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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 26, No. 2, February 1962

AN ION-ASSOCIATION SYSTEM FOR THE SELECTIVE EXTRACTION OF MICROGRAM AMOUNTS OF SILVER FROM AQUEOUS SOLUTION

Silver can be extracted from aqueous solution into hexone as the ion-association system formed between its di-*n*-butylamine complex and stearic acid or salicylic acid. In the presence of an auxiliary complexing agent, anthranilic acid diacetic acid, the latter system is highly selective since only mercury(II) interferes. The procedure is sensitive and extracts silver over the range 5 mg–5 μg (0.05 p.p.m.). No compatible common anion interferes. The extraction is 96–98% complete in one pass.

D. BETTERIDGE AND T. S. WEST, *Anal. Chim. Acta*, 26 (1962) 101–109

SORPTION OF ALDONIC ACIDS FROM ETHYL ALCOHOL–WATER SOLUTIONS ON ANION EXCHANGERS

Aldonic acids can be retained quantitatively from ethyl alcohol–water solutions by means of anion exchangers in the sulfate form. After the sorption step the aldonic acids can be easily displaced by washing with water. The sorption is explained by a partition mechanism of the same type as demonstrated in earlier work with strongly polar non-electrolytes. Precautions have to be taken to prevent uptake by means of an ion exchange mechanism. The method permits a separation from exchangeable anions and from non-adsorbable solutes.

O. SAMUELSON AND R. SIMONSON. *Anal. Chim. Acta*, 26 (1962) 110–119

STUDIES ON THE SOLVENT EXTRACTION OF URANYL BIS(DIBENZOYLMETHANE)

Studies of unmasked and masked extractions of the uranyl bis(dibenzoylmethane)·dibenzoylmethane chelate from aqueous solutions into chloroform containing dibenzoylmethane have been made. Aqueous media containing the following were studied: perchlorate, fluoride, acetate, oxalate, citrate, tartrate, nitrilotriacetate, ethylenediaminetetraacetate. A number of fundamental constants have been determined, these values allowing theoretical interpretations of several of the systems to be made.

G. K. SCHWEITZER AND J. L. MOTTERN, *Anal. Chim. Acta*, 26 (1962) 120–127

A COMPARISON OF THREE COMPLEXOMETRIC METHODS FOR DETERMINATION OF ALUMINIUM

(in German)

The complexometric methods for determination of aluminium of Wänninen and Ringbom, Přibil *et al.* and Sajo are compared. That of Přibil has a relative error of —0.3% and a variance of 0.7% in the region of 2.5 mg Al and is preferable. The salt error for sodium acetate, urotropin, sodium chloride, nitrate and sulfate has been studied for the titration with xylenol orange as indicator (Přibil). The rate of formation of the aluminium complex in strongly acidic medium has been studied in relation to the boiling time.

H. Malissa and H. Kotzian, *Anal. Chim. Acta*, 26 (1962) 128–133

MIXED LIGAND COMPLEXES OF IRON(II) AS NONAQUEOUS ACID–BASE AND AQUEOUS OXIDATION–REDUCTION INDICATORS

The neutral mixed ligand complexes dicyano-bis-(1,10-phenanthroline)–iron(II) and dicyano-bis-(2,2′-bipyridine)–iron(II) are suitable indicators for the titration of various weak bases in nonaqueous solvents. They also serve as practical indicators for certain redox titrations in aqueous solutions; their applicability in the determination of primary aromatic amines is especially noteworthy. Formal potentials of the complexes in different concentrations of sulfuric acid are reported; the results confirm earlier findings that the neutral iron(II) complexes form stable protonated species.

A. A. Schilt, *Anal. Chim. Acta*, 26 (1962) 134–143

REDUCTION OF AMMONIUM NITRATE WITH TITANIUM(III) CHLORIDE IN ACID MEDIA

Investigation of acid ammonium nitrate solutions in the presence of titanous chloride has led to a new mechanism of nitrate reduction. It is proposed that the reduction proceeds through two electron changes and terminates as nitrous oxide in solutions whose acid content is greater than 0.1 *N*. The stronger reducing power of the titanous buffer method previously reported arising from a direct pH affect on the titanous–titanyl couple has been discerned rather as an effect arising from different reduction products in that media. The affects of prolonged reaction at 100° and use of osmium tetroxide catalyst were examined. A pH of 4.5 and 100% excess of titanous was insufficient to reduce nitrate to ammonia quantitatively.

E. A. Burns, *Anal. Chim. Acta*, 26 (1962) 143–147

OXIDIMETRIC DETERMINATION OF URANIUM(III) AND (IV) WITH LEAD TETRAACETATE

(in German)

Uranium(III) or (IV) can be determined by reaction with iron(III) solution in hydrochloric acid medium, the iron(II) produced being titrated potentiometrically with lead tetraacetate solution. As little as 20 μg of uranium(IV) can be determined accurately in a volume of 30 ml.

A. Berka, J. Doležal, I. Němec and J. Zýka, *Anal. Chim. Acta*, 26 (1962) 148–154

TITRIMETRIC METHODS FOR THE MICRO DETERMINATION OF SULPHUR AND HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

III. THE SIMULTANEOUS DETERMINATION OF SULPHUR AND THE HALOGENS

The quantitative absorption of the gaseous products arising from the oxidative degradation of organic materials containing sulphur, halogens, (chlorine, bromine and iodine) oxygen and nitrogen, by the rapid empty tube combustion has been studied further. Satisfactory titrimetric methods for the simultaneous determination of sulphur and any one or two of the halogens in the presence or absence of nitrogen have been developed.

R. Belcher and J. E. Fildes, *Anal. Chim. Acta*, 26 (1962) 155–162

PRECIPITATION FROM HOMOGENEOUS SOLUTION

PRECIPITATION OF MOLYBDENUM AS SULFIDE WITH THIOACETAMIDE

The determination of molybdenum with thioacetamide by precipitation of molybdenum sulfide from homogeneous solution has been studied. The optimum acidity is about 0.75 N in perchloric acid and a two-fold excess of reagent suffices. Pressure flasks and large excesses of reagent are unnecessary. Heating for 60 min at boiling water temperatures yields quantitative precipitation.

F. Burriel-Martí and A. Maceira Vidán, *Anal. Chim. Acta*, 26 (1962) 163–167

METALLIC COPPER FOR THE STANDARDIZATION OF EDTA SOLUTION

The standardization of EDTA solution against metallic copper as primary standard is studied. Six indicators were examined; titration with PAN as indicator at pH 6 is recommended.

T. Iwamoto and K. Kanamori, *Anal. Chim. Acta*, 26 (1962) 167–171

A NEW METHOD FOR THE STUDY OF INTERMETALLIC COMPOUND FORMATION IN MIXED AMALGAMS

A chronoamperometric method is described for the study of mixed amalgams. It is equivalent to measuring the dependence on time of the rate of anodic stripping at controlled potential of one of the metals involved. When applied to amalgams containing cobalt and zinc in various proportions, it reveals the presence of five distinct species containing zinc. One of these is identified as the "free" metal; another has the formula $CoZnHg_x$, and has a dissociation constant, $K = [Co_2][Zn_2]/[CoZnHg_x]^2$, equal to 25 ± 8.

H. K. Ficker and L. Meites, *Anal. Chim. Acta*, 26 (1962) 172–179

THE EFFECT OF SURFACE-ACTIVE AGENTS ON THE POLAROGRAMS OF PYRO- AND TRI-PHOSPHATE COMPLEXES

Camphor and gelatin affect the cathodic steps of metal complexes with pyrophosphate and triphosphate. Camphor displaces them to more negative potentials allowing them to rise in the neighbourhood of its desorption potential. Gelatin (0.1%) virtually obliterates all the steps, while lower concentrations distort them. However, cathodic polarograms relating to thallium(I) and silver(I) from a pyro/triphosphate base electrolyte are not significantly affected by camphor or gelatin.

P. R. SUBBARAMAN, P. S. SHETTY AND J. GUPTA, *Anal. Chim. Acta*, 26 (1962) 179–184

DETERMINATION OF MINUTE QUANTITIES OF WATER AND WATER VAPOR BY THE HYGROPHOTOGRAPHIC METHOD

A more accurate calibration technique is described for the hygrophotographic method for determination of traces of water. The quantity of water absorbed by the hygrophotographic plate is a linear function of the time of exposure up to the state of saturation. Applications include measurement of the permeability of plastic materials.

J. SIVADJIAN AND F. CORRAL, *Anal. Chim. Acta*, 26 (1962) 185–190

SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM IN STEEL WITH STILBAZO

A procedure for the determination of aluminium in steel is described. Aluminium is separated from iron and interfering elements by ion exchange in concentrated hydrochloric acid solution, and finally determined spectrophotometrically with stilbazo.

C. U. WETLESEN, *Anal. Chim. Acta*, 26 (1962) 191–194

AN ION-ASSOCIATION SYSTEM FOR THE SELECTIVE EXTRACTION OF MICROGRAM AMOUNTS OF SILVER FROM AQUEOUS SOLUTION

D. BETTERIDGE* AND T. S. WEST

Chemistry Department, University of Birmingham (Great Britain)

(Received June 1st, 1961)

An examination of the relevant literature reveals that all but two of the very few distribution procedures[1-5] which are available for silver are dependent on chelation systems and consequently are somewhat unselective in action. It appeared to us that the situation could be improved considerably by development of an extractable ion-association system since the latter frequently possess a higher degree of selectivity and a wider working range. Since silver ion has a high propensity for reaction with nitrogen-containing ligands, we first of all examined the alkylamines as reagents for the displacement of coordinated water molecules and subsequently a range of bulky anions to associate firmly with the charged intercalation complex thus formed.

The amine system chosen as a model to guide further investigation was that of the butylamines, *viz.* *n*-butylamine, *sec*-butylamine, *tert*-butylamine and isobutylamine, di-*n*, di-*sec*, diisobutylamine and tri-*n*-butylamine, as it was felt that such an examination might lead to elucidation of the importance of structural effects in relation to extractive behaviour.

Preliminary experiments were done with 10^{-2} *M* silver nitrate solution, using each amine in turn with the solvents toluene, chloroform, isobutylmethyl ketone and tri-*n*-butylphosphate. Each silver amine pair was examined in each solvent over four acidity ranges corresponding to 4 *N* nitric acid, pH 4.6, pH 7 and excess of amine acting as its own buffer. As a result of this work it appeared that the di-*n*-butylamine system in conjunction with isobutylmethyl ketone (hexone) merited closer investigation at the buffered pH produced by its own solubility in water. The addition of an excess of this amine results in the precipitation of *ca.* 30% of the silver as a dark, brown non-extractable complex. However, just under 60% of the silver does partition into the organic phase and analysis shows that the remainder is soluble in the aqueous layer. 13 selected anions were next examined for association with the butylamine complex. In each case an excess of the anion was added to the neutral 10^{-2} *M* silver nitrate solution which was immediately shaken with an equal volume of hexone and a slight excess of di-*n*-butylamine. The results of some of these experiments are

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* Present address: Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia (U.S.A.).

TABLE I

EXTRACTIVE SUITABILITY OF ANIONS FOR ASSOCIATION WITH THE Ag–DI-*n*-BUTYLAMINE COMPLEX

Anion	*% Extracted*	*Observations*
Stearate	99	Dense white emulsion formed which passes cleanly into the organic layer
Salicylate	98	Clean, clear-cut separation
Perchlorate	98	Grey, interfacial precipitate adhering to organic layer
Cinnamate	86	Clean separation
Phenyl salicylate	84	Some precipitation
Suberate	83	Precipitate adheres to glassware
Propionate	65	Marked precipitation of Ag
Tetraborate	65	Rapid, clean separation
n-Octoate	0	White, aqueous emulsion
n-Butyrate	0	Dense brown precipitate

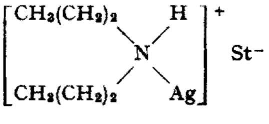
summarised in Table I. Quantitative measurements were made by stripping the organic phase with dilute nitric acid and then titrating the silver in the acid layer by a Volhard procedure.

The extraction figures in Table I should not be interpreted too closely since they were obtained without very close control of experimental variables, but they serve to show that the optimum extraction is obtained with stearate, salicylate and perchlorate. The first two systems were then examined in greater detail.

Nature of extracted stearate complex

In order to carry out more precise work on the extraction system the nature of the extracted complex was next investigated. A fixed silver concentration was taken with excess of stearic acid and the amount of amine was varied. The organic layer was back-extracted with dilute nitric acid (Note 1) and this acid layer and the original aqueous layer were titrated with ammonium thiocyanate. Results obtained by plotting percentage extraction against amount of amine taken show that maximum extraction is obtained at a 1:1 amine ratio. Moreover, the lack of curvature at the equivalence ratio is indicative of a fairly strong bond between the two. It is noticeable that silver is extracted to the extent of nearly 18% by stearate/hexone in the absence of the amine.

The process was then repeated with an excess of amine and variation of the stearate concentration. Once more an overall 1:1 ratio was obtained for Ag: stearate. The curves obtained are shown in Fig. 1. Consideration of these results shows that the extracted species is basically:



$$\left[\mathrm{(CH_3(CH_2)_2)_2N(H)Ag}\right]^+\ \mathrm{St^-}$$

It was observed at this stage that stearic acid was much more effective than sodium stearate in promoting extraction and subsequently it was found that the extent of extraction varied with the nature of the sample of stearic acid. However, several batches from the source specified (B.D.H. Ltd.) all proved equally satisfactory. Subsequently, extraction was carried out with a solution of stearic acid in hexone.

Extraction fell off markedly below pH 7, but appeared to be independent at higher pH levels. The amine itself raises the pH of the aqueous phase to 9–10. Since it was obvious that many metals would interfere with the procedure by precipitating stearate an attempt was made to overcome this difficulty by adding an auxiliary complexing agent to the solution. Several complexans were examined for this purpose and finally anthranilic acid diacetic acid (AADA) was selected. It is also favourable in that it prevents precipitation of silver in the aqueous phase, which tends to slow down the separation. The complexans were examined because they form very weak chelates with silver but act more or less strongly with most other metals. In order to combat loss of silver as its non-extractable silver complexanate, AgY^{-2}, an excess of di-*n*-butylamine (DBA) was added to the solution to maintain equilibrium in reaction (3) well to the right hand side.

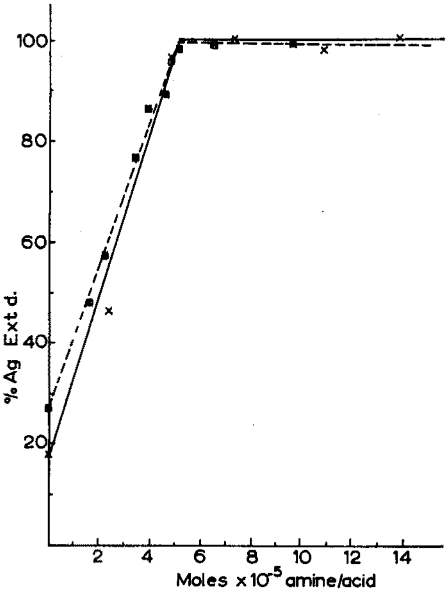


Fig. 1. Extraction of silver. Dependence on (*a*) stearic acid (broken line), (*b*) di-*n*-butylamine (unbroken line). (*a*) $5 \cdot 10^{-5}$ mole $AgNO_3$ + $4 \cdot 10^{-5}$ mole AADA + $15 \cdot 10^{-5}$ mole DBA. Variable concentration of stearic acid. (*b*) Silver and AADA as above, but with $20 \cdot 10^{-5}$ mole stearic acid and variable DBA concentration.

$$Ag^+ + DBA + St^- \rightleftharpoons Ag.DBA.St \quad (1)$$

$$Ag^+ + Y^{-3} \rightleftharpoons AgY^{-2} \quad (2)$$

$$AgY^{-2} + DBA + St^- \rightleftharpoons Ag.DBA.St + Y^{-3} \quad (3)$$

Under the recommended conditions the addition of AADA did not adversely affect the extraction of silver from pure solution, but it prevented the interference of a range of other metals, *e.g.* copper, iron(III), etc. It was not effective in preventing the extraction of mercury(II) however, for results were generally found to be *ca.* 10% high irrespective of the Hg(II) : AADA ratio. The use of a stronger complexan, EDTA, prevents interference of mercury, but if too much is added silver is also rendered non-extractable.

Some metals interfere by forming aqueous gels, and in this respect calcium is particularly troublesome. However, if the solution is made *ca.* 1.5 *M* with respect to sodium nitrate interference from this source by Al^{+3}, Fe^{+3}, Zn^{+2}, Mg^{+2} (and to a lesser extent Co^{+2}) is eliminated, but Ca^{+2} and Ni^{+2} are still troublesome.

TABLE II

COMPARISON OF ACIDS AND OF SODIUM SALTS

($5 \cdot 10^{-5}$ mole Ag, $15 \cdot 10^{-5}$ mole DBA in hexone (5 ml) and $4 \cdot 10^{-5}$ mole of AADA)

Conditions	*Stearic acid*	*% Extraction*	*Palmitic acid*	*% Extraction*	*Lauric acid*	*% Extraction*	*Oleic acid*	*% Extraction*
1 : 1 Acid/ silver (Unilever pure acid)	Separation in 30 min	96	Stood overnight. Separated by addition of $NaNO_3$	95	As palmitic acid	91	As palmitic acid	87
1 : 1 Sodium salt/silver (B.D.H.)	Rapid, clean separation	53	Very poor separation	53	Poor separation	74	Very poor separation	87

Table II summarises an investigation of various fatty acids closely related to stearic acid and also illustrates the less favourable extraction obtained when the sodium salt is used in place of the free acid. As mentioned previously, the efficiency of various batches of these acids varies with their physical state and this must be borne in mind in assessing the data.

Reinvestigation of the behaviour of amines following the more precise working now made possible as a result of fuller understanding of the nature of the system, showed that the highest recovery was obtained with *n*-butylamine closely followed by *sec*-butylamine, but since di-*n*-butylamine is nearly as effective and is more pleasant to use it was not abandoned in favour of the primary amines despite their somewhat higher efficiency.

Nature of extracted silver di-n-butylammonium salicylate

This system was examined by the methods used for stearic acid. In this instance, however, the same simple relationships were not found. Fig. 2 shows that in the presence of excess amine a 1 : 1 silver salicylate complex is formed, but the extent of the extraction varies markedly with the concentration of the amine. On the other hand, when the amount of salicylic acid is maintained constant and the amine is varied (Fig. 2) two breaks are obtained which correspond to abnormally high coordination numbers for silver. Consequently it is more difficult to interpret the nature of the complex. It is probable that the extracted complex is one where the Ag/salicylic acid/DBA ratio is either 1 : 1 : 2 or 1 : 1 : 1.

As a consequence of the above, the competition of the complexan AADA for custody of the silver is much more noticeable in this instance, but if a large excess of DBA is maintained it is possible to obtain 96% extraction in one pass with the remaining 4% accounted for in the aqueous layer. As before, the rate of separation was improved by making the solution 1.5 M with respect to sodium nitrate. Mg^{+2}, Ca^{+2}, Zn^{+2}, Al^{+3}, all of which interfered with the stearate system, showed no interference at the ratio of cation/silver = 0.5. Cu^{+2}, Co^{+2}, Ni^{+2} and Fe^{+3} which would normally interfere were masked by the AADA. Iron(III) required somewhat more AADA because of salicylic acid complexing. Anions tended to improve the separation and cations could all be suppressed with the exception of mercury(II) which behaved as in the stearate system and could be rendered non-extractable only by the addition of exactly the requisite amount of EDTA.

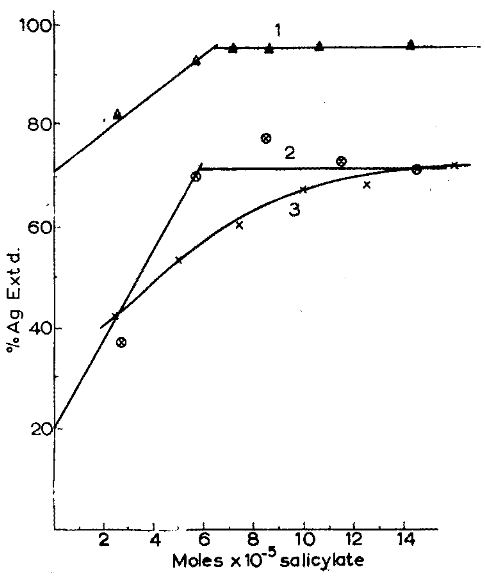


Fig. 2. Extraction of silver. Dependence on salicylate ion. In each experiment $5 \cdot 10^{-5}$ mole $AgNO_3$ + $4 \cdot 10^{-5}$ mole AADA with: Curve 1: $90 \cdot 10^{-5}$ mole of DBA, salicylic acid variable; Curve 2: $15 \cdot 10^{-5}$ mole of DBA, salicylic acid variable; Curve 3: As above but with sodium salicylate in place of salicylic acid.

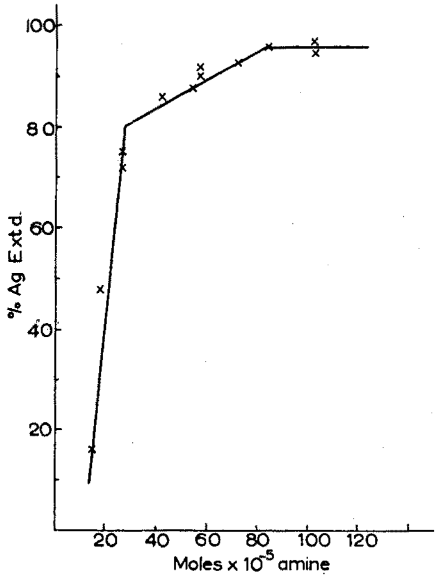


Fig. 3. Extraction of silver/salicylate system. Dependence on DBA. $5 \cdot 10^{-5}$ mole $AgNO_3$ + $4 \cdot 10^{-5}$ mole AADA + 3.75 mole salicylic acid; DBA variable.

Since the freedom from interference of the silver–DBA–salicylic acid system in the presence of AADA obviously presents a separation method for silver which is of practical significance, more detailed experiments were carried out on this system.

Upper and lower limits of extraction procedure

In the presence of AADA, the upper limit of both the salicylic acid and stearic acid systems is governed by the tendency for silver to form an insoluble salt with the complexan. Thus, 0.4 ml of 0.1 M AADA is sufficient to initiate precipitation of silver from 5 ml of $1.5 \cdot 10^{-2}$ M solution. At higher concentrations of silver, a flocculent white precipitate is obtained which is photochemically unstable.

The true lower limit was not successfully investigated since complete extraction was observed within the limits of reproducibility of the most sensitive spectrophotometric method available to us for determining silver in dilute solution. Two colorimetric procedures were investigated, one employing *p*-dimethylaminobenzalrhodanine and the other, dithizone. In the former procedure we were unable to obtain satisfactory results even with pure solutions of silver following the recommendations of SANDELL[6] and also of SNELL AND SNELL[7]. Our experience of the method agrees well with that of PIERCE[2] and subsequent comments in SNELL, SNELL AND SNELL[8].

The dithizone procedure. The dithizone procedure was found to be considerably superior to that with *p*-dimethylaminobenzalrhodanine though still not completely satisfactory for very dilute silver solutions. The carbon tetrachloride solvent used with it must be of A.R. quality and the solution of dithizone must be stored in a brown bottle in a refrigerator.

The silver–dithizone extract is even more unstable so that its extinction must be measured very quickly, whilst it is protected from the disturbing influences of extraneous strong daylight or fluorescent lighting. It is also advisable to avoid a warm laboratory atmosphere. The nitric acid used to strip the silver from the hexone extract must be of A.R. quality and entirely free from nitrogen oxides which readily decompose the dithizone. Sulfuric acid was less satisfactory.

Even with due observation of these precautions we were unable to obtain consistently reproducible results with dithizone and pure $5 \cdot 10^{-6}$ M silver solutions, for although errors within ±0.5 µg may be acceptable in direct analysis they are unsatisfactory in confirming the completeness of extraction of 0.5–2.5-µg amounts of silver. However, the results obtained on the extraction systems at this level were statistically equivalent to the recovery by dithizone from pure solution. On the other hand the extraction method was demonstrably satisfactory for 5-µg amounts of silver in 100 ml of solution, *i.e.* 0.05 p.p.m., *cf.* Experimental. Until a more reliable method is available for the determination of traces of silver, the dithizone procedure is regarded, despite its limitations, as the only practical means of following the course of the extraction by spectrophotometry.

DISCUSSION

The experiments outlined above have shown that it is possible to extract silver from very dilute solution by means of hexone using the silver ion-association systems set up by di-*n*-butylamine and stearate or di-*n*-butylamine and salicylate. The former system is to be preferred for the extraction of silver from "pure" solutions, but it is much more prone to interference from foreign ions because of the tendency for many of these to form stable aqueous emulsions with the stearate ion. Use of the weak complexan anthranilic acid diacetic acid renders the salicylate system specific for silver amongst the range of 9 other typical cations examined except that mercury(II) is still extracted (*ca.* 10%). If, however, the concentration of the latter is known, then the addition of exactly the requisite amount of EDTA prevents even this interference. The addition of sodium nitrate as a salting-out agent improves the speed of phase separation and none of the common anions added, *viz.* sulphate, nitrate, phosphate and carbonate, had an adverse effect. 96–98% extraction was obtained in one pass with silver solutions containing as little as $5 \cdot 10^{-8}$ g of silver/ml. This level — which is below the solubility level for silver chloride — represents, not the lower limit of the procedure, but rather the lowest limit where it was found possible to apply the dithizone procedure unequivocally. The upper limit is *ca.* $5 \cdot 10^{-4}$ g/ml, and is controlled by the insolubility of the silver–anthranilic acid diacetic acid complex.

Finally the procedure was checked by analysis of a series of "unknowns" (*cf.* Table III).

TABLE III

ANALYSIS OF UNKNOWNS CONTAINING FOREIGN IONS

(100 ml of solution containing stated impurities was extracted with 25 ml of 7% DBA in hexone containing 3.2 g salicylic acid/l; 0.4 ml of 0.1 *M* AADA and 10 ml of 5 *M* $NaNO_3$ were also added)

Foreign ion	*µg*	*Silver present* *µg*	*Silver found* *±1.62 µg*
Pb^{+2}	414	6.2	5.5
Fe^{+3}	56		
PO_4^{-3}	1580		
Tannic acid	10^4		
Pb^{+2}	103	18.9	22.1
Fe^{+3}	56		
PO_4^{-3}	1580		
Tannic acid	$5 \cdot 10^3$		
Cu^{+2}	63.5	17.25	16.4
Fe^{+3}	56		
Tl^+	102.2		
PO_4^{-3}	3950	12.4	10.4
CO_3^{-2}	$3 \cdot 10^6$		
Cl^-	35.5	21.6	16.9
Tannic acid	$5 \cdot 10^4$		
Cu^{+2}	63.5	3.78	
Fe^{+3}	56		1.08
Tannic acid	$2 \cdot 10^4$		
Tannic acid	$3.5 \cdot 10^4$	21.6	22.9
Tannic acid	$3.0 \cdot 10^4$	14.6	12.1
Tannic acid	$3.5 \cdot 10^4$	9.7	9.6
Cu^{+2}	63.5	11.9	10.5
Fe^{+3}	56		
CO_3^{-2}	$12 \cdot 10^6$		
Cl^-	17.8		
PO_4^{-3}	790		
Tannic acid	$3 \cdot 10^4$		

It is apparent that this method has potential application to the analysis of traces of silver in natural waters. Since tannin is a normal constituent and is known to form an insoluble silver compound, it was included in several of these solutions. Tannic acid below the level of 0.4% w/v, *i.e.* 0.02 g in 5 ml of $5 \cdot 10^{-5}$ *M* silver solution, showed no adverse effect though precipitation of silver occurred at the 1% level. Its only adverse effect at the non-interfering level was to slow down the phase separation. *n*-Butylamine could profitably replace DBA and perchlorate might be used in place of salicylate since they both follow the same extraction pattern. However no alternative was found to AADA as auxiliary complexing agent.

EXPERIMENTAL

Reagents

Extraction solution A. Dissolve 3.2 g of salicylic acid and 30 ml of di-*n*-butylamine in hexone and make up to 1 l.

Extraction solution B. Dissolve 3.2 g of salicylic acid and 70 ml of di-*n*-butylamine in hexone and make up to 1 l.

$2 \cdot 10^{-3}$ % dithizone in carbon tetrachloride. Dissolve the requisite amount of A.R. reagent in A.R. carbon tetrachloride and store in a well-stoppered brown vessel in a cool, dark cupboard. The solution requires frequent renewal.

AADA 0.1 M. 0.1 mole anthranilic acid diacetic acid dissolved in minimum of 0.1 *M* sodium carbonate and diluted to 1 l.

Apparatus

Unicam SP 600 spectrophotometer operated from a heavy-duty 12-V accumulator.

Glassware. [Note 2] All the separating funnels used were coated with silicone by treatment with a 2% carbon tetrachloride solution of dimethyldichlorosilane in order to minimise loss of silver by adsorption on the glass surface. This compound is supplied as "Repelcote" by Hopkin–Williams Ltd.

pH 4.5 buffer. 103 g of sodium acetate trihydrate (A.R.) + 100 ml of glacial acetic acid diluted to 1 l with distilled water.

Extraction and determination procedures

Procedure A (5–50 µg of silver in 10-ml volumes). Transfer the silver solution to a 50-ml separating funnel and add 0.4 ml of 0.1 *M* AADA and 1 ml of 5 *M* sodium nitrate. Add 5 ml of solution A, stopper the vessel and shake by continuous inversion for 1 min. Allow to stand and run off the aqueous layer when separation is complete. Any precipitate in the organic phase should be ignored. Wash down the walls of the funnel with a jet of distilled water and discard the washing. Add 10 ml of *M* nitric acid to the funnel, shake for 30 sec, allow to settle and run off the aqueous phase into a second 50-ml funnel. Wash the hexone layer with 10 ml of distilled water and combine the washing with the acid extract. Add 5 ml of pH 4.5 buffer to the combined aqueous extracts followed by 10 ml of dithizone solution and shake by continuous inversion for 1 min, taking care to shield the solution from light as much as possible. When the layers have separated, immediately withdraw sufficient of the organic phase and measure its optical density in a 1-cm cell at 460 mµ against the pure dithizone solution. Read the silver content from a calibration curve constructed by following the above procedure with known amounts of silver.

Procedure B (5–50 µg of silver in 100 ml of solution). This is done exactly as in *A* but with a 250-ml funnel, maintaining the solvent/solution ratio by using 20 ml of solution B, and increasing the sodium nitrate volume to 10 ml. The layers separate cleanly within 15–30 min in this instance. Discard the aqueous layer and wash the organic phase with enough distilled water to remove any obvious (coloured) impurities, and discard the washings. Transfer the organic extract to a 50-ml separating funnel. Wash the larger funnel with 10 ml of *M* nitric acid, transfer to the smaller funnel and finally wash the large funnel with 10 ml of distilled water and transfer to the small funnel and shake, etc. Combine the acid extract and washing, add buffer and determine the silver with dithizone as in method *A*.

Notes

(*1*) The acidity of the nitric acid extract of the hexone layer should be checked. If it is neutral or only weakly acid, incomplete recovery of the silver will be found.

(*2*) Considerable controversy exists concerning the adsorption of silver on glassware. SANDELL[6] working absorptiometrically, found the effect to be negligible, but DYRSSEN *et al.*[1] and PIERCE[2] have found radiochemically that adsorption takes place. Continuous use of flasks, etc. might produce a monolayer yielding results consistent with both sets of observations. In these studies the flasks were siliconed — not because we observed increased recoveries, but rather because a cleaner and quicker phase separation resulted.

ACKNOWLEDGEMENTS

One of us (D.B.) is grateful to the Department of Scientific and Industrial Research for a research studentship in aid of this work. We also wish to thank I.C.I. Ltd., for the gift of samples of some of the butylamines, Unilever for supplying samples of the pure fatty acids mentioned in Table II and Mr. R. M. DAGNALL of this Department for independently checking the experimental procedures.

SUMMARY

Silver can be extracted from aqueous solution into hexone as the ion-association system formed between its di-*n*-butylamine complex and stearic acid or salicylic acid. In the presence of an auxiliary complexing agent, anthranilic acid diacetic acid, the latter system is highly selective since only mercury(II) interferes. The procedure is sensitive and extracts silver over the range 5 mg–5 μg (0.05 p.p.m.). No compatible common anion interferes. The extraction is 96–98% complete in one pass.

RÉSUMÉ

Une méthode est décrite pour l'extraction de traces d'argent en solution aqueuse, au moyen de méthylisobutylacétone, à partir des complexes argent-*n*-butylamine + stéarine ou acide salicylique. En présence d'un agent complexant auxiliaire (acide anthranilique diacétique) la méthode devient très sélective. Seul le mercure gêne.

ZUSAMMENFASSUNG

Silber kann aus wässriger Lösung mit Isobutyl-methyl-keton extrahiert werden als Ionen-associationsprodukt aus dem Silber-*n*-Butylaminkomplex mit Stearin- oder Salicylsäure. Durch Zusatz von Anthranilsäure-Diessigsäure als Hilfskomplexbildner wird die Methode sehr selektiv, sodass von anderen Metallen nur noch Quecksilber-(II) stört.

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SORPTION OF ALDONIC ACIDS FROM ETHYL ALCOHOL–WATER SOLUTIONS ON ANION EXCHANGERS

OLOF SAMUELSON AND RUNE SIMONSON

Department of Engineering Chemistry, Chalmers Tekniska Högskola, Göteborg (Sweden)

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INTRODUCTION

As shown in earlier papers, sugars[1–4] and other polar non-electrolytes[5] can be retained by cation exchange resins or anion exchange resins from a mixture of ethyl alcohol and water. The uptake can at least qualitatively be explained by the uneven distribution of alcohol between the resin and solution phases. The lower alcohol concentration inside the resin phase favors the uptake of the polar non-electrolyte[6]. This type of sorption can be utilized in practical analytical work for the quantitative isolation of polar non-electrolytes from complicated mixtures containing interfering electrolytes and less polar non-electrolytes. The elution of the polar non-electrolyte is performed by means of water.

The ionic form of the resin has great influence upon the distribution coefficient. Cation exchangers of the sulfonic acid type in the free acid form are not suitable, whereas those in the potassium form exhibit a strong sorption. Strongly basic anion exchangers in the sulfate form have proved to be the most effective among the anion exchange resins hitherto investigated[2].

The aim of the present work was to demonstrate the applicability of this type of sorption to the isolation of aldonic acids and to give an account of some important factors which may interfere. The application of the method to the determination of aldonic acids in sulfite waste liquor will be described in a subsequent paper.

The experimental work has been limited to anion exchange resins in the sulfate–bisulfate form, which according to earlier experience can be predicted to give more favorable results than most other anionic forms of the resin. Cation exchange resins are not suitable, the reason being that with an ionic form which would give a favorable sorption it is difficult or impossible to avoid a precipitation of salts in the water–alcohol solution.

Aldonic acid solutions

Concentrated solutions were prepared by dissolution of the following substances in distilled, freshly boiled water: Gluconic δ-lactone (Th. Schuchardt, München), D-galactonic γ-lactone (Th. Schuchardt, München), D-mannonic γ-lactone (General Biochemicals Inc., U.S.A.) and D-arabonic γ-lactone (Th. Schuchardt, München). The solutions were stored at a temperature of —10°.

In preparing aldonic acid solutions containing ethyl alcohol, 5 ml of the concentrated solution was transferred with a pipet to a 50-ml volumetric flask. The flask was then filled with ethyl alcohol to the mark. It must be pointed out that the addition of alcohol had to be made immediately before the column operation was run. The ethyl alcohol (spectrographically pure absolute alcohol) was stored in an air-tight bottle and deaerated in vacuum before use.

Titrimetric determination of aldonic acids

Gluconic acid has been determined by periodate oxidation according to FLEURY *et al.*[7,8]. These authors found that the primary reaction (*a*) is followed by a secondary reaction (*b*) according to the following scheme:

$$(a)\quad CH_2OH(CHOH)_4COOH + 4HIO_4 = HCHO + 3HCOOH + CHOCOOH + H_2O + 4HIO_3$$

$$(b)\quad CHOCOOH + HIO_4 = HCOOH + CO_2 + HIO_3$$

To obtain reproducible results it is necessary that reaction (*b*) proceed quantitatively. According to FLEURY, COURTOIS AND WICKSTROM[8] this condition is fulfilled after an oxidation time of 2.5 h at a temperature of 36°. The most suitable range of pH is between 2.5 and 5.5. A pH value of 4 was chosen in the present work.

A few experiments were made in order to adapt this method to galactonic, mannonic, and arabonic acids. As shown from the reaction scheme, 5 moles of periodate are consumed per mol of gluconic acid. Gluconic, galactonic, and mannonic acids are all hexonic acids. For that reason it may be assumed that, if proper conditions are chosen, the same value will be valid for a quantitative oxidation of these acids. Arabonic acid is a pentonic acid. The theoretical value of consumption will, therefore, be 4 moles of periodate per mol of arabonic acid.

In the present work the proper pH values for the periodate oxidation of arabonic, galactonic, and mannonic acids were investigated. The experiments were performed at 36° in different buffer solutions, prepared according to CLARK AND LUBS[9]. For reasonable times of oxidation the consumption of periodate was too low at low temperatures.

TABLE I

PERIODATE OXIDATION OF ARABONIC, GALACTONIC, AND MANNONIC ACIDS

Aldonic acid added	*pH*	*Time of reaction (h)*	*Moles of consumed periodate per mol of added aldonic acid*
Arabonic acid	3.0	3.0	1.07
	4.0	3.0	1.55
	5.0	3.0	3.39
	7.0	3.0	4.09
	8.0	3.0	4.09
Galactonic acid	4.0	1.0	4.41
	4.0	2.0	4.58
	4.0	3.0	4.70
	4.0	4.0	4.81
	7.0	2.0	5.02
	7.0	3.0	5.02
	7.0	4.0	5.02
Mannonic acid	6.0	3.0	5.02
	7.0	3.0	4.99
	8.0	3.0	5.02

Table I shows the influence of the pH and the time of reaction. The determinations were in all other respects performed according to the procedure given below. As seen from the Table, satisfactory results are obtained when working at pH 7. A further investigation of the periodate oxidation was considered to be out of the scope of this work.

Procedure: A portion of the solution to be analysed, containing not more than 0.1 mmoles of aldonic acid, was introduced with a pipet into an Erlenmeyer flask furnished with a stopper. After 40 ml of 0.05 *M* sodium periodate acidified with sulfuric acid and 10 ml of buffer solution (pH 7: KH_2PO_4–NaOH buffer) had been added, the solution was diluted with water to about 150 ml. The flask was pre-heated in a water thermostat, and transferred to an air thermostat (36 ± 1°). The flask was kept in the air thermostat for 3 h. After oxidation, 10 ml of 20% potassium bicarbonate solution, 50 ml of 0.05 *M* sodium arsenite, and 1 ml of 20% potassium iodide solution were added. The pH value of the solution should be about 7.5. After 20 min the excess arsenite was titrated with 0.1 *N* standard iodine in the usual way. Blanks free from aldonic acid were treated in exactly the same way.

The determination of the aldonic acid content in the test solution added to the anion exchanger and the analyses of the eluates were performed in the same way and at the same time. The concentrations were kept at the same level.

Anion exchanger

The strongly basic anion exchange resin Dowex 1 X8 in the form of spherical particles was used. The particle size was in the range 0.08–0.15 mm. The total exchange capacity was found to be 3.51 mequiv./g of dried (at 105°) anion exchange resin in the chloride form[10].

The air-dried resin was sieved to isolate particles of the desired diameter. The resin was treated with 3 *N* hydrochloric acid, 0.5 *N* sodium hydroxide, and 0.5 *M* sulfuric acid. After each treatment, the resin was washed with distilled water. The fines were carefully removed by repeated sedimentations and decantations. Before filling the columns, air was expelled from the resin by the use of vacuum.

The columns were of conventional type and supplied with a pressure device (*cf.*[11]). The column dimensions were 14 × 190 mm and 10 × 83 mm.

Before each experiment the anion exchange resin was converted to the bisulfate–sulfate form by passing 600 (150) ml of 0.01 *M* sulfuric acid through the column. Figures in brackets give values for the column dimensions 10 × 83 mm. Conditioning with ethyl alcohol was performed with 200 (50) ml deaerated ethyl alcohol, 90% by volume. The flow rate during the conditioning steps was 0.7–1.3 ml cm^{-2} min^{-1}.

Influence of the ethyl alcohol conditioning upon the anion exchanger

When sulfuric acid is passed through a column filled with the strongly basic anion exchanger Dowex 1 in the sulfate form, the resin is converted into its bisulfate form. ANDERSON *et al.*[12] showed that the equivalent fraction of bisulfate in the resin phase increases with increasing acid concentration. When the resin is in equilibrium with 0.5 *M* sulfuric acid, the equivalent fraction is about 0.9. By washing with water the resin is easily reconverted into its sulfate form.

Experiments with ethyl alcohol instead of water were carried out to investigate the release of sulfuric acid from an anion exchanger in the bisulfate–sulfate form. A column filled with Dowex 1 X8 in equilibrium with 0.5 *M* sulfuric acid, was treated with ethyl alcohol (90%) in 50-ml portions. The sulfuric acid content in the effluent was determined by titration with standard sodium hydroxide using phenolphthalein as indicator. Finally, the column was washed with distilled water. The results are presented in Fig. 1.

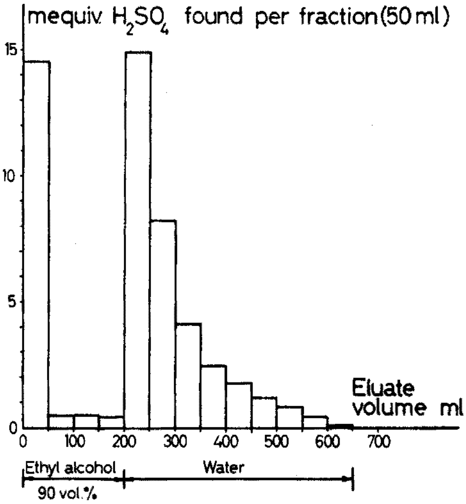

Fig. 1. Elution of sulfuric acid from a resin chiefly in the bisulfate form.

A very high value of the sulfuric acid content was obtained in the first alcohol fraction. This is due to the sulfuric acid present in the free volume of the column at the beginning of the elution. Subsequent fractions contained only small amounts of sulfuric acid, but when the alcohol was exchanged with water there was a sudden increase in sulfuric acid concentration. Evidently, the elution of sulfuric acid with ethyl alcohol is much slower than that brought about by water.

Table II shows the amount of bisulfate ions in the resin calculated according to ANDERSON *et al.*[12] and the amounts of sulfuric acid displaced from the column with

TABLE II

ELUTION OF H_2SO_4 WITH ETHYL ALCOHOL AND WATER FROM AN ANION-EXCHANGE COLUMN

(total exchange capacity 42.3 mequiv.; total volume of resin bed 29.2 ml)

Calculated amount of bisulfate in the resin (0.9 × 42.3)		38.1 mequiv.
Interstitial volume (0.4 × 29.2)	11.7 ml	
Volume of the capillary and the glass wool plug	1.5 ml	
Total free volume	13.2 ml	
Corresponding amount of free H_2SO_4		13.2 mequiv.
Calculated amount of H_2SO_4 in the column before the elution		51.3 mequiv.
Amount of H_2SO_4 eluted		
(*a*) with 90% ethyl alcohol		15.9 mequiv.
(*b*) with water		33.9 mequiv.
Total amount of H_2SO_4 eluted		49.8 mequiv.

ethyl alcohol and by subsequent washing with water. As may be seen from the Table, the amount of sulfuric acid displaced by the alcohol is only slightly higher than the amount of acid present in the free volume of the column. The calculated amount of bisulfate ions in the resin plus the amount of free acid in the column agree very well with the total amount obtained in the eluates.

Sorption and elution of aldonic acids (Proposed procedure)

The sorption of aldonic acids from an ethyl alcohol–water solution was performed as a column operation at room temperature. For final conditioning, 50 (15) ml of deaerated ethyl alcohol, 90% by volume, was added to the column. A constant pressure was applied to obtain the proper flow rate. The ethyl alcohol was forced through the column until the liquid was on a level with the resin bed.

A portion (usually 50 ml) of the freshly prepared test solution, 90% by volume with respect to ethyl alcohol, was carefully introduced with a pipet at the top of the resin bed. The solution passed through the column at a constant flow rate of 1–2 ml cm^{-2} min^{-1}. Then the funnel and the column were washed with 2 × 25 (2 × 10) ml of ethyl alcohol, 90 % by volume, at the same flow rate. The combined effluents were collected in a volumetric flask for analysis.

The aldonic acid retained in the column was eluted with 450 (150) ml of boiled distilled water. No pressure device was used and a flow rate of 0.7–1.3 ml cm^{-2} min^{-1} was obtained. The eluate was collected in a volumetric flask and analysed.

In order to control the completeness of the water elution the resin bed was finally treated with 250 (100) ml of 0.05 *M* sulfuric acid.

To avoid mould formation all aldonic acid solutions were stored in a refrigerator (2–4°) before analysis.

Blanks were run in exactly the same way as the test solutions and corrections have been applied to the values given below. These corrections amount to less than 0.5% of the aldonic acid content found in the eluate. The correction determined for the effluent amounts to 0.5–2% and can largely be ascribed to a release of organic matter from the resin.

Notes

(*1*) The ethyl alcohol concentration has a strong influence upon the uptake of gluconic acid. In an experimental series in which all other factors were kept constant, about 70% of the added gluconic acid was taken up from 75% alcohol, whereas at an alcohol concentration of 96% about 83% was sorbed (*cf.*[1]). A quantitative uptake was obtained in 90% ethyl alcohol.

(*2*) Experiments carried out at 50° showed that, in alcoholic solution, a considerable release of organic material from the anion exchange resin occurred at this temperature. Irregular values of the periodate consumption and high blank values were obtained.

(*3*) The amount of anion exchanger in the larger column (14 × 190 mm) corresponded to 12.1 g dried resin (at 105°) in the chloride form. For the smaller column (10 × 83 mm) the corresponding value was 2.6 g.

(*4*) If not otherwise stated the experiments reported in this paper were performed with the larger column.

Influence of the ionic form of the anion exchanger upon the sorption of gluconic and arabonic acids

The influence of the fraction of bisulfate ions in the anion exchange resin was elucidated by experiments in which the resin had been pretreated with sodium sulfate and with sulfuric acid at different concentrations. Before the sorption step the water solutions were displaced from the columns with ethyl alcohol, 90% by volume. The equivalent fractions of bisulfate ions in the anion exchangers were calculated from a graph given by ANDERSON *et al.*[12]. These values are valid before the conditioning with alcohol, but as already shown, the conditioning will change the composition of the anion exchanger only to a small extent.

The results in Table III (third column) show that the sorption of gluconic acid is quantitative when the resin is present in the sulfate form, whereas with a resin chiefly containing bisulfate ions the sorption is far from complete.

TABLE III

INFLUENCE OF THE SULFATE–BISULFATE EQUILIBRIUM

Pretreatment	*Equiv. fraction of bisulfate in the anion exchanger before conditioning*	*Gluconic acid (in % of added)*		
		Effluent	*Water eluate 450 ml*	*0.05 M H_2SO_4 eluate 250 ml*
1.00 *M* Na_2SO_4	0.0	0.0	99.4	0.6
0.01 *M* H_2SO_4	0.15	0.2	99.8	0.2
0.025 *M* H_2SO_4	0.30	0.6	98.9	0.1
0.05 *M* H_2SO_4	0.47	0.7	97.7	0.0
0.10 *M* H_2SO_4	0.63	1.3	97.5	0.0
0.50 *M* H_2SO_4	0.90	9.1	89.6	0.0

Added: 102.2 mg gluconic acid in 50 ml 90% alcohol. Flow rate in the sorption step: 1.2 ml cm^{-2} min^{-1}

TABLE IV

ELUTION OF ARABONIC ACID FROM AN ANION-EXCHANGER IN THE SULFATE FORM

Added amount of arabonic acid mg	*Flow rate in the sorption step ml cm^{-2} min^{-1}*	*Arabonic acid (in % of added) in different eluates*				
		Water 450 ml	*Water 100 ml*	*0.005 M H_2SO_4 100 ml*	*0.05 M H_2SO_4 250 ml*	*0.05 M H_2SO_4 250 ml*
89.0	0.32	96.6	0.0	—	1.7	0.0
222.4	0.65	97.9	0.0	0.1	1.1	0.0
444.8	0.65	97.7	0.0	0.1	0.8	0.0

On the other hand, the elution with water is not quite complete when working with the sulfate form of the resin. The slight amount of gluconic acid held by the resin after the elution with water is easily eluted with 0.05 *M* H_2SO_4. This behavior is explained by an uptake of gluconate ions by an ion exchange mechanism. To obtain conditions which permit a quantitative sorption and a complete elution with water, a compromise has to be made and in the present work a pretreatment with 0.01 *M* sulfuric acid was found to give satisfactory results in all respects.

Similar difficulties in the elution from a resin in the sulfate form were observed in experiments with arabonic acid. Each column was eluted with different solutions in the sequence given in Table IV. The results presented in the Table show that no arabonic acid appeared in the eluate when the column was further washed with a quantity of water after the first 450-ml portion of water. Detectable amounts of arabonic acid were, however, displaced from the anion exchanger with dilute sulfuric acid. The amounts of arabonic acid in the effluents were negligible.

The low uptake of gluconic acid on a resin chiefly containing bisulfate ions was further elucidated in a series of experiments with anion exchange columns pretreated with 0.5 *M* sulfuric acid and then conditioned with 90% ethyl alcohol. The amounts of gluconic acid in the effluents and the water eluates are presented in Fig. 2.

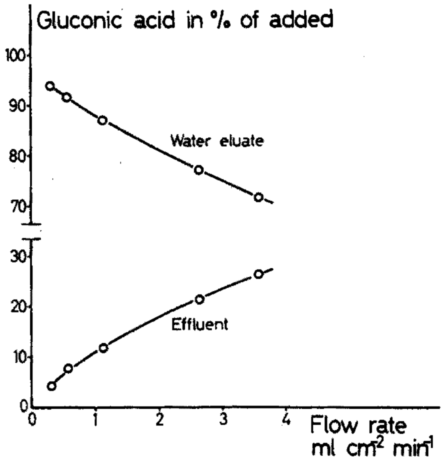

Fig. 2. Sorption of gluconic acid by means of a resin pretreated with 0.5 *M* sulfuric acid. Added: 121.5 mg gluconic acid in 50 ml 90% alcohol.

Influence of the age of the test solution upon the sorption of gluconic acid

An incomplete sorption of gluconic acid was obtained in some experiments even with a resin in the sulfate form. This was explained by formation of ethyl esters of the aldonic acids. In order to eliminate this source of error it is recommended to add the alcohol immediately before the sorption step.

A solution (50 ml) of 29.1 mg of gluconic acid in 90% alcohol was prepared and kept at room temperature for two weeks. The solution was then added to an anion exchange column filled with a resin in the sulfate form. An equal volume of a freshly prepared solution was added to an identical column. The sorption was carried out at a flow rate of 1.0 ml cm^{-2} min^{-1}. The gluconic acid present in the effluent obtained from the column treated with the aged solution amounted to 7.0% of the added acid, whereas the corresponding value for the freshly prepared solution was only 0.4%. The amounts of gluconic acid found in the water eluates were 93.3% and 98.1% respectively.

According to HEDENBURG[13] esterification is obtained from gluconic δ-lactone and ethyl alcohol in the presence of gluconic acid or hydrochloric acid. The melting point[13] for the ester is reported to be 62–63°. The melting point for the gluconic δ-lactone is 153°.

From the aged solution used in the present work, crystals with a melting point of 60–63° were isolated. This value is in good agreement with the value reported for the ethyl gluconate.

Control of the proposed procedure

The maximum amount of gluconic acid taken up by an anion exchange column (10 × 83 mm) was investigated. Different amounts of gluconic acid were added to a number of identical anion exchange columns. The experiments were performed according to the proposed procedure. The results given in Table V show that the recovery of gluconic acid in the eluates is quantitative up to an added amount of about 160 mg of gluconic acid. This value corresponds to about 60 mg of gluconic acid per g of resin.

TABLE V

SORPTION OF VARYING AMOUNTS OF GLUCONIC ACID

Added amount of gluconic acid mg	*Gluconic acid (in % of added)*		
	Effluent	*Water eluate*	*0.05 M H_2SO_4 eluate*
98.4	—	99.5	0.0
163.9	0.3	99.9	0.0
192.7	0.5	98.9	—
308.3	2.0	97.4	—
385.4	3.7	96.6	—
513.8	7.4	92.8	0.1
616.6	14.4	85.5	0.1
770.8	23.3	75.9	0.1

Flow rate in the sorption step: 1.2 ml cm^{-2} min^{-1}

In the investigation of the different factors influencing the sorption and elution of aldonic acids, gluconic acid was used in most experiments. In Table VI results are presented for experiments with other aldonic acids as well. As may be seen from the Table, the recovery of the different aldonic acids in the water eluate is quantitative. The deviations are within the limits of the titration errors.

It should also be mentioned that this method can be used with free aldonic acids as well as lactones. Experiments with gluconic acid, freshly prepared from the calcium salt, and experiments with pure δ-lactone both showed a quantitative sorption and water elution. The same result was obtained with an equilibrium mixture of free acid and lactones.

Separation of gluconic and p-toluene sulfonic acids

The proposed procedure was applied to the separation of gluconic acid from *p*-toluene sulfonic acid in solutions also containing sulfuric and acetic acids. The quantitative determination of *p*-toluene sulfonic acid was made spectrophotometrically in ultraviolet light at 260 mμ using a Beckman spectrophotometer model DU.

Aliquot portions of a stock solution were diluted with proper volumes of distilled water or alkali hydroxide solution. The neutralization was performed with either sodium or lithium hydroxide solutions to different pH-values. The pH-values given in Table VII are valid for the test solutions before the dilution with ethyl alcohol.

TABLE VI

SORPTION AND ELUTION OF ALDONIC ACIDS PERFORMED ACCORDING TO THE PROPOSED PROCEDURE

Aldonic acid added	*Added amount mg*	*Flow rate in the sorption step ml cm^{-2} min^{-1}*	*Aldonic acid (in % of added)*	
			Water eluate	*0.05 M H_2SO_4 eluate*
Arabonic acid	148.8	0.29	100.2	0.0
	148.8	0.60	100.2	0.0
	148.8	1.30	100.2	0.0
	148.8	3.39	100.2	0.0
	148.8	4.81	99.7	0.0
	223.2	1.18	100.1	0.0
	446.5	1.26	99.8	0.0
Galactonic acid	138.3	0.32	99.7	0.0
	138.3	0.72	99.6	0.0
	138.3	1.30	99.9	0.0
	138.3	1.81	99.7	0.0
	138.3	3.61	99.4	0.0
	276.5	0.64	100.3	0.0
	276.5	1.05	100.3	0.0
Gluconic acid	276.2	1.20	99.0	
	441.9	1.30	100.1	
	552.4	1.20	100.0	
	736.5	1.30	100.1	
	1104.8	1.25	99.9	
Mannonic acid	54.6	1.10	99.1	
	54.6	1.94	99.3	

The experiments with mannonic acid were performed with the smaller column type. Periodate titrations of the effluents showed that these were free from aldonic acids.

TABLE VII

SEPARATION OF GLUCONIC ACID (G) AND *p*-TOLUENE SULFONIC (T) ACIDS

Added		*pH*	*Neutralization with*	*Found*						
				Effluent		*Water eluate*		*0.05 M H_2SO_4 eluate*		*3 M HCl eluate*
G mg	*T mg*			*G mg*	*T mg*	*G mg*	*T mg*	*G mg*	*T mg*	*T mg*
389	285	1.05	—	30.8	0	352	0	0.0	0	285
389	285	1.20	NaOH	19.2	0	363	0	0.1	0	280
389	285	2.52	LiOH	4.6	0	384	0	0.0	0	284
389	285	2.98	LiOH	2.7	0	383	0	0.0	0	282

The volume of the test solution before dilution with alcohol was 20 ml for the first two solutions and 40 ml for the solutions at pH 2.52 and 2.98. The added amounts of acetic and sulfuric acids were 240.2 mg and 49.0 mg, respectively. Flow rate in the sorption step: 1.3 ml cm^{-2} min^{-1}.

The results presented in Table VII show that a considerable amount of gluconic acid is present in the effluent when the test solution is not neutralized at all (pH 1.05) or only to a small extent (pH 1.20). This loss of gluconic acid is probably due to the high equivalent fraction of bisulfate ions obtained in the anion exchanger when the column is treated with a strongly acidic solution. As already shown in a previous section, the sorbability of gluconic acid is decreased considerably with increasing equivalent fraction of bisulfate ions.

When the test solutions (*cf.* Table VII) are neutralized with sodium hydroxide to pH-values above 2, a precipitation of sodium salts occurs on dilution with ethyl alcohol. This precipitation will almost clog the column, but the separation may still be accomplished. The precipitate is easily dissolved during the elution with water. When, instead, lithium hydroxide is used as a neutralization agent, no precipitation occurs in the test solutions neutralized to pH 2.52 and 2.98. As seen from the Table, the gluconic acid is in these cases found quantitatively (within the limits of titration errors) in the water eluates.

In all cases a complete separation of gluconic acid from *p*-toluene sulfonic acid was obtained, the latter being quantitatively eluted from the column with 1000 ml of 3 *N* HCl (*cf.*[14]).

ACKNOWLEDGEMENT

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SUMMARY

Aldonic acids can be retained quantitatively from ethyl alcohol–water solutions by means of anion exchangers in the sulfate form. After the sorption step the aldonic acids can be easily displaced by washing with water. The sorption is explained by a partition mechanism of the same type as demonstrated in earlier work with strongly polar non-electrolytes. Precautions have to be taken to prevent uptake by means of an ion exchange mechanism. The method permits a separation from exchangeable anions and from non-adsorbable solutes.

RÉSUMÉ

Une méthode est décrite pour la séparation des acides aldoniques de solutions eau–alcool éthylique, au moyen d'échangeurs d'anions. L'élution s'effectue par lavage à l'eau.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Isolierung von Aldonsäuren aus wasserhaltiger Alkohollösung mit Hilfe eines Anionenaustauscherharzes. Elution erfolgt durch Waschen mit Wasser. Die Adsorption wird durch einen Verteilungsmechanismus erklärt.

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STUDIES ON THE SOLVENT EXTRACTION OF URANYL BIS(DIBENZOYLMETHANE)

GEORGE K. SCHWEITZER AND JACK L. MOTTERN

Department of Chemistry, The University of Tennessee, Knoxville 16, Tenn. (U.S.A.)

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INTRODUCTION

Uranyl ion extractions

In recent years increasing interest has been evidenced in the solvent extraction of metal ions from aqueous media into organic media containing chelating agents. Several theoretical treatments of the equilibria involved have appeared in the literature[1]. The dioxouranium(VI) or uranyl ion has been extracted into several different organic solvents using over 12 different chelating agents[2]. Recently MOUCKA AND STARY[3] have used dibenzoylmethane (1,3-diphenyl-1,3-propanedione) in benzene, carbon tetrachloride, and chloroform to perform such extractions. If the dibenzoylmethane is represented as HR, they found in all cases that the extracting species is $UO_2R_2 \cdot HR$.

Not many studies of the effects of complexing agents in the aqueous phase upon the extraction character of uranyl ion systems have been reported. The work of FREISER AND KRISHEN[4] on the influence of fluoride, tartrate, and ethylenediaminetetraacetate on the extraction of uranyl bis(acetylacetonate) may be cited. In addition, the experiments of STARY[5] on the influence of acetate, oxalate, tartrate, and ethylenediaminetetraacetate on the extraction of uranyl bis(benzoylacetonate) are noteworthy. A few other scattered studies have been carried out, such as the work of TAYLOR[6] using ethylenediaminetetraacetate in extractions of the oxinate of the uranyl ion.

Extraction equations

If one considers the extraction of the uranyl ion from an aqueous phase containing a masking complexing agent X^{-x} into a chloroform phase containing dibenzoylmethane HR, the following equation may be written:

$$\frac{1}{D} = \frac{1}{P_c} + \frac{P_r{}^3 K_r{}^2 (\mathrm{H})^2 Q}{P_c K_c (\mathrm{HR})_0{}^3} \qquad (1)$$

In this equation, the extracting species is assumed to be predominately $UO_2R_2 \cdot HR$ (as has been demonstrated by MOUCKA AND STARY[3]); D is the organic: aqueous distribution ratio of the total metal concentration in the organic phase to that in the aqueous phase; P_c is the organic: aqueous distribution coefficient of the $UO_2R_2 \cdot HR$; P_r is the organic: aqueous distribution of the HR; K_r is the association constant of the HR; K_c is the association constant of the $UO_2R_2 \cdot HR$ which may be expressed as $(UO_2R_2 \cdot HR)/(UO_2)(R)^2(HR)$; (H) is the hydrogen ion concentration in the aqueous phase; $(HR)_0$ is the equilibrium concentration of the HR in the organic phase; and

Q is a term known as the complexing term. This term Q accounts for the complexes in the aqueous phase which mask the extraction; one possible form it might take would be

$$\begin{aligned} Q = 1 &+ K_1(\mathrm{X}) + K_2(\mathrm{X})^2 + K_3(\mathrm{X})^3 + \text{etc.} \\ &+ k_1(\mathrm{OH}) + k_2(\mathrm{OH})^2 + k_3(\mathrm{OH})^3 + \text{etc.} \\ &+ K_b(\mathrm{R}) + K_d(\mathrm{R})^3 + K_e(\mathrm{R})^4 + \text{etc.} \end{aligned} \tag{2}$$

In this exemplary equation K_1, K_2, K_3, etc. are the successive cumulative association constants for complexes between the uranyl ion and the complexing agent X^{-x}; (X) is the equilibrium concentration of the free complexing agent; k_1, k_2, k_3, etc. are the successive cumulative association constants for complexes between the uranyl ion and the hydroxide ion; (OH) is the equilibrium concentration of the hydroxide ion; K_b, K_d, K_e, are the successive cumulative association constants for water-soluble chelates between the uranyl ion and dibenzoylmethane, and (R) is the equilibrium concentration of the singly ionized dibenzoylmethane. In this specific form of Q, all mixed complexes are ignored, and no species other than $\mathrm{UO_2R_2 \cdot HR}$ is considered as extracting into the organic phase. Of course, as RYDBERG[7] has pointed out, a number of the species involved may have one or more molecules of water, chloroform, and/or dibenzoylmethane attached. Further, it should be recognized that $\mathrm{UO_2R(H_2O)^+}$ is stoichiometrically equivalent to $\mathrm{UO_2(HR)(OH)^+}$, and other such equivalencies must also be recognized.

If X^{-x} is an anion of a weak acid, and if $\mathrm{UO_2^{+2}}$ is present in a concentration very small as compared to that of X^{-x}, the free concentration of the anion may be calculated from

$$(\mathrm{X}) = \frac{\text{Total } X^{-x} \text{ concentration}}{1 + K'(\mathrm{H}) + K''(\mathrm{H})^2 + \text{etc.}} \tag{3}$$

where K', K'', etc. are the successive cumulative association constants of the weak acid involved. Likewise, the value of (R) can be obtained from

$$(\mathrm{R}) = \frac{\text{Total HR concentration}}{1 + K_r(\mathrm{H}) + P_r K_r(\mathrm{H})} \tag{4}$$

if the organic and aqueous phases are equal.

When P_c is quite large, as is the case in this work, eqn. (1) may be made to read

$$D \cong \frac{P_c K_c (\mathrm{HR})_0^3}{P_r^3 K_r^2 (\mathrm{H})^2 Q} = \frac{K(\mathrm{HR})_0^3}{(\mathrm{H})^2 Q} \tag{5}$$

Taking logarithms, one arrives at

$$\begin{aligned} \log D &\cong \log P_c + \log K_c - 3 \log P_r - 2 \log K_r + 3 \log (\mathrm{HR})_0 + 2\,\mathrm{pH} - \log Q \\ &= \log K + 3 \log (\mathrm{HR})_0 + 2\,\mathrm{pH} - \log Q \end{aligned} \tag{6}$$

Assuming equal organic and aqueous phases, at 50% extraction of the metal where D equals 1, the pH may be designated the $\mathrm{pH}_{1/2}$, and the following expression results

$$\begin{aligned} 2\,\mathrm{pH}_{1/2} &\cong 3 \log P_r + 2 \log K_r - \log P_c - \log K_c - 3 \log (\mathrm{HR})_0 + \log Q \\ &= -\log K - 3 \log (\mathrm{HR})_0 + \log Q \end{aligned} \tag{7}$$

In many systems eqn. (6) describes a "regular" curve of the sigmoid type when % extraction is plotted against pH. Such a curve might show values as follows: pH 2.00 (1% extraction), 2.25 (3), 2.36 (5), 2.52 (10), 2.70 (20), 2.81 (30), 2.91 (40), 3.00 (50), 3.09 (60), 3.19 (70), 3.30 (80), 3.48 (90), 3.64 (95), 3.75 (97), 4.00 (99). When the organic and aqueous phases are equal, the following relation between D and the % extraction E holds

$$E = \frac{100\,D}{D+1}. \tag{8}$$

Present problem

In this work, the extraction of uranyl ion from aqueous solutions into chloroform containing dibenzoylmethane has been studied using both unmasked and masked conditions. A masked system is one in which the aqueous phase contains a complexing agent which forms water-soluble complexes with the uranyl ion. In addition, the P_r and K_r values of dibenzoylmethane and the P_c value of $UO_2R_2 \cdot HR$ have been determined as aids to the theoretical interpretation of the extractions. Data from several of the extractions allowed estimates of stability constants of some previously unevaluated uranyl complexes.

All solutions were made up with distilled, deionized water using reagent grade chemicals or repeatedly purified reagents. The pH measurements were conducted with a Beckman H2 pH Meter equipped with micro electrodes. All uranium analyses were performed by the method of HORTON AND WHITE[8], after destruction of organic materials with perchloric acid.

FUNDAMENTAL CONSTANTS

Dibenzoylmethane

Samples consisting of 10 ml of 0.1 M sodium perchlorate solution were equilibrated at 30° for 12 h with 10 ml of 0.1 M dibenzoylmethane in chloroform at pH values from 2.0 to 14.0. Both solvents had been saturated previously with the other. Adjustments of pH were made with concentrated solutions of sodium hydroxide and perchloric acid. Percentage extraction was determined by evaporating and weighing aliquots of the chloroform phase after equilibration. When the results of 22 samples were plotted on a curve of E-against-pH, 100% extraction was shown from pH 2.0 to pH 12.0. The curve then dropped according to the following: pH 12.5 (99% extraction), 13.0 (97), 13.3 (95), 13.6 (87).

In order to determine P_r accurately, 4 l of chloroform-saturated water, 0.1 M in sodium perchlorate, was equilibrated at 30° for 12 h with 45 ml of water-saturated chloroform, 1 M in dibenzoylmethane, at a pH of 5.0. The organic phase was separated, and then the aqueous phase was equilibrated for 12 h at 30° with 25 ml of chloroform. 15 ml of this chloroform was evaporated to dryness giving 3.3 mg of dibenzoylmethane. 5 further experiments of this type gave 2.6, 2.7, 3.3, 3.6, and 5.2 mg. On the basis of these 6 values, an average P_r of $10^{5.2}$ was calculated. This value agrees very well with the value of $10^{5.4}$ as determined by MOUCKA AND STARY[3] at 20°.

Utilizing this value of P_r plus values of (H) and distribution coefficient d from the E-against-pH determinations for HR and the following equation

$$\frac{1}{d} = \frac{1}{P_r} + \frac{1}{K_r P_r (\mathrm{H})}$$

the best value of K_r was found to be $10^{9.2}$. The value of K_r as here obtained agrees very well with what might be estimated by an extrapolation of the curves of VAN

UITERT *et al.*[9] who determined K_r in various water–dioxane mixtures. Also it agrees with the value of $10^{9.4}$ as obtained by MOUCKA AND STARY[3] at 20°.

Uranyl bis(dibenzoylmethane)·dibenzoylmethane

Samples consisting of 10 ml of chloroform-saturated aqueous phase, 0.1 M in sodium perchlorate and $10^{-4.1}$ M in uranyl ion were equilibrated for 12 h at 30° with 10 ml of water-saturated chloroform, 0.1 M in dibenzoylmethane, at pH values from 2.0 to 12.0. When the results of 43 samples were plotted as E-against-pH, a curve described by the following values was obtained: pH 2.7 (2% extraction), 3.1 (10), 3.4 (20), 3.7 (50), 4.0 (80), 4.2 (90), 4.7 (99), 5.0 (100), 6.0 (100), 7.0 (100), 8.0 (100), 9.0 (99), 9.5 (97), 10.0 (93), 10.5 (84), 11.0 (63), 11.5 (40). These values do not represent experimental points; they simply describe the shape of the resultant curve. The standard error in each experimental point ran ±0.1 pH units and ±2% extraction. The curve from pH 2.7 to 4.7 is a regular one having a shape and slope as predicted by (6). The $\text{pH}_{1/2}$ value is 3.7, which on substitution into (6) yields a K value of $10^{-4.4}$, assuming Q to be 1. These values of $\text{pH}_{1/2}$ and K agree with those of MOUCKA AND STARY[3] of 3.5 and $10^{-4.0}$ as determined at 20°.

In order to determine P_c, 200 ml of chloroform-saturated water, 0.1 M in sodium perchlorate and $10^{-4.1}$ M in uranyl ion was equilibrated for 12 h at 30° with 20 ml of water-saturated chloroform, 0.1 M in dibenzoylmethane, at a pH of 6.1. Triplicate experiments gave 14.5, 16.0, and 17.7 μg of uranium in the water phase. The average of these values was used to calculate a P_c of $10^{3.4}$.

By putting P_r, K_r and K into eqn. (5), a value of $10^{29.6}$ for P_c K_c was obtained. This compares favorably with the value of $10^{30.9}$ which MOUCKA AND STARY[3] measured at 20°. Then by using the above value of P_c, a value of $10^{26.2}$ is obtained for K_c.

A set of samples similar to that described at the beginning of this section was run except that the dibenzoylmethane concentration was 0.01 M. A regular curve with a $\text{pH}_{1/2}$ value of 5.1 was obtained. This compares with a calculated value of 5.2.

The turning down of the curve in the case of the 0.1 M dibenzoylmethane beyond a pH of 8.8 may be attributed to a negative complex[7,10]. Among the possibilities are $UO_2R_3^-$, $UO_2R_2(OH)^-$, $UO_2R(OH)_2^-$, and $UO_2(OH)_3^-$. Species containing HR and OH^- are thought to be out of consideration since the ratio $(HR)(OH)/(R) = 10^{-4.8}$, this ratio being derived from K_r and the ion product of water. The descending portion of the curve under consideration, that is, the portion from pH 8.8 to 11.5 may be described by using as the dominant term in the Q equation any of the following: $10^{27.6}$ $(R)^3$, $10^{26.2}$ $(R)^2(OH)$, $10^{24.8}$ $(R)(OH)^2$, or $10^{23.4}$ $(OH)^3$. Which of these is applicable or whether any are applicable cannot be determined from the data here obtained.

MASKED EXPERIMENTS

Experimental procedure

Samples consisting of 10 ml of chloroform-saturated water, $10^{-4.1}$ M in uranyl ion, and 0.001, 0.01, 0.1, or 1 M in complexing agent, and made up to an ionic strength of 0.1 with sodium perchlorate if necessary, were equilibrated for 12 h at 30° with 10 ml of 0.1 M dibenzoylmethane in water-saturated chloroform at various pH values. After separation, both phases were analyzed for uranium, E values were calculated, and plots of E-against-pH were made. Table I presents data obtained for 26 different systems. At least 12 points were run in order to define the curve in each system.

Regular curves

All the curves in systems 1–8, 10, 11, 13, 14, and 15 were regular. By using eqns. (1)–(4),(8), a P_c of $10^{3.4}$, a P_r of $10^{5.2}$, a K_r of $10^{9.2}$, a K_c of $10^{26.2}$ and values of complexation constants from Table II, these curves could be predicted very accurately.

As shown by systems 4 and 1, a change in HR concentration from 10^{-1} to 10^{-2} increases the $pH_{1/2}$ from 3.7 to 5.1. Using a K value of $10^{-4.4}$ and a Q of 1, a value of 5.2 is predicted. The slopes of all these regular curves indicate a value of approximately that required for a divalent metal ion, and the observed and calculated $pH_{1/2}$ values agree excellently. Systems 2–5 indicate the effect of ionic strength on the $pH_{1/2}$, there being little influence.

TABLE I

DATA ON URANYL ION EXTRACTIONS

System	*DBM*[a] *Conc.* *M*	*Aqueous*[b] *phase*	$pH_{1/2}$	
			Observed	*Calculated*[c]
1	10^{-2}	10^{-1} M $NaClO_4$	5.1	5.2
2	10^{-1}	10^{-3} M $NaClO_4$	3.7	3.7
3	10^{-1}	10^{-2} M $NaClO_4$	3.7	3.7
4	10^{-1}	10^{-1} M $NaClO_4$	3.7	Std.[c]
5	10^{-1}	10^{0} M $NaClO_4$	3.6	3.7
6	10^{-1}	10^{-3} M NaF	4.9	4.8
7	10^{-1}	10^{-2} M NaF	6.1	6.0
8	10^{-1}	10^{-1} M NaF	7.5	7.6
9	10^{-1}	10^{0} M NaF	10.4[d]	9.6
10	10^{-1}	10^{-3} M NaAc[f]	3.7	3.7
11	10^{-1}	10^{-2} M NaAc	3.7	3.7
12	10^{-1}	10^{-1} M NaAc	5.2[d]	5.2
13	10^{-1}	10^{0} M NaAc	6.9	6.9
14	10^{-1}	10^{-3} M Na_2Ox[g]	6.2	6.2
15	10^{-1}	10^{-2} M Na_2Ox	7.2	7.2
16	10^{-1}	10^{-1} M Na_2Ox	8.2[d]	8.2
17	10^{-1}	10^{-3} M Na_3Ct[h]	7.0[d]	7.0
18	10^{-1}	10^{-2} M Na_3Ct	[e]	
19	10^{-1}	10^{-3} M Na_2Ta[i]	5.6[d]	5.6
20	10^{-1}	10^{-2} M Na_2Ta	[e]	
21	10^{-1}	10^{-1} M Na_2Ta	[e]	
22	10^{-1}	10^{-3} M Na_3Nt[j]	4.7	4.7
23	10^{-1}	10^{-2} M Na_3Nt	[e]	
24	10^{-1}	10^{-3} M Na_2H_2Ed[k]	5.5[d]	5.5
25	10^{-1}	10^{-2} M Na_2H_2Ed	[e]	
26	10^{-1}	10^{-1} M Na_2H_2Ed	[e]	

[a] Dibenzoylmethane concentration in the original chloroform phase.

[b] All aqueous phases were also originally $10^{-4.1}$ M in UO_2^{+2} and made up to an ionic strength of 0.1 with $NaClO_4$, if necessary.

[c] System 4 was used as a standard to calculate a value of K. All other calculated $pH_{1/2}$ values were ascertained using this value of K ($10^{-5.4}$).

[d] Curve irregular, but $pH_{1/2}$ could be read.

[e] Curve irregular, such that no $pH_{1/2}$ could be read.

[f] Sodium acetate.

[g] Sodium oxalate.

[h] Sodium citrate.

[i] Sodium tartrate.

[j] Sodium nitrilotriacetate.

[k] Sodium dihydrogen ethylenediaminetetraacetate.

Irregular curves

The data obtained in system 9 show a curve described by the following: pH 9.4 (2% extraction), 9.6 (11), 10.0 (32), 10.2 (40), 10.5 (57), 10.9 (80), 11.1 (78), 11.4 (67), 11.7 (60). The use of eqns. (1)–(4),(8) with proper complexation constants as taken from Table II predicts a curve exactly like this one but displaced 0.8 pH unit lower. This discrepancy may be due to ionic strength influence on the fluoride complexation constants.

TABLE II

URANYL ION CUMULATIVE COMPLEXATION CONSTANTS

Ligand	*log K_1*	*log K_2*	*log K_3*	*log K_4*	*References*
ClO_4^-	<0	<0	<0	<0	11
OH^-	9.8	18.6			5, 7, 11
F^-	4.6	7.9	10.5	11.9	11, 12
Ac^-	2.4	4.4	6.3		5
Ox^{-2}		11.1			5
Cit^{-3}	9.6[a]				[a]
Ta^{-2}		9.7			5
Nt^{-3}	5.0[a]				[a]
HEd^{-3}	7.3				5

[a] Estimated in this present work

The data obtained in system 12 show a curve described by the following: pH 3.8 (24% extraction), 4.2 (24), 4.6 (24), 5.0 (34), 5.2 (50), 5.5 (80), 5.8 (95), 6.2 (99). It can be seen that this curve is regular in the region above a pH of 5.0. The curve can be predicted precisely with eqns. (1)–(4),(8), proper complexation constants selected from Table II, and a K' value for acetic acid of $10^{4.8}$.

In system 16 the data described a curve which appears as follows: pH 7.2 (2% extraction), 7.6 (5), 7.9 (20), 8.2 (50), 8.4 (68), 9.0 (78), 9.5 (86), 10.0 (88), 10.5 (76). Attempts were made to predict this curve by using equations (1)–(4),(8), the assumption of a simple 1:2 uranyl:oxalate complex, the complexation constants from Table II, and oxalic acid association constants of $10^{4.2}$ and $10^{5.4}$. The lower regular portion of the curve as well as the $pH_{1/2}$ could be predicted, but the upper portion could not. This behavior is presumably due to the formation of complexes other than the simple 1:2 one.

System 17 may be described as a straight line from a pH of 5.5 to 8.3

$$E = 34(\text{pH} - 5.5)$$

and system 18 may likewise be described from a pH of 6.2 to 10.2

$$E = 11(\text{pH} - 6.2)$$

Attempts to predict these curves assuming a simple 1:1 complex, using a K_1 value of $10^{9.6}$, and using citric acid association constants of $10^{3.1}$, $10^{4.8}$, and $10^{6.4}$ were only partly successful, even though this allowed the $pH_{1/2}$ of system 17 to be calculated. However, it is well known that several types of uranyl:citrate complex exist in such solutions[13], and thus these results were not surprising.

System 19 may be described as a straight line from a pH of 3.9 to 6.4,

$$E = 32(\text{pH} - 3.9)$$

and system 20 may likewise be described from a pH of 5.5 to 9.0,

$$E = 15(\text{pH} - 4.6)$$

The curve of system 20 is described as follows: pH 6.0 (9% extraction), 6.5 (9), 7.0 (9), 7.5 (9), 8.0 (10), 8.5 (12), 9.0 (18), 9.5 (28), 10.0 (45). Attempts to predict the tartrate curves using tartaric acid association constants of $10^{4.2}$ and $10^{7.1}$ were largely unsuccessful, undoubtedly due to the formation of complexes other than simple ones. However, there is a fair degree of similarity between the observed and theoretical curves for system 19.

The data obtained in system 22 can be approximated by a straight line equation which applies between pH values of 3.5 and 5.3,

$$E = 44(\text{pH} - 3.5)$$

The data of system 23 show a curve as follows: pH 5.0 (20% extraction), 5.2 (26), 5.4 (36), 5.7 (42), 6.0 (50), 6.5 (51), 7.0 (48), 7.5 (45), 8.0 (42), 8.5 (35), 9.0 (28). Association constants of $10^{1.9}$, $10^{2.5}$, and $10^{9.7}$ were employed to make theoretical calculations. By using a K_1 value of $10^{5.0}$, assuming the complexing species to be the doubly-ionized entity, and assuming the complex to be 1 : 1, the calculated curve fits the observed data of system 22 fairly well. However, the behavior of system 23 defies simple theoretical analysis. Studies on complexes in this system indicate complicated hydrolysis phenomena at higher pH values, which could be involved[14].

System 24 may be described approximately in the pH region 4.4 to 6.7 by a straight line equation

$$E = 35(\text{pH} - 4.1)$$

system 25 between pH values of 5.3 and 7.8 by

$$E = 23(\text{pH} - 5.2)$$

and system 26 between pH values of 6.5 and 10.0 by

$$E = 13(\text{pH} - 6.3)$$

For attempted theoretical interpretation, it was assumed that the complexing species was the triply-ionized entity, and acid association constants of $10^{2.0}$, $10^{2.7}$, $10^{6.2}$, and $10^{10.3}$ were employed. The data for system 24 fit the theoretical curve fairly well, but attempts with systems 25 and 26 failed completely. Again it may be noted that several complexes may exist and that hydrolysis phenomena are probably important in the higher pH ranges[15,16].

COMPARISONS

Acetylacetone, benzoylacetone, and dibenzoylmethane make up a series of compounds which have now been used as chelating agents for the solvent extraction of the uranyl ion into chloroform[3-5,7,10]. There is an increasing trend in the P_r values of these three compounds ($10^{1.4}$, $10^{3.6}$, $10^{5.2}$) and the K_r values are quite similar ($10^{9.0}$, $10^{8.7}$, $10^{9.2}$). The $\text{pH}_{1/2}$ values for the extraction of UO_2^{+2} using a 0.1 M reagent solution are 4.6 (ref.[7]), 3.7 (ref.[10]), and 3.7. In each case the predominant extracting species is $UO_2R_2 \cdot HR$, showing extraction constants K of $10^{-6.2}$, $10^{-4.4}$, and $10^{-4.4}$. In the three systems, the values of $P_c\,K_c$ are $10^{16.1}$, $10^{23.8}$, and $10^{29.6}$. The K_c and P_c values in this work are not in agreement with the estimates made by STARY[3]; it appears to the present authors that his P_c value is too high and his K_c value too low.

The shifts in $pH_{1/2}$ observed in the presence of acetate, oxalate, tartrate, and ethylenediaminetetraacetate agree favorably with the shifts observed by STARY[10] using benzoylacetone as the extractant. Likewise the shifts in $pH_{1/2}$ observed here in the presence of fluoride, tartrate, and ethylenediaminetetraacetate may be compared with those observed by KRISHEN[4] using acetylacetone as both the chelating agent and the non-aqueous solvent.

SUMMARY

Studies of unmasked and masked extractions of the uranyl bis(dibenzoylmethane)·dibenzoylmethane chelate from aqueous solutions into chloroform containing dibenzoylmethane have been made. Aqueous media containing the following were studied: perchlorate, fluoride, acetate, oxalate, citrate, tartrate, nitrilotriacetate, ethylenediaminetetraacetate. A number of fundamental constants have been determined, these values allowing theoretical interpretations of several of the systems to be made.

RÉSUMÉ

Les auteurs ont effectué une étude de l'extraction du complexe uranyl-bis(dibenzoylméthane), à partir de solutions aqueuses, dans du chloroforme contenant du dibenzoylméthane. Les milieux aqueux renfermant: perchlorate, fluorure, acétate, oxalate, citrate, tartrate, nitrilotriacétate, éthylènediaminetétracétate, ont été examinés. Un certain nombre de constantes ont été déterminées, permettant des interprétations théoriques de plusieurs des systèmes.

ZUSAMMENFASSUNG

Es wird das Verhalten des Uranyl-bis-(dibenzoylmethan)-dibenzoylmethan bei der Extraktion mit Chloroform aus wässriger Lösung in Abwesenheit und Gegenwart chelatbildender Substanzen (Perchlorat, Fluorid, Acetat, Oxalat, Citrat, Tartrat, Nitrilotriacetat, Aethylendiaminotetraacetat) untersucht. Es wurde ferner eine Anzahl wichtiger Konstanten bestimmt, die eine theoretische Behandlung einiger der Systeme ermöglichen.

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VERGLEICH DREIER KOMPLEXOMETRISCHER ALUMINIUMBESTIMMUNGSMETHODEN

H. MALISSA UND H. KOTZIAN

Institut für analytische Chemie der Technischen Hochschule, Wien (Österreich)

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Aus der Vielzahl der Methoden[1-8] zeichnen sich die von WÄNNINEN UND RINGBOM[3], von PŘIBIL *et al.*[2] und die von SAJO[1] vor allem durch ihren guten Umschlagspunkt aus. Es handelt sich wegen der relativ langsamen Umsetzung des in wässriger Lösung vorliegenden Aluminiumions beziehungsweise dessen Komplexen mit Äthylendiaminotetraessigsäure jeweils um Rücktitrationen.

Zur Theorie der Aluminiumkomplexonkomplexbildung und des bei derartigen Rücktitrationen zu erwartenden Fehlers wurde schon oftmals Stellung genommen, so dass hier darauf verzichtet werden kann[9-11].

METHODEN

Bestimmung nach WÄNNINEN UND RINGBOM[3]

Bei einem pH-Wert um 4.5 wird ein bekannter Überschuss einer Komplexonlösung mit Zinksulfat-Masslösung gegen Dithizon als Indikator rücktitriert. Wesentlich für die Schärfe des Umschlagpunktes des Indikators, der durch Bildung von Zinkdithizonat entsteht, ist die Anwesenheit von 40 bis 50 Volumsprozent an Alkohol bei der Titration.

Bestimmung nach PŘIBIL *et al.*[2]

Die indirekte Bestimmung von Aluminium mit Xylenolorange als Indikator erfolgt über die Titration des überschüssigen Komplexons bei pH 5 in einer acetat- oder urotropingepufferten Lösung mit Zinksulfat. Ein pH-Wert über 3 ist hier, abgesehen von der Stabilitätsverminderung des Al-Komplexes, auch deshalb wichtig, weil der Indikator ansonsten mit Aluminium einen beständigen roten Farblack bildet.

Bestimmung nach SAJO[1]

Die komplexometrische Titration des Aluminium mit Ferri–ferrocyanid als Indikator führt ebenfalls über die Rücktitration des überschüssigen Komplexons, die im pH-Bereich 5 bis 7 stattfindet und mit Zinkacetatmasslösung durchgeführt wird. Den Endpunkt liefert das Redoxsystem Ferro- Ferricyanid und Benzidin. Durch den ersten überschüssigen Tropfen Zinklösung wird Ferrocyanid gebunden, wodurch das Gleichgewicht des Systems gestört wird und den Farbumschlag zur Folge hat.

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DURCHFÜHRUNG DER BESTIMMUNGEN

Methode I[3,12]

Die wässrige Aluminiumchloridlösung (2.50 mg Aluminium) wurde mit 0.01 *M* Komplexonlösung im Überschuss versetzt, mit 10 ml Acetatpuffer ein pH-Wert von 4.5 (*M* Essigsäure: *M* Natriumacetat = 4:1) eingestellt, zwecks besserer Komplexbildung kurz aufgekocht, rasch abgekühlt und nach Zugabe eines gleichen Volumens an Äthylalkohol und einigen[5-8,12,13] Tropfen Indikatorlösung (0.05%ig Dithizon in Trichloräthylen) von blau nach hellrosa mit Zinksulfatlösung titriert.

TABELLE I

BESTIMMUNG VON 2.50 mg ALUMINIUM NACH METHODE I AUS WÄSSRIGER ALUMINIUMCHLORIDLÖSUNG

	0.01 M Komplexonlösung	*0.001 M Komplexonlösung*
mg Aluminium gefunden	2.42	2.483
	2.44	2.489
	2.36	2.490
	2.39	2.480
	2.36	2.485
	2.40	2.482
	2.42	2.478
	2.40	2.481
	2.39	2.477
	2.41	2.485
	2.36	2.485
Mittelwert	2.395	2.483
Fehler in Rel. %	—4.0	—0.7
Varianz[13] in %	2.8	1.2

Gearbeitet wurde mit einer 50-ml Bürette mit 0.1-ml Teilung für die Titration mit 0.01 *M* Zinksulfatlösung und mit einer 10-ml Bürette mit 0.02 ml Teilung für die Titration mit 0.001 *M* Zinksulfatlösung.

TABELLE II

BESTIMMUNG VON 2.50 mg ALUMINIUM NACH METHODE II AUS WÄSSRIGEN ALUMINIUMCHLORIDLÖSUNGEN

	Puffer	
	Acetat	*Urotropin*
mg Aluminium gefunden	2.489	2.484
	2.489	2.490
	2.499	2.484
	2.501	2.484
	2.499	2.495
	2.499	2.495
	2.501	2.486
	2.492	2.490
	2.489	2.495
	2.485	2.484
	2.499	2.495
Mittelwert	2.494	2.491
Fehler in Rel. %	—0.3	—0.3
Varianz[13] in %	0.72	0.64

Methode II[2]

Ansatz. (*a*) Acetatpuffer (*M* Essigsäure: *M* Natriumacetat = 1:2), (*b*) Urotropinpuffer (0.1 g Urotropin und 0.1 ml *N* Essigsäure).

Durchführung. Die reine wässrige Lösung von Aluminiumchlorid (2.50 mg Aluminium) wurde mit 10 ml Pufferlösung und Komplexonlösung im Überschuss versetzt, kurz aufgekocht, rasch gekühlt, ein pH-Wert von 5.0–5.2 eingestellt, auf etwa 150 bis 180 ml verdünnt und gegen Xylenolorange (5–10 Tropfen 1% Xylenolorange in verdünntem Alkohol) als Indikator von gelb und rot mit 0.001 *M* Zinksulfatlösung titriert. Gearbeitet wurde mit einer 10-ml Bürette mit 0.02-ml Teilung.

Methode III[1]

Im Hinblick auf die Möglichkeit, die Bestimmung der Summe von Aluminium und Titan einerseits und Aluminium allein andererseits zu erzielen, wurde untersucht, welche Genauigkeit für die Aluminiumwerte erhältlich ist, wenn nach Sajo[1] in bereits zu Ende geführten Lösungen der Aluminium–Komplexon-Komplex durch Kochen mit 20 ml gesättigter Natriumfluoridlösung zerstört und das in Freiheit gesetzte Komplexon mit Zinksulfat gegen Xylenolorange titriert wird. Des besseren Vergleiches wegen auf ebenfalls theoretisch 2.50 mg Aluminium berechnet, ergab sich als Mittelwert von 6 Bestimmungen 2.30 mg Aluminium; bei einer Varianz von 9.5%

TABELLE III

BESTIMMUNG VON 2.50 mg ALUMINIUM NACH METHODE III AUS WÄSSRIGEN ALUMINIUMCHLORID-LÖSUNGEN

mg Aluminium	2.32	2.38
	2.46	2.32
	2.38	2.46
	2.46	2.50
	2.56	2.54
	2.38	—
Mittelwert	2.43	
Fehler in Rel. %	2.8	
Varianz[18] in %	9.6	

TABELLE IV

GEGENÜBERSTELLUNG DER DREI VERSCHIEDENEN ALUMINIUMBESTIMMUNGSMETHODEN AUS REINEN LÖSUNGEN

(Bezogen auf 2.50 mg Al)

Methode	*Indikator*	*Puffer*	*$ZnSO_4$ (M)*	*Fehler (Rel. %)*	*Varianz (%)*
I	Dithizon	Acetat	0.01	−4.0	2.8
	Dithizon	Acetat	0.001	−0.7	1.2
II	Xylenolorange	Acetat	0.001	−0.3	0.72
	Xylenolorange	Urotropin	0.001	−0.3	0.64
III	Ferri–ferrocyanid	Acetat	0.001	−2.8	9.6

betrug der relative Fehler —8.0%. Daraus ist ersichtlich, dass ein derartiges Verfahren den Genauigkeitsansprüchen nicht genügt.

Ansatz. 2.50 mg Aluminium; 5 ml Indikatorlösung (Mischung aus 20 ml 1%igem Ferricyanid und 5 ml 1%igem Ferrocyanid); 20 ml Acetatpuffer (500 g Natriumacetat, 20 ml Eisessig auf 1000 ml mit destilliertem Wasser aufgefüllt); 0.5 ml Benzidinlösung (1 g Benzidin in 100 ml Eisessig).

Tabelle III zeigt, dass die einzelnen Werte stark vom theoretischen Wert abweichen, was auch auf den schlecht sichtbaren Titrationsendpunkt zurückzuführen ist.

Ein Vergleich der 3 beschriebenen Methoden gibt, wie Tabelle IV zeigt, Aufschluss über ihre Brauchbarkeit.

Methode II ist den beiden anderen deutlich überlegen. Ausser der höheren Genauigkeit ist sie gemäss[2] gegen Anwesenheit grösserer Salzmengen am wenigsten empfindlich, dieser Umstand war mit entscheidend, dass sie für alle weiteren Bestimmungen herangezogen wurde. Hat man nämlich eine aluminiumhaltige Lösung vorliegen, aus der schon auf verschiedenen Wegen eine Reihe von Ionen abgetrennt wurden, so ist es unvermeidlich, dass sie mehr oder weniger salzhaltig ist.

DER EINFLUSS VERSCHIEDENER SALZE AUF DIE TITRATION VON KOMPLEXONLÖSUNG MIT ZINKSULFAT

Wie gefunden ist[2,12], kann der Einfluss anwesender Salze auf die Ausbildung des Aluminium–Komplexon-Komplexes dadurch ausgeschaltet werden, dass man vor der Titration kurz aufkocht. Nun zeigten sich aber schon bei der Titration von Komplexon mit Zinksulfat, bei Verwendung von Xylenolorange als Indikator, folgende in Tabelle V zusammengefasste Salzeffekte.

TABELLE V

TITRATION VON 1 ml 0.01 *N* KOMPLEXONLÖSUNG MIT 0.001 *M* ZINKSULFAT BEI ANWESENHEIT VERSCHIEDENER SALZE

Urotropin		*Natriumacetat*		*Natriumchlorid*		*Natriumnitrat*		*Natriumsulfat*	
g	*ml*	*g*	*ml*	*g*	*ml*	*g*	*ml*	*g*	*ml*
0	10.0	0	10.0	0	10.0	0	10.0	0	10.0
0.4	10.4	0.66	10.6	5	10.5	5	10.45	5	10.3
1	10.8	1.65	11.1	10	11.5	10	11.0	10	10.6
2	11.2	3.30	11.8	15	13.0	15	11.6	15	10.9
4	11.7	5.0	12.3	20	22.0	—	—	—	—

Man sieht, dass der Einfluss der als Puffersubstanz mit eingesetzten Salze Natriumacetat und Urotropin wesentlich bedeutender ist, als der der übrigen Salze. 4 g Urotropin, bzw. 3 g Natriumacetat entsprechen bereits einem ebenso grossen Mehrverbrauch, wie etwa 10 g NaCl, 15 g $NaNO_3$ oder mehr als 15 g $Na_2SO_4 \cdot 10\ H_2O$. Abb. 1 zeigt den durch Zugabe verschiedener Salze notwendig gewordenen Mehrverbrauch an Zinksulfatlösung.

Um diese mögliche Fehlerquelle bei der Aluminiumbestimmung auszuschalten, wurde bei der Titerstellung der Zinksulfatlösungen jeweils etwa die gleiche Menge an Kochsalz und die gleiche Menge an Puffer zugegeben, die bei der Titration dann vorhanden sein musste.

Eine weitere Fehlermöglichkeit konnte noch in der starken Komplexbildungsverzögerung der Aluminiumkomplexonverbindung bei Anwesenheit grosser Mengen an Salzsäure festgestellt werden. Abb. 2 zeigt die Abhängigkeit der vollständigen Aluminium-Komplexon-Komplexbildung von der Kochzeit der Lösung nach Extraktion des Aluminiums mit Acetylaceton. Daraus ist zu entnehmen, dass bei diesen

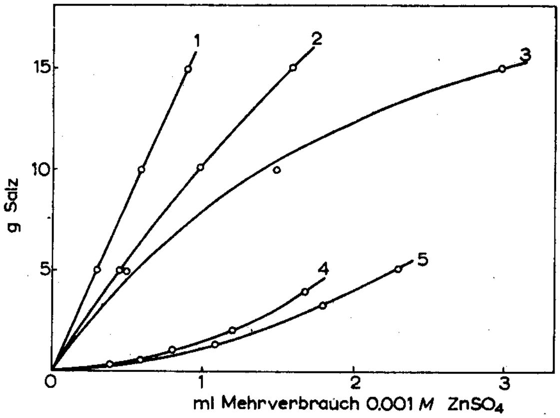

Abb. 1. Einfluss verschiedener Salze auf die Titration mit Xylenolorange als Indikator. 1, $Na_2SO_4 \cdot 10\ H_2O$; 2, $NaNO_3$; 3, NaCl; 4, Urotropin; 5, CH_3COONa.

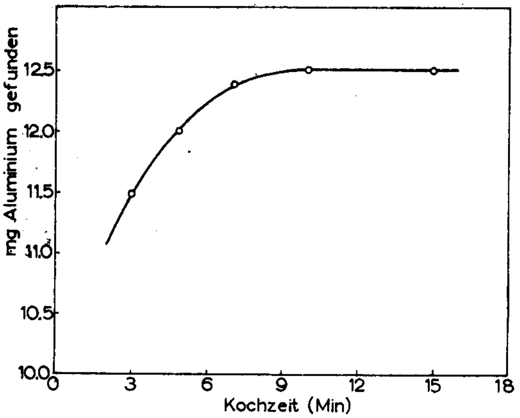

Abb. 2. Der Einfluss der Kochzeit auf die Bildungsgeschwindigkeit des Aluminium-Komplexon-Komplexes. Gefunden nach Extraktion des Aluminiums mit Acetylaceton.

stark sauren Lösungen, die nach Zerstörung des Aluminiumacetylacetonkomplexes mit Salzäure und Brom zu pH-Werten kleiner als 0 führen, eine Kochzeit von 10 Min nötig ist, um eine vollständige Bildung des Komplexes zu gewährleisten.

Um die komplexometrische Aluminiumbestimmung nach Methode II schnell und einfach bei Anwesenheit von Neutralsalzen durchführen zu können, ist es also vorteilhaft, die Lösung vorerst auf den zur Aluminiumkomplexonkomplexbildung günstigen pH-Wert von 1–2 zu bringen.

EMPFOHLENE ARBEITSVORSCHRIFT

Die zu untersuchende Lösung wird mit Natronlauge oder Salzsäure auf pH 1–2 gebracht, ein Überschuss an 0.01 M Komplexonlösung zugefügt und 5 Min gekocht. Hierauf wird in der noch heissen Lösung die noch vorhandene Säure mit verdünnter Natronlauge abgestumpft und rasch unter fliessendem Wasser gekühlt. Zur pH-Einstellung auf 5.0–5.2 gibt man 5 ml N Essigsäure und 1 g Urotropin zu. Stimmt der pH-Wert nicht ganz, so wird er mit verdünnter Lauge oder Säure korrigiert. 5–10 Tropfen der Xylenolorangelösung zugegeben und das überschüssige Komplexon mit 0.001 M Zinksulfat zurücktitriert.

ZUSAMMENFASSUNG

Es werden die komplexometrischen Aluminiumbestimmungsmethoden von WÄNNINEN UND RINGBOM, PŘIBIL *et al.* und SAJO verglichen. Die von PŘIBIL ist im Bestimmungsbereich von 2.5 mg Al bei einem Fehler von —0.3 Rel. % und einer Varianz von 0.7% den beiden anderen überlegen. Für Natriumacetat, Urotropin, Natriumchlorid, Natriumnitrat und Natriumsulfat wurde der Salzfehler für die Titration gegen Xylenolorange als Indikator (nach PŘIBIL) festgestellt. Die Bildungsgeschwindigkeit des Aluminiumkomplexonkomplexes in stark salzsaurem Milieu in Abhängigkeit der Kochzeit wurde untersucht.

SUMMARY

The complexometric methods for determination of aluminium of WÄNNINEN AND RINGBOM, PŘIBIL *et al.* and SAJO are compared. That of PŘIBIL has a relative error of —0.3% and a variance of 0.7% in the region of 2.5 mg Al and is preferable. The salt error for sodium acetate, urotropin, sodium chloride, nitrate and sulfate has been studied for the titration with xylenol orange as indicator (PŘIBIL). The rate of formation of the aluminium complex in strongly acidic medium has been studied in relation to the boiling time.

RÉSUMÉ

Les auteurs ont examiné et comparé les 3 méthodes complexométriques de WÄNNINEN ET RINGBOM, PŘIBIL *et al.* et SAJO, pour le dosage de l'aluminium. La vitesse de formation du complexe, en milieu fortement acide, a été étudiée en fonction du temps d'ébullition.

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MIXED LIGAND COMPLEXES OF IRON(II) AS NONAQUEOUS ACID-BASE AND AQUEOUS OXIDATION-REDUCTION INDICATORS

ALFRED A. SCHILT

Department of Chemistry, University of Michigan, Ann Arbor, Mich. (U.S.A.)

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Studies conducted on the preparation and properties of the complexes of iron(II) and (III) with cyanide and aromatic diimine mixed ligands[1-3] indicate that they may be useful in a variety of ways in chemical analysis. Thus far analytical use has been made only of the neutral dicyano-bis-(1,10-phenanthroline)-iron(II) complex and of its 4,7-diphenyl-1,10-phenanthroline homolog. A highly selective, sensitive colorimetric method for the determination of cyanide based on formation and extraction of the former has been described[4]. The homologous phenyl-substituted complex was shown to be a suitable form in which trace amounts of iron can be quantitatively separated from copper and measured spectrophotometrically[5]. In the present study it is found that dicyano-bis-(1,10-phenanthroline)-iron(II) and dicyano-bis-(2,2'-bipyridine)-iron(II) are useful as acid-base and oxidation-reduction indicators. Future studies are anticipated which may lead to the use of the charged species in this series of mixed ligand complexes as precipitation reagents. The tetracyano-mono-(1,10-phenanthroline)-ferrate(II) anion, for example, which forms insoluble salts with a number of the heavy metal ions, may prove to be a practical and selective precipitation reagent. The tetracyano complex and its salts are highly colored; thus small amounts could be measured colorimetrically.

For simplicity and convenience, the trivial names ferrocyphen and ferrocypyr are proposed for dicyano-bis-(1,10-phenanthroline)-iron(II) and dicyano-bis-(2,2'-bipyridine)-iron(II), respectively; the cationic iron(III) species, obtained on oxidation of these neutral complexes, may then be referred to respectively as ferricyphen and ferricypyr.

It is believed that this marks the first time a metal complex of any kind has been found to be effective as an acid-base indicator. In any case, the use of a metal complex for such a purpose is sufficiently novel to prompt some elaboration as to its conception. During a recent investigation[3] it was found that ferrocyphen and ferrocypyr react rapidly and reversibly with strong acids to give stable mono-and diprotonated species. Acid exchange measurements, carried out in glacial acetic acid, indicated that ferrocyphen and ferrocypyr are similar to *o*-chloroaniline in basicity. In acetic acid solvent, the monoprotonated species proved to be very much weaker than *o*-chloroaniline, somewhat weaker than thiourea, yet considerably stronger than the solvent in competition for perchloric acid. Since the visible absorption characteristics, as well as the basicities, of the protonated and neutral species differ markedly, the neutral complexes should be able to function as acid-base indicators. This contention is confirmed by the results of the present study. It is shown that the complexes are applicable as indicators for titrating certain bases in various nonaqueous solvents. Their possible applications in spectrophotometric titrations and in aqueous systems have yet to be investigated.

Formal redox potentials for ferrocyphen and ferrocypyr were measured in various concentrations of sulfuric acid. Confirming the fact that only the iron(II) species exhibit measurable basicities, the formal potentials are found to increase with increasing acid concentration. Interestingly, just the opposite trend is observed for the formal potentials of the ferroin complexes tris-(1,10-phenanthroline)-iron(II), tris-(5-nitro-1,10-phenanthroline)-iron(II), etc.[6].

The results of this investigation show the neutral mixed ligand complexes of iron(II) to be suitable for use as redox indicators. Several practical titrations are described. The suitability of ferrocyphen as an indicator for the titration of aromatic amines with sodium nitrite is especially notable.

Previous work has been reported concerning the properties of the tetracyano species. GEORGE, HANANIA AND IRVINE[7] found a value of 0.541 V for the standard reduction potential of the following couple (where bipy represents 2,2′-bipyridine):

$$[\mathrm{Fe\ bipy\ (CN)_4}]^- + e = [\mathrm{Fe\ bipy\ (CN)_4}]^{-2}$$

In 0.2 *M* HCl a formal potential of 0.619 V was found. More positive potentials arise in acid because the iron(II) complex forms stable acid species whereas the iron(III) complex does not. The visible absorption characteristics of the iron(II) and iron(III) tetracyano species are not greatly different[2]; hence they are not believed to be suitable redox indicators. They could find application in spectrophotometric titrations, but this possibility has yet to be explored.

An interesting trend is apparent in the formal redox potentials of the complexes: a decrease in potential of approximately 0.2 V results each time an aromatic diimine ligand is displaced from coordination with iron by two cyanide ligands. To illustrate, complexes in the iron-cyanide-2,2′-bipyridine system and their approximate formal potentials in strong acid solutions are $[\mathrm{Fe\ bipy_3}]^{+3}/[\mathrm{Fe\ bipy_3}]^{+2}$, 1.0 V; $[\mathrm{Fe\ bipy_2(CN)_2}]^+/[\mathrm{Fe\ bipy_2(CN)_2}]$, 0.8 V; $[\mathrm{Fe\ bipy(CN)_4}]^-/[\mathrm{Fe\ bipy(CN)_4}]^{-2}$, 0.6 V; $[\mathrm{Fe(CN)_6}]^{-3}/[\mathrm{Fe(CN)_6}]^{-4}$, 0.4 V.

APPARATUS AND REAGENTS

A Beckman pH meter, Model G, was used for potentiometric titrations. For nonaqueous acid-base titrations a conventional glass electrode and silver-silver chloride reference electrode were used. When titrations were performed in acetic anhydride the silver-silver chloride electrode was immersed in a saturated acetic anhydride solution of silver and lithium chlorides which was in electrical contact with the solution titrated by means of a capillary-fibre junction[8]. For all other titrations the reference electrode was immersed directly in the solution titrated. A platinum electrode and saturated calomel reference electrode (fibre-capillary type) were employed for aqueous redox titrations.

Procedural details for the synthesis of dicyano-bis-(1,10-phenanthroline)-iron(II) dihydrate (ferrocyphen) and dicyano-bis-(2,2′-bipyridine)-iron(II) trihydrate (ferrocypyr) are given elsewhere[2]. Solutions of the solid complexes were prepared as indicators. For acid-base titrations, 25 mg of the solid complex was dissolved in 100 ml of the solvent to be used for the titration and 1 ml of this indicator solution added to approximately every 25 ml of solution to be titrated. For aqueous redox titrations, 0.3 g of the solid complex was dissolved in 100 ml of concentrated acid, of the kind to be used in the titration, and 1 ml of this indicator solution was added to approximately every 100 ml of solution to be titrated. Limited solubilities preclude preparation of more concentrated indicator solutions in both cases.

The nonaqueous solvents used were of reagent quality; no basic impurities were detectable.

Standard perchloric acid in acetic acid

A 0.1 *M* solution was prepared by the method of FRITZ[9] and standardized by potentiometric titration against potassium acid phthalate in acetic acid.

Standard perchloric acid in acetic anhydride–acetic acid mixture

A 0.05 *M* solution was prepared as described by STREULI[8] and standardized with potassium acid phthalate by potentiometric titration in acetic acid.

Standard ceric sulfate solution

A solution 0.05 *M* in cerium(IV) and approximately 0.9 *M* in H_2SO_4 was prepared using ceric hydroxide (G. Frederick Smith Chemical Co.) and the procedure described by DIEHL AND SMITH[10]. Arsenious oxide was employed for standardization.

Standard potassium dichromate, 0.1 N

This was prepared by dissolving a weighed sample of dry, primary standard grade $K_2Cr_2O_7$ and diluting to a known volume with distilled water.

Standard vanadium(V) solution, 0.02 M

A 2.4-g sample of ammonium vanadate was dissolved in 16 ml of concentrated sulfuric acid and diluted to 1 l with distilled water. The molarity of the final solution was determined by potentiometric titration *versus* a standardized solution of ferrous ammonium sulfate.

Sodium nitrite solution, 0.1 M

Reagent grade $NaNO_2$ was dried at 110° for 2 h; a weighed sample was dissolved and diluted to exactly 1 l with distilled water; the molarity was calculated, assuming absolute purity.

EXPERIMENTAL

Acid–base titrations in nonaqueous solvents

Preliminary tests were carried out to determine which solvents of those commonly employed for nonaqueous titrations might prove suitable in conjunction with the use of the neutral complexes as indicators. Criteria for suitability were the following: (*1*) the solvent should dissolve a sufficient amount of the complex to be colored thereby, (*2*) the addition of 1–3 drops of the 0.1 *M* perchloric acid titrant to the solution should result in a pronounced and easily recognized color change, and (*3*) the color change should be reversible on adding a weak base. Acetone, dioxane, ethyl acetate, and benzene failed to dissolve the complexes. Varying degrees of solubility were observed in isopropyl alcohol, ethylene glycol, and diethyl cellosolve; however excessive amounts of acid were necessary to produce significant color changes. Solvents which provided all of the sought-for characteristics are glacial acetic acid, acetic anhydride, chloroform, chlorobenzene, nitrobenzene, nitromethane, and acetonitrile.

A variety of titrations were performed to evaluate the applicability and effectiveness of ferrocyphen and ferrocypyr as acid–bases indicators. Four different solvents and a number of selected weak bases were employed. The general procedure was the same in every case. Table I gives the pertinent data and results.

TABLE I

TITRATIONS IN NONAQUEOUS SOLVENTS

Solvent	*Substance titrated*	*g per aliquot*	*Method*[a]	*E (mV) or color*[b] *vs. extent neutralization*				*Purity found (%)*	
				0%	*50%*	*99%*	*101%*		
Acetic acid	$NaC_2H_3O_2$	0.2885	pot	185	230	363	511	99.6	
			phen	R	R	O	Y	99.5	99.6
			pyr	P	P	O	Y	99.4	
Acetic acid	Pyridine[c]	0.2750	pot	180	215	350	550	99.1	
			phen	R	R	R	Y	99.1	
			pyr	P	P	P	Y	99.0	99.1
Acetic acid	1-Naphthylamine	0.4273	pot	190	218	346	492	99.5	
			phen	R	R	O	Y	99.5	99.7
			pyr	P	P	O	Y	99.7	
Acetic acid	*p*-Bromoaniline	0.5045	pot	192	219	352	483	99.0	
			phen	R	R	O	Y	98.8	98.1
			pyr	P	P	pale R	Y	98.3	98.7
Acetic acid	*o*-Chloroaniline	0.3544	pot	280	324	446	495	99.3	
			phen	R	O	OY	Y	99.6	
			pyr	P	R	OY	Y	100.1	98.7
Acetic acid	2,4-Dichloro-aniline	0.4756	pot	337	389	472	489	98.1	
			phen	R	O	OY	Y	96	
			pyr	P	O	OY	Y	99	
Acetic anhydride	LiCl	0.0118	pot[d]	426	516	715	910	79.5	
			phen	P	P	O	Y	80.1	
			pyr	V	V	OY	Y	78.1	
Acetic anhydride	KBr	0.0174	pot[d]	410	683	880	966	99	
			phen	P	O	Y	Y	—	
			pyr	V	O	Y	Y	—	
Acetic anhydride	$NaC_2H_3O_2$	0.0257	pot[d]	299	390	619	960	99.9	
			phen	P	P	R	Y	100.1	99.9
			pyr	V	V	pale R	Y	100.3	
Acetic anhydride	Pyridine	0.0204	pot[d]	330	484	679	935	99.0	
			phen	P	P	O	Y	98.7	98.9
			pyr	V	V	OY	Y	98.5	

TABLE I (Cont.)

Solvent	*Substance titrated*	*g per aliquot*	*Method*[a]	*E (mV) or color*[b] *vs. extent neutralization*				*Purity found (%)*	
				0%	*50%*	*99%*	*101%*		
Chloroform	Pyridine	0.3089	pot	—342	223	343	565	99.0	
			phen	V	P	R	Y	99.0	99.0
			pyr	B	B	P	Y	99.1	99.0
Chloroform	1,10-Phenanthroline[c]	0.0628	pot	—148	320	370	531	100.0	
			phen	V	P	R	Y	100.0	100.6
			pyr	B	P	R	OY	100.3	100.9
Chloroform	*o*-Chloroaniline	0.3506	pot	—294	360	469	520	99.9	
			phen	V	O	Y	pale Y	97.7	98.6
			pyr	B	R	Y	pale Y	99.3	
Chloroform	2,4-Dichloroaniline	0.4771	pot	—370	418	514	533	99.3	
			phen	V	O	pale Y	pale Y	~97	
			pyr	B	O	pale Y	pale Y	~97	
Chlorobenzene	1-Naphthylamine	0.0470	pot	—340	268	405	497	99.6	
			phen	V	R	O	Y	99.6	99.4
			pyr	B	R	O	OY	100.3	
Chlorobenzene	2,2′-Bipyridine[c]	0.1726	pot	—276	300	437	560	99.9	
			phen	V	V	V	Y	99.7	
			pyr	B	P	P	Y	99.9	99.7
Chlorobenzene	*o*-Chloroaniline	0.2045	pot	—170	381	488	521	99.4	
			phen	V	O	OY	Y	100	
			pyr	B	R	OY	Y	101	

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[a] Potentiometric titrations are designated by "pot"; unless otherwise noted, the glass and Ag–AgCl electrodes were immersed directly in the solution titrated. Visual titrations are indicated by the notation "phen" where ferrocyphen and by "pyr" where ferrocypyr was used as indicator.

[b] Colors: V(violet), B(blue), P(purple), R(red), O(orange), OY(golden), Y(yellow).

[c] Perchlorate salt precipitates during titration.

[d] Glass electrode *vs.* Ag–AgCl in acetic anhydride saturated with lithium chloride and silver chloride as the reference electrode.

General procedure. Weigh out a 0.01–0.02 mole sample of the base to be titrated, dissolve it in the solvent selected, and dilute to 250.0 ml in a volumetric flask. Pipet 50.0 ml of this solution into the titration vessel, add 50 ml more of the solvent and 4 ml of ferrocyphen or ferrocypyr indicator solution, and titrate with standard perchloric acid solution. For titrations in acetic anhydride use the 0.05 *N* perchloric acid–acetic anhydride–acetic acid solution; for all others, use the standard 0.1 *N* perchloric acid in acetic acid solution. Record both the potentiometric data and the solution color as a function of the titrant added. Then titrate successive aliquots visually using the appropriate color response of the indicator, ascertained from the first titration, to detect the equivalence point. Determine and correct for the amount of acid consumed by the indicator; calculate the percent purity of the sample.

Determination of formal redox potentials

Solutions of the complexes, prepared in sulfuric acid of known concentration, were titrated potentiometrically using platinum and saturated calomel electrodes, standard ceric sulfate titrant, and a 5-ml buret. Since the solid complexes were very slow to dissolve in the more dilute acid solutions, the weighed samples were first dissolved in 0.5 ml of concentrated acid and then diluted with a known volume of sulfuric acid of the desired concentration. Some solutions were prepared by shaking an excess of the solid complex with the sulfuric acid for several min and then filtering off the undissolved solid. Although this did not permit use of weighed samples, it served to give crude estimates of solubilities and to check on the reliability of the other dissolution procedure. Limited solubility of the iron(II) complexes precluded potentiometric measurements both in neutral solutions and in acid solutions more dilute than those employed here.

Formal reduction potentials (*versus* the standard hydrogen electrode) for the Fe(III)/Fe(II) complex systems and the Ce(IV)/Ce(III) couple were determined from the 50% and 200% experimental titration points, respectively. Potentiometric measurements prior to the end-point could be taken almost immediately after the addition of each increment of titrant; beyond the end-point the electrode response was quite slow so that considerable time was required for the gradually increasing readings to attain reasonably constant values. The formal potentials found for the Ce(IV)/Ce(III) couple may be slightly low in some cases for this reason. However the main interest in these was to test the reliability of the potentiometric measurements; in most cases the agreement with previously determined values is satisfactory. As a further check of the procedure, the amount of complex found was compared with that taken for titration. The results are compiled in Table II.

TABLE II

FORMAL REDOX POTENTIALS AT 25° IN SULFURIC ACID SOLUTIONS

H_2SO_4		*Weight of complex*		*Formal potentials (V)*	
M	*Volume (ml)*	*Taken (g)*	*Found (g)*	*Ce(IV)/Ce(III)*	*Fe(III)/Fe(II)*
		A. Ferrocypyr			
12	50	0.0512	0.0519	1.54	0.979
10	50	0.0537	0.0540	1.47	0.901
6	50	0.0321	0.0323	1.43	0.817
	100	a	0.0770	1.42	0.824
4	100	0.0220	0.0221	1.43	0.794
	100	a	0.0175	1.44	0.780
2	200	0.0200	0.0200	1.44	0.791
	200	a	0.0193	1.43	0.781
		B. Ferrocyphen			
12	50	0.0501	0.0490	1.53	0.990
10	50	0.0390	0.0396	1.47	0.925
6	100	0.0209	0.0220	1.42	0.852
	100	a	0.0210	1.40	0.852
4	100	0.0058	0.0062	1.40	0.822
	100	a	0.0030	1.41	0.814
2	200	0.0050	0.0052	1.40	0.806
	200	a	0.0057	1.41	0.806

[a] Amount necessary to nearly saturate the solution with the complex; excess solid filtered off before titrating supernatant solution.

Oxidation–reduction titrations

A brief survey of the more common oxidants and reductants was made to ascertain which would undergo sufficiently rapid reaction with the reduced and oxidized forms of the proposed indicators to be suitable in titrations. In strongly acidic solutions, ferrocyphen and ferrocypyr are oxidized reversibly and with great rapidity by Ce(IV), V(V), $Cr_2O_7^{-2}$, BrO_3^-, IO_4^-, or HONO. Oxidation under similar conditions occurs much more slowly and at various rates using IO_3^-, H_2O_2, $S_2O_8^{-2}$, or HNO_3. The oxidized indicators ferricyphen and ferricypyr are readily reduced in strong acid solutions by Fe(II), Sn(II), Cu(I), Sb(III), I^-, and hydroquinone. Reduction by As(III), SO_2, hydroxylamine, or hydrazine is extremely slow except in very dilute acid or neutral solutions.

All of the titrations were performed using ferrocyphen as the indicator. Since ferrocyphen and ferrocypyr have nearly identical formal reduction potentials and exhibit similar color changes on oxidation, it is assumed that they can be used interchangeably.

Titration of iron(II). Preliminary titrations, performed potentiometrically in the presence of added ferrocyphen, demonstrated the need for adding phosphoric acid to lower the formal potential of iron(II) (and thus the equivalence point potential) so that the indicator response would coincide with potentiometric end-points. Subsequent titrations were performed according to the following directions: pipet 10.00 ml of the iron solution (in this case a solution containing 39.216 g Mohr's salt per l), add 5 ml of concentrated phosphoric acid followed by sufficient concentrated sulfuric or

TABLE III

STANDARDIZATION OF 0.1 *N* $FeSO_4$ USING FERROCYPHEN INDICATOR

Titrant	*Solution*	*End-point recognition*	*Normality*
$K_2Cr_2O_7$	1 *M* H_2SO_4	Potentiometric	0.1001
	1 *M* H_2SO_4	Orange → yellow green	0.0999
	2 *M* H_2SO_4	Orange → yellow green	0.1000
	4 *M* H_2SO_4	Yellow green → green	0.1002
	6 *M* H_2SO_4	Green → blue green	0.1004
	1 *M* HCl	Indistinct color change	—
	2 *M* HCl	Yellow → green	0.0999
	4 *M* HCl	Yellow → green	0.1001
	5 *M* HCl	Indistinct color change	—
HVO_3	4 *M* H_2SO_4	Potentiometric	0.1002
	1 *M* H_2SO_4	Yellow → pale blue	0.0999
	2 *M* H_2SO_4	Yellow → pale blue	0.1004
	4 *M* H_2SO_4	Yellow → pale blue	0.1003
	6 *M* H_2SO_4	Yellow → pale blue	0.1003
	1 *M* HCl	Orange → pale blue	0.1002
	2 *M* HCl	Yellow → pale green	0.1003
	4 *M* HCl	Indistinct color change	—
$Ce(SO_4)_2$	6 *M* H_2SO_4	Potentiometric	0.1001
	1 *M* H_2SO_4	Orange → pale blue	0.0999
	6 *M* H_2SO_4	Yellow → pale blue	0.1002
	1 *M* HCl	Orange → pale blue	0.1001
	2 *M* HCl	Yellow → pale yellow	0.0997
	4 *M* HCl	Indistinct color change	—

hydrochloric acid and water to give 100 ml of the desired acid concentration, add 1 ml of indicator solution (0.3 g ferrocyphen in 100 ml of concentrated phosphoric acid, and titrate with standard oxidant to the first distinct, sharp change in color (see Table III for specific details). Blank titrations were made to correct for the amount of titrant necessary for oxidation of the indicator.

Tests performed on the solutions retained after titration showed the indicator reaction to be reversible. Prolonged storage in an excess of either oxidant or reductant produced no deleterious effect on indicator behavior.

Titration of hydroquinone. Potentiometric titration of hydroquinone in the presence of added ferrocyphen with the vanadium(V) titrant demonstrated that the visual and potentiometric end-points coincide almost exactly, even as the acid concentration is varied. Using cerium(IV) as the titrant, visual end-points were observed to occur slightly before the potentiometric inflection points. The differences were in the range of 1000–2000 p.p.m. and hence are within the expected limits of experimental error.

Visual titrations were performed according to the directions: weigh a 0.03–0.04-g sample, dissolve in 100 ml of acid (either hydrochloric or sulfuric, 1–6 *M*), add 1 ml of indicator (0.3 g ferrocyphen in 100 ml of concentrated sulfuric acid), and titrate with the standard oxidant to the first distinct, sharp change in color. Blank titrations are necessary to correct for the amount of titrant consumed by the indicator. The results are given in Table IV.

TABLE IV

TITRIMETRIC ASSAY OF HYDROQUINONE USING FERROCYPHEN INDICATOR

Titrant	*Solution*	*End-point recognition*	*% Purity*
$Ce(SO_4)_2$	1 *M* H_2SO_4	Orange → colorless	99.4
	6 *M* H_2SO_4	Yellow → very pale yellow	101.3
	1 *M* HCl	Orange → colorless	99.9
	1 *M* H_2SO_4	Potentiometric	99.7
HVO_3	1 *M* HCl	Orange → pale green	99.7
	2 *M* HCl	Yellow → pale green	99.6
	0.5 *M* H_2SO_4	Orange → pale green	99.6
	4 *M* H_2SO_4	Yellow → pale green	99.5
	1 *M* HCl	Potentiometric	99.6

Tests performed on the solutions retained after titration demonstrated that the indicator reaction behaves reversibly. Storage for several hours of the solutions to which an excess of either hydroquinone or titrant had been added was without noticeable effect on the indicator or its response.

Titration of primary aromatic amines. Samples of various amines were titrated using the following procedure: weigh out a 2–3- mmol sample of the amine, dissolve in 100 ml of 6 *M* hydrochloric acid, add 1 ml of indicator solution (0.3 g ferrocyphen in 100 ml of concentrated hydrochloric acid), and titrate with standard sodium nitrite to a violet colored end-point that will persist for at least 3 min. A titration blank was measured to correct for the amount of titrant consumed by the indicator. Results are given in Table V.

From the behavior of the indicator during the titrations it is evident that its reaction responds reversibly with respect to the titration reaction. Upon rapid addition of large increments of titrant, prior to the equivalence-point, ferrocyphen underwent complete and rapid oxidation followed more slowly by a gradual return to the reduced condition. Such behavior could be produced many times throughout the course of any given titration, and apparently, without adversely affecting the ability of the indicator to function properly. Since reduction of ferricyphen cannot be effected by the aromatic amines in question, it appears that one of the diazotization products or reaction intermediates is responsible for the reversibility of the indicator in this case. No attempt was made to elucidate the indicator reaction mechanism.

TABLE V

TITRIMETRIC ASSAY OF PRIMARY AROMATIC AMINES USING FERROCYPHEN INDICATOR

Amine	*HCl* *M*	*Replicate determinations* % *Purity*[a]
Aniline	4	98.9 (98.9)
Aniline	6	99.3 99.5 99.4 (99.2)
Aniline	8	99.3 (99.1)
Aniline	9	99.2 99.9
p-Bromoaniline	6	100.1 99.7
o-Chloroaniline	6	99.9 100.1
1-Naphthylamine	6	b
2,4-Dichloroaniline	6	100.2 100.1

[a] Values given in parentheses were obtained by potentiometric titration.
[b] Visual end-point detection was impossible because titration gives colored products.

Aniline was titrated potentiometrically in the presence of ferrocyphen to determine the color of the indicator in the immediate neighborhood of the electrometric end-point. The change in color of the indicator from light yellow to pale violet was observed to coincide almost exactly with the potentiometric end-point in each of three different hydrochloric acid concentrations employed: 4, 6 and 8 *M*. Considerable time, up to 1 h, was required to complete each potentiometric titration, because either or both chemical and electrode systems were slow to reach equilibrium and, of course, many equilibrium measurements were needed. No deleterious effect on the reversibility of the indicator after this time was noticeable.

A modest saving of time could be achieved by using 6 *M* hydrochloric acid as the solvent medium. Total elapsed time to complete the titration of aniline, for example, in 6 *M* HCl by visual end-point detection was approximately 10 min; in 4 *M* and 9 *M* acid the respective times averaged 15 and 10 min.

SUMMARY

The neutral mixed ligand complexes dicyano-bis-(1,10-phenanthroline)-iron(II) and dicyano-bis-(2,2'-bipyridine)-iron(II) are suitable indicators for the titration of various weak bases in nonaqueous solvents. They also serve as practical indicators for certain redox titrations in aqueous solutions; their applicability in the determination of primary aromatic amines is especially noteworthy. Formal potentials of the complexes in different concentrations of sulfuric acid are reported; the results confirm earlier findings that the neutral iron(II) complexes form stable protonated species.

RÉSUMÉ

Les complexes fer(II)-dicyano-bis-(1,10-phénanthroline) et fer(II)-dicyano-bis-(2,2'-dipyridine) conviennent très bien, comme indicateurs aux titrages de diverses bases faibles en milieu non-aqueux, de même qu'à certains titrages redox en solutions aqueuses et tout spécialement au dosage d'amines aromatiques primaires.

ZUSAMMENFASSUNG

Die neutralen Mischkomplexe Dicyano-bis-(1,10-phenanthrolin)-eisen(II) und Dicyano-bis-(2,2'-bipyridin)-eisen(II) eignen sich als Indikatoren für die Titration schwacher Basen in nicht-wässrigen Lösungsmittel sowie für gewisse Redox Titrationen in wässriger Lösung. Auf ihre Anwendung bei der Bestimmung von aromatischen primären Aminen wird besonders hingewiesen.

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REDUCTION OF AMMONIUM NITRATE WITH TITANIUM(III) CHLORIDE IN ACID MEDIA*

EUGENE A. BURNS

Space Sciences and Propulsion Division, Stanford Research Institute, Menlo Park, California (U.S.A.)

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Investigation of the determination of nitrate in acid media using an indirect titanous titration has led to the proposal of a new mechanism of nitrate reduction. It has been shown that the reduction of nitrate to ammonium ion as proposed by KNECHT AND HIBBARD[1] is not quantitative when only a moderate excess (50 to 100%) of the titanous salt is present.

TOMIČEK[2] reported that the direct potentiometric titration of nitrate solutions with titanous chloride is not possible because the reaction takes place very slowly. Therefore, to eliminate the time dependence when a small excess is present, a back-

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titration method similar to that found to be successful for the determination of perchlorate[3] was investigated: the sample was boiled with a known excess of titanous chloride solution contained in an Erlenmeyer flask which was protected from atmospheric oxidation; the solution was cooled and the excess titanous was titrated with standard ferric ammonium sulfate solution using potassium thiocyanate as end-point indicator.

The use of titanous solutions for the determination of organic nitrates of nitroesters[4] and nitroglycerin[5,6] has been reported. OLDHAM[4] found that 7.5 moles of titanous ion were consumed per mole of nitrate. SHANKSTER AND WILDE[5] found only 18 moles of titanium consumed per mole of nitroglycerin, and postulated that the nitrogen had been reduced to the —1 state (corresponding to hydroxylamine). The excellent work of FAINER[6] showed that two of the nitrates of nitroglycerin are reduced to the amine, the third to the +3 state, which is hydrolyzed to nitrous acid and subsequently disproportionates without consuming additional titanous salt. FAINER[6] also found that at very high acid concentrations (*e.g.* greater than 20 *N* sulfuric acid) the nitrate is reduced to nitric oxide (a 3-electron change). WELLINGS[7] observed that inorganic nitrates were quantitatively reduced to nitric oxide by action of hydrous titanous oxide. The wide divergence of findings in the literature indicates that the sequence of reduction steps, together with the ease of reaction, is quite sensitive to the acid concentration. Little or insufficient care was exercised to obviate atmospheric oxidation of the titanous solutions employed by previous researchers, and hence a certain doubt of the credulity of the interpretation of the data obtained by these workers exists. For these reasons the following carefully controlled experimental investigation was undertaken in an attempt to resolve the discrepancies.

EXPERIMENTAL

Reagents

A stock solution of titanous chloride was prepared from titanium hydride by action of excess hydrochloric acid in accord with the procedure described by BURNS AND MURACA[3]. The solution, approximately 0.3 *N* in titanous ion and 2.7 *N* in hydrogen ion, was standardized against potassium dichromate using sodium *p*-diphenylamine sulfonate as end-point indicator. A 0.33 *N* solution of ferric ammonium sulfate was prepared in 1 *N* sulfuric acid and standardized against standard titanous chloride using ammonium thiocyanate as end-point indicator. A 1.5 *N* sodium hydroxide–2 *F* sodium acetate solution was prepared; when equal amounts of this solution and a solution which contains 2.7 *N* hydrochloric acid are mixed, the resulting concentration of ingredients in the mixture (pH 4.5) are sodium chloride 1.35 *F*, acetic acid 0.6 *F*, and sodium acetate 0.4 *F*. A 2 *N* sodium hydroxide –*F* sodium sulfate solution was prepared; when equal amounts of this solution and a solution which contains 2.7 *N* hydrochloric acid are mixed, the resulting concentration of ingredients in the mixture (pH 1.0) are sodium chloride 1.35 *F*, sodium bisulfate 0.35 *F*, and sodium sulfate 0.15 *F*. A solution containing 2 mg/ml of osmium tetroxide in 2 *N* sulfuric acid was prepared to be used as a catalyst.

Apparatus

An apparatus similar to that described by BURNS AND MURACA[3] was employed to protect titanous solutions from air oxidation.

Procedure

In order to facilitate the experimental work and to ensure the highest possible degree of accuracy, stock solutions containing 70 to 80 mg of ammonium nitrate in a 25-ml aliquot were used. The aliquot was transferred to the reduction flask together with a 50-ml portion of reagent-grade deaerated hydrochloric acid, sulfate–sodium hydroxide, or acetate–sodium hydroxide to give the desired acidic conditions. The vessel was flushed with carbon dioxide and 50 ml of the titanous solution was added. The reduction was carried out in the presence and absence of osmium tetroxide and for varying durations of boiling to ascertain the effects of these parameters. The remainder of the procedure was performed in accordance with that described before[3].

RESULTS AND DISCUSSION

Table I summarizes the results obtained for the reduction of ammonium nitrate in 5.8 *M* HCl, pH 1, and pH 4.5 solutions as a function of time of boiling and whether or not the reaction was performed in the presence of osmium tetroxide. The reduction in 5.8 *N* acid and at pH 1.0 indicates that 3.7 to 3.9 equiv. of titanous chloride are required, and at pH 4.5, 6 to 7 equiv. of titanous chloride are required. There is no apparent effect using osmium tetroxide as a catalyst and/or to prolonged boiling. The boiling time of 10 min appears to be sufficient.

From this work, it is evident that, in strongly or moderately acidic solutions, the nitrate is reduced predominately, but not quantitatively, to the +1 state by titanous ions. It is logical to propose that the reduction goes through two-electron changes and the products are nitrous acid (eqn. 1), nitrous oxide (eqn. 2), hydroxylamine acid ion (eqn. 3), and ammonium ion (eqn. 4):

TABLE I

EQUIVALENTS OF TITANOUS CHLORIDE PER MOLE OF AMMONIUM NITRATE REQUIRED FOR REDUCTION OF AMMONIUM NITRATE

Sample weight (g)	*Acidity*		*Boiling time (min)*	*Osmium tetroxide catalyst*	*Equivalents Ti^{+3} consumed*
	HCl N	*pH*			
0.07393	5.8		10	Yes	3.72
0.07393	5.8		30	Yes	3.72
0.07393	5.8		60	Yes	3.81
0.07393	5.8		30	No	3.76
0.07393	5.8		10	No	3.84
0.07126		1.0	10	Yes	3.89
0.07126		1.0	30	Yes	3.69
0.07126		1.0	30	No	3.78
0.07126		4.5	10	No	6.43
0.07126		4.5	30	No	6.21
0.07393		4.5	10	Yes	6.92
0.07393		4.5	30	Yes	6.40
0.07393		4.5	30	Yes	6.72
0.07126		4.5	60	No	6.18
0.07126		4.5	60	No	6.68

$$H_2O + HNO_2 = NO_3^- + 3H^+ + 2e \qquad E^\circ = -0.94 \tag{1}$$

$$3H_2O + N_2O = 2HNO_2 + 4H^+ + 4e \qquad E^\circ = -1.29 \tag{2}$$

$$2NH_3OH^+ = N_2O + H_2O + 6H^+ + 4e \qquad E^\circ = +0.05 \tag{3}$$

$$H_2O + NH_4^+ = NH_3OH^+ + 2H^+ + 2e \qquad E^\circ = -1.35 \tag{4}$$

Standard potentials and notation are those of LATIMER[8].

It is observed that the +1 to −1 step (eqn. 3) has the greatest potential to be overcome in the reduction. For titanous–titanyl couple:

$$Ti^{+3} + H_2O = TiO^{+2} + 2H^+ + e \qquad E^\circ = -0.1 \tag{5}$$

Hence, it appears likely that the reduction may be stopped at the +1 state in moderately and strongly acidic solutions. On the other hand, LATIMER[8] states that the reduction stops at the +2 state, nitric oxide (eqn. 6) because of its "remarkable inertness". Indeed, FAINER[6] found that at extremely high acid concentrations (greater than 20 N), reduction ceases with the formation of nitric oxide; however, he also concurs with the findings of the present work at an acid concentration of 5.7 N (4.3 equiv. of titanium were consumed). The proposal that the acid reduction proceeds through two-electron changes is not unreasonable because in alkaline solution there is abundant evidence that the reduction takes this course[8].

$$H_2O + NO = HNO_2 + H^+ + e \qquad E^\circ = -1.00 \tag{6}$$

The titanous couple is a function of the acidity and ratio of titanyl to titanous ions. At 25°,

$$E = -0.1 - 0.059 \log \left(\frac{TiO^{+2}}{Ti^{+3}}\right) + 0.118\ \text{pH} \tag{7}$$

and as the pH is raised, or the ratio TiO^{+2}/Ti^{+3} is made smaller, the potential becomes more reducing.

It has been stated that the titanous chloride buffer method for reducing nitro groups to amines [9–14] utilizes the principle of operating at a higher pH, as explained in the previous paragraph. However, this is not the explanation for the further reduction of nitro or nitrato groups which occurs in more alkaline solution. The potential of eqn. (3) is also a function of pH and would increase more than the potential of eqn. (5). Therefore, the products which form in more alkaline solution *must be different*, *i.e.*, the formation of hyponitrous acid for the +1 state instead of nitrous oxide. The reactions represented by eqns. (8) and (9) can serve as a suitable explanation,

$$2H_2O + H_2N_2O_2 = 2HNO_2 + 4H^+ + 4e \qquad E^\circ = -0.86^9 \tag{8}$$

$$2NH_3OH = 2H_2N_2O_2 + 6H^+ + 4e \qquad E^\circ = -0.50^9 \tag{9}$$

A better approach to increase the potential of the titanous–titanyl couple lies in using a very large excess of titanous ion, hence the ratio TiO^{+2}/Ti^{+3} is very small throughout the entire reduction; however, this expedient has experimental limitations because the small difference between the two large ferric titrations of blank and sample will have a large relative error.

The data of Table I shows that reduction did not proceed to ammonium ion at pH

4.5, and hence the results at this pH are not adequately interpretable. Clearly, a 50 to 100% excess of titanous chloride is insufficient to drive the reaction to the quantitative production of ammonium ion. It is quite probable that this reaction is very slow as the —3 oxidation state is approached. More probable, however, is the termination of reduction to be a mixture of lower oxidation states, —3, —1, to give the effective —1 to —2 oxidation state. There is also the possibility that at higher pH values, some spurious reduction of hydrogen ion takes place.

SUMMARY

Investigation of acid ammonium nitrate solutions in the presence of titanous chloride has led to a new mechanism of nitrate reduction. It is proposed that the reduction proceeds through two electron changes and terminates as nitrous oxide in solutions whose acid content is greater than 0.1 *N*. The stronger reducing power of the titanous buffer method previously reported arising from a direct pH affect on the titanous–titanyl couple has been discerned rather as an effect arising from different reduction products in that media. The affects of prolonged reaction at 100° and use of osmium tetroxide catalyst were examined. A pH of 4.5 and 100% excess of titanous was insufficient to reduce nitrate to ammonia quantitatively.

RÉSUMÉ

Des recherches sur le comportement de solutions acides de nitrate d'ammonium, en présence de chlorure titaneux, ont conduit à un nouveau mécanisme de réduction des nitrates; deux électrons entrent en jeu, avec formation d'oxyde nitreux. L'influence du tétroxyde d'osmium, comme catalyseur, a été examinée. D'autre part, un pH de 4.5 et un excès de sel titaneux de 100% n'ont pas permis une réduction quantitative du nitrate en ammoniac.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Mechanismus der Reduktion von Nitraten zu Ammoniak mit Titan(III)-chlorid. Der Einfluss der Säurekonzentration, Erhitzungsdauer und von Osmiumtetroxyd als Katalysator wurde untersucht.

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DIE OXYDIMETRISCHE BESTIMMUNG VON DREI- UND VIERWERTIGEM URAN MIT Pb(IV)-AZETAT

A.BERKA, J. DOLEŽAL, I. NĚMEC UND J. ZÝKA

Institut für analytische Chemie der Karlsuniversität, Praha (Tschechoslowakei)

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Zur oxydimetrischen Bestimmung von Uran (nach vorgehender Reduktion zu vierwertigem Uran) wurde eine Reihe von Oxydationsmitteln verwendet, z.B. Permanganat[1], Cerisulphat[2,3], Vanadat[4-7], Eisen(III)-Cyanid in alkalischem Medium[8], dreiwertiges Eisen[9] u.s.w. Die Erkentnisse über die Reduktion von sechswertigem Uran mittels Reduktoren[10] und Amalgamen[11] wurden unlöngst übersichtlich zusammengefasst.

In der vorliegenden Arbeit haben wir die Oxydation von drei- und vierwertigem Uran mit Pb(IV)-Azetat untersucht, dass wir schon in der vorgehenden Arbeit[12] zur massanalytischen Bestimmung von einigen einfacheren anorganischen Systemen verwendet haben.

Wir haben gefunden, dass die direkte potentiometrische Titration von drei- und vierwertigem Uran mit Pb(IV)-Azetat nur in einem engen Aziditätsbereich verläuft, und dass sie wenig genau ist. Da aber, nach unseren Erkenntnissen es möglich ist, mit Pb(IV)-Azetat verlässlich zweiwertiges Eisen zu titrieren[12], haben wir eine Methode ausgearbeitet, bei der das drei- oder vierwertige Uran mit überschüssigem Eisen(III)-Chlorid oxydiert wird, und das entstandene zweiwertige Eisen potentiometrisch mit Pb(IV)-Azetat titriert wird. Dieses Prinzip wird des öfteren zur Uranbestimmung angewendet, auch wenn Kaliumbichromat[13-16] oder Cerisulphat[17] als Massreagentien angewendet werden. Die von uns vorgeschlagene Methode eignet sich auch zur Mikrotitration von vierwertigem Uran.

EXPERIMENTELLER TEIL

Reagenzien

Chlorwasserstoffsäure, Schwefelsäure, Essigsäure (p.a. Merck, Lachema). Die zur Mikrobestimmung verwendete Chlorwasserstoffsäure wurde durch Destillation einer azeotropen Mischung, oder durch isothermale Diffusion nach Abrahamczik[18] gereinigt.

Zweiprozentige wässerige Ferrichlorid-Lösung (p.a. Lachema).

Die Vorbereitung der 0.1 *N* und 0.01 *N* Lösung von Pb(IV)-Azetat in Eisessigsäure und die Bestimmung des Faktors wurde in vorgehenden Mitteilungen beschrieben[12,19]. Der Faktor von 0.01 *N* Lösungen wurde durch Titration von Fe(II)-Sulphat kontrolliert, dessen Faktor seinerseits mit Bichromat bestimmt wurde[20], sowie durch Titration von einwertigem Thallium[21] (Tl(I)-Karbonat wurde in verdünnter Schwefelsäure gelöst).

Die 0.0002 N Lösung von zweiwertigem Eisen (für die Mikrobestimmungen) in 1 N HCl wurde durch genaues Verdünnen einer 0.02 N Fe(II)-Sulphat Lösung bereitet, deren Faktor mittels Titration mit Kaliumbichromat[20] bestimmt wurde.

Die Lösung von U(IV)-Sulphat 0.1 N in 1 N H_2SO_4 wurde durch Reduktion einer entsprechenden Einwaage von Uranyl-Azetat (p.a. Lachema) mit Zinkamalgam bereitet. Das eventuell entstanden dreiwertige Uran wurde durch das Durchströmen von Luft zu vierwertigem Uran oxydiert. Der Faktor der Lösung wurde bichromatometrisch[13] bestimmt. Die 0.0002 N U(IV)-Sulphat Lösung in 1 N HCl wurde durch genaues Verdünnen der 0.1 N Lösung bereitet. Aus der verwendeten 1 N Chlorwasserstoffsäure wurde vorher Sauerstoff durch das Durchströmen von Stickstoff entfernt. Der Titer der Lösungen niedrigerer Normalität wurde durch Titration mit Pb(IV)-Azetat bestimmt. Dabei haben wir immer solche Volumina der Lösungen von niedrigerer Normalität abgemessen, die Uranmengen enthielten die wir bereits unter Verwendung von Lösungen höherer Normalität verlässlich bestimmt haben.

Eine 0.03 N Lösung von dreiwertigem Uran in 1 N HCl wurde mittels Reduktion von Uranylazetat mit amalgamiertem Zink[22] in einer Reduktor-Bürette nach DOLEŽAL UND ZÝKA[23] (in der die Lösung auch unter Stickstoffatmosphäre aufbewahrt wurde) bereitet. Der Faktor wurde bichromatometrisch[22] bestimmt.

Apparatur

Apparatur und Einrichtung für Mikrotitrationen wurde in den vorgehenden Mitteilungen beschrieben[21].

ÜBERSICHT DER RESULTATE

Zuerst versuchten wir die direkte Titration von sowohl vier- als auch dreiwertigem Uran mit Pb(IV)-Azetat mit potentiometrischer Indikation des Titrationsendpunktes. Auch durch Abänderung der Titrationsbedingungen erzielten wir keine zufriedenstellende Resultate. Die Titration des vierwertigen Urans verlief am besten in Medien von 0.01 N bis 0.3 N HCl oder H_2SO_4. Aber auch unter diesen Bedingungen waren die Resultate mit positiven Fehlern behaftet (bis 15%). Bei der Titration von dreiwertigem Uran waren die Resultate ausserdem durch die Titrationsgeschwindigkeit beeinflusst. Wir nutzten also unsere guten Erfahrungen mit der Titration von zweiwertigem Eisen mit Pb(IV)-Azetat zur indirekten Bestimmung von vier- und dreiwertigem Uran.

Bestimmung von vierwertigem Uran

Bei der Bestimmung von vierwertigem Uran oxydierten wir das vierwertige Uran in mit Chlorwasserstoffsäure angesäuerten Lösungen mit einem Überschuss an Fe(III)-Chlorid, und titrierten potentiometrisch das entstandene zweiwertige Eisen mit Pb(IV)-Azetat. Wir arbeiteten in der Weise, dass wir zu 0.7 ml bis 38 ml einer 2% Fe(III)-Chlorid Lösung 2 ml einer 0.02 N bis 20 ml einer 0.1 N U(IV)-Lösung zugaben, und soviel Chlorwasserstoffsäure zugaben, um ihre Normalität in der Lösung auf 0.5 bis 1.5 N zu bringen. Diese Säurekonzentration ist für die Oxydation von vier- zu sechswertigem Uran optimal. Die Titration des entstandenen zweiwertigen Eisens verläuft aber am besten in etwa 2 N HCl. Wir haben also nach 30 Sek die Azidität durch Zugabe von weiterer Säure auf diesen Wert erhöht, und nachdem mit Pb(IV)-Azetat titriert. Das Volumen der titrierten Lösung war bei unseren Versuchen 30 bis 70 ml. Das Potenzial stellt sich während der ganzen Titration, auch in der Nähe des Equivalenzpunktes sofort ein. Die Potenzialänderung in der Equivalenz ist bedeutend, das Inflexionspotenzial liegt in der Nähe von 760 mV.

1 ml 0.1 *N* Pb(IV)-Azetat entspricht 11.9035 mg U. Beispiele der Bestimmungen sind in Tabelle I angegeben.

TABELLE I

BESTIMMUNG VON URAN(IV) MIT 0.1 *N* $PbAc_4$ IN EINEM MEDIUM VON 2 *N* HCl

(4.96–249.55 mg U)

Gegeben (mg)	*Gefunden (mg)*	*Abweichung (%)*	*Potenzialänderung im Equivalenzpunkt (mV)*	*Inflexions-potenzial (mV)*
4.96[a]	4.95	—0.20	120[d]	740
4.96[a]	4.98	+0.40	135[d]	750
49.91[b]	49.88	—0.06	100[e]	745
49.91[b]	49.95	+0.08	110[e]	765
124.77[b]	124.52	—0.20	180[f]	760
124.77[b]	124.42	—0.28	110[f]	775
249.55[c]	248.72	—0.33	100[f]	740
249.55[c]	248.83	—0.29	110[f]	775

[a] 30 ml Volumen
[b] 50 ml Volumen
[c] 70 ml Volumen
[d] 0.005 ml Massreagens
[e] 0.01 ml Massreagens
[f] 0.02 ml Massreagens

Bestimmung von dreiwertigem Uran

Die quantitative Reduktion von sechswertigem Uran zu dreiwertigem hat in letzter Zeit KENNEDY[22] beschrieben. Laut seiner Arbeit kann das sechswertige Uran quantitativ im Reduktor nach JONES mit amalgamiertem Zink in 1 *N* HCl oder 1 *N* $HClO_4$ zu dreiwertigem reduziert werden. Quantitativ können höchstens 0.01 *M* Lösungen des sechswertigen Urans reduziert werden. Die Quantität der Reduktion wird gleichfalls durch höhere Konzentration von Zn^{+2} Ionen in der Lösung ungünstig beeinflusst. In der vorliegenden Arbeit haben wir eine Lösung von dreiwertigem Uran durch Reduktion nach KENNEDY[22] in der obgenannten Reduktorbürette[23] bereitet, in der wir die Lösung in Gegenwart der reduzierenden Füllung längere Zeit aufbewahrten. Obzwar in unserem Falle die Zn^{+2} Ionen-Konzentration die bei der Uranreduktion entstanden waren durch längere Berührung der saueren Lösung mit der Reduktorfüllung erhöht war, erreichten wir 98% Reduktion des sechswertigen Urans zu dreiwertigem. Wir haben die Lösung in streng inerter Stickstoffatmosphäre (in der Reduktorbürette) aufbewahrt, und haben gefunden, dass sich ihr Wert nach 4 Tagen nicht geändert hat. Auch in Abwesenheit des Zinks ist die Lösung von dreiwertigem Uran, bei Aufbewahrung in streng inerter Atmosphäre, ganz beständig. Selbst nach 12 Stunden wurde keine Änderung des Faktors beobachtet.

Bei der Bereitung von Lösung des dreiwertigen Urans haben wir immer so gearbeitet, das wir 1 l 0.01 M Uranylazetat in 1 N HCl in der mit amalgamiertem Zink gefüllten Reduktorbürette reduzierten, in der das Strömen der Lösung durch stete Zufuhr von Stickstoff ermöglicht wurde. In allen Fällen wird die gelbe Lösung zuerst grün, nach etwa 15 Min wird die hellgrüne Lösung grau (vierwertiges Uran wird bereits zum Teile zu dreiwertigem Uran reduziert). Die quantitative Reduktion zu dreiwertigem Uran ist an der rot-violetten Farbe zu erkennen (nach etwa 6 Stunden). Das Prozent des zur Dreiwertigkeit reduzierten Urans haben wir so bestimmt, dass wir zuerst den gesamten Urangehalt bichromatometrisch[13] (nach Oxydation des gesamten Urans zu U^{+4}) und danach das dreiwertige Uran ebenfalls bichromatometrisch[22] bestimmt haben. Dieserweise haben wir in sechs Versuchen bei der Reduktion von etwa 2.38 g U(VI) die Reduktion zu U(III) von bis 97.9–98.8% erreicht.

Bei der eigentlichen Bestimmung des dreiwertigen Urans mit Pb(IV)-Azetat sind wir so vorgegangen, dass wir zu 7 bis 13 ml einer 2% Fe(III)-Chlorid Lösung (die vorher mit Stickstoff durchströmt wurde) in inerter Atmosphäre aus der Reduktorbürette 5 bis 25 ml einer 0.03 N Lösung von dreiwertigem Uran (in 1 N HCl) zugaben. Danach stellten wir die Lösung mit Chlorwasserstoffsäure auf eine Konzentration von 2 N HCl in 50 ml Volumen der Lösung, und titrierten potentiometrisch mit 0.1 N Pb(IV)-Azetat. Der Verlauf der Titration war ähnlich, wie im Falle der Bestimmung von vierwertigem Uran.

1 ml 0.1 N Pb(IV)-Azetat entspricht 7.93566 mg Uran. Beispiele der Bestimmung sind in Tabelle II angeführt.

TABELLE II

BESTIMMUNG VON Uran(III) MIT 0.1 N $PbAc_4$ IN EINEM MEDIUM VON 2 N HCl

(11.63–58.15 mg U; 50 ml Volumen)

Gegeben (mg)	*Gefunden (mg)*	*Abweichung (%)*	*Potenzialänderung im Equivalenzpunkt für 0.01 ml Massreagens (mV)*	*Inflexionspotenzial (mV)*
11.63	11.64	+0.09	120	760
11.63	11.63	+0.00	100	750
34.89	34.92	+0.09[a]	140	750
34.89	34.90	+0.03	150	750
58.15	58.11	—0.07	120	755
58.15	58.22	+0.12	100	735

[a] Mittlere relative Abweichung berechnet von 10 Bestimmungen von 34.89 mg U(III) war 0.11%.

Mikrobestimmung von vierwertigem Uran

Der gute Verlauf der potentiometrischen Titration, grosse Potenzialänderungen im Equivalenzpunkt sowie die gute Reproduzierbarkeit der Resultate führten uns dazu, die Bestimmung von vierwertigem Uran im Mikromasstab zu versuchen.

Zuerst untersuchten wir die Titration kleiner Mengen von zweiwertigem Eisen mit einer 0.01 N Pb(IV)-Azetat Lösung, und den Einfluss von Uranylionen und überschüssigen Fe(III)-Ionen auf den Verlauf der Titration. Im Medium von 2 N HCl haben wir potentiometrisch 10 bis 100 μg Fe in einem Volumen von 30 ml mit Hilfe einer Mikrobürette titriert, ohne dass die angeführten Ionen sich störend ausgewirkt hätten. Zu Anfang der Titration haben wir grössere Mengen des Reagens zugegeben (das Potenzial stellt sich sofort ein), mit nähernder Equivalenz haben wir den Titrationsschritt stets bis zu 0.001 ml (im Falle der Titration von 100 μg Fe), bzw. zu 0.0004 ml (im Falle von 10 μg Fe) in der Nähe des Equivalenzpunktes herabgesetzt. Auf die Potenzialeinstellung haben wir höchstens 30 Sek gewartet.

0.001 ml 0.01 *N* Pb(IV)-Azetat entspricht 0.5585 μg Fe.

Bei der Titration muss aber die Reagensmenge abgezogen werden, die zur Oxydation von reduzierenden Stoffen verbraucht wird, die auch in der gereinigten Säure anwesend sind, und die zusammen mit dem zweiwertigen Eisen oxydiert werden. Die Menge an reduzierenden Stoffen haben wir durch einen Blindversuch ermittelt, bei dem wir die angeführten Stoffe mit Pb(IV)-Azetat zum Potenzialwert der Equivalenz bei der eigentlichen Titration titriert haben. Die Resultate der Mikrotitration von Eisen haben wir übersichtlich in Tabelle III zusammengefasst.

TABELLE III

MIKROTITRATION VON EISEN(II) MIT 0.01 *N* $PbAc_4$ IN EINEM MEDIUM VON 2 *N* HCl

(30 ml Volumen)

Gegeben (μg)	*Verbrauch ml 0.01 N PbAc₄*			*Gefunden (μg)*	*Abweichung (%)*	*Potenzialänderung im Equivalenzpunkt (mV)*
	bei der eigentlichen Titration	*bei dem Blindeversuch*	*Differenz die der Oxydation von Fe⁺² entspricht*			
98.90	0.1824	0.0040	0.1784	99.64	+0.75	60[b]
98.90[a]	0.1868	0.0090	0.1778	99.30	+0.40	50[b]
24.72[a]	0.0540	0.0085	0.0455	25.41	+2.79	20[c]
24.72	0.0493	0.0040	0.0453	25.30	+2.35	30[c]
9.89	0.0211	0.0042	0.0169	9.44	—4.55	30[c]
9.89[a]	0.0257	0.0083	0.0174	9.72	—1.72	18[c]
9.89[a]	0.0265	0.0083	0.0182	10.16	+2.73	20[c]
9.89	0.0227	0.0040	0.0187	10.44	+5.56	20[c]
9.89[a]	0.0255	0.0085	0.0170	9.49	—4.04	15[c]
9.89	0.0220	0.0042	0.0178	9.94	+0.51	25[c]

[a] 30 ml der titrierten Lösung enthalten 0.2 ml 2% $FeCl_3^{+3}$ und 1 ml 0.001 *M* UO_2Ac_2.
[b] Für 0.001 ml Massreagens
[c] Für 0.0004 ml Massreagens

Die guten Resultate der Eisen-Mikrobestimmung haben wir zur Mikrobestimmung von vierwertigem Uran angewandt. Wir sind so vorgegangen, dass wir zu 0.2 ml einer 2% Fe(III)-Chlorid Lösung etwa 5 ml 0.5–1.5 *N* HCl, und danach die zu bestimmende Lösung des vierwertigen Urans (1 bis 10 ml der 0.0002 *N* Lösung) zugegeben haben, und nach 30 Sek mit Chlorwasserstoffsäure so einstellten, dass das Endvolumen 30 ml war und die Lösung zugleich 2 *N* an Chlorwasserstoffsäure wurde. Die solcherart bereitete Lösung haben wir potentiometrisch mit einer Mikrobürette mit einer 0.01 *N* Pb(IV)-Azetat Lösung titriert, in derselben Weise wie bei der Eisen-Mikrobestimmung. Ebenso wie im Falle des Eisens haben wir einen Blindversuch durchgeführt, mit dem wir die Menge der Verunreinigungen in den verwendeten Reagenzien bestimmten, die zusammen mit dem zu bestimmendem Stoff oxydiert werden, und den ermittelten Reagensverbrauch haben wir von dem Reagensvolumen abgezogen, das bei der eigentlichen Titration verbraucht wurde.

0.001 ml 0.01 *N* Pb(IV)-Azetat entspricht 1.19035 μg U. Die Resultate der Uranmikrobestimmung sind in Tabelle IV angeführt.

TABELLE IV

MIKROTITRATION VON URAN(IV) MIT 0.01 *N* PbAc$_4$ IN EINEM MEDIUM VON 2 *N* HCl

(30 ml Volumen)

Gegeben (µg)	*Verbrauch ml 0.01 N PbAc$_4$*			*Gefunden (µg)*	*Abweichung (%)*	*Potenzialänderung im Equivalenzpunkt (mV)*
	bei der eigentlichen Titration	*bei dem Blindversuch*	*Differenz die der Oxydation von U^{+4} entspricht*			
205.73	0.1838	0.0092	0.1746	207.83	+1.02	60[a]
205.73	0.1837	0.0092	0.1745	207.72	+0.97	50[a]
102.86	0.0947	0.0091	0.0856	101.89	—0.94	15[b]
102.86	0.0967	0.0090	0.0877	104.39	+1.49	12[b]
51.43	0.0535	0.0091	0.0444	52.85	+2.76	13[b]
32.91	0.0368	0.0088	0.0280	33.33	+1.28	15[b]
20.57	0.0259	0.0086	0.0173	20.59	+0.10	22[b]
20.57	0.0269	0.0086	0.0183	21.78	+5.88	20[b]
20.57	0.0255	0.0084	0.0171	20.35	—1.07	15[b]
20.57	0.0264	0.0084	0.0180	21.43	+4.18	12[b]

[a] Für 0.001 ml Massreagens
[b] Für 0.0004 ml Massreagens

SCHLUSSFOLGERUNGEN

In der vorliegenden Arbeit haben die weiteren Anwendungsmöglichkeiten des Pb(IV)-Azetats als oxydimetrischen Reagens für die Bestimmung von anorganischen Systemen untersucht. Schon in unseren früheren Arbeiten haben wir darauf aufmerksam gemacht, dass dieses Reagens zur direkten potentiometrischen Titration in geeignet angesäuerten wässerigen Lösungen verwendet werden kann, in solchen Fällen wo die eigene Oxydations-Reduktions Reaktion schneller verläuft als die Hydrolyse des Pb(IV)-Salzes.

In der vorliegenden Arbeit ist es uns nicht gelungen mit Hilfe dieses Reagens Uran mittels direkter oxydimetrischer Titration zu bestimmen. Wir haben aber eine indirekte Bestimmung ausgearbeitet, bei der Uran mit einem Überschuss an Fe(III)-Chlorid oxydiert wird, und das entstandene zweiwertige Eisen mit Pb(IV)-Azetat titriert wird. Unsere früheren Voraussetzungen, dass dank der Grösse der Potenzialsprünge, Geschwindigkeit der Reaktion und guter Reproduzibilität der Resultate das Pb(IV)-Azetat auch zu Mikrotitrationen verwendet werden kann wurden bestätigt. Wie aus den Resultaten die in der Arbeit angeführt werden zu ersehen ist, haben wir in 30 ml Volumen durch direkte potentiometrische Titration noch 10 µg Fe und durch indirekte Titration noch 20 µg U bestimmt. Bei der Bestimmung von kleineren Mengen dieser Stoffe haben die Verunreinigungen die in den Reagentien anwesend waren einen störenden Einfluss auf die Bestimmung ausgeübt. (Der Verbrauch bei dem Blindversuch war höher als die Menge des Reagens die der Oxydation des zu bestimmenden Stoffes entsprach).

Wir haben gefunden, dass auch 0.01 *N* Pb(IV)-Azetat Lösungen in Eisessigsäure, die für die Mikrotitration geeignet sind, genügend beständig sind. Ihr Wert braucht nicht öfter als einmal wöchentlich kontrolliert werden, sofern natürlich (mit Hinsicht auf den Wärmedillatationskoeffizienten der Essigsäure) bei der gleichen Raumtemperatur gearbeitet wird.

Massanalytische Bestimmungen weiterer Systeme, und die Möglichkeiten weiterer Mikrotitrationen mit Pb(IV)-Azetat werden an unserem Arbeitsplatz weiter verfolgt.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Uranium(III) und (IV) mit Eisen(III)-lösung. Das bei der Reaktion gebildete Eisen(II) wird potentiometrisch mit Bleitetraacetat bestimmt.

SUMMARY

Uranium(III) or (IV) can be determined by reaction with iron(III) solution in hydrochloric acid medium, the iron(II) produced being titrated potentiometrically with lead tetraacetate solution. As little as 20 µg of uranium(IV) can be determined accurately in a volume of 30 ml.

RÉSUMÉ

L'uranium(III) et (IV) peut être dosé au moyen d'une solution chlorhydrique de fer(III). Le fer(II) formé est ensuite titré potentiométriquement au moyen du tétracétate de plomb.

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TITRIMETRIC METHODS FOR THE MICRO DETERMINATION OF SULPHUR AND HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

III. THE SIMULTANEOUS DETERMINATION OF SULPHUR AND THE HALOGENS

R. BELCHER AND J. E. FILDES*

Chemistry Department, The University, Birmingham (Great Britain)

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INTRODUCTION

In the previous paper of this series[1] titrimetric methods for the simultaneous micro-determination of the halogens (chlorine, bromine and iodine) in organic substances were described. Because sulphur and the halogens are often found together in organic compounds, studies were extended to the determination of sulphur simultaneously with the halogens. Titrimetric procedures have been suggested[2-5] for the concurrent determination of one halogen (chlorine, bromine or iodine) with sulphur, but no methods seem to have been described for the simultaneous determination of sulphur and more than one halogen. The present paper deals with suitable titrimetric methods for the determination of all such combinations of these elements.

For simultaneous micro-determinations of sulphur with all three halogens, the required accuracy would not be attained if 4 aliquots of a single absorption solution were used, hence it appeared preferable to burn two samples, one for the determination of sulphur and the other for the three halogens together.

As in the simultaneous determination of the halogens[1], it is important that satisfactory absorption conditions should be established for the gaseous products of combustion. In addition, difficulties arise in the choice of methods for the determination of sulphur in the presence of nitrogen. For convenience, the methods are considered under two general headings (*A*) non-nitrogenous and (*B*) nitrogenous organic compounds containing sulphur and halogens.

DISCUSSION

A. The simultaneous determination of sulphur and halogens in non-nitrogenous compounds

(1) Sulphur in the presence of one halogen

When compounds which contain sulphur with only one halogen are burned, a mixture of sulphuric and the corresponding hydrohalic acid is produced when the combustion products are absorbed in dilute hydrogen peroxide. If the total acidity

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* Present address: Department of Medical Chemistry, Australian National University, Canberra, A.C.T. (Australia).

of such a solution and the halide concentration are determined, the sulphur content can be obtained by difference. The mercuric oxycyanide method of VIEBÖCK[6] for halide makes it possible to determine both elements very simply[2] because both the procedures involve alkalimetric titrations; the titrations are done successively on the same solution and it is not necessary to divide into aliquots.

Previous studies[7] have shown that alkaline solutions of hydrogen peroxide are more efficient than neutral solutions for the absorption of halogen combustion products. When the efficiency of these two absorption solutions was compared with compounds containing sulphur and chlorine or bromine, the sulphur values were invariably 0.5 to 1.5% low with neutral peroxide solutions, although the halogen values were satisfactory. When alkaline peroxide solutions were used, satisfactory values were obtained for both elements. The gaseous combustion products from this type of sample formed heavy white mists which passed through the neutral peroxide solution without being completely absorbed. (HALLETT AND KUIPERS[8] have reported similar difficulties). The results shown in Table I show that satisfactory analytical values can be obtained for both sulphur and chlorine or bromine if alkaline peroxide solutions are used as absorbents.

Attempts to exploit a similar direct procedure for compounds containing sulphur and iodine were unsuccessful, owing to side-reactions interfering with the alkalimetric determination of iodine. The determination of sulphur, under these circumstances, was more satisfactory by the 4-amino-4′-chlorodiphenyl hydrochloride method[9,10]. As the use of this reagent is discussed more fully under *B*, a general method for the simultaneous determination of sulphur and iodine will be outlined there.

TABLE I

Compound	*Sample Wt. (mg)*	*% Halogen (Cl or Br)*		*% Sulphur*	
		Found	*Calculated*	*Found*	*Calculated*
2-Naphthalene-1-sulphonyl chloride	5.451	15.55	15.64	14.11	14.13
	5.402	15.69		13.95	
p-Toluene sulphonyl chloride	4.587	18.63	18.59	16.60	16.81
	4.163	18.48		16.71	
Bis-benzylthiotoluene	3.114				
+ hexachlorobenzene	1.710	74.65	74.70	18.92	19.06
2,5-Dibromobenzene sulphonic acid trihydrate	8.354	43.40	43.20	8.59	8.66
	7.844	43.26		8.61	
Benzyl disulphide	3.050				
+ *p*-bromobenzoic acid	3.814	39.64	39.75	25.91	26.03
Sulphonal	3.427				
+ *p*-bromobenzoic acid	5.872	39.88	39.75	28.20	28.09

(2) Simultaneous determination of sulphur, chlorine, and bromine

These three elements can be determined simultaneously by first titrating the total acidity and then evaluating the chlorine and bromine by the procedures outlined previously. Two aliquots of the neutralized absorption solution are required, one being used for the iodometric determination of bromide[7], and the other for the determination of total halide by the method of VIEBÖCK[6]; after the bromide acid equivalent has been deducted the chloride content can be ascertained by a modified VIEBÖCK procedure[11]. The sulphur value is calculated by difference from the initial total acidity. Alkaline peroxide solution again proved to be the most dependable absorbent.

TABLE II

Compound	*Sample Wt. (mg)*	*% Chlorine*		*% Bromine*		*% Sulphur*	
		Found	*Calculated*	*Found*	*Calculated*	*Found*	*Calculated*
p-Bromobenzene sulphonyl	6.580	14.01	13.87	31.32	31.27	12.32	12.54
chloride	8.059	13.99		31.36		12.39	
Dibenzyl sulphone	3.270						
+ *p*-bromochlorobenzene	3.224	18.40	18.52	41.52	41.74	13.04	13.02
p-Toluene sulphonyl chloride	3.346						
+ *p*-bromobenzoic acid	4.107	18.44	18.59	39.65	39.75	16.69	16.81

In Table II are shown some typical analytical values obtained by this method. The accuracy of ±0.15% achieved for all three elements must be considered very satisfactory in view of the dependence of the method on difference calculations.

B. The simultaneous determination of sulphur and the halogens in nitrogenous compounds

Direct titration of total acidity is of no value when nitrogen is present in the organic sample. In recent years several direct micro titrations for sulphate have been suggested[12-14] in which barium solutions are used in conjunction with adsorption indicators, such as thorin and sodium alizarin-3-sulphonate. However, these methods seemed less attractive for our purpose because the titrations must be carried out in a high concentration of organic solvent and in the absence of such interfering anions as nitrate and chloride. Although the titration with thorin as indicator yields excellent results after flask combustion, it is much less reliable after decomposition in the empty tube, for more nitrogen oxides are formed and may interfere seriously. We therefore preferred to use the organic reagent, 4-amino-4′-chloro-diphenyl hydrochloride in the method of simultaneous determination.

Previous work[9,10,15] had shown that this reagent is not only more sensitive than barium chloride towards sulphate ions, but is also less subject to interferences from nitrate and halide ions. Because the sulphate concentrations in the aliquots taken would be within the range of 0.5 to 1.5 mg, this reagent seemed to offer the best reasonably straightforward titrimetric method for sulphur.

The method is based on the precipitation from hydrochloric acid solution of 4-amino-4′-chlorodiphenyl sulphate, which, after filtration and washing, is dissolved in boiling water and titrated alkalimetrically.

Although the precipitate is virtually insoluble in the presence of excess of reagent, it is sparingly soluble in water and the washing procedure must be done with great care. It must be emphasized that the reliability of this sulphate determination depends on strict adherence to the recommended precipitation and titrimetric procedures. When the total volume of the absorption solution was kept within 50 ml, aliquots of 15 or 20 ml gave satisfactory sulphate recoveries over the 0.5–1.5 mg range.

We confirmed earlier work which showed that neither nitrogen nor any combination of halogens interfered in this method on the micro scale.

(1) *The determination of sulphur in the presence of the three halogens*

After it was found that the simultaneous quantitative absorption of the three halogens can be effected only in strongly alkaline bisulphite medium[1], no further attempts were made to develop a simultaneous method for the determination of sulphur and all three halogens.

For determinations of sulphur in the presence of these halogens, quantitative absorption could be obtained in an alkaline peroxide medium. However, it was essential that all excess of peroxide be destroyed before the precipitation with 4-amino-4′-chlorodiphenyl because some free halogen was released under the prevailing acid conditions and the organic precipitant was partially oxidised. When excess of peroxide was removed, satisfactory values were obtained (Table III).

TABLE III

DETERMINATION OF SULPHUR IN THE PRESENCE OF CHLORINE, BROMINE AND IODINE

Compound	*Sample Wt. (mg)*	*% Sulphur*	
		Found	*Calculated*
A. Non-nitrogenous			
p-Bromobenzene sulphonyl chloride	7.058	12.27	12.54
+ *o*-iodobenzoic acid	3.782		
Sulphonal	3.146	27.90	28.09
+ *p*-bromophenacyl bromide	2.327		
+ *p*-chloroiodobenzene	4.602		
B. Nitrogenous			
7-Iodo-8-hydroxyquinoline-5-sulphonic acid	8.261	9.03	9.13
+ *p*-chlorobromobenzene	5.381		
S-Benzyl thiouronium chloride	4.292	15.73	15.82
+ 2,4,6-Tribromoiodobenzene	5.972		

TABLE IV

Compound	*Sample Wt. (mg)*	*% Halogen (Cl, Br or I)*		*% Sulphur*	
		Found	*Calculated*	*Found*	*Calculated*
2-Chlorobenzidine sulphate	5.747	11.26	11.20	10.27	10.13
2,2′-Dichlorobenzidine sulphate	5.530	20.36	20.18	9.30	9.13
S-Benzyl thiouronium chloride	7.364	17.45	17.49	15.91	15.82
α-Diacetylamino-2,5-dichloro-4-nitrophenyl-β-thiolactic acid	7.838	18.18	17.94	7.97	8.11
3-Bromobenzidine sulphate	6.218	22.01	22.12	8.78	8.87
p-Bromobenzene sulphonaniside	7.238	23.43	23.35	9.32	9.37
2,2′-Dibromobenzidine sulphate	7.130	36.22	36.31	7.20	7.28
7-Iodo-8-hydroxyquinoline-5-sulphonic acid	9.842	36.04	36.14	9.08	9.13
Phenyl thiourea	3.643				
+ *o*-iodobenzoic acid	4.584	51.22	51.17	20.97	21.07
Benzyl disulphide	3.005				
+ *o*-iodobenzoic acid	4.772	51.20	51.17	25.98	26.03
Sulphonal	3.590				
+ *o*-iodobenzoic acid	4.419	50.96	51.17	28.00	28.09

(2) *Simultaneous determination of sulphur and chlorine or bromine*

To ensure the quantitative absorption of the total sulphur and halogen combustion products, an alkaline peroxide absorption medium was used.

The two procedures selected for the determination of sulphur and one halogen (chlorine or bromine) in nitrogenous compounds cannot be operated on the same solution hence it is essential to take two separate aliquots. Chlorine or bromine was determined satisfactorily on a neutralized aliquot by means of the appropriate mercuric oxycyanide titration procedure[6,7]. Sulphur was determined on the other aliquot by the 4-amino-4'-chlorodiphenyl method. Some typical results (Table IV) indicate that sulphur can be determined with an accuracy of ±0.10% and the chlorine and bromine with an accuracy of ±0.15% by this procedure.

(3) Simultaneous determination of sulphur and iodine

This method has been developed as a general procedure for the micro determination of sulphur and iodine in their non-nitrogenous as well as their nitrogenous compounds. Alkaline peroxide solutions effectively absorbed the combustion products of both elements, but to avoid losses of iodine, all traces of peroxide have to be removed before the evaluation of iodine by the LEIPERT method[16]. The use of two aliquots for the individual determinations of sulphur and iodine gave values such as those included in Table IV, which are of similar accuracy to those reported for the analogous chlorine and bromine combinations.

Simultaneous determination of sulphur and any two halogens

Alkaline peroxide solutions were quite satisfactory absorbents for the determination of sulphur and any two of the three halogens in organic compounds. Before the elements were evaluated all excess of peroxide had to be decomposed. Three aliquots were needed for these three elemental determinations, the sulphur in all cases being precipitated as 4-amino-4'-chlorodiphenyl sulphate.

(4) Simultaneous determination of sulphur, chlorine and bromine

For the determination of chlorine and bromine, two separate aliquots were analysed according to the procedures outlined under *A(2)* namely: bromine by the hypochlorite oxidation method and chlorine by the mercuric oxycyanide comparison titration procedure.

(5) Simultaneous determination of sulphur, chlorine and iodine

The LEIPERT method for iodine was again applied. The chlorine was then determined on a separate aliquot by the mercuric oxycyanide titration procedure after deducting the iodide acid equivalent.

(6) Simultaneous determination of sulphur, bromine and iodine

These two halogens were satisfactorily determined on separate aliquots by the iodometric procedures described previously[1], *i.e.* iodine by the LEIPERT method and total iodine and bromine by the hypochlorite oxidation procedure.

Because no suitable test compounds were available for determinations listed under *B(4–6)* mixtures of appropriate compounds had to be used. Despite the unfavourable reduction in the concentration of each element being analysed by the three aliquot procedures, we were able to obtain quite acceptable values for all three elements (Table V).

TABLE V

Compound	*Element*	*Elements*			
		Present (mg)	*Found (mg)*	*Theor. (%)*	*Found (%)*
Benzyl disulphide + *p*-chloroiodobenzene	S	0.262	0.261	26.03	25.93
	Cl	0.307	0.304	14.87	14.73
	Br	—	—	—	—
	I	1.100	1.106	53.22	53.32
S-Benzyl thiouronium chloride + *p*-bromobenzoic acid	S	0.148	0.147	15.82	15.70
	Cl	0.164	0.165	17.49	17.62
	Br	0.585	0.584	39.75	36.69
	I	—	—	—	—
7-Iodo-8-hydroxyquinoline-5-sulphonic acid + *p*-bromophenacyl bromide	S	0.234	0.232	9.13	9.02
	Cl	—	—	—	—
	Br	0.790	0.787	57.50	57.31
	I	0.928	0.927	36.14	36.13

EXPERIMENTAL

Procedure for A(1)

Burn off the weighed sample (3–7 mg) as previously described[3,7], using as absorbent an exactly measured volume of standard 0.01 *N* sodium hydroxide with a known amount of 30% hydrogen peroxide (0.5–1.0 ml), for which an alkali blank deduction may be required. After the combustion, the absorption solution and the aqueous washings of the absorber are transferred to a 100-ml conical flask and treated with a known excess of standard 0.01 *N* sulphuric acid and a few drops of aqueous saturated methyl red indicator solution. The mixture is boiled for 2–3 min, cooled and finally back-titrated with 0.01 *N* sodium hydroxide in the presence of 8–10 drops of screened methyl red–methylene blue indicator solution. The volume representing the total acidity is ascertained from the total consumption of alkali after deduction of the added acid and peroxide blank.

The halogen is then determined on this neutralized solution, the chlorine by the mercuric oxycyanide comparison titration[11] and the bromine by the VIEBÖCK method[6].

$$1 \text{ ml of } 0.01\ N\ \text{NaCl} \equiv 0.3546 \text{ mg Cl}^-$$

$$1 \text{ ml of } 0.01\ N\ \text{H}_2\text{SO}_4 \equiv 0.7992 \text{ mg Br}^-$$

Calculation for sulphur: mg of S = total acidity titre — ml of 0.01 *N* NaCl (or H_2SO_4) · 0.1603.

Procedure for A(2)

The combustion and absorption of the weighed sample are carried out as described under (*1*) and the total acidity is determined. The resulting neutral solution is diluted to 50 ml in a graduated flask and two 20-ml aliquots are taken for the two halogen evaluations. Sodium hydroxide (1 ml of 1 *N*) is added to the 20-ml aliquot in 250-ml stoppered, conical flask and the excess of peroxide is destroyed by boiling. The solution is cooled, neutralized with 1 *N* phosphoric acid in the presence of aqueous methyl red indicator and finally subjected to the hypochlorite oxidation procedure as described earlier[1,7].

Total halide and chlorine determination. These are determined as in Part II by the modified mercuric oxycyanide titration.

Sulphur determination. This is calculated from the total acidity value, after the acid equivalents of the chlorine and bromine have been deducted.

Reagents for B

(*a*) 0.24% solution of 4-amino-4′-chlorodiphenyl hydrochloride in 0.05 *N* HCl[9,10]. (*b*) Saturated aqueous solution of 4-amino-4′-chlorodiphenyl sulphate which is prepared by shaking some freshly precipitated amine sulphate with distilled water at room temperature. The solution is kept stored in a brown bottle and filtered just before use. (*c*) Mixed indicator solution of 0.04% aqueous phenol red (Na salt) and 0.04% aqueous bromothymol blue (Na salt) in ratio of 3 : 2 by volume.

Procedure for B(1)

The weighed sample (3–5 mg) is burned as before using 7–8 ml of 0.1 *N* sodium hydroxide and 1.0 ml of 30% hydrogen peroxide as absorption solution. Afterwards, the absorbent and the aqueous washings from the absorber are run into a 100-ml conical flask and boiled for several minutes to destroy all excess of peroxide. The volume should not exceed 30 ml. Hydrochloric acid (2 ml of 1 *N* for acidity adjustment) and a small amount of filter paper pulp are added to the cooled solution, followed by a two-fold excess of the 0.24% 4-amino-4′-chlorodiphenyl hydrochloride solution (40–50 ml). The contents of the flask are mixed well and allowed to stand for 20–30 min. The sulphate precipitate is then filtered off and evaluated titrimetrically[10].

$$1 \text{ ml } 0.01\ N \text{ NaOH} \equiv 0.1603 \text{ mg S}$$

Procedure for B(2)

Burn the sample (5–8 mg) as usual and absorb in 7–8 ml of 0.01 *N* sodium hydroxide and 0.5–1.0 ml of 30% hydrogen peroxide. The absorption solutions and the aqueous rinsings from the absorber are transferred to a graduated flask and made up to 50 ml. Two aliquots of 20 ml are taken for the two determinations.

Sulphur determination. The 20-ml aliquot is placed in a 100-ml conical flask and boiled for several minutes to destroy all traces of excess peroxide. 1.5 ml of 1 *N* hydrochloric acid and paper pulp are added as above, followed by 30–32 ml of the 4-amino-4′-chlorodiphenyl hydrochloride solution. The determination is then completed as previously described[10].

Chlorine or bromine determinations. The second aliquot is neutralized with 0.01 *N* sulphuric acid and the chloride or bromide content determined by the appropriate mercuric oxycyanide titration (see *A* (*1*) above).

Procedure for B(3)

Burn the sample (5–7 mg) and absorb in 7–8 ml of 0.1 *N* sodium hydroxide solution and 0.5 ml of 30% hydrogen peroxide, the excess of the latter being decomposed by boiling the contents of the absorber for several minutes after transference. The absorption solution is then made up to 50 ml and the sulphur and iodine determined separately on 20-ml aliquots.

Sulphur. The 20-ml aliquot is treated with 1.5 ml of 1 *N* hydrochloric acid in a 100-ml conical flask and the precipitation carried out as in *B (2)* above.

Iodine. The second 20-ml aliquot placed in a 250-ml stoppered, conical flask, is neutralized in the presence of aqueous methyl red indicator solution with 0.1 *N* sulphuric acid; then 5 ml of 24% potassium dihydrogen phosphate solution and 1.0–1.5 ml of saturated bromine water are added and the mixture is allowed to stand stoppered for 5 min. The removal of the excess bromine and the iodometric titration are carried out as previously described[7].

Procedure for B(4–6)

The weighed sample is burned as usual and the combustion products are absorbed as in *B(3)* above. After excess of peroxide has been removed the solution is cooled and neutralized with 0.1 *N* nitric acid, using aqueous methyl red as indicator. The solution is then made up to 50 ml and 15-ml aliquots taken for each of the three elemental determinations.

Sulphur. The 15-ml aliquot is diluted to 20 ml in a conical flask and the acidity is adjusted with 1 ml of 1 *N* hydrochloric acid. A small quantity of filter paper pulp and 25–27 ml of the 2.4% 4-amino-4′-chlorodiphenyl hydrochloride solution are added and the evaluation is completed as previously described.

Halogen determinations. The individual halogen determinations in each of the three possible two-halogen combinations are carried out on the 15-ml aliquots by the appropriate methods already outlined in Part II.

SUMMARY

The quantitative absorption of the gaseous products arising from the oxidative degradation of organic materials containing sulphur, halogens, (chlorine, bromine and iodine) oxygen and nitrogen, by the rapid empty tube combustion has been studied further. Satisfactory titrimetric methods for the simultaneous determination of sulphur and any one or two of the halogens in the presence or absence of nitrogen have been developed.

RÉSUMÉ

Les auteurs ont examiné l'absorption des produits gazeux formés lors de l'oxydation de substances organiques, renfermant soufre, chlore, brome, iode, oxygène et azote, dans la combustion rapide en tube vide. Des méthodes titrimétriques sont proposées pour le dosage du soufre et des halogènes.

ZUSAMMENFASSUNG

Es werden titrimetrische Methoden beschrieben zur Gleichzeitigen Bestimmung von Schwefel und Halogenen in organischen Substanzen nach der Verbrennung im leeren Rohr.

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PRECIPITATION FROM HOMOGENEOUS SOLUTION

PRECIPITATION OF MOLYBDENUM AS SULFIDE WITH THIOACETAMIDE

F. BURRIEL-MARTÍ AND A. MACEIRA VIDÁN

Department of Analytical Chemistry, Faculty of Sciences and High Council of Scientific Research, Madrid (Spain)

(Received June 5th, 1961)

The use of thioacetamide as a substitute for hydrogen sulfide for the precipitation of metal sulfides in homogeneous solution has increased in recent years. The general advantage of the method is widely recognized. FLASCHKA AND JAKOBLJEVICH[1] were the first to study precipitation of sulfides by thioacetamide from homogeneous solution; they considered the general application of the method in quantitative analysis, as well as the particular case of precipitation of molybdenum sulfide. Molybdenum was determined in both acid and ammoniacal solutions. In the former case, the solution was made 1 *N* in sulfuric or hydrochloric acid, the thioacetamide was added as a 2% aqueous solution, and the precipitation was done by heating for 1 h at 100° under pressure.

In later work, MCNERNEY AND WAGNER[2] determined molybdenum using thioacetamide in homogeneous solution with a concentration of 1 *N* sulfuric acid; pressure flasks were not considered necessary but a very large excess (5–10-fold) of thioacetamide was employed. A similarly large excess was used by LEHRMAN AND SCHNEIDER[3] with solutions which were 0.5 *N* in sulfuric acid, again without a pressure flask.

SWIFT AND ANSON[4] have referred to these investigations of the precipitation of molybdenum with thioacetamide; they state that the mechanism of the precipitation has not yet been elucidated. The present paper describes an investigation of the optimum conditions for the precipitation of molybdenum with thioacetamide. The variables which have been studied are the acid concentration, the excess of thioacetamide, the temperature and time of reaction, and the conditions needed to obviate the use of pressure flasks.

EXPERIMENTAL

Reagents

Standard molybdenum solution: (1 ml = 0.665 mg Mo). Dissolve 1 g of MoO_3 (reagent grade, Merck) in about 50 ml of 20% ammonium hydroxide, neutralize with perchloric acid to methyl orange indicator and dilute to 1 l.

Thioacetamide solution: Prepare a 1% solution of thioacetamide (Schuchard, München) in water, filtering off any insoluble material. The theoretical amount to precipitate 10 mg MoO_3 (*i.e.* 6.6 mg Mo) is 1.5 ml.

Perchloric acid: 60% (Mayer), $d = 1.54$.

Procedure

Several aliquots of the standard solution (10 to 100 ml) were transferred to Erlenmeyer flasks of capacity such that the solution could be shaken easily without losses. Acid, water and thioacetamide were then added in rapid succession and the flasks were closed as rapidly as possible. They were then placed in holders and held in a hot water bath. Sufficient water had to be added to the solutions to ensure that the relative concentration of MoO_3 did not exceed about 0.066 g % in volume. The stopper and the flask were protected by a cloth so that the flask and holder could be shaken without being removed from the bath.

The precipitate obtained (MoS_3) was dense and settled readily so that it could be filtered on a porous porcelain crucible (Berlin 2A2). The crucible was previously heated to constant weight at 650°. After filtration, the precipitate was washed with 1% perchloric acid solution and then 2–3 times with distilled water. It was then dried at 110° for 30–60 min and ignited very carefully in an oven, the temperature of which was raised slowly to 500° in order to avoid the spurting of the precipitate which can happen if it is not properly dried. Finally, the ignition was completed at 500–550° for 15 min and the residue was weighed as MoO_3.

RESULTS AND DISCUSSION

Determinations of molybdenum were carried out by precipitation from solutions which contained 1 *N*, 0.75 *N* and 0.5 *N* perchloric acid, with an excess of thioacetamide equivalent to the theoretical amount for precipitation. Precipitation was allowed to proceed for 60 min but the results were not quantitative. Under the same conditions but with a two-fold excess of thioacetamide, satisfactory recoveries were obtained in some cases. It was observed that the time and temperature of the reaction had an effect on the results. For example, with 1 *N* perchloric acid media, recoveries were quantitative in 90 min (see Table I) but not in 60 min. When the solution was 0.5 *N* in perchloric acid and a two-fold excess of thioacetamide was added, a time of 60 min sufficed but some molybdenum(VI) was reduced to the pentavalent state at boiling water temperatures, so that the solution became dark blue. It proved necessary to heat at about 60° in order to obtain quantitative recoveries. However, when the solution was 0.75 *N* in perchloric acid and contained a two-fold excess of thioacetamide a time of 60 min at the temperature of boiling water proved quite satisfactory (see Table II).

TABLE I

PRECIPITATION FROM 1 *N* PERCHLORIC ACID MEDIA FOR 90 MIN

Mo present *mg*	*Mo found* *mg*	*Difference* *mg*
6.6	6.6	0.0
13.3	13.1	—0.2
26.6	26.6	0.0
26.6	26.7	+0.1
26.6	26.4	—0.2
26.6	26.8	+0.2
39.9	39.9	0.0
39.9	39.9	0.0
66.5	66.4	—0.1

It was therefore concluded that a time of 60 min at the temperature of boiling water was adequate for the quantitative precipitation of molybdenum. The fact that the time required for a solution which is 0.75 *N* in perchloric acid is less than that needed for 1 *N* solutions is not surprising in view of the studies made by SWIFT and his collaborators[5,6] on the hydrolysis of thioacetamide in other acid solutions for precipitation of other metallic ions.

TABLE II

PRECIPITATION FROM 0.75 *N* PERCHLORIC ACID MEDIA FOR 60 MIN

Mo present *mg*	*Mo found* *mg*			*Difference* *mg*		
6.6	6.6	6.6	6.7	0	0	+0.1
13.3	13.3	13.3	13.1	0	0	—0.2
26.6	26.5	26.5	26.7	—0.1	—0.1	+0.1
39.9	39.9	39.8	39.7	0	—0.1	—0.2
66.5	66.6	66.4	66.4	+0.1	—0.1	—0.1

Limits of acidity and time required

Although the acidity of a solution which is 0.5 *N* in perchloric acid is not sufficient to allow determinations of molybdenum by hydrolysis of thioacetamide at boiling water temperature, this acidity was taken as a starting point for a series of experiments designed to fix the limit at which molybdenum(VI) is not reduced to molybdenum(V). The normality of the perchloric acid was raised in steps of 0.05 *N* until the solution did not become blue after being maintained at boiling water temperature for 60 min. The lower limit of acidity proved to be 0.65 *N* in perchloric acid.

TABLE III

PRECIPITATION AT DIFFERENT ACIDITIES FOR DIFFERENT TIMES

$HClO_4$ *N*	*Time* *min*	*Mo present* *mg*	*Mo found* *mg*	*Difference* *mg*
0.65	45	6.6	6.6	0.0
		13.3	13.3	0.0
		26.6	26.5	—0.1
		39.9	39.7	—0.2
		66.5	66.7	+0.2
0.70	50	6.6	6.5	—0.1
		13.3	13.2	—0.1
		26.6	26.5	—0.1
		39.9	39.8	—0.1
		66.5	66.7	+0.2
0.75	55	6.6	6.6	0.0
		13.3	13.3	0.0
		26.6	26.4	—0.2
		39.9	39.9	0.0
		66.5	66.7	+0.2
1.0	80	6.6	6.6	0.0
		13.3	13.1	—0.2
		26.6	26.7	+0.1
		39.9	39.9	0.0
		66.5	66.7	+0.2

When this limit was fixed, the minimum time required was then studied. The solution was made 0.65 N in perchloric acid, as a reference, since it was assumed that the minimum time would be less with this concentration, given that the time required for a 0.75 N solution was less than that needed for a 1 N solution. It was found that recoveries of molybdenum were quantitative with a heating time of 45 min; recoveries were low after heating for 40 min.

Table III shows the results obtained after heating for 45 min. Also shown are the results obtained when the acidity was increased in steps of 0.05 N and the time was increased in steps of 5 min. Precipitation was quantitative from 0.7 N perchloric acid solution after heating for 50 min and from 0.75 N perchloric acid solution after heating for 55 min; it should be noted that recoveries were not quantitative under these conditions when the heating times were reduced by 5 min.

If the time of heating were plotted against the perchloric acid normality in the above series of experiments, three points in a straight line would be obtained. It would also be observed that the points obtained from the preliminary experiments, *i.e.* 0.75 N and 1 N perchloric acid for 60 and 90 min respectively, lay far off the line. Experiments were therefore carried out with 1 N perchloric acid solutions with a heating time of 80 min as indicated by the plot. The results (Table III) were completely satisfactory, although low results were obtained on heating for 75 min. It has thus proved possible to establish a quantitative relationship between time and normality.

CONCLUSIONS

The minimum excess of thioacetamide for quantitative precipitation of molybdenum is only two-fold, at least over the range of molybdenum concentration between 6.6 mg and 66.5 mg.

The limit of acidity is about 0.65 N in perchloric acid; below this limit, precipitation is not quantitative at the temperature of boiling water, since molybdenum(VI) is reduced. Within the range 0.65–1 N in perchloric acid, a linear relationship exists between the acidity and the time of heating required for complete precipitation; hence given a certain acidity, the time can be chosen appropriately.

Finally, it should be noted that pressure flasks are not necessary; all the above work was done with ordinary glass-stoppered Erlenmeyer flasks.

SUMMARY

The determination of molybdenum with thioacetamide by precipitation of molybdenum sulfide from homogeneous solution has been studied. The optimum acidity is about 0.75 N in perchloric acid and a two-fold excess of reagent suffices. Pressure flasks and large excesses of reagent are unnecessary. Heating for 60 min at boiling water temperatures yields quantitative precipitation.

RÉSUMÉ

Les auteurs ont étudié le dosage du molybdène au moyen de thioacétamide, avec précipitation du sulfure de molybdène. Un chauffage de 60 min, au bain-marie bouillant permet d'obtenir une précipitation quantitative sans qu'il soit nécessaire de chauffer en vase clos et d'utiliser un grand excès de réactif.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Bestimmung von Molybdän mit Thioacetamid. Zur quantitativen Ausfällung des Sulfids genügt eine Erhitzungsdauer von einer Stunde auf dem Wasserbad und ein offenes Gefäss anstelle einer Druckflasche.

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METALLIC COPPER FOR THE STANDARDIZATION OF EDTA SOLUTION

TOSCHITAKE IWAMOTO AND KEN KANAMORI*

Department of Chemistry, Faculty of Science, The University of Tokyo,
Bunkyo-ku, Tokyo (Japan)

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Several substances have been tested as primary standards for chelatometric titrations with EDTA (disodium dihydrogen ethylenediaminetetraacetate) and some have proved of general use; for example, metals such as very pure zinc, copper, nickel or mercury, and metal salts such as zinc sulfate heptahydrate, calcium carbonate, lead chloride or dipyridinozinc thiocyanate, etc.[1–5].

BLAEDEL AND KNIGHT[1] proved that the reaction between copper or zinc ion and ethylenediaminetetraacetate ion is strictly stoichiometric by means of a high frequency titration. In practice, however, the end-point of a titration is usually determined visually by means of a metal indicator added to the titrated solution and the selection of a suitable indicator is of primary importance.

One of the visual methods of standardization now in common use is the titration of a standard zinc(II) solution prepared from pure zinc metal using XO** or EBT as indicator[4]. VŘEŠŤÁL *et al.*[5] examined twelve pure metals and metal compounds as primary standards and recommended lead chloride. However, only three indicators, murexide, pyrocatechol violet and XO were tested.

Despite its ready availability, ease of purification and preservation in a pure state, copper has not been used so generally owing to the lack of good indicators for it. Recently, some excellent indicators for the titration of copper have been proposed *e.g.* PAN[6], PAR[7,8], GCR[9], GTB[10], and we therefore re-examined the use of metallic copper with those indicators; we also compared the results with those obtained by the use of metallic zinc with EBT[3,11] or XO[12] as indicator.

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* Present address: Hirohata Works, Fuji Iron & Steel Co. Ltd., Himeji, Hyogo.
** See Table I for the abbreviation of indicators.

Among six indicators tested, PAN, PAR, MTB[13], GCR, GTB and XO–Phen[14], we found PAN the best because of the accuracy and precision of the results, the sharpness of color change at the end-point, the wide range of pH (2 to 10) which could be tolerated, and the applicability to many metal cations which form colored chelates with PAN. For metal cations that do not form colored chelates with PAN it is possible to use the combined indicator system Cu–PAN[15], which is an equivalent mixture of copper–EDTA and PAN.

EXPERIMENTAL

Reagents

Copper: 99.999% Oxygen-free copper was dissolved in the minimum amount of redistilled nitric acid and diluted with deionized water to give a 0.01 *F* solution.

Zinc: 99.998% Zinc foil was dissolved in a small amount of redistilled nitric acid and diluted with deionized water to give a 0.01 *F* solution.

Metal indicators: These were supplied by Dojin Pharmaceutical Laboratories, Kumamoto; the preparation of the solutions are indicated in Table I.

Other chemicals used were of reagent grade. Deionized water was used throughout.

Buffers of pH 4, 6 and 10 were prepared from acetic acid–ammonium acetate, acetic acid–sodium acetate and ammonia–ammonium chloride mixtures, respectively.

TABLE I

INDICATORS

Abbreviation	*Name (trivial: chemical)*	*Preparation*
PAN	1-(2′-pyridylazo)-2-naphthol	1% Cu–PAN in 50% isopropanol or 0.1% PAN in 95% ethanol
PAR	4-(2′-pyridylazo)-resorcinol	0.1% PAR in 95% ethanol
MTB	Methylthymolblue: 3,3′-bis-[N,N-di(carboxymethyl)-aminomethyl]-thymolphthalein, sodium salt	diluted 1 : 100 with K_2SO_4
GCR	Glycinecresolred: 3,3′-bis-(N-carboxymethyl-amino-methyl)-*o*-cresolsulfonphthalein	diluted 1 : 100 with KNO_3
GTB	Glycinethymolblue: 3,3′-bis-(N-carboxymethyl-aminomethyl)-thymolsulfonphthalein	diluted 1 : 100 with KNO_3
XO	Xylenol orange: 3,3′-bis-[N,N-di(carboxymethyl)-aminomethyl]-*o*-cresolsulfonphthalein, sodium salt	0.1% XO in 50% ethanol
Phen	*o*-Phenanthroline	0.5% in 5% methanol
EBT	Eriochrome black T: 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid, sodium salt	diluted 1 : 100 with K_2SO_4

Procedure

To an aliquot of the metal salt solution was added 2–4 ml of the buffer solution, deionized water to dilute the solution to 50–100 ml, and a suitable amount of the indicator. The mixture was titrated with an EDTA solution from a 10-ml buret graduated at 0.02-ml intervals. The exact conditions used are listed in Table II.

TABLE II

CONDITIONS OF TITRATION

Metal	*Indicator*	*pH*	*°C*	*Color change at end-point*
Zn	XO	6	40	red to yellow, excellent
Zn	EBT	10	40	wine-red to blue. excellent
Cu	PAN	4, 6, 10	80	reddish violet to yellow, excellent
Cu	PAR	4, 10	80	reddish violet to yellow, good
Cu	MTB	4, 6	40	blue to greenish yellow, rather obscure
Cu	GCR	4, 6	40	reddish violet to yellow, good
Cu	GTB	6	40	blue to greenish yellow, rather obscure
Cu	XO-Phen	6	40	reddish violet to yellow, rather obscure

TABLE IIIa

TITRATION OF COPPER

Indicator	*pH*	*Cu added μmoles*	*Cu found μmoles*	*Standard deviation*	*Relative error %*
PAN	4	50.1_1	49.9_6	0.06	−0.2
PAN	6	79.9_3	79.8_3	0.07	−0.1
PAN	6	50.1_1	50.0_9	0.08	0.0
PAN	10	47.5_6	47.3_7	0.03	−0.3
PAN	10	39.6_6	39.5_7	0.06	−0.2
PAR	4	50.1_1	50.3_3	0.01	+0.4
PAR	10	79.9_3	79.9_8	0.07	0.0
PAR	10	50.1_1	50.5_4	0.12	+0.8
PAR	10	39.9_6	39.8_2	0.06	+0.4
MTB	4	50.1_1	49.6_8	0.03	−0.8
MTB	6	79.9_3	79.6_0	0.09	−0.4
MTB	6	50.1_1	49.8_0	0.06	−0.6
GCR	4	79.9_3	79.4_3	0.17	−0.4
GCR	4	50.1_1	49.9_0	0.03	−0.4
GCR	6	79.9_3	79.4_3	0.06	−0.6
GTB	6	47.5_6	47.3_9	0.11	−0.9
XO-Phen	6	47.5_6	47.5_5[a]		0.0

[a] Corrected for added amount of Phen

RESULTS AND DISCUSSION

Accuracy of the titration of copper

With six different indicators the accuracy of the titration of copper was examined with the EDTA solution standardized against zinc metal as the primary substance. The results are listed in Tables IIIa and b.

PAN used at pH 6 gave the most accurate results. Two species of thymolblue dyes, MTB and GTB, gave rather obscure end-points because of the mixing of three colors, *viz.*, blue (Cu-indicator), yellow (free indicator) and greenish yellow (Cu–EDTA). The XO–Phen system was also inadequate and complicated. PŘIBIL[14] pointed out that XO forms a blocked chelate with copper and so does not have a reversible reaction, but that the addition of a trace amount of *o*-phenanthroline to the system makes reversibility possible. However, we found that the more *o*-phenanthroline was added, the clearer was the color change, up to the point where the increased green color of the copper–*o*-phenanthroline chelate made it difficult to observe the end-point; moreover, the apparent titer had to be corrected for the added amount of *o*-phenanthroline (see Table IIIb).

TABLE IIIb

TITRATION OF COPPER IN XO–PHEN SYSTEM

Cu added μmoles	*Cu found μmoles*	*Difference μmoles*	*Phen added*	$\frac{\text{Phen added}}{\text{Cu captured}}$	*Cu corrected μmoles*
47.5_6	47.3_5	0.2_1	1 drop		47.5_5 (extrapolated to 0 drop)
	47.1_2	0.4_4	2 drops		
	46.9_6	0.6_0	3 drops		
47.5_6	45.4_7	4.6_4	13.4 μmoles	2.8	
	41.4_8	8.6_3	26.8 μmoles	3.1	

Comparison of the standardizations against zinc(II) and copper(II)

The factors of an EDTA solution determined by three methods: (*1*) zinc with EBT at pH 10, (*2*) zinc with XO at pH 6, (*3*) copper with PAN at pH 6, agreed within the normal limits of error in titrimetric analysis; in each case ten aliquots were titrated (Table IV). The accuracy and precision of the titration of copper(II) were similar to those of zinc(II), so that the use of copper is as reliable as that of zinc. We recommend the following procedure because of the ease with which very pure metallic copper can be obtained commercially or by electrolytic deposition in the laboratory, and because of the wide applicability of the copper–PAN indicator system.

TABLE IV

COMPARISON OF FACTORS

Method	*Factor found*	*Probable error*	*Standard dev.*
Zn: EBT at pH 10	1.095_9	0.0005	0.002_2
Zn: XO at pH 6	1.095_8	0.0003	0.001_4
Cu: PAN at pH 6	1.096_3	0.0006	0.002_6

RECOMMENDED PROCEDURE

Prepare a 0.01–0.1 *F* solution by dissolution of cleaned and weighed metallic copper in a small amount of nitric acid and by suitable dilution with water. To a suitable aliquot, add buffer solution pH 6, dilute with distilled water to 50–100 ml, and add a few drops of PAN or Cu–PAN indicator. Heat the mixture to about 80° and titrate with the EDTA solution from a semi-micro buret. The color change at the end-point is reddish purple to yellow.

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SUMMARY

The standardization of EDTA solution against metallic copper as primary standard is studied. Six indicators were examined; titration with PAN as indicator at pH 6 is recommended.

RÉSUMÉ

Les auteurs ont examiné la possibilité d'utiliser le cuivre métallique comme étalon pour la détermination du titre de solutions d'EDTA. Parmi les indicateurs étudiés, le (pyridylazo-2')-1-naphtol-2 (PAN) semble le meilleur.

ZUSAMMENFASSUNG

Die Verwendung von metallischem Kupfer als Urtiter zur Standardisierung von ÄDTE-Lösungen wurde studiert. Von sechs verwendeten Indicatoren hat sich PAN bei pH 6 als der beste erwiesen.

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A NEW METHOD FOR THE STUDY OF INTERMETALLIC COMPOUND FORMATION IN MIXED AMALGAMS

HAROLD K. FICKER* AND LOUIS MEITES**

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, N. Y. (U.S.A.)

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INTRODUCTION

One of us[1] recently described a method for the determination of very small amounts of zinc by coulometry at controlled potential. It involved the deposition of metallic zinc from an ammoniacal citrate solution into a mercury cathode, then the measurement of the quantity of electricity consumed in the quantitative anodic stripping of the zinc. Though the polarographic half-wave potentials of metal ions in this medium[2] suggested that a similar procedure would be well suited to the determination of zinc in the presence of many other metals, this expectation was not borne out by experiment. On the contrary, each of a number of other co-deposited metals was found to prevent the quantitative stripping of zinc unless the concentrations of both zinc and the foreign metal were extremely low.

It appeared that this behavior was probably attributable to intermetallic compound formation between zinc and the foreign metal. The occurrence of such compound formation in mixed amalgams was studied by RUSSEL, CAZELET AND IRVIN[3], and has been confirmed by KEMULA *et al.*[4] and by KOZLOVSKII *et al.*[5-7].The present paper describes a new method for the study of the formulas and stabilities of such compounds and also describes some results that have been obtained with mixed amalgams of cobalt and zinc.

EXPERIMENTAL

Controlled-potential electrolyses were carried out with an Analytical Instruments, Inc. (Wolcott, Conn.) potentiostat. The double-diaphragm cell[8] and general technique[1] employed have been described previously.

Solutions containing known amounts of cobalt(II) and zinc, in a supporting electrolyte consisting of 1 F ammonium citrate and 2 F ammonia, were electrolyzed with a mercury cathode having a volume of 35.0 ± 0.1 ml at —1.45 V *vs.* S.C.E. Both metals are quantitatively deposited at this potential[1,9]. After a suitable period of electrolysis, which in some experiments was as long as 140 h, the working electrode potential was changed to —0.50 V *vs.* S.C.E., where zinc is quantitatively reoxidized when present alone, and measurements of current as a function of electrolysis time

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[*] Based on a thesis submitted by HAROLD K. FICKER to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the B. S. degree, June, 1960.

[**] To whom correspondence and requests for reprints should be addressed.

were made during the stripping by reading the register of an Analytical Instruments, Inc., current integrator. These readings were made at times so closely spaced that the error of reading the moving register was always comparable with the error involved in equating the current at the midpoint of an interval with the ratio of quantity of electricity consumed during that interval to the interval duration. In principle this is equivalent to periodic direct measurement of the electrolysis current, as was done by MacNevin and Baker[10]. In our hands, however, the present technique has given both smoother current-time curves and better values for the current integral. This is because it serves to average out the unavoidable momentary fluctuations in electrolysis current that are caused by fluctuations of stirring efficiency and electrode area.

When the stripping was complete, as indicated by the total cessation of motion of the integrator register for a prolonged period, the total quantity of electricity consumed was recorded in order to provide a check on the quantity calculated by the procedure described below. Special experiments showed that no additional detectable quantity of zinc could be stripped by prolonging the electrolysis for up to 24 h more, or by changing the working-electrode potential to a more positive value. For example, in one experiment the working-electrode potential was reset to —0.15 V *vs.* S.C.E. after the completion of the electrolysis at —0.50 V, and at the same time the electrolyte was replaced by a fresh portion of ammoniacal citrate which had been freed from zinc by the procedure previously described[1]. At this potential an anodic current flowed, due to the oxidation of mercury. After an hour the amalgam was withdrawn from the cell and replaced by fresh mercury, and the mercury previously oxidized was re-reduced at —0.50 V. Polarographic examination of the aqueous phase then indicated the absence of any detectable concentration of zinc(II).

These observations do not disagree with Kemula's report that different compounds are stripped at different potentials. The time required to complete a controlled-potential stripping at —0.50 V is so long that any equilibrium involving free zinc (or any other substance that can be stripped at that potential) is essentially completely displaced. This would not have been true in Kemula's experiments because of the far smaller time for equilibration permitted by his technique.

All measurements were made at 25 ± 1°. Mercury was purified by the procedure of Meites and Moros[11], and then contained too little zinc to be detected in this work. Reagent-grade chemicals were used throughout. On the scale of these experiments the concentration of zinc in the supporting electrolyte was too small to require purification or correction. Oxygen was scrupulously excluded from all solutions by a rapid stream of prepurified nitrogen which had been scrubbed twice with acidic chromous chloride to remove traces of oxygen and then with a portion of supporting electrolyte to minimize loss of ammonia from the solution being studied. The stirring speed was carefully controlled as described below.

ANALYSIS OF THE DATA

Fig. 1 is a plot of the logarithm of stripping current against time for a typical experiment, in which the original concentrations of cobalt and zinc in the amalgam phase were approximately 20 mM and 1.2 mM, respectively. Contrary to what is predicted by the simple theory[12] of the current–time curve for a controlled-potential electrolysis in which no detectable background current is involved, the curve is not linear. It can, however, be dissected into well-defined linear segments by the following procedure.

In every experiment the log i — t curve became linear after a sufficiently long period of electrolysis. In the experiment of Fig. 1, this linear portion began at about 2000 sec and continued for at least 4000 sec more. This linear portion defines a straight line whose equation is of the form

$$\log i_3 = \log i_3^{\circ} - k_3 t \qquad (1)$$

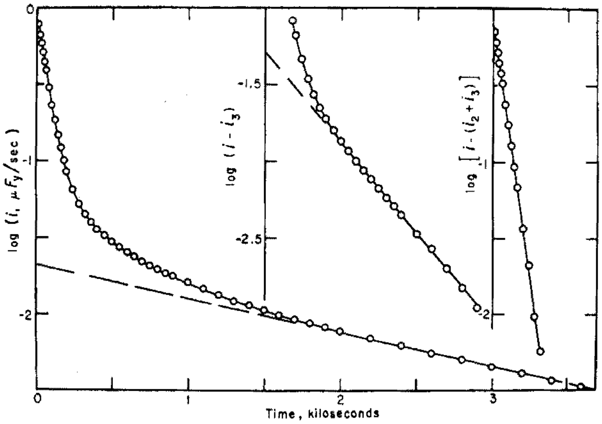

Fig. 1. Dissection of the current–time curve for the stripping of zinc at —0.50 V *vs.* S.C.E. from 35 ml of an amalgam containing 40.5 μgatoms of zinc and 664 μgatoms of cobalt into an aqueous phase containing 2 F ammonia and 1 F ammonium citrate. The curve extending across the width of the figure is a plot of the logarithm of the total observed electrolysis current, i; the dashed line (which continues to account for the experimental data out to total times of at least 6000 sec) is a plot of log i_3 against time according to the equation given in the text. The curve in the upper central portion of the figure is a plot of log $(i - i_3)$ against time for the same experiment; it also begins at $t = 0$, and each division on the horizontal axis corresponds to 0.5 ksec. The dashed line on this curve is a plot of log i_2 against time (see text). The curve at the upper right is a plot of log $[i - (i_2 + i_3)]$ against time, beginning at $t = 0$ and with each division on the horizontal axis corresponding to 0.5 ksec. The solid line here is a plot of log i_1 against time according to the equation given in the text.

For the data of Fig. 1, when currents are expressed in μF_y/sec (1 μF_y/sec = 0.0965 A) and times are expressed in sec,

$$\log i_3 = -1.68 - 2.22 \cdot 10^{-4} t$$

Subtracting the currents predicted by this equation for values of t smaller than 2000 sec from the currents actually observed and plotting the logarithm of the difference $(i_t - i_3)$ *versus* time yielded another curve. This had a linear portion extending from 400 to 1500 sec; at times between 1500 and 2000 sec the values of $(i_t - i_3)$ were so small that they scattered considerably around the extrapolation of this line, but no systematic deviation could be detected. In this way a second straight line was obtained which obeyed the equation

$$\log i_2 = \log i_2^{\circ} - k_2 t \qquad (2)$$

where log $i^\circ_2 = -1.29$ and $k_2 = 1.18 \cdot 10^{-3}$ for these data. Repeating the process once more, plotting log $[i_t-(i_2+i_3)]$ *versus* time, gave a straight line, which obeyed the equation

$$\log i_1 = \log i^\circ_1 - k_1 t \tag{3}$$

with log $i^\circ_1 = -0.083$ and $k_1 = 6.76 \cdot 10^{-3}$ obeyed within experimental error up to about $2/k_1$ (usually about 400) sec. Fig. 1 shows plots of i_3, i_2, and i_1 against time. An equation of this form was always obeyed.

The number of linear segments into which an experimental current–time curve was dissected by this process depended systematically on the amounts of cobalt and zinc present in the amalgam at the start of the stripping process. With 1.2 m*M* zinc and less than about 5 m*M* cobalt, only the initial linear portion was obtained. However, with about 5 m*M* zinc and 20 m*M* cobalt, four straight-line relationships were required to reproduce the data: the fourth one appeared at times longer than about 7000 sec.

The value of k_1, the slope of the line corresponding to electrolysis times between 0 and 400 sec, was always in good agreement with that obtained for the stripping of zinc from cobalt-free amalgams. Because the rate of this process under optimum stirring conditions[9] ($k = 1.7 \cdot 10^{-2}$ sec^{-1}) was so high that the data needed to define this portion of the curve adequately could only have been obtained with some difficulty, a slower and carefully controlled stirrer speed was used throughout this work. Experiments with zinc alone gave an average k of $(5.2 \pm 0.3) \cdot 10^{-3}$ sec^{-1}; the average value of k_1 obtained with mixed amalgams was $(4.7 \pm 1.2) \cdot 10^{-3}$ sec^{-1}. This agreement leaves no doubt that i_1 is the current corresponding to the oxidation of free zinc in the amalgam. The mean values of the other rate constants obtained were $k_2 = (1.03 \pm 0.25) \cdot 10^{-3}$, $k_3 = (2.4 \pm 0.7) \cdot 10^{-4}$, and $k_4 = (6.0 \pm 1.3) \cdot 10^{-5}$ sec^{-1}.

Integrating these equations by means of the relationship

$$Q_n = \int_0^\infty i_n \mathrm{d}t = \frac{i^\circ_n}{2.303\, k_n} \tag{4}$$

gave values of the quantities of electricity, Q_1, Q_2, Q_3, and Q_4 corresponding to these four processes. In the experiment described by Fig. 1, $Q_4 = 0$, and $Q_1+Q_2+Q_3 = 59.9$ μF$_y$, whereas the total quantity of electricity registered by the current integrator was 60.60 μF$_y$. The mean difference between these values was ± 4%; in view of the much greater complexity of the current–time curves involved here, this may be considered to compare satisfactorily with the accuracy obtained with a similar procedure by MacNevin and Baker[10].

However, the total quantity of electricity obtained was always smaller than that expected for the quantitative stripping of the zinc present: the symbol Q_5 is used below to denote the difference.

RESULTS AND DISCUSSION

Solutions containing 40 μgatoms (about 2.4 mg) of zinc and 660 μgatoms (about 39 mg) of cobalt were electrolyzed at −1.45 V *vs.* S.C.E. for varying lengths of time in order to determine the rate of approach to equilibrium in the amalgam phase. Under these conditions Q_4 was undetectably small; Fig. 2 shows the variations of Q_1,

Q_2, Q_3, and Q_5 with amalgam age. It may be mentioned that the deposition of cobalt and zinc was always essentially complete within 40 min. A reduction period of at least 1 h was always allowed in order to eliminate any anomalies that might otherwise have resulted from differences in reaction rates near the beginning of the deposition, when the concentrations of the metals in the amalgam were far from their final values.

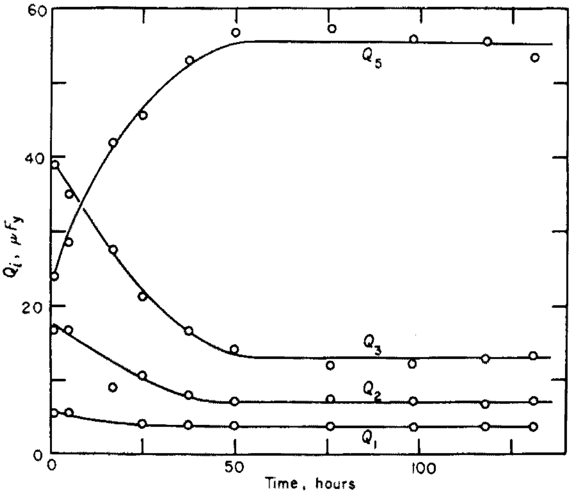

Fig. 2. Variations of Q_1, Q_2, Q_3 and Q_5 with amalgam age for amalgams containing 40.5 μgatoms of zinc and 664 μgatoms of cobalt in 35 ml of mercury.

Fig. 2 indicates that, although the value of Q_1 becomes constant within a very few hours, final equilibrium is not reached in this case until at least 60 h have elapsed. This is a surprising result, and one which is difficult to understand except on the basis of the assumption that one or more solids must be involved. It seems highly probable that the slow increase in Q_5, which is reflected in the decreases of Q_2 and Q_3, reflects the occurrence of a slow aggregation process. This would be in accord with the report by BABKIN AND KOZLOVSKII[7] of the formation of a colloidal substance in copper–zinc amalgams.

An important conclusion from the behavior shown in Fig. 2 is that KEMULA's technique[4], which involves a short deposition and immediate rapid stripping, cannot yield information concerning the equilibrium compositions of these amalgams or even about the formulas of the intermetallic compounds that they contain. All of the following data, on the contrary, were obtained after the reductions had been so greatly prolonged (never less than 40 h) that the quantities measured did not change further on longer standing.

Measurements were made of Q_1 and Q_2 for amalgams in which the cobalt concentration varied from 0.002 to 0.07 M while the zinc concentration varied from 0.0003 to 0.014 M. The cobalt:zinc ratio in these experiments varied from 0.5 to 30, and the ratio Q_1/Q_2 varied from 18 to 0.2. It was found that the results could be described by assuming the existence of an equilibrium of the form

$$a\,\mathrm{Co} + b\,\mathrm{Zn} + x\,\mathrm{Hg} \rightleftharpoons \mathrm{Co}_a\mathrm{Zn}_b\mathrm{Hg}_x$$

Assuming, since the amalgams are fairly dilute, that the activity of mercury is unity, and equating the activities of the other substances with their concentrations, this corresponds to an equilibrium constant of the form

$$K = \frac{[\mathrm{Co}_a\mathrm{Zn}_b\mathrm{Hg}_x]}{[\mathrm{Co}]^a[\mathrm{Zn}]^b}$$

The concentration of $\mathrm{Co}_a\mathrm{Zn}_b\mathrm{Hg}_x$ was taken as $Q_2/2bV$, where V is the volume of the amalgam phase in l; that of free zinc was similarly taken as $Q_1/2V$.

The concentration of free cobalt was taken as $N^{\circ}_{\mathrm{Co}}/V$, where N°_{Co} is the number of moles of cobalt originally deposited into the amalgam. This involves two assumptions: (*1*) only a small fraction of the total amount of cobalt present is bound by zinc, and (*2*) the solubility of cobalt in mercury is at least 0.07 *M*. The first of these is justified by the fact that the cobalt: zinc ratio was usually considerably greater than 1 in these experiments. When it was not, most of the zinc remained in the uncombined state; in one experiment with an amalgam containing 83 µmoles of cobalt and 161 µmoles of zinc, the value of Q_1 indicated that 147 µmoles of free zinc were still present at equilibrium. The second, which contradicts a long-standing belief that cobalt is nearly insoluble in mercury, is justified by two kinds of evidence. One is the appearance of the amalgams, which were always perfectly clean and bright, quite unlike amalgams of elements such as manganese, which clearly evince the presence of a solid phase with amounts of metal far smaller than were involved here. The other is the fact that the distribution of zinc among its various forms was markedly changed by varying the amount of cobalt while holding that of zinc constant. This could hardly be the case if the reactivity of cobalt were constant by virtue of a limited solubility.

The concentrations of cobalt, free zinc, and $\mathrm{Co}_a\mathrm{Zn}_b\mathrm{Hg}_x$ at equilibrium are given in Table I for a few of the amalgams studied. Writing the equilibrium constant expression in the form

TABLE I

VALUES OF Q_1 AND Q_2 AT EQUILIBRIUM FOR SOME COBALT–ZINC AMALGAMS

µgatoms Co Taken	*µgatoms Zn Taken*	*Reduction time h*	Q_1 μF_v	Q_2 μF_v
83	161.1	38	293.6	16.50
332	10.1	69	0.28	1.72
332	40.5	96	15.4	11.8
664	40.5	118	6.30	6.8
664	40.5	131	5.70	8.6
664	161.1	93	119.2	30.2
2496	496.1	51	124.0	85.4

$$\log K + \log 2^{b-1}\,V^{a-1} = \log Q_2 - (a \log N^{\circ}_{\mathrm{Co}} + b \log Q_1)$$

whose left-hand side is constant as long as V remains unchanged, as was the case in these experiments, it is possible to use the experimental results to obtain pairs of simultaneous equations from which values of *a* and *b* can be calculated.

When this was done it was found that the mean values of *a* and *b* were 0.63 ± 0.11

and 0.43 ± 0.04, respectively. Values more nearly equal to each other and to 0.50 were obtained by similar calculations in which it was assumed that each gatom of bound zinc corresponded to one gatom of bound cobalt, which can scarcely lead to a sensible error in the concentration of free cobalt. Thus assuming that

$$[\mathrm{Co}] = [N^{\circ}_{\mathrm{Co}} - (N^{\circ}_{\mathrm{Zn}} - Q_1/2)]/V$$

gave $a = 0.57 \pm 0.06$ and $b = 0.47 \pm 0.02$.

It seems impossible to escape the conclusion that $a = b = 0.5$. This indicates that the equilibrium involved is actually

$$2\ \mathrm{CoZnHg}_x = \mathrm{Co}_2 + \mathrm{Zn}_2 + x\ \mathrm{Hg}$$

The equilibrium constant of this reaction,

$$K = \frac{[\mathrm{Co}_2][\mathrm{Zn}_2]}{[\mathrm{CoZnHg}_x]^2}$$

is given by our data, after correcting for bound cobalt as just described, as 25 ± 8. This mean deviation is within the limits of error of these experiments as indicated by the data shown in Fig. 2.

There appears to be no precedent in the literature for this unexpected conclusion that both cobalt and zinc form diatomic molecules when dissolved in mercury. However, an exploration of this possibility would seem likely to furnish information that would be valuable in interpreting the properties of simple as well as of mixed amalgams. It may be pointed out that the majority of the amalgams studied were relatively concentrated.

These experiments appear to contradict the assertion by RUSSELL, CAZELET AND IRVIN[3] that intermetallic compounds are generally insoluble in mercury.

SUMMARY

A chronoamperometric method is described for the study of mixed amalgams. It is equivalent to measuring the dependence on time of the rate of anodic stripping at controlled potential of one of the metals involved. When applied to amalgams containing cobalt and zinc in various proportions, it reveals the presence of five distinct species containing zinc. One of these is identified as the "free" metal; another has the formula CoZnHg_x, and has a dissociation constant, $K = [\mathrm{Co}_2][\mathrm{Zn}_2]/[\mathrm{CoZnHg}_x]^2$, equal to 25 ± 8.

RÉSUMÉ

Une méthode chronoampérométrique est décrite pour l'étude d'amalgames renfermant deux ou phusieurs métaux dissolus. Avec des amalgames renferment du cobalt et du zinc en diverses proportions, elle montre la présence de 5 espèces distinctes renfermant du zinc. L'une d'elles est identifiée comme métal "libre", une autre a la formule CoZnHg_x, avec une constante de dissociation $K = [\mathrm{Co}_2][\mathrm{Zn}_2]/[\mathrm{CoZnHg}_x]^2$ égale à 25 ± 8.

ZUSAMMENFASSUNG

Beschreibung einer chronoamperometrischen Methode zur Untersuchung von gemischten Amalgamen. Sie beruht auf der Messung der Zeitabhängigkeit der anodischen Entfernung eines der Metalle bei controlliertem Potential. Bei Amalgamen mit wechselnden Mengen Kobalt und Zink konnten 5 verschiedene zinkhaltige Komponenten festgestellt werden. Eine dieser Komponenten wurde als "freies" Metall identifiziert, eine andere besitzt die Zusammensetzung CoZnHg_x mit einer Dissociationskonstanten $K = [\mathrm{Co}_2][\mathrm{Zn}_2]/[\mathrm{CoZnHg}_x]^2 = 25 \pm 8$.

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THE EFFECT OF SURFACE-ACTIVE AGENTS ON THE POLAROGRAMS OF PYRO- AND TRI-PHOSPHATE COMPLEXES*

P. R. SUBBARAMAN, P. S. SHETTY AND J. GUPTA

Inorganic Chemistry Division, National Chemical Laboratory, Poona (India)

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The need for caution in the use of surface-active agents for suppressing polarographic maxima has been recognized for some time. The so-called maximum suppressors alter the polarograms obtained at the dropping mercury electrode (DME) in several ways. Their effect is comparatively slight on the reversible waves of uncomplexed (hydrated) metal ions, though it is noticeable even in the reduction of thallium(I). From a potassium nitrate supporting electrolyte, the half-wave potential ($E_{1/2}$) of thallium(I) is shifted[1] from —0.472 V to —0.483 V by Triton X-100. Polarograms of complexed metal ions, especially those resulting from irreversible reduction of their anionic complexes, undergo a greater change. The effects vary, ranging from a simple change in the $E_{1/2}$, the limiting current or the slope of the wave, to a combination of all the three to such an extent as to obliterate the wave completely. A few examples of such drastic changes are the effects of (*1*) camphor and gelatin on the reduction of cystine[2], (*2*) camphor on that of chloroplatinate[3], (*3*) gelatin on that of copper(II)[4] in tartrate, (*4*) camphor on that of molybdenum(VI)[5] in tartrate, (*5*) gelatin on that of bismuth[6] in EDTA and (*6*) quinoline on that of copper(II)[7] in citrate. The precise reasons for these effects are not fully understood. Two different mechanisms are generally invoked. One attributes the effect to a change in the bulk of the solution caused by the

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surface-active agent interacting with the reducible species either physically (adsorption) or chemically (complex formation). For instance, the decrease in the limiting current[8] on the polarograms of lead, cadmium and cobalt(II) in presence of gelatin is supposed to be due to the complexing of these cations by the imidazole and carboxyl groups of gelatin. The mobility of the simple ions may also be retarded by possible physical adsorption on the gelatin macro-molecule. The other physical mechanism, which may be more important, assumes that electro-reduction is hindered by adsorption of the surface-active agent on the DME–electrolyte interface.

During investigation of the polarographic behaviour of uranium(VI) from an aqueous sodium triphosphate supporting electrolyte, it was noticed[9] that camphor and gelatin altered the polarogram somewhat similarly. Increasing amounts of camphor shifted the $E_{1/2}$ to more negative potentials besides rendering the wave very steep. On the other hand, the incorporation of 0.01% gelatin in the supporting electrolyte seriously distorted the polarogram, while 0.1% gelatin virtually obliterated the wave. Since the triphosphate as well as the pyrophosphate complexes of metals carry a multiple negative charge and generally give irreversible[10] cathodic steps, it was felt that the pronounced effect of gelatin and camphor may not be peculiar to the uranyl triphosphate complex but may be a common feature of many pyrophosphate/triphosphate complexes. An experimental verification of this idea formed the basis of this investigation.

EXPERIMENTAL

All the reagents used were polarographically pure. Sodium triphosphate hexahydrate was prepared by controlled heating of a mixture of disodium hydrogen phosphate and phosphoric acid in the molar ratio 5 : 1, followed by repeated crystallization from aqueous alcohol. Its purity was confirmed by the modified BELL method[11]. Sodium pyrophosphate decahydrate was prepared by heating disodium hydrogen phosphate and crystallizing from alcohol in a similar way.

The apparatus and experimental set-up were as described earlier[9].

Polarograms of silver(I) in pyro- as well as triphosphate were taken using a conventional cup cell containing a mercury pool as anode. The polarograms of Tl(I), Cu(II), Cd(II), Pb(II), Fe(III), Bi(III), Ti(IV), Nb(V), Mo(VI) and U(VI) were taken with an H-type cell carrying SCE as the reference electrode.

RESULTS AND DISCUSSION

Certain common features are observed in the polarograms of the metals examined in aqueous solutions of both sodium pyrophosphate and sodium triphosphate. The cathodic steps are generally irreversible, becoming increasingly so with increasing pH. They are free from apparent maxima. For a given metal, the waves from pyrophosphate and from triphosphate are also strikingly similar, differing slightly[10] in $E_{1/2}$ only, presumably because of a slight difference in the stabilities of the two complexes. The lead polarograms in Fig. 1 illustrate this similarity very clearly.

Niobium(V), which does not give a satisfactory step from many complex-forming media, shows a fairly distinct reduction step from both pyrophosphate and triphosphate. The wave from triphosphate is traced in Fig. 2. The diffusion plateau (Fig. 2A) is not well-defined, being too near the discharge potential of the supporting electrolyte. The step is, however, well separated in the derivative polarogram (Fig. 2B).

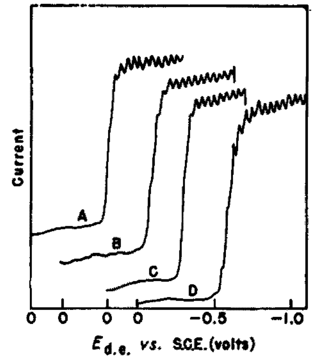

Fig. 1. Polarograms of 0.5 mM Pb^{+2} in A, 0.1 M $Na_4P_2O_7$, pH 5; B, 0.1 M $Na_4P_2O_7$, pH 7; C, 0.1 M $Na_5P_3O_{10}$, pH 5; D, 0.1 M $Na_5P_3O_{10}$, pH 7; ionic strength adjusted to 1.2 with $NaClO_4$ in all cases.

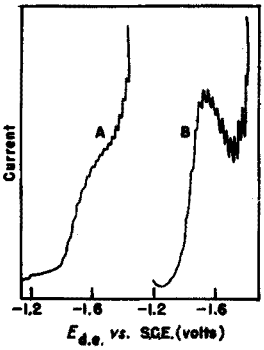

Fig. 2. Polarograms of 1.0 mM Nb^{+5} in 0.2 M $Na_5P_3O_{10}$, 0.2 M $NaClO_4$, pH 7. A, direct; B, derivative. ($E_{d.e.}$ vs. $di/dE_{d.e.}$).

When a little camphor or gelatin is added to the polyphosphate electrolyte, the polarogram usually changes remarkably. This is illustrated in Fig. 3 for bismuth. By the addition of 0.01% camphor, the wave is pushed to a more negative potential, the $E_{1/2}$ changing from —0.344 to —1.01 V, and also becomes very steep. With 0.1% camphor, the $E_{1/2}$ is still more negative (—1.3 V) and the current rise is also more abrupt. A similar effect is produced by camphor on polarograms of other metal polyphosphate complexes. The change in $E_{1/2}$ for a few cathodic steps is listed in Table I. Notwithstanding differences in the $E_{1/2}$ values of the original waves, it is

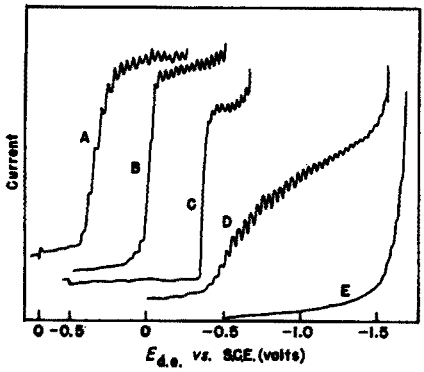

Fig. 3. Polarograms of 0.5 mM Bi^{+3} in 0.1 M $Na_5P_3O_{10}$, pH 5. A, no surface-active agent; B, 0.01% camphor; C, 0.1% camphor; D, 0.01% gelatin; E, 0.1% gelatin. Ionic strength adjusted to 1.2 with $NaClO_4$ in all cases.

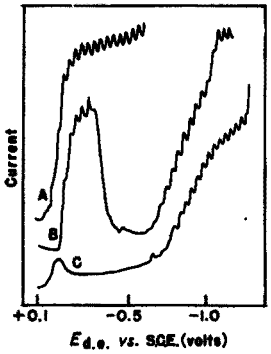

Fig. 4. Polarograms of 0.5 mM Fe^{+3} in 0.1 M $Na_4P_2O_7$, pH 2. A, no surface-active agent; B, 0.01% camphor; C, 0.1% camphor. Ionic strength adjusted to 1.2 with $NaClO_4$ in all cases.

interesting to note that 0.01% camphor shifts the $E_{1/2}$ of all the waves to around —1.0 V and 0.1% camphor to around —1.3 V. The only exception appears to be niobium(V), which will be discussed separately.

The effect of gelatin is also shown in Fig. 3, taking bismuth as the typical example. A distorted, slowly rising wave results with 0.01% gelatin, whereas with 0.1% gelatin the wave is practically obliterated. This applies to all the polarograms referred to in Table I, including niobium(V).

TABLE I

REDUCTION OF PYRO- AND TRIPOLY-PHOSPHATE COMPLEXES IN PRESENCE OF CAMPHOR AT THE DROPPING MERCURY ELECTRODE

Electrolyte composition: 0.5 mM depolariser under test, 0.1 M pyro-/tripolyphosphate of sodium, ionic strength adjusted to 1.2 with sodium perchlorate. T = 30° ± 1°

Depolariser	*pH*	*Buffer*	*$E_{\frac{1}{2}}$ vs. SCE in pyrophosphate (V)*		*$E_{\frac{1}{2}}$ vs. SCE in tripolyphosphate (V)*	
			No suppressor	*0.01% camphor*	*No suppressor*	*0.01% camphor*
Pb^{+2}	5	Phthalate	—0.485 reversible	—1.0	—0.524	—0.97
Bi^{+3}	5	Acetate	—0.277 irreversible	—0.98	—0.344	—1.01
Ti^{+4}	2		—0.372 irreversible	—1.0	—0.316	—1.02
Nb^{+5}	7		*ca.* —1.6 irreversible	*ca.* —1.6	*ca.* —1.6	*ca.* —1.6
U^{+6}	9				—1.06 irreversible	—1.19

In the case of Nb^{+5}, the tripolyphosphate concentration was 0.2 M, hence the ionic strength was higher. Figures for uranium are quoted from a previous paper[9].

It is possible to interpret the above results by assuming that the surface-active agent is adsorbed on the DME. For example, camphor is known to be adsorbed[2,3] in the potential range —0.1 to —1.3 V from aqueous solutions saturated (*ca.* 0.1%) with it. With more dilute solutions of camphor, the potential range of its adsorption may become less extended. The residual current curve from aqueous sodium triphosphate saturated with camphor also shows two inflexions at the appropriate potentials corresponding to the adsorption and desorption of camphor. The cathodic steps listed in Table I, with the exception of niobium(V), all occur in the potential range where camphor is adsorbed on the DME and all are therefore pushed to a potential where camphor is desorbed. The niobium(V) wave rising at —1.4 V is obviously in a potential range where camphor is not adsorbed, hence camphor has no effect on this polarogram. On the other hand, gelatin remains adsorbed[1,12,13] on the DME throughout the range from the dissolution potential of mercury to the discharge potential of the alkali metals. Consequently all the reductions listed in Table I including that of niobium(V) are suppressed by gelatin.

If this interpretation of the observed effects is correct, then waves which begin to rise at potentials less negative than the adsorption potential of camphor (*ca.* —0.1 to —0.2) will also be altered by this agent to an extent which can be qualitatively predicted. They will continue to rise till adsorption of camphor sets in, then fall, showing a minimum where adsorption of camphor is strongest. An example of the effect of camphor on such steps is shown in Fig. 4. The limiting current of the wave due to reduction of iron(III) from pyrophosphate at pH 2 is attained around —0.2 V (Fig. 4A). The wave also rises to almost its full height in presence of 0.01% camphor (Fig. 4B), but before a diffusion plateau is attained, the wave descends as the adsorption of camphor on the DME sets in. The polarogram shows a minimum at about —0.6 V where adsorption of camphor is strongest. After this, the current again begins to rise as the adsorption of camphor weakens. The effect of 0.1% camphor (Fig. 4C), though qualitatively similar, is more drastic because adsorption sets in earlier, desorption is effected at a more negative potential and the coverage of the DME by the surface-active agent is more effective.

The effect of camphor on the copper-triphosphate and bismuth-triphosphate reduction waves at pH 2 is very similar. It thus appears that the shape of the polarogram obtained in presence of camphor is dependent on the position of the cathodic step in the potential scale in the absence of the surface-active agent, that is, whether it occurs in the region where camphor is adsorbed or outside this region. This is confirmed for copper(II), lead, cadmium, bismuth, iron(III), titanium(IV), niobium(V), uranium(VI), and molybdenum(VI) from both pyrophosphate and triphosphate supporting electrolytes.

The effect of gelatin has also been studied on all the above metal-polyphosphate systems. Its action is less drastic on the reversible waves, *e.g.*, those for copper(II) and lead at low pH, but in sufficient concentration (0.1%), it practically obliterates all waves.

Only two instances have been noted in the present investigation where gelatin and camphor are both without effect. In 0.1 *M* sodium triphosphate (0.1 *M* $NaClO_4$, 0.5 m*M* $AgNO_3$) silver gives a well-defined, reversible wave with $E_{1/2} = —0.07$ V *vs.* mercury pool, and a similar one with $E_{1/2} = —0.04$ V from 0.1 *M* sodium pyrophosphate. From both pyrophosphate and triphosphate (0.1 *M* phosphate, borate buffer, pH 9), thallium(I) gives a well-defined reversible wave with an $E_{1/2}$ —0.518 V and —0.520 V respectively. These waves are not altered by the addition of camphor or gelatin to the base electrolytes. Perhaps the low stability of the complexes formed from the two univalent cations, and their reversible, one-electron reductions, may have caused this apparent immunity.

The difference in the effects of camphor and gelatin may also arise from a difference in the type of film formed on the DME; that formed by camphor may be compact whereas that formed by gelatin is probably porous[14] owing to the size and irregular shape of the gelatin molecule. Protracted waves such as those obtained in the presence of low concentrations of gelatin (0.01%) may well result from a porous film which renders the electrode surface only partly accessible.

Polarograms in orthophosphate supporting electrolytes do not seem to be affected by either gelatin or camphor. The cathodic step of ferric orthophosphate complex (0.5 m*M* Fe(III), 1 *M* Na_2HPO_4, 1 *M* H_3PO_4, $E_{1/2} + 0.1$ V), for instance, shows no appreciable change on the addition of either of these agents. Further study is in progress, and other peculiarities observed in the polarograms of metal polyphosphate complexes will be reported in subsequent communications.

SUMMARY

Camphor and gelatin affect the cathodic steps of metal complexes with pyrophosphate and triphosphate. Camphor displaces them to more negative potentials allowing them to rise in the neighbourhood of its desorption potential. Gelatin (0.1%) virtually obliterates all the steps, while lower concentrations distort them. However, cathodic polarograms relating to thallium(I) and silver(I) from a pyro/triphosphate base electrolyte are not significantly affected by camphor or gelatin.

RÉSUMÉ

Les auteurs ont effectué une étude de l'influence d'agents tensio-actifs (camphre et gélatine) sur les polarogrammes de complexes phosphoriques.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von Campher und Gelatine auf das Polarogramm von Pyro- und Triphosphat Komplexen.

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DETERMINATION OF MINUTE QUANTITIES OF WATER AND WATER VAPOR BY THE HYGROPHOTOGRAPHIC METHOD*

JOSEPH SIVADJIAN AND FRANCISCO CORRAL

Institut Pasteur, Paris (France)

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In an earlier paper[1], one of us (J.S.) described a hygrophotographic method for the determination of very small amounts of water, and indicated a simple and rapid process of calibration of the hygrophotographic plates, which could be applied even without an analytical balance. Thus were obtained values which were approximate but perfectly acceptable.

The calibration was done by saturating some circles of cellophane No. 600 with water vapor from pure water and by laying these disks on the hygrophotographic plate; the stain obtained on the plate from the small amount of water given off by the cellophane disk to the gelatine of the plate was then compared with the stains of a densitometric scale established by using pure water and five solutions of sodium bromide of concentration 1, 2.5, 3, 4.5 and 5 *M*.

The vapor pressure of these solutions at a temperature of 25° has been determined with great accuracy by PEARCE, TAYLOR AND BARTLETT (see ref. [1]). On the plate used, a circular, relatively large stain was obtained; its surface area, as well as the amount of water having caused the stain, could be estimated. At the same time 6 other circular stains, smaller and of gradually diminishing intensity, were obtained.

When the hygrophotographic plate was exposed to the action of the water vapor released by these 6 types of liquid of which the vapor pressure diminishes progressively from pure water to the 5-*M* sodium bromide solution, it was noticed that the absorption of the water vapor given off by the pure water was equal to that obtained by putting the plate on the cellophane disk saturated with water.

Since the amount of water given off by the disk to the gelatine as well as the surface area of the disk were approximately known, it was easy to calculate, from the vapor pressure of the other solutions, the amounts of water evaporated at the same time by these solutions. SIVADJIAN assumed that these amounts of water were entirely absorbed by the plate. This rapid simple method of determination permitted one to follow, for example under field conditions, the variation of the transpiration of plant leaves according to their different physiological states.

In order to apply the same hygrophotographic method to the measurement of small amounts of moisture diffusing through plastic materials, we sought a more precise method of calibration and investigated the direct weighing of a small piece of

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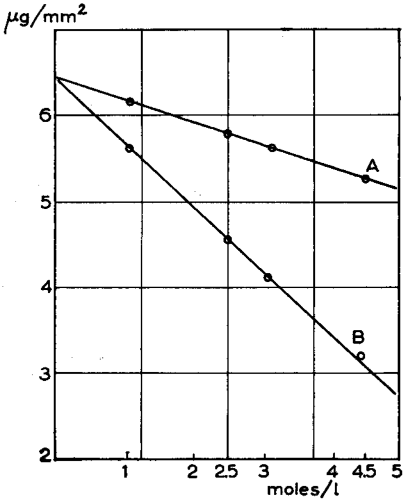
hygrophotographic plate before and after absorption by the plate of a definite amount of water vapor.

When we weighed the amount of water absorbed by a hygrophotographic plate which had been placed over pure water and over the five solutions of sodium bromide of increasing concentrations for a definite period of time, we found that the amounts of water absorbed by the plate from these different solutions coincided with the theoretical amounts calculated from the vapor pressures of the pure water and of the dilute bromide solutions. However, deviations were found for the more concentrated solutions; the deviations between the theoretical and experimentally found weights increased as the concentration of the solutions increased. Table I and the related Fig. 1 illustrate very well the results obtained in experiments carried out at 22°, the surface area of the absorbing disk on the gelatine being 346 mm².

TABLE I

Solution	*M*	*Water absorbed (µg)*	*Vapor pressure (mm Hg)*	*Water absorbed per mm²*	*Calculated*	*Difference*
Pure water		2230	23.493	6.44	6.44	0
NaBr	1	1970	22.723	5.69	6.23	0.54
NaBr	2.5	1510	21.435	4.35	5.88	1.53
NaBr	3	1390	20.950	4.01	5.75	1.74
NaBr	4.5	1100	19.289	3.18	5.29	2.11
NaBr	5	930	18.671	2.68	5.12	2.44
Pure water		1940	23.493	5.60	5.60	0
NaBr	1	1720	22.723	4.97	5.42	0.45
NaBr	2.5	1290	21.435	3.72	5.11	1.39
NaBr	3	1210	20.950	3.49	5.00	1.51
NaBr	4.5	760	19.289	2.19	4.60	2.41
NaBr	5	715	18.671	2.06	4.45	2.39



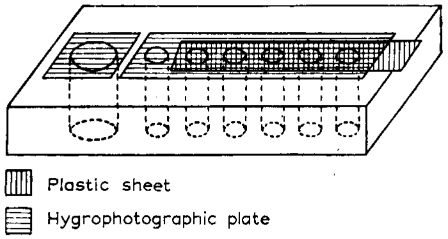


Fig. 2. Plexiglas block for calibrating.

Fig. 1. A: calculated curve of the amounts of water absorbed by the gelatine; B: Experimental curve.

These results can be explained as follows. If the evaporation of water in terms of its vapor pressure follows a linear law so that the amount of water given off by a solution of a certain concentration can be calculated from data obtained with another solution, then the absorption of this vapor by the gelatine in terms of the same vapor pressure likewise follows a linear law (Fick's law). However, the angular coefficient of the latter is different from that of the former. Hence the amounts of water vapor absorbed by the gelatine at the lowest pressure deviate considerably from those calculated with reference to the amount of water vapor absorbed at the highest pressure, *i.e.* from the most dilute solutions. The lower the pressure of the water, the less the gelatine of the plate absorbs.

We have therefore replaced the use of salt solutions in the elaboration of the densitometric scale by another technique in which only pure water is used. In this method the time of exposure of the plate to the action of the water vapor is varied progressively.

It has been shown that the quantity of water absorbed by the plate is a linear function of the time of exposure up to a certain limit, which depends on the temperature of the experiment, when the amount absorbed remains constant; that is, the state of saturation is obtained. The stains obtained were compared with a densitometric scale corresponding to 6 rates of staining. These were obtained by means of gradually reduced quantities of water.

EXPERIMENTAL

Apparatus

A circular cavity, 19.4 mm in diameter and 12 mm deep, is bored in a perspex (plexiglas) block 19 mm thick, 140 mm long and 50 mm wide (Fig. 2). 6 smaller cavities, 9 mm in diameter and 12 mm deep, are also provided at intervals. These cavities are filled with pure water to the same level, which should be (in our arrangement) 4 mm from the top of the perspex block.

Procedure for calibration of the hygrophotographic plate

A narrow strip, 23 mm wide, is cut lengthwise from a plate 9 × 12 cm in size, which has previously been blackened by exposure to daylight (or an intense source of light), then placed in a desiccator under vacuum over phosphorus pentoxide and stored in a dark room to remove all moisture from the gelatine. A square is then cut from one end of the strip; this is the piece to be calibrated. Another square of the same size is cut from an unserviceable hygrophotographic plate and the two squares are fitted together on the gelatine side. They are held together with a clip provided with a hook and suspended on a suitable microbalance. The combined plates are then weighed against a tare consisting of two identical pieces (unserviceable).

The piece of plate to be calibrated is then placed above the large perspex cavity, whose diameter, and therefore area, is known. The plate is held firmly in position by setting weights on it for 18 min; it must be protected from strong light and covered, if need be, with black paper. The time mentioned above may vary within broad limits depending on the room temperature. We found that at an average of 22–23°, the "exposure" required 12–18 min, this being the time during which moisture absorption by the plate retains its linear relationship to time.

A circular stain appears on the plate, which is promptly removed from the block;

the gelatine surface of the plate to be calibrated is immediately covered by the gelatine surface of the other piece and joined by means of the clip. Both are then weighed again. The difference between the two weighings represents the quantity of water absorbed by the hygrophotographic plate. The second plate prevents any weight loss of the plate to be calibrated, by evaporation of moisture, for this is absorbed by the other plate. Since the area of the stain and the quantity of water absorbed by it are known, the quantity of water fixed per unit area can readily be determined.

The remaining part of the narrow strip is then placed on the perspex portion which has 6 identical cavities filled with pure water to the above-mentioned level. 5 of these cavities are shielded with a very thin, suitably rigid, transparent and impermeable plastic sheet. The strip of hygrophotographic plate is pressed against the block with a suitable weight, so that the sensitized surface of the plate is in contact with the vapor given off from the sixth cavity. The pressure is maintained for 3 min exactly. Then, the pressure is reduced and, without moving the plate, the next cavity is uncovered by removing the plastic material. To do this correctly, a piece of paper is stuck underneath the transparent block, the paper being marked with equidistant lines to show the point up to which the plastic sheet can be removed in order to fully uncover a cavity without uncovering the next one.

After 3 min, the remaining cavities are uncovered successively every 3 min until, eventually 6 round spots are obtained which are of gradually decreasing intensity since they have been exposed to water vapor for periods of 18, 15, 12, 9, 6 and 3 min, respectively. The narrow strip is then removed and covered with the gelatine surface of another unserviceable strip of the same size, during a time equal to that needed for the weighing. It is then joined to the calibrated piece.

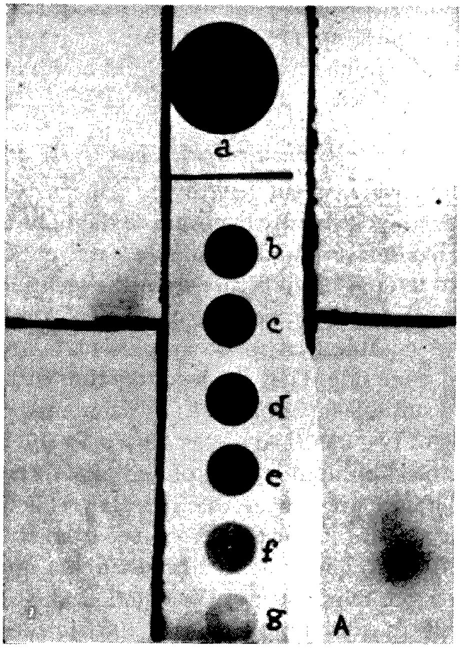


Fig. 3. Hygrophotographic recording of the water diffused through a polyethylene plastic sheet (A), with the densitometric scale (a–g) for comparison.

Under these conditions, and provided that the requirements mentioned are duly met, the maximum stain of this densitometric scale is identical with that of the calibrated piece, since the exposure times are identical (18 min). It is thus clear that the quantity of water absorbed by the plate which has been placed over the small cavity for 18 min is the same per unit area as the quantity of water fixed by the large circular reference area which is used for calibrating. It should be mentioned that identical stains can also be achieved at other portions of the densitometric scale.

As soon as the experiment is complete, the various fragments of the 9 × 12 cm plate, comprising the recorded densitometric scale, are joined together. They are then photographed on standard silver bromide paper or, better still, on a transparency for densitometric measurements. The prints are made using the contact process, the hygrophotographic plate serving as negative.

In the densitometric scale (Fig. 3), the reference value shown in Fig. 3a, obtained by means of a known quantity of water, is identical with that in Fig. 3b, which is the maximum stain of the scale.

Since the diameter of this reference area, which is pure yellow in the hygrophotographic plate and black in the positive, is 19.4 mm, its area is 295.5 mm^2. The quantity of water absorbed was 3690 μg, hence the amount fixed is 12.49 μg/mm^2. Since the absorption of water vapor by gelatine conforms to a linear law within the chosen limits of time and temperature (18 min at an average of 22–23° in this case), the quantities of water fixed per unit area in the other portions of the densitometric scale can be readily determined, these portions being exposed during 15, 12, 9, 6 and 3 min, respectively.

When 12.49 μg/mm^2 is divided by the longest exposure (18 min), the quantity of water absorbed per mm^2 of area/min, i.e. 0.69 μg/mm^2/min, is obtained.

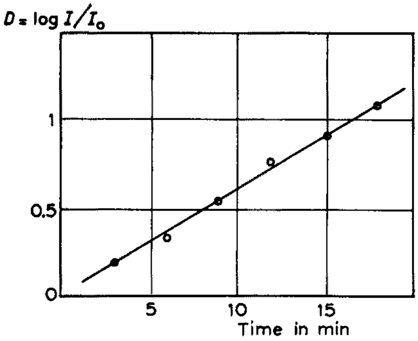


Fig. 4. Plot, every division of which shows the quantity of water absorbed per min per unit surface area.

In Fig. 4 the various times of exposure of the densitometric scale are shown as abscissae, and the densities of the stains, expressed as the logarithm of the ratio between the incident and transmitted light (I/I_0) are shown on the ordinate. The unit density is that which will let through one tenth of the incident light. Each division of the linear plot obtained shows the quantity of water absorbed each min per unit surface area, *i.e.*, in the present instance, 0.69 μg.

An example of the use of this scale is as follows: the stain caused by moisture percolating through a sheet of a plastic material over a period of 87 h and 15 min (87.25 h) in water (A in Fig. 3) was identical with that shown in Fig. 3g of the densitometric scale. This was obtained after a 3-min exposure, hence the stain corresponds to an absorption of $3 \cdot 0.69 = 2.07$ µg of water per mm². Since this quantity of water is absorbed by the hygrophotographic plate after 87.25 h at normal temperature, the permeability of the plastic material is $2.07/87.25 = 0.023$ µg of water per mm² per h.

SUMMARY

A more accurate calibration technique is described for the hygrophotographic method for determination of traces of water. The quantity of water absorbed by the hygrophotographic plate is a linear function of the time of exposure up to the state of saturation. Applications include measurement of the permeability of plastic materials.

RÉSUMÉ

Les auteurs ont mis au point une méthode de calibrage pour leur méthode hygrophotographique et démontré que l'absorption de l'eau par la plaque hygrophotographique a lieu suivant une loi linéaire, tant qu'on n'a pas atteint la saturation. Application à la mesure de la perméabilité des matières plastiques.

ZUSAMMENFASSUNG

Es wird ein genaueres Verfahren zur Standardisierung der hygrophotographischen Methode zur Bestimmung von Spuren von Wasser beschrieben. Zwischen der Menge absorbierten Wassers und der Dauer der Einwirkung bis zur Sättigung bestehen lineare Beziehungen.

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SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM IN STEEL WITH STILBAZO

C. U. WETLESEN

Central Institute for Industrial Research, Oslo (Norway)

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Stilbazo in weakly acid solutions gives with aluminium a red-brown color which has been made the basis of a colorimetric method[1,2]. The present work deals with the application of stilbazo for the determination of aluminium in steel.

EXPERIMENTAL

Apparatus and special reagents

Spectrophotometer. A Beckman spectrophotometer, model DU, with 1-cm cells was used.

Ion exchange column. The column was constructed of a glass tube with inner diameter 1.3 cm. It was equipped with a stopcock at the bottom. The resin was supported by a 1-cm glass-wool plug. The column was filled with a 15-cm layer of 100–200 mesh Dowex 1 X8 resin.

Reagent solution. Dissolve 0.200 g of stilbazo in 1 l of distilled water.

Sodium acetate solution. Dissolve 24 g of sodium acetate trihydrate in 1 l of distilled water.

Procedure

Separation and determination of aluminium

Dissolve 1 g of steel in 1:1 hydrochloric acid. Oxidise iron with nitric acid and evaporate to dryness. Add 3 ml of concentrated hydrochloric acid and again evaporate to dryness. Redissolve in 1:1 hydrochloric acid and filter. Wash the residue with distilled water. Reserving the filtrate, ignite the residue in a platinum crucible Fuse the oxides with 1 g of sodium carbonate and dissolve the melt in hydrochloric acid. Heat to boiling, make the solution just ammoniacal and filter. After washing with very dilute ammonia, dissolve the hydroxides on the filter in warm 1:1 hydrochloric acid. Combine the solution with the reserved filtrate and evaporate to dryness (do not bake). Dissolve the salts in concentrated hydrochloric acid; 2 ml of water may be added to aid the dissolution of salts. Make up to volume in a 25-ml volumetric flask with hydrochloric acid (sp.gr. 1.18). Transfer a 5-ml aliquot to the ion exchange column which has previously been washed with concentrated hydrochloric acid. After draining to the resin bed level, elute the aluminium with 25 ml of hydrochloric acid (sp.gr. 1.18). Evaporate the eluate to near dryness. Add 10 ml of distilled water and add from a pipette 10 ml of the reagent solution. Then add sodium acetate solution dropwise to pH 4.8 ± 0.05 (use a pH-meter). The pH may be adjusted with 10% acetic acid and 10% ammonia. Transfer the solution to a 50-ml volumetric flask and make up to volume with distilled water. Read the absorbance at 500 mμ against a reagent blank.

Determination of aluminium without separation

Dissolve the sample as described. To a suitable aliquot of the weakly acid solution add 1 ml of 5% ascorbic acid and 1 ml of 1% sodium thiosulfate solutions. Add 10 ml of reagent solution and add sodium acetate to give pH 4.8. Make up to volume in a 50-ml volumetric flask. Immediately read the absorbance at 500 mμ. Obtain the percentage content from a calibration graph plotted after applying the procedure to series of aluminium standards containing the same amount of iron as the sample aliquot.

Effect of variables

The absorption of the aluminium–stilbazo complex is dependent on pH and close control of the pH using a pH-meter is required[2]. The absorbance may be read at higher pH which makes the method more sensitive, but at such pH values, the method is more sensitive to interferences. Stilbazo absorbs at 500 mμ[2]. Consequently the reagent solution is added to blanks and samples using a pipette or burette.

The absorption of the complex is independent of the sodium acetate concentration.

In pure aluminium solutions the color is stable for at least 30 min. The molar extinction coefficient at pH 4.8 is 13.500. The presence of iron and ascorbic acid reduces the color intensity and affects the stability of the complex.

RESULTS AND DISCUSSION

A method for the determination of aluminium in steel without separation has been worked out by AGRINSKAYA[3]. In this method iron is masked with ascorbic acid. The present author, however, has found that iron and ascorbic acid reduce the color intensity and make the complex unstable. The calibration curve consequently must be constructed with the same amount of iron and ascorbic acid present as in the sample aliquot. The absorption must be read without delay.

Stilbazo is not a specific reagent for aluminium. Table I lists the degree of interference encountered when foreign ions are present. In the absence of interfering ions, however, the direct method may be used for rapid semi-quantitative determination of aluminium. The addition of sodium thiosulfate prevents the interference from copper.

For exact aluminium determinations and for determination of aluminium in steels containing interfering elements, the ion exchange separating procedure is performed. Aluminium is thus separated from iron and several interfering elements. Aluminium, scandium, yttrium, thorium, rare earths, arsenic, lead, manganese, chromium, nickel, alkaline earths, and the alkalies are not retained in the column[4]. Of these elements only scandium, yttrium, thorium, rare earths and large amounts of chromium will interfere with the spectrophotometric determination. Except for chromium these elements are not common in steels. Titanium is slowly eluted from the column with hydrochloric acid[4]. Experiments demonstrated, however, that at least 10 mg of titanium may be present without contaminating the eluate.

Representative results for aluminium determination in National Bureau of Standards samples are listed in Table II.

TABLE I

EFFECT OF FOREIGN IONS ON ALUMINIUM–STILBAZO COMPLEX

(50 μg aluminium present)

Foreign ion	*Amount of foreign ion (μg/50 ml)*	*Aluminium found (μg)*	
		A	*B*[a]
Mg	10,000	50	—
Ca	10,000	50	—
Sc	70	57	52
La	150	52	—
Ti	50	75	90
Zr	30	61	61
Th	75	55	57
V	50	65	75
Cr	500	48	48
Mo	85	60	62
W	75	58	—
Mn	2,500	50	50
Cu	150	53	—
Cu	6,500	—	50
Zn	6,500	50	—
Sn(IV)	50	75	—
Sn(II)	50	75	60
Pb	2,500	53	51
As(III)	3,700	50	—
Fe(II)	5,000	—	45
Fe(III)	50	67	—
Ni	6,000	50	—
Co	1,500	50	—
PO_4	500	46	—
F	25	36	—

[a] Ascorbic acid and thiosulfate present

TABLE II

DETERMINATION OF ALUMINIUM IN STEELS

Sample	*% Aluminium*	
	Certificated value	*Found*
National Bureau of Standard Sample No. 100 A	0.040	0.039
National Bureau of Standard Sample No. 106 A	1.08	1.10
National Bureau of Standard Sample No. 33 C	0.032	0.034
National Bureau of Standard Sample No. 22 C	0.116	0.115

SUMMARY

A procedure for the determination of aluminium in steel is described. Aluminium is separated from iron and interfering elements by ion exchange in concentrated hydrochloric acid solution, and finally determined spectrophotometrically with stilbazo.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique de l'aluminium dans l'acier. On procède d'abord à la séparation d'avec le fer et d'autres éléments gênants par échangeur d'ions, en solution HCl concentré.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Aluminium in Stahl. Die Abtrennung von Eisen und anderer störenden Elemente erfolgt durch Ionenaustausch in konzentrierter Salzsäure.

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Book Reviews

Treatise on Analytical Chemistry, Éditée par I. M. KOLTHOFF ET P. J. ELVING, avec l'aide de E. B. SANDELL, Part II, Vol. 3, *Chimie analytique des éléments*, Interscience Publishers, New York 1961, 380 pp., prix US $13.25 (subscription price: US $12.00).

Nous avons présenté le premier volume de cet ouvrage dans le fascicule d'août 1960 de ce journal. La volume 2 de la deuxième partie n'ayant pas encore paru, nous ferons donc la récension du volume 3 que nous venons de recevoir.

Dans un tableau périodique placé sur la couverture, chaque élément est accompagné d'un chiffre indiquant le numéro du volume dans lequel il est traité. Pour le volume 3, ce sont dans l'ordre et avec les auteurs respectifs: le cuivre (W. C. COOPER), le magnésium (G. B. WENGERT, P. F. REIGLER ET A. M. CARLSON), le zinc (J. H. KANZELMEYER), le cadmium (Q. FERNANDO ET H. FREISER), le mercure (J. F. COETZEE) et l'étain (M. FARNSWORTH ET J. PEKOLA).

Comme on le voit, chaque élément est présenté par un ou plusieurs spécialistes; c'est-à-dire que, d'une part, on ne retrouve pas une parfaite homogénéité, tant en ce qui concerne l'ordre que l'importance de chaque paragraphe, mais c'est-à-dire aussi que les méthodes proposées ont été choisies avec soin et compétence. Nous ne sommes pas en présence, comme c'est si souvent le cas, d'une simple compilation; chaque chapitre a en effet été l'objet d'un remarquable travail de synthèse, ce qui a permis aux auteurs d'éliminer une foule de choses inutiles, de documents sans valeur. Cet ouvrage, ainsi épuré, aéré, rendra les plus grands services aux chimistes de l'industrie, car on y trouve, décrites avec soin, les méthodes les plus sûres et un bibliographie fort bien faite. Quant aux chimistes de recherche, ils consulteront avec profit un ouvrage qui leur apporte une abondante documentation.

Prenons comme exemple, le zinc, dont l'exposé comme pour les autres éléments est d'une parfaite clarté, on y trouve des renseignements fort précieux tels que: le survoltage de l'hydrogène, la tension de vapeur, la chaleur latente, l'abondance isotopique, le produit de solubilité des composés inorganiques (14) et des composés organiques (49), un tableau très complet des potentiels ox/red et des $E_{\frac{1}{2}}$ polarographiques, les spectres d'émission, etc. En outre, on peut très rapidement se faire une idée des principales méthodes d'identification et de détection, des dosages chimiques et physicochimiques, micro et macro, sans oublier la détermination des traces. Quant à la présentation, elle est parfaite.

D. MONNIER (Genève)

Anal. Chim. Acta, 26 (1962) 194–195

Entwicklungsgeschichte der analytischen Chemie (Az analitikai kémia módszereinek kialakulása), von F. SZABADVÁRY, Verlag der Ung. Akademie der Wissenschaften, Budapest, 1961, 418 Seiten, 100 Abbildungen (ungarisch), 100 Forints.

Obwohl die analytische Chemie zweifelsohne der älteste Zweig der chemischen Wissenschaften ist, gab es bisher keine selbstständige, dabei aber umfassende Schilderung der Geschichte dieses Wissenszweiges. Die wohlbekannte Kopp'sche Geschichte der Chemie befasst sich zwar in einem selbstständigen Kapitel mit diesem Thema, kann aber mit seinen bis zur Hälfte des vorigen Jahrhunderts reichenden und zu kurz gefassten Daten ebenso wie andere kleinere Werke, die nur Teilprobleme der Geschichte der analytischen Chemie behandeln, bloss als Einleitung betrachtet werden. Das vorliegende Buch von SZABADVÁRY kann also mit Recht als ein lückenfüllendes, bis jetzt entbehrtes Werk begrüsst werden. Die, nach den einzelnen Gebieten der analytischen Chemie eingeteilte Entwicklungsgeschichte erlaubt eine besonders leichte Handhabung des Werkes und sichert auch dessen leichte Lesbarkeit. So werden die analytischen Kenntnisse des Altertums, des Mittelalters, die Anfänge der Analyse in wässrigen Lösungen, die Anwendung des Lötrohrs, die Anfänge der Gasanalyse noch zuzeiten der Phlogiston-Theorie, das Zeitalter von Berzelius und die Entwicklung der qualitativen Analyse, der Gravimetrie, der Titrimetrie, der Elektrogravimetrie sowie der optischen Verfahren eingehend behandelt. Nach einer Würdigung der Auswirkung der theoretischen Behandlung der analytischen Chemie werden auch die modernen Zweige derselben, wie die elektrometrischen Methoden (Potentiometrie, Konduktometrie, Polarographie, Amperometrie, Coulometrie, usw.), dann die Entwicklung der radiochemischen Analyse, der Gebrauch von Ionenaustauschern und die Entwicklung der chromatographischen Verfahren besprochen. Die biographischen Daten bedeutender Analytiker werden mitunter — wenn auch kurz — angegeben. Zitate aus den Originalarbeiten gewähren einen Einblick in die wissenschaftliche Tätigkeit hervorragender Analytiker.

Die reiche Biographie (über 2000 Literaturhinweise) erhebt wesentlich den Wert und somit die Brauchbarkeit des Buches, welches als kurzes Nachschlagewerk besonders von denen, die analytische Chemie dozieren, zu schätzen ist, obwohl die Behandlung der einzelnen Kapitel nicht ganz gleichmässig tief gehalten zu sein scheint. Eine deutsche und eine englische Ausgabe des Werkes ist vorgesehen.

E. SCHULEK (Budapest)

Anal. Chim. Acta, 26 (1962) 195

An Introduction to Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra, by JOHN D. ROBERTS, W. A. Benjamin, Inc., New York, 1961, vii + 116 pp., $ 4.95.

The pragmatic approach of organic and analytical chemists to their increasing dependence on instrumentation has been eminently successful. A person may use infrared spectra quite adequately with little or no knowledge of theory, and applications of optical rotary dispersion have far outstripped the development of theory. But complex nuclear magnetic resonance spectra demand some knowledge of the underlying theory of spin-spin splitting for their maximum utilization in organic chemical problems. The intent of this book is to present a simplified theory of spin-spin splitting so that the ideas become accessible to organic chemists, "who are in fact by far the most important users of the theory."

Although the book is for the student with serious intent, the first chapter presents a quick, informative summary of many aspects of n.m.r. in such a way as to be helpful even to the person who wants only to be conversant with this important development in the field of structure elucidation. The other three chapters, depending more on the language of mathematics, cover quantum mechanical treatment of spin-spin interaction between two nuclei, three-spin systems and a four-spin system. Some familiarity with n.m.r. is assumed, but little prior knowledge about the actual mathematics of quantum mechanics is required. The completeness of the treatment in the text is indicated by the absence of appendices. In the Preface, Professor Roberts deplores the fact that students all too frequently "make the transition between knowing and not knowing . . . hard for themselves by their failure to work problems or to work through even simple derivations." To overcome the temptation of students to avoid such things, the author has inserted exercises and problems right in the text at appropriate places, nearly an average of one per page. These exercises are intriguing and so cleverly placed that even the would-be casual reader is virtually trapped into attempting the solutions. Strong resolve is needed not to succumb to Professor Roberts' able leading from not knowing to knowing.

The book is attractively printed, well illustrated, and written in a pleasantly readable style. In addition to numerous other spectra used throughout the book, a set of 21 spectral problems illustrating the use of n.m.r. in organic qualitative analysis follow Chap. 1.

Professor Roberts closes his book with a quotation: "The Promised Land always lies on the other side of the wilderness." His contributions undoubtedly ensure that chemists interested in n.m.r. should emerge from the wilderness in shorter time than did the ancient Hebrews following Moses.

JAMES G. TRAYNHAM (Baton Rouge)

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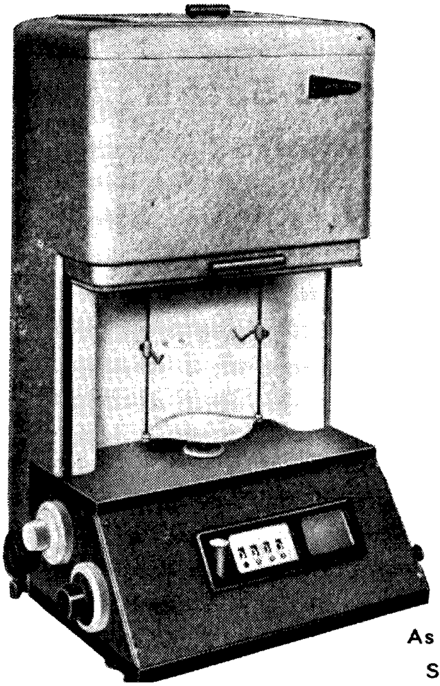

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