ltd., Model H-760, was used with 1-cm cells and an Ilford No. 608 filter. A Beckman Model G pH meter was used for pH measurement.

TABLE II

NON-INTERFERING CATIONS

Ion	*Added as*	*Maximum amount added (mg)*
Pb^{2+}	Nitrate	50[a]
Hg^{2+}	,,	40
Bi^{3+}	,,	10
Zn^{2+}	,,	50
Al^{3+}	,,	10
Sr^{2+}	,,	10
Ca^{2+}	,,	10
Mg^{2+}	,,	50
Be^{2+}	,,	50
Li^{+}	,,	50
K^{+}	,,	50
NH_4^{+}	,,	50
Fe^{3+}	Chloride	4[b]
Ni^{2+}	Sulphate	6
Co^{2+}	,,	30
Ce^{4+}	,,	2
Cr^{3+}	,,	3
Cd^{2+}	Nitrate	50
Mn^{2+}	Sulphate	20
UO_2^{2+}	Nitrate	20

[a] The precipitate formed was filtered off before the absorbance was measured.
[b] Larger amounts may be masked with fluoride or phosphate.

Reagents

EEDTA solution. Prepare a 5% solution by dissolving 5 g of the acid in sufficient 1 *M* sodium hydroxide at 60°; dilute to 100 ml and, if necessary, filter through a Schleicher and Schull 589 blue-band paper. The pH of the solution is 3.50.

Clark and Lubs buffer pH 2. Mix 5.3 ml of 0.2 *N* hydrochloric acid and 25 ml of 0.2 *N* potassium chloride and dilute to 100 ml.

Standard copper solution. Prepare a 0.1 *M* solution of copper sulphate pentahydrate. The solution can be standardized by electrolytic deposition.

Procedure

Transfer an aliquot of the test solution to a 25-ml volumetric flask, and add 2 ml of EEDTA solution. Adjust the pH to about 2 by dropwise addition of 1 *M* ammonium hydroxide or 2 *M* hydrochloric acid and add 10 ml of buffer solution. Dilute to the mark with water. Prepare a similar blank solution. Measure the absorbance in a suitable spectrophotometer at 720 mμ or use an absorptiometer with an appropriate filter. Determine the copper content from a calibration curve prepared in the usual way.

Procedure for the analysis of silver solders

Clean the alloy from grease, transfer a 0.5-g sample to a porcelain dish and heat with 20 ml nitric acid (1 :4) until dissolution is complete. Expel nitrogen oxides by evaporation, dilute with water, boil and add dilute hydrochloric acid dropwise to precipitate all the silver. Avoid an excess of precipitant. Allow the mixture to cool in the dark, check that precipitation is complete, filter on a Gooch crucible and wash with nitric acid (1 :200) and water. Silver can be determined in the precipitate.

Treat the filtrate with 5 ml of concentrated sulphuric acid and evaporate to fumes of sulphur trioxide. Transfer to a volumetric flask and dilute to 100 ml with distilled water. Determine the copper in a 2-ml aliquot (or in a suitable aliquot depending on the amount of copper in the sample) by the method given above.

RESULTS AND DISCUSSION

Typical results obtained by the absorptiometric method are shown in Table III. The accuracy of the method is usually better than ±2%. Analysis of a silver solder gave results of 26.40% copper compared with a value of 26.60% obtained by electrolytic deposition.

TABLE III

ACCURACY OF THE PROPOSED METHOD

Copper taken $\mu g/ml$	*Copper found* $\mu g/ml$	% *Error*
54	53	−1.85
108	107	−0.92
216	216	0.00
324	324	0.00
378	376	−0.52
532	532	0.00
640	644	+0.62

It is of interest to compare the performance of the three reagents DCTA, EGTA and EEDTA in the spectrophotometric determination of copper.

DCTA is the most sensitive of the three[5] but neither DCTA nor EGTA can be used below pH 5; DCTA is used at pH 5 and EGTA at pH 7.5[6]. The present reagent can be applied at pH 1–3 which is a considerable advantage over the earlier reagents. EEDTA is also superior from the point of view of interfering ions. For example, up to 160 μg of iron(III) and 240 μg of nickel(II) per ml of solution can be tolerated with EEDTA whereas these ions must be previously masked or eliminated when the DCTA or EGTA procedure is applied. Interferences are remarkably few so that the method should be applicable to a great variety of materials.

SUMMARY

A spectrophotometric determination of copper with 2,2'-diaminodiethylether-N,N,N',N'-tetraacetic acid is proposed. Maximum absorbance is obtained at 720 mμ at pH 2 (1–3) and 25–650 μg Cu/ml can be determined. The reaction is unaffected by temperature or time of standing, and very few ions interfere. A 1 : 1 copper–EEDTA complex is formed.

RÉSUMÉ

Un dosage spectrophotométrique du cuivre au moyen de l'acide 2-2'-diamino-diéthyléther-N,N,N',N'-tétraacétique est proposé. On peut ainsi doser 25 à 650 μg Cu/ml. La réaction est stable et d'une bonne sélectivité.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur spektrophotometrischen Bestimmung von Kupfer mit 2,2'-Diaminodiäthyläther-N,N,N',N'-tetraessigsäure. Es können hiermit Mengen von 25–650 μg/ml bestimmt werden.

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OBSERVATIONS IN ATOMIC ABSORPTION SPECTROSCOPY

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In the course of studies on atomic absorption spectroscopy, several observations have been made which appear to be worthy of notice. These are outlined below.

Spectral slit widths

The degree of resolution required for the most sensitive determination of a particular metal is a function of the spectrum of that metal. When a hollow cathode or other suitable emission-type lamp is used as the source it is necessary to isolate the absorbed line from the other unabsorbed lines in the spectrum. The resolution required to do this is a function of the hollow cathode spectrum itself and depends on the proximity and intensity of unabsorbed lines in the immediate vicinity of the absorbed line.

For alkali metals and alkaline earths, usually the absorbed lines are somewhat remote from other parts of the spectrum of the light source and it is probable that a simple light filter would be perfectly satisfactory for their determination. However, hollow cathodes made from transition elements exhibit much more complex spectra than alkali metals. A high resolution prism or grating is probably necessary.

It will be appreciated of course that spectral emission lines may originate in the sample, *e.g.* when a flame atomizer is used. If the instrument is modulated, the detector will not be sensitive to these lines and high resolution is unnecessary. However, if the instrument is not modulated they will interfere directly with the measurement of absorption by acting as unabsorbed light. This interference can be

TABLE I

EFFECT OF SPECTRAL SLIT WIDTH ON THE SENSITIVITY OF Ni 3414 Å

Inlet slit (*mm*)	*Spectral slit width (measured) at 1/2 wave height* (*Å*)	*Limit of detection* (I_0–I_1 = 2 *divs.*) (*p.p.m.*)
0.03	3.2	5
0.05	3.2	5
0.075	3.9	6
0.1	4.7	6
0.2	7.7	6
0.3	11.8	7
0.4	16.1	7
0.6	24.7	10
1.0	No resolution	50
1.5	No resolution	100

reduced with high resolution, but in view of the complex spectra of metals it would be difficult to eliminate this source of error completely by high resolution.

The effect of slit widths on the absorption of the nickel 3414 Å line was studied by progressively decreasing the slit widths of the monochromator. The spectral slit widths were measured at half-wave height of the emission line. The results are shown in Table I.

The instrument was not set under conditions for maximum sensitivity. The sensitivity levels are therefore not representative of the ultimate limits of detection of this metal, but do serve to illustrate the relative sensitivity at various slit widths.

The results indicated that as the spectral slit width was decreased, the sensitivity increased. It would seem therefore that for the transition elements good resolution is required for high sensitivity. A prism or grating would appear to be suitable for use in these circumstances.

Spark as an alternative atomizer

In the past, the flame has been used principally for the atomization of liquid samples. A serious disadvantage of the use of a flame is that many metals form refractory oxides during combustion and are not reduced to the metallic state. This prevents their detection and determination by atomic absorption spectroscopy. It was anticipated that if these metals could be broken down to the atomic state by an alternative means, then they could be determined by this process.

The metal studied in this case was aluminum. Attempts to reduce this to the atomic state in a flame have been unsuccessful, even using oxycyanogen flames which generate very high temperatures (4500°) and might be expected to break up the oxide. This metal was particularly interesting because it has been observed that in an oxycyanogen flame it will emit intense lines ascribed to transitions to the ground state. This would indicate the presence of aluminum atoms which had attained the atomic state. However, using the same burner and flame conditions, it was not possible to detect aluminum atoms by atomic absorption. These two observations seem to be completely contradictory unless (a) aluminum cannot absorb at the expected wavelength, and (b) the life time of the aluminum atom is extremely short.

An ARL Quantometer was used as the spark and detection system merely for demonstration purposes. The optical alignment is shown in Fig. 1.

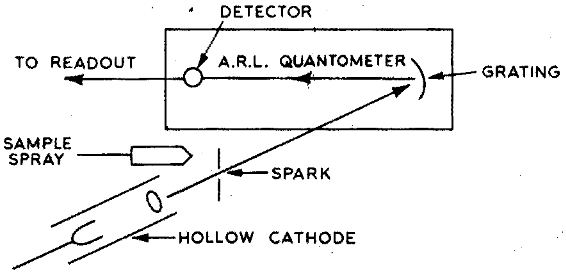


Fig. 1. Optical alignment for spark and spray atomization of aluminum.

The sample was sprayed into the discharging spark using an insulated forced feed burner. When the electrodes were discharged across a flame containing a sample no visible discharge occurred and no absorption by the metal was detected. This indicated that the metal oxides were not broken down by electrical discharge across a flame. This is presumably because the high conductivity of the flame changes the effect of the discharge. However, when the metal was merely sprayed into the electrical discharge appreciable absorption took place. The results (Table II) indicated that both intense absorption and emission by aluminum took place, illustrating the efficiency of this system for producing excited and unexcited metals in the atomic state. It was seen that aluminum is a strong absorber at the expected wavelength. Its lack of ability to absorb in a flame may be due to an extremely short atom life before oxidation. An alternative explanation may be that different electrons are involved in spectral emission and chemical combination in this case.

TABLE II

ABSORPTION OF ALUMINUM USING A LIQUID SPRAY AND ELECTRICAL DISCHARGE SYSTEM

	Signal
Hollow cathode only	$50 = I_0$
Hollow cathode + spark + spray	162
Spark + spray	120
Signal from hollow cathode after absorption =	$42 = I_1$
Signal noise level =	4 units
Conc. of solution =	10 p.p.m.
Sensitivity =	3 p.p.m. (or lower)
Wavelength =	3944 Å

In the course of running this experiment, it was noted that violent inductive fields were set up during spark discharge. When this was carried out in the proximity of a normal spectrophotometer, wild variations of signal were obtained, presumably because of pickup by the wiring of the instrument. Attempts to screen the discharge with homemade equipment were unsuccessful but did indicate that the problem could be overcome.

With the ARL Quantometer, however, this problem is eliminated. It was seen that the signal noise associated with spark discharge was low and that quantitative analytical procedures could be developed based on this technique.

Flame adapter

The extent of absorption by metal atoms is a direct function of the number of atoms in the light path. In an attempt to increase this number, an adapter was designed to fit over a narrow burner such as the Beckman atomizer. A schematic

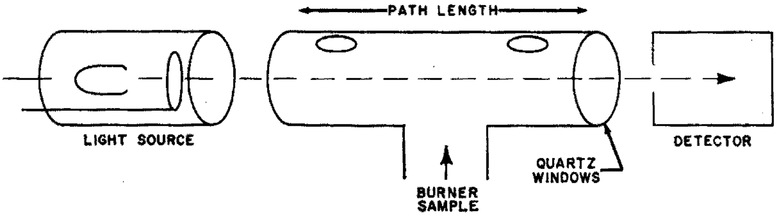


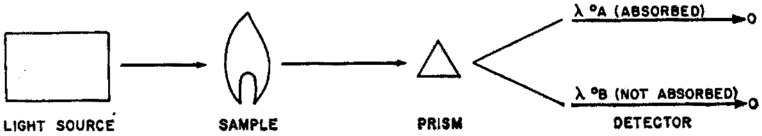
Fig. 2. Flame adapter (schematic).

diagram of this adapter is shown in Fig. 2. It was hoped that by using this adapter the number of atoms in the light path would be increased, but the number of excited atoms in the light path would be decreased. This would lead to an increase in the absorption signal, but a decrease in the emission signal from the flame, and may even eliminate the necessity for modulation in atomic absorption equipment.

The flame used was an oxyhydrogen flame and the samples were in aqueous solution. In preliminary tests using sodium and nickel, however, the adapter was not successful, since neither of these metals were detected. Presumably, both elements were oxidized before reaching the pertinent part of the adapter. However, when an aqueous solution of platinum was aspirated, a 10-fold increase in absorption was observed. The results lead us to conclude that the adapter could not be used for the determination of the alkali metals and some of the transition metals. However, it should be useful for determination of low quantities of the noble metals. Further, it is anticipated that if flame conditions could be regulated to prevent the formation of metal oxides on the metal in the upper portions of the flame, its use may be extended to some of the transition elements.

Double wavelength system

Work carried out by Menzies[1] and independently by the author shows that there are certain advantages to the 'Double Wavelength' System. In this system, two spectral lines of the metal being determined are monitored, as shown in Fig. 3.



SIGNAL AT λ °A $= I_1$ (SAMPLE)
SIGNAL AT λ °B $= I_0$ (INTERNAL STANDARD)

Fig. 3. Two-wavelength system (schematic).

One line is an absorbed line and falls on detector A. The second line is unabsorbed and falls on detector B. The signal from the two detectors is balanced with no sample present. The sample is then aspirated into the burner, and the ratio of the signals from the detectors is measured. From this the analysis of the sample is calculated. One problem with the method is the choice of the standard or unabsorbed line. It is important that the intensity of this line does not vary significantly relative to the absorption line with variation of voltage to the hollow cathode. To investigate this point, the ratio of various lines from an iron hollow cathode was examined. The voltage to the source was changed 100 %. Twenty-seven lines were compared to the Fe 3719 Å absorption line; twenty-two remained constant in ratio, but five varied in relative intensity. It appears therefore that the procedure can be safely used if sufficient care is taken to choose the correct unabsorbed line.

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SUMMARY

Four features of atomic absorption have been studied. Results show that spectral slit width markedly affects sensitivity; an electrical discharge can be used for sample atomization; a flame adapter can be used to increase the sensitivity of noble metals, and the double-wavelength system is satisfactory under some conditions.

RÉSUMÉ

Quelques observations, faites au cours de recherches sur la spectroscopie par absorption atomique, ont été communiquées. Elles se rapportent à l'influence de la largeur de la fente sur la sensibilité, à l'application de l'étincelle au lieu de la flamme et à l'utilisation de la flamme pour augmenter la sensibilité des métaux nobles. Puis, on discute les avantages du système à "double longueur d'onde"

ZUSAMMENFASSUNG

Es werden einige Beobachtungen, die bei Untersuchungen über atomare Absorptions-Spektroskopie gemacht wurden, mitgeteilt. Diese beziehen sich auf den Einfluss der Spaltbreite auf die Empfindlichkeit, auf die Anwendung des Funkens an Stelle der Flamme (besonders bei Aluminium) und Anwendung der Flamme bei der Bestimmung der edlen Metalle. Ferner werden die Vorteile der "Doppel-Wellenlängen" Methode erwähnt.

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DETERMINATION OF RHENIUM AND TECHNETIUM BY INFRARED SPECTROSCOPY

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(Received March 5th, 1962)

In the course of investigations of new analytical methods for technetium and rhenium, new techniques have been applied to meet the requirements of an accurate and simple method for determining the two elements[1].

Although an appreciable number of spectrophotometric methods are available for the determination of rhenium, few are known for technetium. The thiocyanate ion has been used in a colorimetric method for technetium[2] and rhenium[3] but, unfortunately, this reagent forms coloured species with a large number of metallic ions. Recently[4] potassium ferrocyanide has been used for the spectrophotometric determination of rhenium and technetium after reduction. Up to the present, however, infrared spectroscopy has not been one of the techniques used for the determination of these elements. The application of this technique in the systematic qualitative and quantitative analysis of inorganic compounds in general has been neglected until recently when potassium bromide disc techniques were suggested[5–7]. By means of this technique, it has been possible to detect a number of anions by precipitating them with tetraphenylarsonium chloride and pressing into a disc with potassium bromide before determining the infrared spectra[8].

The success achieved in this work suggested the possibility of using it for the determination of technetium and rhenium, since these two elements, as pertechnetate and perrhenate, form precipitates with tetraphenylarsonium chloride (T.P.A.C.).

In the present work the method developed is based on the precipitation of perrhenate and pertechnetate with T.P.A.C. in the presence of potassium perchlorate as carrier. The filtered precipitate is dried, mixed and pressed with potassium bromide into a disc, and examined in the infrared spectrophotometer. The results of this work are presented below.

EXPERIMENTAL

Reagents

Potassium perchlorate. A solution containing 1 mg of 'AnalaR' Grade salt per ml.

Potassium perrhenate. A standard solution containing 0.372 mg Re/ml of 'Specpure' potassium perrhenate.

Caesium pertechnetate. A standard solution containing 0.100 mg Tc/ml.
All other reagents used were of 'AnalaR' Grade.

Apparatus

The infrared spectra were recorded on a Perkin Elmer ('Infracord') Spectrophotometer, Model 137.

Potassium bromide discs were prepared with a Perkin Elmer die using an 'Apex' hydraulic press with a 10-ton capacity on a ram of $2\frac{1}{8}$ inch diameter. Before use the potassium bromide was dried at 150° for 24 h and ground to pass BSS 100-mesh.

Procedure

To the sample which contains 20–300 μg of perrhenate or pertechnetate ions in 5–20 ml of solution, add 2 ml of perchlorate solution and enough sodium chloride to make the solution approximately 1 M. Heat the solution and neutralise with ammonium hydroxide solution, using a strip of litmus paper as indicator. Add 1 ml in excess, followed by a measured excess of the aqueous 5% tetraphenylarsonium chloride reagent. Stir the solution and allow to stand for several hours in a cool place. Filter the precipitate on a 10-ml sintered crucible (porosity 4) and wash twice with 1-ml portions of cold sodium chloride solution, then with 1 ml of ice water. Dry at 110° to constant weight. Break up any lumps with a small spatula, and mix a known weight, around 2 mg, intimately with about 300 mg of potassium bromide, to form a mixture of 300 mg. Place this mixture in an agate mortar and mix to a homogeneous form. Transfer the finely-divided mixture to the die and form it into an even layer with the plunger. It is not necessary to transfer the mixture quantitatively, since the optical density of the finished disc is corrected to the 300-mg disc. Replace the plunger of the die, evacuate the whole die for 2 min, and apply a total pressure of 10 tons for 5 min. The disc should be a little opaque but clear. Fix the finished disc into a suitable holder and place it in the sample beam of the 'Infracord' using a pure potassium bromide disc of similar weight in the reference beam. The spectrum is recorded over the range 10–12 μ.

To calculate the optical density, a base-line technique was used (Fig. 1). A line is drawn at the base of the band and the optical density calculated from the incident (I_0) and transmitted (I) intensities. This was corrected to a 300-mg basis by multiplying by the factor 300/W, where W is the weight of the disc in mg. The concentration of rhenium or technetium is determined by preparing a calibration curve of optical density against concentration of rhenium or technetium (*cf.* Fig. 2). From this curve the concentration of rhenium or technetium in the original sample may be obtained.

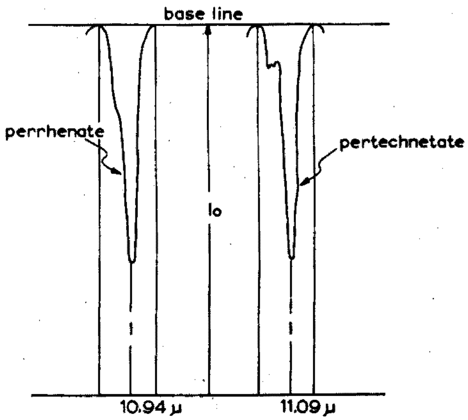

Fig. 1. Calculation of the optical density of Tc and Re by the base-line technique.

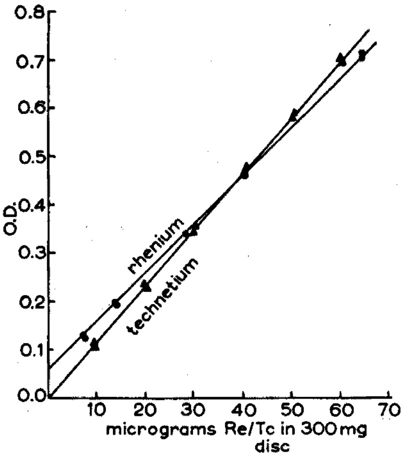

Fig. 2. Calibration curve: Optical density *vs.* concentration of Tc and Re in μg.

DISCUSSION AND RESULTS

Tetraphenylarsonium chloride is a well-known precipitating reagent for perchlorate, perrhenate[9], pertechnetate[10], and other polyatomic ions. Unfortunately, the gravimetric determination of both perrhenate and pertechnetate is subject to interference from a large number of anions which necessitates laborious methods of separation. Further, μg quantities of these ions cannot be precipitated unless a carrier is present.

During the study of tetraphenylarsonium (T.P.A.) complexes of a number of anions[8] by infrared spectroscopy it was found possible to use this method for the determination of perrhenate and pertechnetate, as well as the other ions. The precipitation of both perrhenate and pertechnetate when present in μg amounts, is assisted by the presence of XY_4^- groups which form a precipitate with T.P.A.C. In the infra-red spectrophotometer, perrhenate and pertechnetate ions, in T.P.A. complexes, show strong and sharp bands at 10.94 and 11.09 μ respectively. These bands are assignable to metal–oxygen stretching frequencies.

The advantages of using T.P.A.C. in this work have been discussed in the previous work[8].

Permanganate, perrhenate and pertechnetate ions all exhibit strong bands in the same region. This necessitates their separation, if present in admixture, by suitable methods[11,12]. The elimination of the interference of permanganate ion is simply achieved by treating the acidified solution with hydrogen peroxide solution which reduces the permanganate to manganese(II).

Infrared spectroscopy with a potassium bromide disc has been applied in quantitative analysis by a number of workers[5-7]. KIRKLAND[13] has studied grinding methods and pressing techniques in detail. He used 3 modes of particle size reduction: (*1*) ball-milling the sample with potassium bromide, (*2*) grinding the material in a mortar with powdered potassium bromide and, (*3*) grinding the substance with potassium bromide in a mechanical vibrator–grinder with the help of steel balls. He concluded that the vibrator–grinding method produced the highest and most reproducible band absorptivities. The grinding time was also studied.

In the present work 2 grinding methods were used: (*a*) grinding the sample with powdered potassium bromide in a mortar for 10 min, and (*b*) mixing the sample and the powdered potassium bromide in a stainless steel capsule of approximately 1.2 × 3 cm dimension with the aid of two small steel balls and a laboratory-type vibrator–shaker, again for 10 min. The results of these two grinding methods showed that there is a slight improvement in the absorptivities in the case of mechanical grinding. Equally good results can however be obtained using mortar and pestle.

INTERFERENCES

Tetraphenylarsonium chloride forms precipitates with a considerable number of ions[8,9] which interfere in the gravimetric determination of both rhenium and technetium. Fortunately, these precipitates do not exhibit strong absorption bands at 11 μ with the exception of permanganate. The effects of molybdate, tungstate, metavanadate, bromide, nitrate and thiocyanate on the rhenium determination are shown in Table I.

TABLE I

EFFECT OF VARIOUS IONS

(Rhenium added 223.2 μg)

Interfering ion	*concentration, μg*	*added as*	*Re found, μg*	*% error*
Mo^{6+}	5,000	Na_2MoO_4	219.3	—1.7
W^{6+}	3,600	Na_2WO_4	214.6	—3.8
V^{5+}	5,000	$NaVO_3$	231.0	+3.5
Br^-	4,000	KBr	221.2	—0.9
NO_3^-	6,000	KNO_3	219.0	—1.8
SCN^-	1,000	KSCN	216.6	—2.9

Sulphate, phosphate, acetate, tartrate, citrate, oxalate, iodate, bromate and uranyl ions do not interfere with the determinations of rhenium and technetium.

Metallic complexes of halides such as $[HgI_4]^{2-}$ do not form precipitates under ammoniacal conditions. Thiocyanate, persulphate, chlorate, perchlorate, and periodate, all form precipitates with T.P.A.C. under the proposed conditions, but do not show strong absorption bands at 11 μ and therefore, do not interfere.*

SUMMARY

The determination of μg amounts of rhenium, as perrhenate, and technetium, as pertechnetate, by infrared spectroscopy is described. The species are precipitated with tetraphenylarsonium chloride in presence of potassium perchlorate as carrier; the precipitate is filtered, dried, and pressed with potassium bromide into a disc for examination. The tetraphenylarsonium complexes of perrhenate and pertechnetate show strong sharp bands at 10.94 and 11.09 μ respectively.

RÉSUMÉ

Une méthode est décrite pour le dosage du rhénium (comme perrhénate) et du technétium (comme pertechnétate) par spectroscopie infrarouge. Ces éléments sont précipités au moyen de chlorure de tétraphénylarsonium, en présence de perchlorate de potassium.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Rhenium und Technetium durch IR-Spektroskopie nach Fällung mit Tetraphenylarsoniumchlorid in Gegenwart von Kaliumperchlorat.

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* It is worthy of mention that certain anions which form a precipitate with T.P.A.C., *e.g.* thiocyanate, periodate and perchlorate, exhibit a very weak band at approximately 10.8 μ. With μg amounts of these anions no problem arises but, in the determination of rhenium, 2 mg of perchlorate is mixed with potassium bromide to form the 300-mg disc. At this concentration of perchlorate a measurable optical density (*ca.* 0.08) is recorded; because of this the calibration curve does not pass through the origin (Fig. 2). However, this need cause no trouble if a constant weight of TPA-perchlorate is always used in the KBr disc. Any interference from the other anions may be eliminated in the same way, since these ions also behave as carriers.

DIFFERENTIAL THERMAL ANALYSIS OF DIVALENT METAL 8-HYDROXYQUINOLINE CHELATES

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Although there have been several studies of the thermal decomposition behavior in air[1-3] of 8-hydroxyquinoline chelates (oxinates), there has been little published regarding the heat stabilities of these compounds in inert atmospheres. Previous experience in this laboratory has shown that results obtained under the latter conditions are often markedly different from those obtained in air. We describe here data obtained by differential thermal analysis (DTA), in an atmosphere of argon, for a number of the divalent metal oxinates. DTA is based on the detection of heat given off or taken up during chemical or physical changes of the material being heated[4]. The technique is useful, therefore, to detect phase changes, as well as to establish temperature regions for decomposition.

EXPERIMENTAL

Apparatus

The differential thermal analysis apparatus employed is shown diagrammatically in Fig. 1. The sample was contained in the lower part of a cylindrical quartz tube, 1.0 cm in diameter. The bottom of the tube was indented to accept one junction of a differential chromel–alumel thermocouple. Sample and junction were thus separated by a layer of quartz. The sample tube was connected by means of a standard taper quartz joint and rubber pressure tubing to a glass reservoir (capacity 200 ml). The latter was provided with a stopcock arrangement to permit evacuation and filling with argon. The size of the reservoir was sufficient to prevent excessive pressure build-up in the closed system when the sample tube was heated. Alumina, as the reference material, was contained in a second tube, identical to the sample tube, except that the reference tube was allowed to remain open to the air.

The two quartz tubes fit loosely within holes bored longitudinally in a cylindrical stainless steel block (2.6 cm diameter) which rested on a base constructed from asbestos and refractory cement. The base acted as support for the two junctions of the differential thermocouple and also for another chromel–alumel thermocouple which was used to measure the temperature of the stainless steel block. The metal block and base assembly were suspended within a Hoskins tube furnace. The temperature of the furnace was raised with time by means of a motor-driven Variac variable transformer. By using an initial Variac setting of 60 V the temperature–time relationship for the metal block was nearly linear, above 100°, at 12°/min.

The output from the differential thermocouple was recorded as a function of time with a Leeds and Northrup Speedomax 1 mV recorder. No amplification of the thermocouple output was necessary. The temperature of the furnace block was recorded simultaneously using a second recorder.

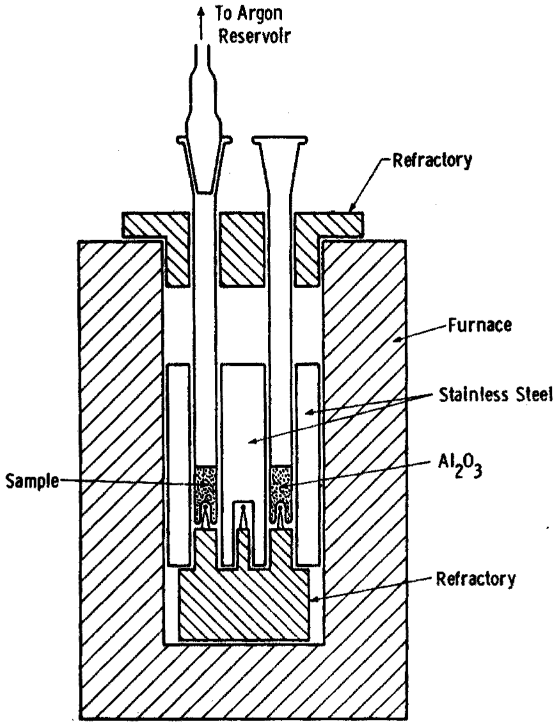


Fig. 1. Cross-section of DTA apparatus.

Procedure

A 400-mg sample of the finely powdered metal oxinate (dried at room temperature) was placed in the sample tube and dehydrated by heating for at least 2 h in a vacuum oven at 150°. The cooled tube was attached to the gas reservoir and alternately evacuated and filled with argon to displace the air. It was finally filled to a pressure of about 525 mm Hg with argon and sealed off. The tube was tapped repeatedly to insure even (though somewhat loose) packing about the thermocouple well. An equal volume of ignited alumina was placed in the comparison tube, and the apparatus assembled as in Fig. 1.

In order to establish more accurately the temperatures at which some of the DTA peaks occur, a series of calibration runs was carried out. Compounds were employed which exhibit known melting and phase transition points in the temperature region 25–800°. The relation found between the reported[4] temperature (T) for the transitions and the observed furnace block temperature (T_f) at the endotherm maximum is given by:

$$T = 0.980\,(T_f - \Delta T)$$

where ΔT is the observed temperature difference between the sample and reference material. The plot of $(T_f - \Delta T)$ *vs.* T given in Fig. 2 was used to obtain the corrected melting point data given in Table I.

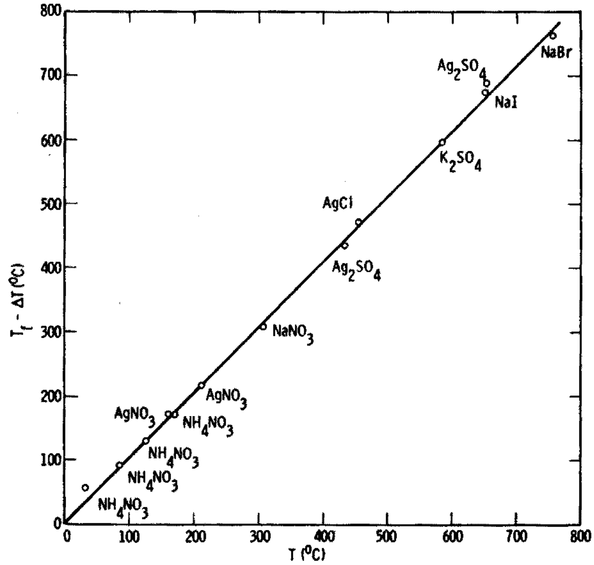


Fig. 2. Calibration curve for DTA apparatus.

Preparation of compounds

Magnesium, calcium and strontium oxinates were prepared as previously described[5]. Barium oxinate, prepared as described elsewhere[5], gave the hydrate which underwent partial hydrolysis upon heating. A different procedure was used in the present work which circumvented this difficulty. The oxide coating was removed, by machining, from about 2 g of pure barium metal rod. Subsequent operations were performed in a glove box filled with dry argon. The barium was dropped into 200 ml of absolute ethanol. When hydrogen evolution had ceased, the solution was filtered through filter paper. To the resulting clear filtrate was added a solution of 4.5 g of 8-hydroxyquinoline in 100 ml of absolute ethanol. A yellow precipitate formed immediately. The mixture was allowed to stand for an hour. The solid was filtered off on filter paper and was then washed with 50 ml of absolute ethanol. The wet solid was transferred rapidly to a vacuum desiccator and dried overnight over calcium chloride. Yield 5.3 g (about 85% of the theoretical). Calculated for $(C_9H_7ON)_2Ba$: Ba, 32.27%; N, 6.56%. Found: Ba, 32.2%; N, 6.51%, 6.56%.

The remainder of the metal oxinates were prepared by precipitation from aqueous solution, utilizing adaptations of conventional procedures[6,7]. With the exception of the barium compound all the oxinates precipitated as hydrates.

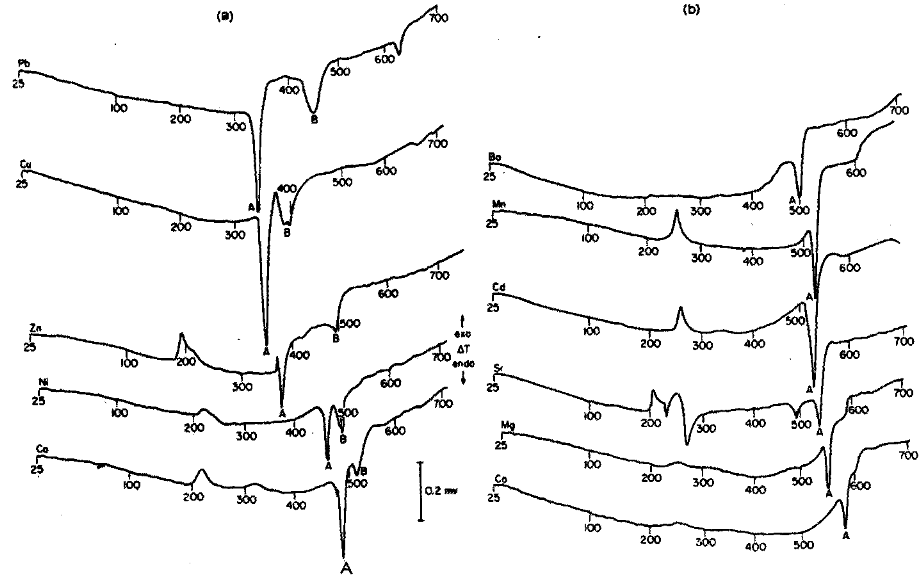
Extraction experiments

At the required temperature the DTA sample tube was removed from the furnace and the contents cooled rapidly to room temperature under the atmosphere of argon.

The contents of the tube were then heated gently with 100 ml of 1 M aqueous hydrochloric acid until complete solution was obtained, or for 2 h if a residue remained. The extract was filtered through filter paper and diluted quantitatively to 300 ml with 0.1 M hydrochloric acid. This solution was diluted successively 15:100 and 1:100. For comparison, solutions were prepared from 400-mg samples of the unheated oxinates, using the same dilution procedure. Optical absorbance at 252 mμ was measured for each of the diluted solutions using a Cary model 14 recording spectrophotometer and 1 cm quartz cells.

RESULTS AND DISCUSSION

The DTA curves obtained are shown in Figs. 3(a) and 3(b). The most prominent feature of each of the curves is the sharp endotherm marked *A* in the figures. The position of *A* along the temperature axis is a function of the nature of the bonded metal. To determine whether the endotherms *A* are due to phase changes, or to decomposition, a second series of DTA runs was carried out. Each of these runs was terminated 5 to 10° above the endotherm maximum. After cooling, the contents of the sample tube were extracted with dilute hydrochloric acid and the optical absorbance of the quantitatively diluted solution was compared (at 252 mμ) with that of a solution prepared from unheated oxinate. The amount of undecomposed oxinate shown in Table I was calculated on the assumption that decomposition products do not contribute to the absorption at 252 mμ[5].



Figs. 3(a) and (b). DTA curves for metal 8-hydroxyquinolates heated in argon. Numbers refer to furnace temperature (°). The curves are displaced along the ordinate.

Table I shows that the Cu, Pb, Zn, Ni and Co oxinates are not appreciably decomposed upon passing through the endotherms *A*. Inspection of the tubes immediately upon removal from the furnace showed the contents to be mobile liquids

TABLE I

DIFFERENTIAL THERMAL ANALYSIS DATA FOR DIVALENT METAL OXINATES

Metal	*Apparent melting point (°)*[a]	*% Oxinate not decomposed at melting point*
Ca	554	26
Mg	527	23
Sr	516	83
Cd	506	60
Mn	502	63
Ba	481	86
Co	466	97
Ni	450	98
Zn	356	100
Cu	334	97
Pb	321	100

[a] Average of 2 to 5 determinations in each case. Average deviation from the mean was ±5° for each.

for these oxinates. The contents solidified upon cooling. In a separate run, lead oxinate was heated just above *A* and then was allowed to cool in the DTA apparatus. An exotherm corresponding to *A* was observed on cooling. This is good evidence for the reversibility of the transition which takes place at *A*.

The endotherms *A* must be due to simple melting for these five compounds. There appears to have been no previous report of the melting behavior of metal oxinates.

Table I shows that appreciable, but not complete, decomposition takes place when the DTA runs for the other oxinates are terminated immediately beyond the endotherms *A*. This suggests that the endotherms here are due primarily to melting; but that melting is followed closely by thermal decomposition in these cases. This behavior may indicate that the compounds are more susceptible to pyrolysis in the liquid phase than in the solid.

Listed in Table I are the apparent melting points for the oxinates as determined from the endotherms *A* and Fig. 2. The melting point increases in the order Pb < Cu < Zn < Ni < Co < Ba < Mn < Cd < Sr < Mg < Ca. There is a rough correspondence between this order and the order of decreasing volatility for the oxinates, determined previously[8]. The results suggest an increase in intermolecular attraction in the solid as one ascends the oxinate series from lead to calcium.

For the Cu, Zn, Ni, Co and Pb oxinates the additional well-defined endotherms *B* occur to the high temperature side of *A* (Fig. 3(a)). We interpret these endotherms to be the result of thermal decomposition. For the remainder of the oxinates (Fig. 3(b)), distinct endotherms do not occur above *A* and it is reasonable to assume that the decomposition endotherms are here superimposed upon *A*. From this assumption and the position of *B*, where it is observed, one arrives at the order of decreasing heat stability Ca > Mg > Sr > Cd > Mn > Ba > Co > Ni > Zn > Pb > Cu. This order is the same as that found in previous studies involving thermogravimetric, gas evolution, and sealed tube experiments[5,7]. In the latter work, however, decomposition was found to occur at appreciably lower temperatures than observed here, presumably because of the more prolonged heating at the lower temperatures. Thus decomposition can occur for the oxinates below the melting points reported here, if the temperature rise is not sufficiently rapid[5].

For a number of the curves in Figs. 3(a) and 3(b) small exotherms occur in the temperature region 200–300°. These seem to be due to the crystallization of the initially amorphous dehydrated compounds. In support of this interpretation X-ray powder patterns were obtained for manganese oxinate heated just above and just below this exotherm. The high temperature sample gave a much sharper and better defined pattern than did the sample heated at the lower temperature. That the thermal effect was not reversible was shown by a DTA run with manganese oxinate which was terminated just above the exotherm. A corresponding endotherm was not observed on cooling.

The curve for strontium oxinate (Fig. 3 (b)) exhibits a number of additional peaks in addition to those discussed above. These have not been fully interpreted. However, the endotherm at about 270° seems to be due to vaporization of 8-hydroxyquinoline produced by hydrolysis during the dehydration of the oxinate[5]. The small endotherm at about 490° was shown not to involve decomposition of the oxinate by comparing the ultraviolet spectrum of an acid solution of the compound heated to this temperature with the spectrum characteristic of the unheated compound. It was observed visually that strontium oxinate does not melt at 490°.

ACKNOWLEDGEMENT

The writer is grateful to Miss Antoinette Perrotto for help in the experimental portion of this work.

SUMMARY

DTA curves were obtained for a number of anhydrous metal chelates derived from the important analytical reagent 8-hydroxyquinoline. The compounds were heated in an inert atmosphere to avoid interaction with oxygen or water vapor. The Cu, Pb, Zn, Ni and Co chelates melted without decomposition, under the conditions used, while the remainder of the compounds underwent partial decomposition upon melting. The order of increasing melting point is Pb $<$ Cu $<$ Zn $<$ Ni $<$ Co $<$ Ba $<$ Mn $<$ Cd $<$ Sr $<$ Mg $<$ Ca. The order of decreasing heat stability is Ca $>$ Mg $>$ Sr $>$ Cd $>$ Mn $>$ Ba $>$ Co $>$ Ni $>$ Zn $>$ Pb $>$ Cu.

RÉSUMÉ

Des courbes d'analyse thermique différentielle ont été tracées pour un certain nombre de chélates métalliques de l'hydroxy-8-quinoléine. Les composés ont été chauffés dans une atmosphère inerte pour éviter une interaction de l'oxygène ou de la vapeur d'eau.

ZUSAMMENFASSUNG

Es wird das Verhalten einer Anzahl Metall-oxinate bei der Differential Thermo-analyse beschrieben (Kurven). Unter den angegebenen Versuchsbedingungen schmelzen die Oxinate von Kupfer, Blei, Zink, Nickel und Kobalt ohne Zersetzung, während bei den übrigen untersuchten Oxinaten eine teilweise Zersetzung beim Schmelzvorgang auftritt.

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THE DISTRIBUTION COEFFICIENT OF CUPFERRON

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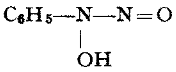
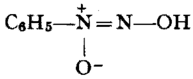
Commercial "cupferron" is the ammonium salt of the weak organic acid nitrosophenylhydroxylamine. This acid is said to exist in 2 forms (I and II)[1,2]



$$C_6H_5{-}\underset{\substack{|\\ OH}}{N}{-}N{=}O$$

I

nitrosohydroxy form



$$C_6H_5{-}\underset{\substack{|\\ O^-}}{\overset{+}{N}}{=}N{-}OH$$

II

amine oxide form

It has been suggested[1] that the marked acidic character of the compound is due to its existing largely in the amine oxide form (II). ELVING AND OLSON[2] suggested that this form is favoured in solutions varying from neutral to slightly acidic (pH 4) and that the nitrosohydroxy form appears to predominate in more strongly acidic solution (pH 1–2).

The acid is a white unstable solid (m.p. 51°[1]) and is said to decompose spontaneously into nitrosobenzene, benzenediazonium nitrate, 4,4'-dinitrodiphenylamine and other products[3]. In this article the name "cupferron" will be used for the acid and the ammonium and sodium salts will be designated ammonium and sodium cupferrate respectively.

In quantitative solvent extraction studies with cupferron it is essential to know the distribution coefficient of the acid between the organic solvent and aqueous solutions as well as the ionization constant of the acid. The value of the ionization constant seems to be fairly well established (Table I). The distribution coefficient on

TABLE I

THE IONIZATION CONSTANT OF CUPFERRON

pK_a	*Temp.*	*Reference*
4.28	25	7
4.16	25	5
4.11	25	2
4.10	room?	8
4.13		

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the other hand seems to be less well known and there is a rather large discrepancy between the 2 reported values for chloroform. FURMAN *et al.*[4] determined the distribution coefficient of cupferron between chloroform and sulphuric acid solutions spectrophotometrically and reported a value of 211. DYRSSEN[5] reports a value of 151 ± 4 for the same solvent and perchloric acid solution, determined by a potentiometric method. (A value of 284 for the distribution coefficient between ethyl acetate and aqueous solutions was reported recently[6].) In view of the great difference in reported values it was considered necessary to develop an independent method for determination of the distribution constant.

With the pK_a and K_D values reported by DYRSSEN a theoretical curve for the distribution of cupferron between chloroform and aqueous solutions as a function of pH was constructed. (Fig. 1.). This curve shows clearly that the distribution should be practically constant below pH 2.5. Above this pH, ionization becomes increasingly important. Consequently the amount of cupferron in the aqueous phase increases with increasing pH, slowly at first up to a pH of about 4, and then much more rapidly until it finally tails off again to a constant value above pH approximately 9.

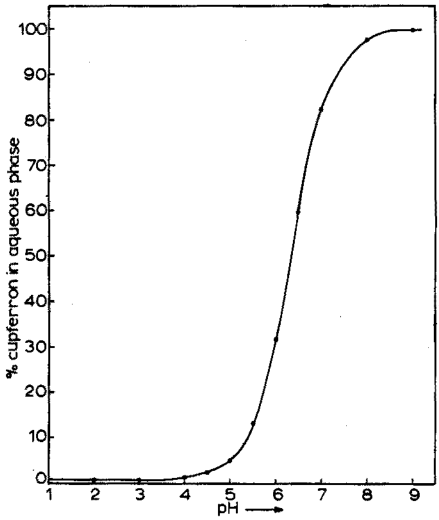

Fig. 1. Distribution of cupferron between equal volumes of chloroform and aqueous solution.

From this it is evident that if the amount of cupferron in one or both phases is determined at pH values below 2.5, it can be used directly in the calculation of K_D. At pH values above 3.5 the ionization of the acid has to be taken into account and K_D can then be determined only if the ionization constant of the acid is known.

It was thus decided to determine K_D at low pH values (<2.5) and also at a higher pH (between 4 and 5), the distribution coefficient in the latter case being calculated from existing values of pK_a (for this calculation the pK_a value of DYRSSEN (4.16) was accepted as a good representative value). Chloroform was selected as solvent, for it is most often used in cupferron extractions.

In their work on uranium cupferrates, FURMAN *et al.*[9] used sodium pentacyanoammine ferrate(II) as a test for the nitroso group. Preliminary experiments with this reagent indicated that it was suitable for the spectrophotometric determination of small amounts of cupferron under suitable conditions.

EXPERIMENTAL

$Na_3[Fe^{II}(CN)_5NH_3]$

The reagent was prepared as follows[10]: 30 g of sodium nitroprusside and 150 ml of 35% ammonia solution were mixed in an Erlenmeyer flask and left in an ice bath for about 20 h with occasional shaking. The precipitate was filtered with suction, washed once with 35% ammonia and sucked dry. It was then recrystallized once by precipitation from concentrated aqueous solution with ethanol, filtered and washed with ethanol. After being sucked dry it was transferred to a desiccator and left overnight.

Ammonium cupferrate

A good quality product was selected and recrystallized 2–3 times from 95% ethanol[11]. The crystals were filtered with suction and sucked dry. They were transferred to a glass-stoppered flask, ether was added and the flask shaken vigorously. The crystals were filtered and the ether treatment repeated once or twice more. After removal of the ether by filtration and suction, the ammonium cupferrate was transferred to an amber bottle containing a small bag with ammonium carbonate in the bottom.

A solution of ammonium cupferrate in oxygen-free water was prepared just before use and used for not more than 3 h after preparation. Sometimes the solid was used directly but the results obtained did not differ appreciably from those obtained with solutions. In a few cases sodium cupferrate was used. The preparation of this compound will be described in a subsequent paper.

Ammonium perchlorate

Prepared by neutralizing Analar perchloric acid with ammonia and evaporating. The crystals were recrystallized twice from water.

Potassium perchlorate

Recrystallized twice from water.

Water

All reagent solutions were prepared with demineralized water distilled from permanganate solution in a quartz still.

Nitrogen

Oxygen-free nitrogen was used. As a precautionary measure the gas was passed through a wash bottle containing chromous sulphate followed by 2 wash bottles containing water.

All other chemicals were of reagent grade or similar quality.

Apparatus

pH measurements were made with a Cambridge battery operated pH-meter, using a glass-saturated calomel electrode system. The meter was calibrated with a series of acids of known concentration at constant ionic strength.

A Unicam SP 500 battery operated spectrophotometer and 1-cm cells were used.

Colorimetric procedure

The sodium pentacyanoammine ferrate(II) reagent produces an intense violet colour with cupferron under proper experimental conditions with a maximum absorbance at 530 mμ (Fig. 2). The colour was developed by slightly acidifying an ammoniacal solution of the reagent and cupferron with 3 N acetic acid and heating on a water bath to 35–40°. After addition of 5 drops more of acetic acid, the mixture was left for at least 15 min before dilution and measurement of the extinction at 530 mμ against a blank treated in exactly the same way except that no cupferron was present.

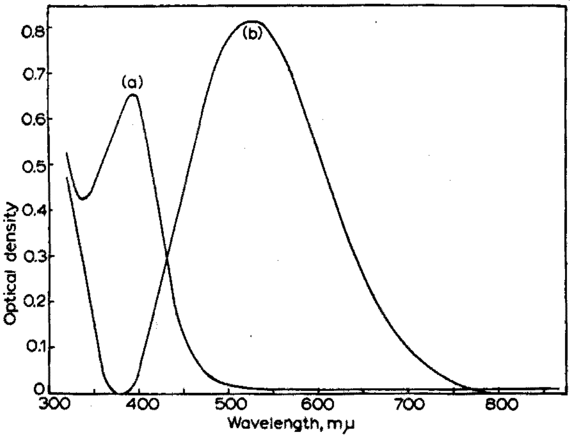

Fig. 2. Absorption spectrum of: (*a*) reagent and (*b*) cupferron complex.

It was found that several factors influence the intensity of the colour:

(*a*) *Reagent concentration.*

At any particular concentration of reagent there seem to be 2 reactions which lead to different optical densities at higher cupferron concentrations (Fig. 3). The first part of the curve indicates a straight line through the origin up to a certain point, after which the increase in optical density is also linear but with a different slope (Fig. 3, curve 1). With further increase in cupferron concentration a point is finally

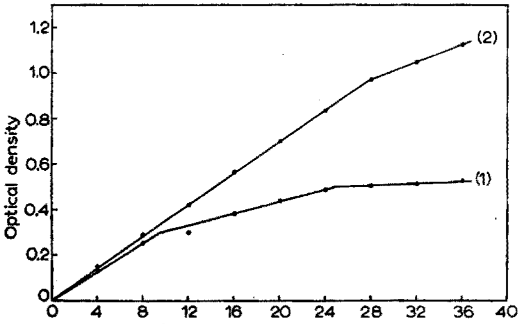

Fig. 3. Effect of reagent concentration; (*1*) 2 ml 0.25% reagent/50 ml; (*2*) 2 ml 1.1% reagent/50 ml.

reached after which practically no increase in absorption is observed. Increasing the reagent concentration changes the slope of the first part of the curve slightly and also shifts the inflection point to a higher cupferron concentration. (The molar extinction coefficient increases from about $5 \cdot 10^3$ for curve 1 to about $6 \cdot 10^3$ for curve 2.) Because of uncertain composition of the reagent and until further work has been done on this phenomenon, no definite conclusions can be drawn.

However, if identical experimental conditions were used, reproducible results could be obtained, and it was decided to use concentrations covering the first part of the curve, because of greater sensitivity.

(*b*) *Acetate concentration*

Increasing the acetate concentration in the reaction mixture under otherwise identical conditions, results in an increase in the colour intensity up to an acetate concentration of about 0.1 *M*. Further increase appears to have no effect. This was investigated by adding increasing amounts of ammonia to mixtures of reagent and cupferron and developing the colour as described above. The optical density in this particular case increased from about 0.45 at 0.02 *M* acetate to a constant value of about 0.6 above 0.1 *M* acetate. This increase was definitely due to the presence of increasing amounts of acetate, for ammonium chloride or perchlorate up to a concentration of about 0.1 *M* did not affect the colour intensity.

The previous experiments indicated the experimental conditions for reproducible colour development, *i.e.* 2 ml of 1% reagent and 2 ml of 2.5 *M* ammonia for every 50 ml of final solution.

Determination of distribution coefficients

Distribution coefficients were determined in 2 pH ranges: below pH 2.5 and between pH 3.5 and 5. Measurements were made in both hydrochloric acid–chloride and perchloric acid–perchlorate media. Equal volumes of organic and aqueous phases were used.

(*a*) *pH below 2.5*

All reagents were measured from 5 or 10-ml burettes into the extraction apparatus

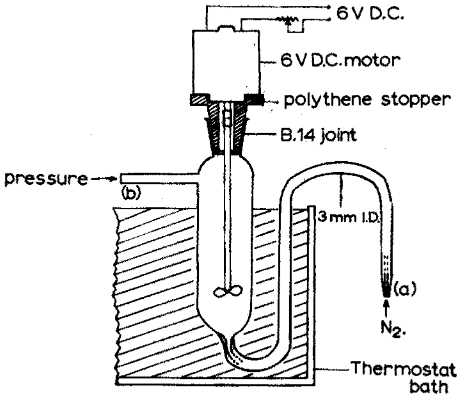

Fig. 4. Extraction apparatus.

(Fig. 4), which was then inserted into a thermostat bath at 20 ± 0.1°. The solution was purged with nitrogen (oxygen-free) through tube (a) for a few min. After addition of standard cupferron solution from a 5-ml burette, the solution was stirred vigorously for 1–2 min while nitrogen was bubbled through at a lower rate. The nitrogen supply was then disconnected and separation was achieved, after settling of the 2 phases, by applying slight pressure through the side tube (b) with a rubber bulb. The aqueous phase was centrifuged immediately in a 10-ml centrifuge tube after which a final separation was made using a pipette to draw off most of the aqueous phase. This was transferred to a 10-ml beaker and its pH measured. A known aliquot of this solution was transferred to a suitable volumetric flask and neutralized with ammonia to methyl red indicator. The solution was then set aside for colour development at a convenient time.

Procedure for colour development and measurement: For every 50 ml of final solution 2 ml of 1% reagent and 2 ml of 2.5 M ammonia were added. The solution was neutralized with 3 N acetic acid until the colour began to change and then 2 drops more were added. The solution was heated on a water bath to 35–40° with continuous shaking, 5 drops more of acetic acid were added and the solution was left for about 15 min before dilution to volume with distilled water. The extinction was measured against a blank at 530 mμ.

From the measured extinction the cupferron concentration in the aqueous phase was derived from a calibration curve constructed in the usual way. Although relatively large amounts of ammonium salts (chloride or perchlorate) did not interfere, the solutions were nevertheless all adjusted to the same salt concentration before colour development by addition of the appropriate ammonium salt.

(*b*) *pH between 3.5 and 5*

These experiments were carried out at an ionic strength of 0.08, the ionic strength being made up when necessary by addition of potassium perchlorate in case of perchlorate media or potassium chloride in case of chloride media. The procedure was exactly the same as that described under (*a*).

TABLE II

DISTRIBUTION COEFFICIENT IN HCl MEDIA. pH RANGE *ca.* 3.5–5

(Total amount of cupferron used = 80 mg)

No.	*pH*	*Cupf. in aq.* *mg*	*Cupf. in org.* *mg*	*HCupf in aq.* *mg*	*HCupf in org.* *mg*	*D*
1	2.4	0.581	0.0099	0.570	79.42	139
2	2.74	0.549	0.0195	0.530	79.45	144
3	3.30	0.597	0.072	0.525	79.40	151
4	3.90	0.897	0.317	0.580	79.10	137
5	4.22	1.254	0.74	0.514	78.75	153
6	4.25	1.134	0.625	0.509	79.87	157
7	4.48	1.702	1.15	0.552	78.30	142
8	4.66	2.09	1.59	0.503	77.91	155
9	4.88	3.39	2.84	0.550	76.61	139
10	4.90	3.605	3.05	0.555	76.39	138
					Mean:	145

RESULTS AND DISCUSSION

The results of the above experiments in the pH range 3.5–5 as well as a few outside this range are presented in Tables II and III. The results in chloride media tend to be slightly higher than those in perchlorate media though the difference is so small that it is difficult to say whether it is a true effect or due to experimental error. However, the agreement between these results and the distribution coefficient of 151 reported by DYRSSEN is good. On the other hand, the value of 211 reported by FURMAN *et al.* seems to be too high unless the distribution coefficient is different in sulphuric acid media, which seems unlikely.

TABLE III

DISTRIBUTION COEFFICIENT IN $HClO_4$ MEDIA, pH RANGE *ca.* 3.5–5

(Total amount of cupferron used = 80 mg)

No.	*pH*	*Total Cupf in aq.* *mg*	*Cupf. in org.* *mg*	*HCupf in aq.* *mg*	*HCupf in org.* *mg*	*D*
1	2.82	0.555	0.029	0.526	79.44	150
2	3.22	0.616	0.061	0.555	79.38	143
3	4.66	2.41	1.83	0.58	77.59	134
4	4.66	2.29	1.74	0.55	77.71	141
5	4.73	2.67	2.10	0.57	77.33	135
6	5.05	5.09	4.51	0.58	74.91	129
7	5.08	5.33	4.75	0.58	74.67	129
8	5.20	5.84	5.35	0.49	74.16	151
						Mean: 139

From the results of the present work and those of DYRSSEN, it seems reasonable to assume a distribution coefficient of 145 for cupferron between chloroform and aqueous solutions of hydrochloric and perchloric acids in the pH range above 3.

In the pH range below 2.5 the distribution coefficient is lower than the values obtained at lower acidities for both perchlorate and chloride media. Table IV shows some results in this region. It is again noticeable that the results in perchlorate media appear to be lower than those in chloride media.

TABLE IV

DISTRIBUTION COEFFICIENT IN $HClO_4$ AND HCl MEDIA, pH RANGE < 2.5

(Total cupferron = 80 mg; extraction time = 0.5 min.)

	$HClO_4$			*HCl*		
No.	*pH*	*HCupf in aq.*	*D*	*pH*	*HCupf in aq.*	*D*
1	0.76	0.696	114	0.78	0.635	125
2	0.92	0.665	119	1.23	0.594	134
3	1.14	0.677	117	1.54	0.602	132
4	1.55	0.660	120	2.04	0.602	132
5	2.0	0.670	118	2.44	0.606	132

The reason for this peculiar behaviour, if indeed it is real, is not immediately obvious; several factors may contribute. No correction has been applied for mutual solubility of the 2 phases and this could be a source of error. Furthermore, there seems to be a slight tendency for the results to be lower at higher acidities. A possible explanation for this could be increasing decomposition of cupferron with increasing acidity, provided that the cupferron decomposes into a nitroso compound with a smaller distribution coefficient that cupferron itself. To investigate this, a series of extractions was made at constant pH and increasing extraction time. The results are recorded in Table V. These results indicate that in both cases the distribution coefficient appears to remain constant up to extraction times of about 2 min, after which it decreases fairly rapidly with increasing extraction time. As the extraction time in the above determinations never exceeded 2 min, this does not support the decomposition theory, unless the initial rate of decomposition is very high and reaches low values within a few seconds or less. As can be seen from the results even an extraction time of 15 sec does not produce the high values obtained over the higher pH ranges.

TABLE V

VARIATION OF DISTRIBUTION COEFFICIENT WITH EXTRACTION TIME

(pH = *ca.* 1.14; 80 mg cupferron total)

	$HClO_4$			HCl		
No.	*Time*	*HCupf in aq.*	*D*	*Time*	*HCupf in aq.*	*D*
1	15 sec	0.658	120	15 sec	0.636	125
2	30 ,,	0.675	118	30 ,,	0.628	126
3	1 min	0.657	121	1 min	0.616	129
4	2 ,,	0.680	117	2 ,,	0.597	133
5	3 ,,	0.685	114	3 ,,	0.659	120
6	6 ,,	0.715	111	6 ,,	0.738	108

The effect of increasing ionic strength was also investigated; as can be seen from Table VI, this does not affect the distribution appreciably.

TABLE VI

INFLUENCE OF IONIC STRENGTH ON DISTRIBUTION COEFFICIENT

(pH = *ca.* 1.14; 80 mg cupferron total)

	perchlorate			*chloride*		
No.	$[NH_4^+]$ *g mol/l*	*HCupf in aq. mg*	*D*	$[NH_4^+]$ *g mol/l*	*HCupf in aq. mg*	*D*
1	0.0	0.661	120	0.10	0.640	124
2	0.10	0.620	128	0.20	0.595	133
3	0.30	0.639	124	0.40	0.585	136
4	0.50	0.645	123	0.50	0.598	133

Another factor which might explain the lower results at lower pH is the fact that cupferron exists in 2 forms. According to ELVING AND OLSON[2] the nitrosohydroxy form predominates at low pH values, *i. e.* in the region where the low results were obtained. But if this is a contributory factor, it would mean that the nitrosohydroxy form has a lower distribution coefficient than the amine oxide form.

From the above it is obvious that further investigations are necessary to explain these phenomena. Development of a more rapid and precise method and one suitable for measurement at much higher acidities (4 N or more) is desirable, because several metal cupferrates are extracted readily at these higher acidities where cupferron decomposes more rapidly.

Calculation of the distribution coefficient

At pH values below 2.5 the distribution coefficient is given by:

$$K_D = \frac{[\mathrm{HCupf}]_{\mathrm{org}}}{[\mathrm{HCupf}]_{\mathrm{aq}}} \qquad (1)$$

$[\mathrm{HCupf}]_{\mathrm{aq}}$ is determined experimentally and the value of $[\mathrm{HCupf}]_{\mathrm{org}}$ is calculated by difference.

At pH values above 3, the ionization of the acid has to be taken into account:

The ionization of cupferron can be presented as:

$$\mathrm{HCupf} \rightleftharpoons \mathrm{H^+} + \mathrm{Cupf^-} \qquad (2)$$

The equilibrium constant for this reaction is given by:

$$K_a = \frac{[\mathrm{H^+}][\mathrm{Cupf^-}]}{[\mathrm{HCupf}]} \qquad (3)$$

Substituting

$$[\mathrm{HCupf}]_{\mathrm{aq}} = [\mathrm{Cupferron}]_{\mathrm{aq,\ total}} - [\mathrm{Cupf^-}]_{\mathrm{aq}} \qquad (4)$$

one obtains

$$K_a = \frac{[\mathrm{H^+}][\mathrm{Cupf^-}]}{[\mathrm{HCupf}]_{\mathrm{aq,\ total}} - [\mathrm{Cupf^-}]_{\mathrm{aq}}} \qquad (5)$$

This can easily be simplified to

$$[\mathrm{Cupf^-}] = \frac{[\mathrm{Cupferron}]_{\mathrm{aq,\ total}}}{[\mathrm{H^+}]/K_a + 1} \qquad (6)$$

After calculation of $[\mathrm{Cupf^-}]$, $[\mathrm{HCupf}]_{\mathrm{aq}}$ can be calculated from eqn. (4). As the total amount of cupferron in the aqueous phase is known (experimentally) $[\mathrm{HCupf}]_{\mathrm{crg}}$ can be calculated by difference. K_D is then calculated using eqn. (1).

ACKNOWLEDGEMENTS

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SUMMARY

A spectrophotometric method for the determination of the distribution coefficient of cupferron, based on a colour reaction of cupferron with sodium pentacyanoammine ferrate(II), is described. A value of 142 was obtained above pH 3 for chloroform and aqueous solutions of perchloric and hydrochloric acid. At higher acidities lower values (120–135) were obtained. Some possible causes for this are briefly discussed.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour la détermination du coefficient de partage du cupferron; elle est basée sur la réaction colorée de ce composé avec le pentacyanoamminoferrate(II) de sodium. Une valeur de 142 a été obtenue pour des solutions dans l'eau et dans le chloroforme, en milieux perchlorique et chlorhydrique.

ZUSAMMENFASSUNG

Die Farbreaktion des Kupferrons mit Natriumpentacyano-ammin-ferrat-(II) wurde zur spektrophotometrischen Bestimmung des Verteilungskoeffizienten des Kupferrons herangezogen. Für die Verteilung zwischen Chloroform und wässriger Perchlorsäure bezw. Salzsäure wurde der Wert 142 bei pH > 3 erhalten. Stärker saure Lösungen geben tiefere Werte.

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TITRIMETRIC DETERMINATION OF THIOCYANATES WITH SULFATOCERIC ACID

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The determination of thiocyanate by its quantitative oxidation to sulfate and cyanide with iodate has been studied by several investigators. Jamieson *et al.*[1] determined copper by precipitation as thiocyanate, dissolution in 6 *N* hydrochloric acid and titration with iodate solution to the iodine monochloride end-point. He later extended the method for the determination of zinc and mercury by precipitation as $Zn[Hg(SCN)_4]$ and titration with standard iodate solution[2]. Lang[3], however, found that direct titration gave erroneous results and recommended the addition of a known excess of iodate with a subsequent iodometric titration. According to Fenwick *et al.*[4], the direct titration gave good results provided that the final hydrochloric acid concentration was about 10%. Since high acidity brings about decomposition of thiocyanate, Hammock *et al.*[5] recommended the addition of thiocyanate to an excess of iodine monochloride solution followed by titration with iodate. Gauguin[6] employed potentiometric titrations to determine macro amounts of thiocyanate in 1 *N* hydrochloric acid. Joshi[7] recommended that an acid concentration of 1.5–3 N hydrochloric acid be used to obtain reliable results.

Because of the multiplicity of different recommended procedures, the present study was undertaken in an effort to determine the accuracy of the method. An attempt was made to correlate the divergent views expressed previously by determining the manner in which errors arise and the extent to which different sources of error affect the direct oxidative titration of thiocyanate. Sulfatoceric acid was selected as the titrant, partly because of the high oxidation potential and partly because the cerium(IV) – thiocyanate system has not been investigated.

PRELIMINARY TESTS

It is contended that a direct titration of thiocyanate leads to low results because of the acid decomposition and aerial oxidation of thiocyanate[8]. A number of different sample solutions of thiocyanate ($M/60$) were taken and hydrochloric acid was added to give a final acid concentration of 0.2–7 N. The solutions were allowed to stand for different lengths of time and then titrated with sulfatoceric acid after adding 6 ml of 0.02 M iodine monochloride, or with potassium iodate to the iodine monochloride end-point. The comparative data thus obtained showed that neutral and slightly acid thiocyanate solutions do not undergo noticeable decomposition or oxidation in 10 h. Thiocyanate solutions containing 4–5 N hydrochloric acid showed detectable oxidation and decomposition while solutions with higher acidity, and in particular those solutions exposed to the air, underwent decomposition at a rate of approximately 10% per h. However, acidified solutions contained in stoppered iodine flasks showed only a loss of 1.1% in 10 h, confirming that acidity alone does not cause rapid decomposition. Thus, the extent to which these sources of error may affect the results during normal titration times would be expected to be less than the range of variations observed by different investigators[3,5,7].

The fact that increasing the acidity led to lower and lower results for thiocyanate indicated the loss of volatile intermediates, possibly from sulfide and sulfite. Tests were made with thiocyanate solutions containing different amounts of acid (1.5–7 N) by adding varying, but less than equivalent, amounts of cerium(IV) or iodate. Pure dry nitrogen was bubbled into the solution through a fritted disc to flush any gases into a trap made from a long spiral of glass tubing. The gases were frozen in the trap and then transferred to a 5-cm infrared cell. When the initial concentration of thiocyanate was not less than 0.2 M, the infrared spectra showed weak absorption bands for sulfur dioxide and hydrogen sulfide. The bands were stronger when the solutions contained greater than 4 N hydrochloric acid. After some time, free sulfur appeared both in the trap and in the infrared cell. At thiocyanate concentrations of the order of $M/60$, the concentrations of gases appeared to be too small to be detected.

Thiocyanate is visualized as existing in 3 resonance forms[9], each contributing approximately equally to the structure. At high acid concentrations, the resonance form with the negative charge on the sulfur may become comparatively more important, thus giving a possible explanation for the elimination of hydrogen sulfide. This elimination results in the use of less oxidant; however, the rate of loss of hydrogen sulfide or sulfur dioxide under normal titration procedures must be too slow to affect the final results to an appreciable extent. This is especially the case when an excess of oxidant is added as recommended by LANG[3], since these side reactions are less likely and the reaction is more quantitatively complete. The titrations should be performed after the solutions are made ice-cold. It is therefore contended that direct titration can give good results provided that the various sources of errors are controlled. By taking precautions to eliminate air oxidation and the escape of hydrogen sulfide and sulfur dioxide, results within ± 0.1% can be obtained by ordinary titrimetric methods.

EXPERIMENTAL

Reagents

All compounds used in the course of this study were analytical reagents of highest purity; in addition, the reagents were standardized by conventional methods[10]. Potassium thiocyanate was standardized against silver nitrate conductimetrically and then diluted to obtain several concentrations. All volumetric glassware employed was calibrated although some had been manufactured to comply with the National Bureau of Standards tolerances.

Determination of thiocyanate, cobalt(II), zinc(II) and mercury(II)

A known amount of each substance to be determined was dissolved in 20 ml of distilled water. Potassium thiocyanate was titrated directly, while cobalt(II) and zinc(II) were precipitated with a sufficient quantity of 0.1 *M* $K_2[Hg(SCN)_4]$ and mercury(II) with a mixture of 0.4 *M* potassium thiocyanate and 0.1 *M* zinc sulfate

TABLE I

DETERMINATION OF THIOCYANATE, COBALT, ZINC AND MERCURY

	Substance taken (g)	*Volume of 0.1033 N $H_2Ce(SO_4)_3$ used (ml)*	*Substance found (g)*
KSCN			
	0.01786	10.68	0.01786
	0.02010	12.00	0.02010
	0.02520	15.05	0.02517
	0.03218	19.20	0.03212
	0.04100	24.50	0.04099
$CoCl_2 \cdot 6H_2O$			
	0.01985	19.37	0.01983
	0.02575	25.13	0.02573
	0.03072	30.00	0.03072
	0.03970	38.75	0.03969
	0.05000	48.45	0.04962
$ZnSO_4 \cdot 7H_2O$			
	0.01098	8.87	0.01098
	0.01408	11.38	0.01408
	0.02490	20.10	0.02487
	0.02745	22.20	0.02747
	0.03520	28.45	0.03521
$HgCl_2$			
	0.01170	10.00	0.01169
	0.01690	14.45	0.01688
	0.02220	19.00	0.02220
	0.02860	24.50	0.02863
	0.03506	30.00	0.03506

solution. The solutions were allowed to stand for 3 h, and filtered. The precipitates were washed with 0.01 M $K_2[Hg(SCN)_4]$ and finally twice with distilled water. The precipitates were dissolved and leached from the filter paper with a sufficient amount of ice-cold dilute hydrochloric acid to give a final concentration of 3–4 N. Five ml of 0.02 M iodine monochloride and 5 ml of chloroform or carbon tetrachloride were added to the cold solution. The titration was performed by adding standardized cerium-(IV) solution rapidly until the equivalence point was nearly reached as indicated by a distinct appearance of iodine color in the solution. Thus loss of hydrogen sulfide or sulfur dioxide was decreased as much as possible. The titration was completed by dropwise addition of oxidizing agent until the iodine color disappeared from the organic solvent layer. The results of some of the determinations made for each case are recorded in Table I.

SUMMARY

The direct oxidative titration of thiocyanate has been investigated in order to correlate the divergent views previously expressed. Sulfatoceric acid was used as the oxidant with iodine monochloride as a preoxidant and indicator. The low results at high acidities observed by previous investigators are attributed to loss of hydrogen sulfide and sulfur dioxide, which can be detected by infrared spectra. Cobalt(II), zinc(II), and mercury(II) were also determined by titrating the precipitated complex thiocyanates. Accurate and reproducible results were obtained in hydrochloric acid concentrations ranging from 1.7–4.5 N.

RÉSUMÉ

Une méthode volumétrique est décrite pour le dosage des thiocyanates au moyen de cérium(IV), en présence de monochlorure d'iode comme préoxydant et indicateur. Le cobalt, le zinc et le mercure(II) peuvent être dosés par titrage de leur thiocyanate complexe précipité.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Thiocyanaten mit Cer-(IV)-lösung. Die bei höherer Acidität erhaltenen zu niedrigen Resultate werden auf einen Verlust an Schwefelwasserstoff und Schwefeldioxyd zurückgeführt. Die Methode kann auch zur Bestimmung von Kobalt, Zink und Quecksilber-(II) über deren Thiocyanate verwendet werden.

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ANALYTISCHE UNTERSUCHUNG DER REAKTION VON THALLIUM(III) UND HYDRAZINSULFAT

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Zur volumetrischen Thallium-Bestimmung wurden bereits eine ganze Reihe von Methoden ausgearbeitet, die auf der Oxydation von einwertigem Thallium zu dreiwertigem, oder umgekehrt auf der Reduktion von dreiwertigem Thallium zu einwertigem, berühen. Die Möglichkeit der oxydimetrischen Bestimmung von einwertigem Thallium haben wir in einer unlängst veröffentlichten Mitteilung[1] behandelt. Zur Bestimmung von dreiwertigem Thallium durch direkte Titration kann als reduktometrisches Reagenz *z.B.* Titanium(III)-Chlorid[2], Thiosulfat[3], Askorbinsäure[4] oder Hydrochinon[5] herangezogen werden. In den zwei erstgenannten Fällen muss jedoch die Bestimmung bei erhöhter Temperatur ausgeführt werden, während nur Hydrochinon die Bedingung einer an der Luft beständigen Masslösung erfüllt.

In der vorliegenden Arbeit untersuchten wir die Möglichkeit der Bestimmung von dreiwertigem Thallium mittels Hydrazinsulfat, aus dem sich sehr beständige Masslösungen herstellen lassen und das sich auch des öfteren als energisches reduktometrisches Reagenz bewährt hat[6].

EXPERIMENTELLER TEIL

Reagenzien

Lösungen von $Tl_2(SO_4)_3$ wurden durch Oxydation von Tl_2SO_4 mit Bromat in salzsaurer Lösung bei erhöhter Temperatur bereitet. Das dreiwertige Thallium wurde dann mit Ammoniak als Hydroxyd gefällt, der Niederschlag zur Entfernung der Chloride gut ausgewaschen und anschliessend in der nötigen Menge verdünnter Schwefelsäure (1:1) gelöst. Der Faktor der auf diese Weise erhaltenen Lösung wurde komplexometrisch unter Verwendung von 1-(2-Pyridylazo)-2-naphtol als Indikator[7] bestimmt.

Die 0.01 *M* EDTA-Lösung und die 0.1 *N* Hydrazinsulfat-Lösung wurden aus gereinigten Präparaten bereitet. Die verwendete Schwefelsäure und Ammoniak waren mit p.a. bezeichnete Präparate.

Apparatur

Die potentiometrischen Titrationen wurden mit einem Kompensations-Potentiometer der Type P4 ausgeführt. Es wurden folgende Elektrodenpaare verwendet:

Pt–ges. Kalomelelektrode, C–ges. Kalomelelektrode, Pt–C. Als Graphitelektroden wurden Graphitstifte der Fa. L. und C. Hardmuth Koh-i-Noor (Tschechoslowakei) verwendet. Bei den Messungen mit der Kalomelelektrode wurde eine Nitrat-Brücke angewandt.

DISKUSSION DER RESULTATE

(1) *Titration von dreiwertigem Thallium mit Hydrazinsulfat*

Während die oxydimetrische Bestimmung von einwertigem Thallium oft in salzsaurer Lösung durchgeführt wird, in der wegen der Bildung von Chlorokomplexen der Potentialwert des Systems Tl^{3+}/Tl^{+} stark verschoben ist, eignet sich für die Reduktion von dreiwertigem Thallium besser ein schwefelsaure Lösung, in der das Oxydations-reduktions Potential des Systems Tl^{3+}/Tl^{+} den Wert 1.22 V besitzt[9].

In der vorliegenden Arbeit haben wir zunächst die Reduktion von dreiwertigem Thallium mit Hydrazinsulfat in Lösungen mit wechselndem Gehalt an Schwefelsäure mittels direkter potentiometrischer Titration untersucht, wobei wir die Platinelektrode als Indikations- und die Kalomelelektrode als Vergleichselektrode verwendeten. Wir fanden bei diesen Versuchen, dass die Reaktion nach folgender Gleichung verläuft:

$$2\,Tl^{3+} + N_2H_4 \rightarrow 2\,Tl^{+} + N_2 + 4\,H^{+},$$

dass aber in der Nähe des Aequivalenzpunktes die Einstellung des Potentials sehr langsam ist (etwa 15 Minuten für den letzten Reagenztropfen), und dass selbst nach Erreichen des Aequivalenzpunktes das Potential nicht absolut konstant ist, und nach längerer Zeit den ursprünglichen Wert erreicht. Da die Titration in weniger saueren Lösungen schneller verläuft, erhofften wir bessere Resultate in der Weise zu erzielen, dass wir entweder die sauere Tl(III)-Lösungen mit Ammoniak soweit neutralisierten, bis sie durch ausfallendes $Tl(OH)_3$ eben getrübt wurde, und den entstandenen Niederschlag mit möglichst wenig Schwefel- oder Essigsäure wieder lösten, oder durch Einstellung des pH der Lösung mittels Pufferlösungen. Es wurde aber in keinem Fall eine Verbesserung des Titrationsverlaufes erreicht. Die Resultate waren immer mit positiven Fehlern behaftet (bis + 10 %). Wenn die Messungen bei erhöhter Temperatur ausgeführt wurden, kam es zuerst zu einer Hydrolyse des Tl(III)-Salzes, so dass die Säurekonzentration in der Lösung erhöht werden musste, was eine langsamere Reaktion zur Folge hatte.

Da in schwach saueren Lösungen schon bei Zimmertemperatur sofort nach Zugabe des Reagens die Entwicklung eines Gases (N_2) beobachtet wurde, konnte angenommen werden, dass der unbefriedigende Titrationsverlauf eher durch die ungeeignete Indikationsmethode als durch den langsamen Verlauf der eigentlichen Reaktion bedingt war. Wir haben deshalb Orientierungsversuche ausgeführt, bei denen zuerst die Platinelektrode und dann die Kalomelelektrode durch eine Graphitelektrode ersetzt wurde. In beiden Fällen wurde eine schnelle Einstellung des Potentials während des ganzen Titrationsverlaufes beobachtet. Da in dem ersten Fall (bei Verwendung des Elektrodenpaares Graphit–gesättigte Kalomelelektrode) die Potentialänderung im Aequivalenzpunkt kleiner war, und etwa 80 mV für 0.1 ml 0.1 *N* $N_2H_4{\cdot}H_2SO_4$ betrug, während bei Verwendung des Systems Platin–Graphit dieser Wert etwa 350 mV betrug, arbeiteten wir anschliessend nur noch mit dem Elektrodensystem Pt–C.

Bei der Untersuchung des Einflusses des Säuregehaltes auf die Geschwindigkeit und den quantitativen Verlauf der Reaktion fanden wir, dass die Reaktion sowohl in Lösungen, die nur die zur Lösung des Thalliumhydroxyds benötigten Mengen an Schwefelsäure enthielten, als auch in Gegenwart von 10 Gewichtsprozenten H_2SO_4 quantitativ verläuft. Die Reaktionsgeschwindigkeit jedoch wird durch die Säurekonzentration stark beeinflusst, mit wachsenden Säuregehalt der Lösung verläuft die Reaktion langsamer. So muss in einem Medium von 1.5 % H_2SO_4 in der Nähe des Aequivalenzpunktes nach Reagenszugabe eine Minute lang auf die Einstellung des Potentials gewartet werden, während in einem Medium von 10% H_2SO_4 die Einstellung des Potentials etwa 15 Minuten beansprucht. Die bei der Titration von Lösungen mit verschiedener Schwefelsäurekonzentration erhaltenen Resultate sind in Tabelle I zusammengestellt.

TABELLE I

TITRATION VON DREIWERTIGEM THALLIUM MIT HYDRAZINSULFAT IN LÖSUNGEN VON VERSCHIEDENER SCHWEFELSÄUREKONZENTRATION (40 ml VOLUMEN)

Medium % (gew.) H_2SO_4	*mg Tl^{3+}*		*Abweichung (%)*	*Potentialeinstellung im Aequivalenzpunkt nach Min*
	gegeben	*gefunden*		
1.5	83.40	84.01	+0.73	1
1.5	125.10	125.34	+0.19	1
1.5	166.80	167.22	+0.25	1
2.5	83.40	83.69	+0.35	3
2.5	125.10	125.56	+0.37	3
2.5	166.80	166.88	+0.05	3
9	83.40	83.78	+0.45	15
9	125.10	125.82	+0.58	15
9	166.80	167.19	+0.23	15
+	83.40	83.58	+0.22	1
+	125.10	125.40	+0.24	1
+	166.80	167.33	+0.32	1

+ = Die Lösung wurde mit Ammoniak bis zur Trübung durch Thallium(III)-Hydroxyd neutralisiert, dieses wurde anschliessend in der kleinsten notwendigen Menge H_2SO_4 (1 : 1) wieder gelöst.

Folgende Arbeitsweise hat sich am besten bewährt: Sauere Thallium(III)-Salzlösungen werden mit Ammoniak neutralisiert bis zur beginnenden Trübung durch $Tl(OH)_3$. Dieses wird mit einigen Tropfen H_2SO_4 (1:1) wieder gelöst und die Lösung anschliessend potentiometrisch mit einer Hydrazinsulfat-Masslösung unter Verwendung von Pt und C Elektroden titriert (siehe Tabelle I). Unter den angeführten Bedingungen ist es in der Regel nicht nötig, länger als eine Minute auf die Einstellung des Potentials zu warten. Die Potentialänderung im Aequivalenzpunkt beträgt etwa 300 mV für 0.03 ml 0.1 N $N_2H_4{\cdot}H_2SO_4$; das Inflexionspotential, dessen Lage sich mit sinkender Säurekonzentration zu negativeren Werten verschiebt, liegt im Medium von 9 % H_2SO_4 bei etwa 150 mV. 1 ml 0.1 N $N_2H_4{\cdot}H_2SO_4$ entspricht 10.2195 mg Tl^{3+}.

Aus Tabelle I folgt, dass die Resultate aller Bestimmungen mit positiven Fehlern behaftet sind. Diese Tatsache stimmt mit den theoretischen Überlegungen überein[7], nach denen die zur Standardisation von Tl^{3+}-Lösungen angewandte komplexometrische Titration etwas zu niedrige Werte liefert.

Wie unsere Resultate zeigen, wird die Bestimmung von einer ganzen Reihe Ionen nicht gestört, so *z.B.* Be^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Pb^{2+}, Ag^{+}, Fe^{3+}, As^{5+}, Ga^{3+}, In^{3+}, Ti^{4+}, Li^{+}, NO_3^-, F^-, SiO_3^{2-} und PO_4^{3-} (siehe Tabelle II). In einigen Fällen wird natürlich die Titration durch Anwesenheit einer grösseren Salzmenge verlangsamt.

TABELLE II

TITRATION VON 83.40 mg Tl^{3+} MIT 0.1 *N* HYDRAZINSULFAT IN GEGENWART VON VERSCHIEDENEN IONEN (40 ml VOLUMEN)[a]

Anwesend mg		*Gefunden mg*	*Abweichung in %*
Be^{2+}	92	83.58	+0.22
Zn^{2+}	84	83.64	+0.29
Cr^{3+}	76	83.55	+0.18
Al^{3+}	79	83.74	+0.41
Mn^{2+}	95	83.64	+0.29
Ni^{2+}	105	83.67	+0.32
Co^{2+}	96	83.76	+0.43
Ca^{2+}	105	83.58	+0.22
Sr^{2+}	80[b]	83.45	+0.06
Ba^{2+}	94[b]	83.70	+0.36
Mg^{2+}	110	83.81	+0.49
Cu^{2+}	92	83.47	+0.08
Cd^{2+}	84	83.67	+0.32
Bi^{3+}	78	83.60	+0.24
Pb^{2+}	70[c]	83.42	+0.02
Ag^{2+}	75	83.77	+0.44
As^{5+}	90	83.67	+0.32
Fe^{3+}	85	83.47	+0.08
Ga^{3+}	90	83.62	+0.26
In^{3+}	100	83.73	+0.40
Ti^{4+}	75	83.76	+0.43
Li^{+}	60	83.69	+0.35
NO_3^-	150	83.61	+0.25
F^-	50	83.79	+0.47
SiO_3^{2-}	65	83.75	+0.42
PO_4^{3-}	200	83.71	+0.37

[a] Die Lösung wurde mit Ammoniak bis zur Trübung durch $Tl(OH)_3$ neutralisiert, dass anschliessend mit der gerade notwendigen Menge von H_2SO_4 (1 : 1) gelöst wurde.

[b] $Tl(OH)_3$ wurde mit HNO_3 gelöst.

[c] Der $PbSO_4$ Niederschlag verlangsamt die Reaktion, es muss daher langsam titriert werden.

Die Titration wird gestört durch Ionen, die mit Thallium Komplexe bilden und dadurch das Redoxpotential herabsetzen, oder die Thallium ausfällen, wodurch die Titration verlangsamt oder unmöglich gemacht wird, sowie schliesslich durch Systeme, die selbst durch Hydrazinsulfat reduziert werden (Cl^-, Br^-, I^-, MoO_4^{2-}, WO_4^{2-}, VO_3^- und $Cr_2O_7^{2-}$).

(2) Bestimmung von Hydrazinsulfat mit Thallium(III)-Masslösungen

Masslösungen von dreiwertigem Thallium können unter Verwendung des im vorgehenden beschriebenen Elektrodensystems zur direkten potentiometrischen

Titration von 0.1 N wässerigen Hydrazinsulfatlösungen benutzt werden, ohne besondere Modifikation des Mediums, und mit derselben Genauigkeit wie bei der umgekehrten Titrationsrichtung. In der Nähe des Aequivalenzpunktes muss etwa 3 Minuten auf die Einstellung des Potentials gewartet werden. In saueren Lösungen verläuft die Reaktion langsam, was leicht zur Ueberschreitung des Endpunktes führen kann. 1 ml 0.1 N $Tl_2(SO_4)_3$ Masslösung entspricht 0.80125 mg N_2H_4.

Nach unseren Resultaten kann Hydrazinsulfat sehr gut auf indirektem Wege komplexometrisch bestimmt werden. Es wird dabei in der Weise vorgegangen, dass zu der Hydrazinsulfatlösung ein zweifacher Ueberschuss an Thallium(III)-Sulfat Masslösung (auf die Normalität bezogen) gegeben wird; der weitere Verlauf ist derselbe wie bei der komplexometrischen Bestimmung von dreiwertigem Thallium[7]. Die Lösung wird mit Ammoniak bis zum Auftreten einer gelben Färbung neutralisiert, anschliessend wird Essigsäure bis zum Klarwerden der Lösung zugegeben, und nach Zusatz von 1-(2-Pyridylazo)-2-naphtol als Indikator wird mit einer 0.1 N EDTA-Lösung bis zum Farbumschlag vom violett nach zitronengelb titriert. Der Titrationsverbrauch wird von dem bei einem Blindversuch ermittelten Verbrauch abgezogen, wodurch die Menge von EDTA, *bzw.* von dreiwertigem Thallium errechnet wird, die der anwesenden Hydrazinmenge entspricht. Die aus 10 Bestimmungen berechnete mittlere relative Abweichung betrug 0.05%. 1 ml 0.1 N EDTA entspricht 0.80125 mg N_2H_4.

ZUSAMMENFASSUNG

Eine Untersuchung über die Reaktion von dreiwertigem Thallium mit Hydrazinsulfat ergab, dass in schwach schwefelsauren Lösungen die Reaktion schnell und quantitativ verläuft, sodass sie sowohl zur direkten potentiometrischen Titration von Tl^{3+} wie auch zur Bestimmung von Hydrazinsulfat mit Thallium(III)-Masslösungen angewandt werden kann. Es wird empfohlen das Elektrodensystem Pt–C zur Titration zu verwenden.

Hydrazinsulfat kann ebenfalls auf indirektem Wege durch Zugabe eines Ueberschusses von Thallium(III)-Salz bestimmt werden, dessen unverbrauchte Menge komplexometrisch bestimmt wird.

SUMMARY

The reaction of thallium(III) with hydrazine sulphate has been studied. In solutions slightly acidified with sulphuric acid the reaction is rapid and quantitative; direct potentiometric titration of thallium(III) with hydrazine sulphate solutions is possible as well as the reverse titration. The electrode system Pt–C is recommended.

Hydrazine sulphate may also be determined indirectly by oxidation with excess of thallium(III) which is then titrated compleximetrically.

RÉSUMÉ

Les auteurs ont examiné la réaction du thallium(III) avec le sulfate d'hydrazine. Le thallium(III) peut ainsi être dosé potentiométriquement par l'hydrazine, soit directement, soit par titrage en retour. Le systême Pt–C est recommandé comme électrode. Il est possible aussi de doser l'hydrazine par le thallium(III) en excès, et titrage en retour par compleximétrie.

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ANALYTICAL APPLICATIONS OF THE REACTION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID

PART V. DETERMINATION OF SILVER

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ERDEY AND BUZÁS have described a direct method for the determination of silver[1], in which silver ions are reduced to the metal in hot solution with ascorbic acid; the end-point of the titration is detected with variamine blue. However, the simplicity and accuracy of the titration of hexacyanoferrate(III) with ascorbic acid suggested that this reaction could be utilized also for the indirect determination of silver. The titration has already been shown to be advantageous for indirect determinations of a number of oxidizing and reducing agents[2], where the favourable redox potential of the hexacyanoferrate(III)-hexacyanoferrate(II) system can be applied.

Hexacyanoferrate(III) and hexacyanoferrate(II) are well known as precipitants, this property being widely utilized in qualitative and quantitative analysis. Both ions form precipitates with several metals of groups 1–3. It is interesting to note that metal hexacyanoferrate(II) precipitates are generally less soluble than the corresponding hexacyanoferrate(III) precipitates, and that metal hexacyanoferrate(III) precipitates generally contain only one metal ion, whereas the hexacyanoferrate(II) compounds are usually double salts.

We have therefore extended the previous investigations on oxidation-reduction reactions[2] to cover reactions involving precipitation. In such methods, the precipitate of metal hexacyanoferrate(III) is determined by a titration with ascorbic acid. The determination of silver provides an excellent example of such a procedure.

Silver ions in neutral or nitric acid-containing medium form a reddish brown precipitate with hexacyanoferrate(III)[3,4]. The precipitate is difficult to filter, though the situation can be improved by the addition of foreign electrolytes (*e.g.* ammonium nitrate). The precipitate can be washed with ammonium nitrate solution. If ammonium hydroxide is added to the washed precipitate, it partly dissolves quite quickly, and dissolves completely after some time. However, when sodium hexacyanoferrate(II) solution is added to the precipitate, which has been mixed with ammonium hydroxide, a precipitation exchange reaction takes place and a yellowish-white silver hexacyanoferrate(II) precipitate is formed:

$$Ag_3\,Fe(CN)_6 + K_4\,Fe(CN)_6 = KAg_3\,Fe(CN)_6 + K_3\,Fe(CN)_6$$

The hexacyanoferrate(III) ions, which are so dissolved, can be separated from the precipitate by filtration, and can be titrated with ascorbic acid. The amount of hexacyanoferrate(III) released and titrated is therefore directly proportional to the amount of silver present in the original solution. Thus the equivalent weight of silver in this method is three times its atomic weight.

EXPERIMENTAL

Reagents

0.1 N Silver nitrate solution. Dissolve 16.99 g of pure silver nitrate in water and dilute to 1 l. The solution can be standardized with standard 0.1 *N* sodium chloride as follows: to 20.00 ml of standard 0.1 *N* sodium chloride solution add 10 ml of buffer (10.2 ml of glacial acetic acid and 2.8 g of crystalline sodium acetate diluted to 1 l), then add 3 drops of freshly prepared 1% variamine blue acetate solution. Titrate the mixture with silver nitrate until the violet colour appears[5].

0.1 N Ascorbic acid standard solution. Dissolve 8.9 g of ascorbic acid in water and dilute to 1 l. Glass-distilled water must be used. The solution can be standardized as follows: to 20.00 ml of standard 0.1 *N* potassium hexacyanoferrate(III) add 1 g of potassium hydrogen carbonate and 1 ml of 0.1% 2,6-dichlorophenolindophenol indicator (or 0.5 g of the solid mixture). Titrate the solution with ascorbic acid solution until the blue colour disappears[2].

2,6-Dichlorophenolindophenol indicator. A filtered aqueous 0.1% solution or a solid 1:500 mixture of 2,6-dichlorophenolindophenol with pure dry sodium chloride[2].

Procedure

(*a*) *Precipitation of silver hexacyanoferrate(III).* The solution containing 100–550 mg of silver may be neutral or may contain some nitric acid. Add 1–2 g of solid ammonium nitrate, and shake to dissolve. Precipitate silver as the hexacyanoferrate(III) salt with 20 ml of 5% potassium hexacyanoferrate(III) solution. Let the precipitate settle for 5–10 min, filter on a medium-pored filter paper, and wash 5–6 times with 1% ammonium nitrate. Discard the filtrate.

(*b*) *Precipitation exchange reaction.* Return the filter paper containing the precipitate to the original beaker. Add 20 ml of 2 *N* ammonium hydroxide, and break the filter paper up as much as possible with a glass rod. Dissolve 1 g of solid ammonium nitrate in this mixture, and then add 10 ml of 5% potassium hexacyanoferrate(II) solution. Immediately a yellowish-white precipitate appears, and the last traces of the red silver hexacyanoferrate(III) precipitate disappear. Add 2 drops of phenolphthalein indicator, and neutralize the solution cautiously with 1 : 1 nitric acid. To the mixture add 1 g of solid potassium hydrogen carbonate, and after 10 min filter the precipitate. Wash 5–6 times thoroughly with 1% ammonium nitrate and collect the filtrate in a titration flask.

(*c*) *Titration.* Add to the solution 2 g of solid potassium hydrogen carbonate and 1 ml or 0.5 g of the indophenol indicator, and titrate with 0.1 *N* ascorbic acid solution. The initial green colour changes gradually to deep blue and at the end-point the solution becomes colourless. 1 ml 0.1 *N* ascorbic acid is equivalent to 32.364 mg Ag.

Summarized results of some silver determinations are shown in Table I. The standard deviation of the method, calculated from these results, is ± 0.34%, while the standard deviation of the mean of 12 parallel determinations is 0.1%.

TABLE I

Ag taken (mg)	*Ag found (mg)*	*Error (mg)*	
		maximum	*minimum*
107.88	107.77 (3 results)	— 0.43	— 0.11
215.76	216.34 (11 results)	+ 1.40	+ 0.11
323.64	325.04 (3 results)	+ 2.59	+ 0.32
539.40	341.55 (3 results)	+ 3.02	+ 1.07

SUMMARY

Silver is determined titrimetrically after precipitation from neutral or dilute nitric acid solution as silver hexacyanoferrate(III). The filtered precipitate is converted to silver hexacyanoferrate(II) and the hexacyanoferrate(III) ions released are eventually titrated with ascorbic acid.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'argent, par précipitation sous forme d'hexacyanoferrate(III), transformation en hexacyanoferrate(II) et titrage des ions hexacyanoferrates(III) libérés au moyen d'acide ascorbique.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Silber durch Umsetzung mit Kalium-hexacyano-ferrat-(III). Das gebildete Silbersalz wird abgetrennt, mit Hexacyano-ferrat-(II) Lösung behandelt und das hierbei in Freiheit gesetzte Hexacyano-ferrat-(III) mit Ascorbinsäure titriert.

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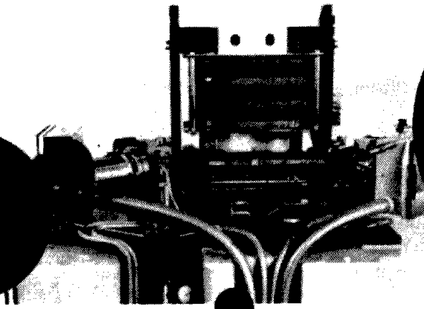

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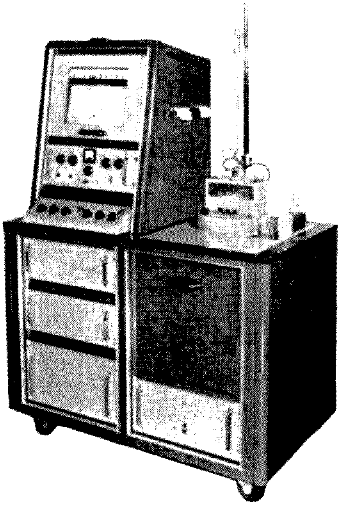

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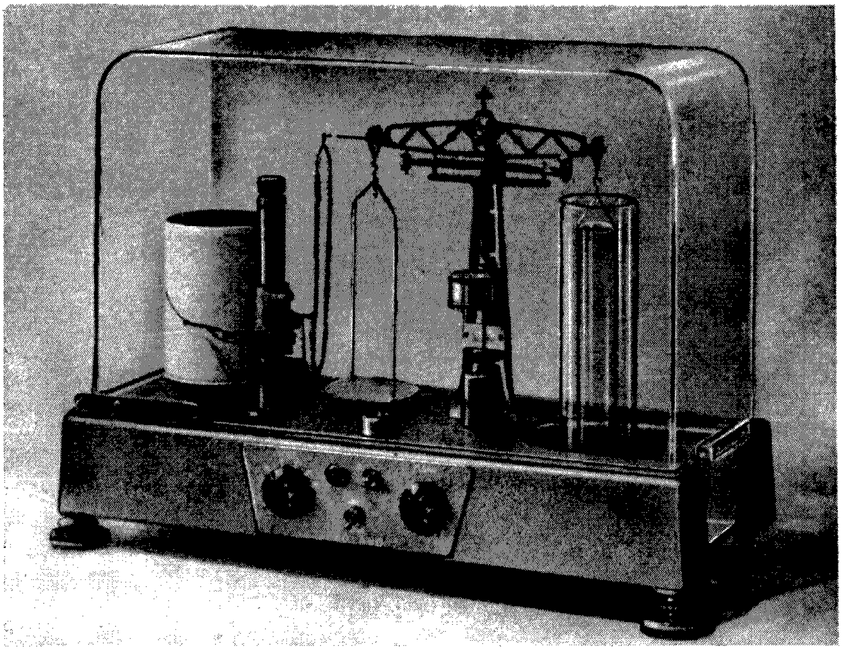

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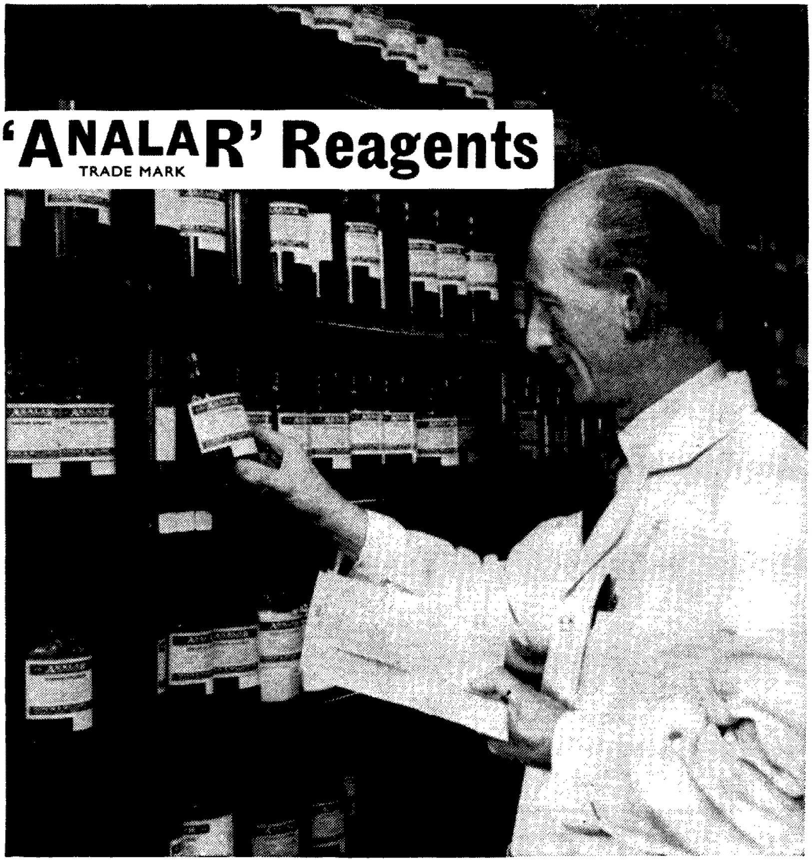

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