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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 28, No. 2, February 1963

DETERMINATION OF SULFATE AND SULFUR IN INORGANIC AND ORGANIC MATERIALS

Sulfate is determined by titration with lead nitrate solution in aqueous acetone solutions buffered with nitric acid–pyridine, in presence of dithizone indicator. Sulfate is titrated directly or after separation from interfering ions and other materials on a column containing aluminum oxide and cation-exchange resin. The titration and separation are also applied to determination of sulfur in organic compounds after oxygen flask combustion. Details of the methods are fully discussed.

W. J. Kirsten, K.-A. Hansson and S. K. Nilsson, *Anal. Chim. Acta*, 28 (1963) 101–117

A RAPID AND PRECISE HETEROMETRIC METHOD FOR THE DETERMINATION OF TRACES OF PHOSPHORIC OR ARSENIC ACID WITH NITRON AND MOLYBDATE

The precipitation of phosphomolybdate or arsenomolybdate with nitron was studied by heterometry at various acidities. A rapid and precise heterometric method is presented for the determination of 0.03–0.08 mg of phosphorus (or 0.06–0.16 mg of arsenic). Foreign salts can be tolerated often in 100–200-fold molar amounts. No interference is caused by Ca, Ba, Mg, Zn, Cr^{3+}, Fe, Mn, Co, Ni, Al, U(VI), Cd, Cu, Pb, Hg^{2+}, Ag, Zr or Th. Iodide, silicic acid, tartrate or pyrophosphate can also be tolerated.

The titration time is 10–15 min and the error is usually less than 1%.

M. Bobtelsky and I. Barzily, *Anal. Chim. Acta*, 28 (1963) 118–126

STUDIES ON COORDINATION POLYMERS

II. COORDINATION POLYMERS OF 1,6-DIHYDROXYPHENAZINE

Coordination polymers of 1,6-dihydroxyphenazine (I) with Cu(II), Zn(II), Ni(II), Co(II) and Hg(II) were prepared and studied. All the polymers formed were dark blue to black powders, very insoluble in the common solvents, apparently of low molecular weight, and decomposed at temperatures ranging from 200 to 280°. The zinc polymer was the most stable, mercury the least. Infrared studies confirmed the proposed chelation reaction between the metal ion and (I). The polymers of Co and Hg were amorphous, whereas those of Cu, Zn, and Ni were crystalline. When used as a spot test reagent, (I) gave instant color reactions with 15 common ions but neither the sensitivity nor selectivity of the reagent is impressive.

E. W. Berg and A. Alam, *Anal. Chim. Acta*, 28 (1963) 126–131

SYSTEMATIC STUDY OF THE SOLVENT EXTRACTION OF METAL OXINATES

The extraction of 32 metals (Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, V, Nb, Cr, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Al, Ga, In, Tl, Pb and Bi) with oxine solution has been studied. The effects of pH, oxine concentration and water-soluble complexing agents (oxalic acid, tartaric acid, hydrocyanic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid and 1,2-diaminocyclohexanetetraacetic acid) have been investigated. From these results the extraction constants and stability constants of the metal complexes with the various complexing agents investigated have been calculated.

J. Starý, *Anal. Chim. Acta*, 28 (1963) 132–149

COLORIMETRIC DETERMINATION OF LIGANDS BY THE EFFECT OF THEIR COBALT(II) COMPLEXES ON REDOX INDICATORS

Coordination of cobalt(II) with ligands facilitates oxidation to the trivalent state by an oxidizing agent such as 3-*p*-iodophenyl-2-*p*-nitrophenyl tetrazolium chloride (INT). Since the formazan produced by the reduction of the tetrazolium chloride is highly colored, a sensitive measure of the amount of ligand (ethylenediamine or cyanide) present is obtained.

J. S. Hanker, M. D. Sulkin, M. Gilman and A. M. Seligman,
Anal. Chim. Acta, 28 (1963) 150–155

SPECTROPHOTOFLUORIMETRIC DETERMINATION OF FORMALDEHYDE AND ACROLEIN

COMPARISON WITH OTHER METHODS

Highly sensitive spectrophotofluorimetric methods for the determination and estimation of formaldehyde and acrolein have been described. Formaldehyde and acrolein can be estimated in amounts as low as 0.0005 μg formaldehyde and 0.01 μg acrolein. Quinaldinium salts have been shown to have high sensitivity for the spectrophotometric determination of formaldehyde. The procedure in which these salts are used has a high potentiality for further improvement. Twelve different methods for the determination of formaldehyde have been compared.

E. Sawicki, T. W. Stanley and J. Pfaff, *Anal. Chim. Acta*, 28 (1963) 156–163

THE USE OF THE MASS SPECTROMETER FOR THE QUANTITATIVE ANALYSES OF MIXTURES OF AMINO ACIDS

The quantitative analysis of a low vapor pressure unstable solid mixture of amino acids is possible by putting the solid mixture in a crucible which is then placed directly into the ionization chamber of a mass spectrometer. Relative sensitivities for the various acids in a mixture can be established by the proper use of a particular amino acid as an internal calibrating standard. The success of the method depends upon: (1) the reproducibility of the mass spectra of the pure components, (2) the ideal vapor pressure behavior of the solid mixture, (3) the preparation of an intimate solid mixture by rapid freezing of the water solution of the acids with subsequent vacuum sublimation of the ice and ball-milling the dried mixture.

G. JUNK AND H. SVEC, *Anal. Chim. Acta*, 28 (1963) 164–169

FURTHER OBSERVATIONS IN ATOMIC ABSORPTION SPECTROSCOPY

Three observations have been made pertinent to atomic absorption spectroscopy. With a flame atomizer, it is shown that (*1*) the absorption profile is controlled by metal oxide formation, (*2*) organometallic compounds give rise to greater absorption than metal salts, and (*3*) absorption by hydroxyl bands affects the apparent metal absorption in certain spectral regions.

J. W. ROBINSON AND L. J. KEVAN, *Anal. Chim. Acta*, 28 (1963) 170–175

THE DETERMINATION OF PERIODATE BY INFRARED SPECTROSCOPY

An infrared method has been developed to determine periodate on the microgram scale. Periodate is precipitated in slightly acid solution with tetraphenylarsonium chloride and in presence of perchlorate as carrier. The precipitate is mixed with powdered potassium bromide and pressed into a disc. The base-line absorbance of the periodate band at 11.68 μ is calculated in order to find the concentration of periodate from a calibration curve. No interference is caused by perchlorate, permanganate, perrhenate, chlorate, iodate or bromate.

M. AL-KAYSSI AND R.J. MAGEE, *Anal. Chim. Acta*, 28 (1963) 176–178

THE ANALYTICAL APPLICATIONS OF DISTILLATION OF CARBON DIOXIDE

PART III. DECARBOXYLATION REACTIONS IN AQUEOUS SOLUTION

(in German)

Carboxylic acids which decompose spontaneously on boiling or by oxidation in aqueous solutions can be determined by titration of the carbon dioxide formed after distillation as described previously. Acetonedicarboxylic acid and *p*-aminosalicylic acid are determined by spontaneous decarboxylation. Hydrolysis must precede the determination for acetoacetic ester, phenylethylcyanoacetic acid ethyl ester and for carbonic acid esters. Oxidative decarboxylation allows determinations of glyoxylic acid, aldonic acids, sugar dicarboxylic acids, formic acid, oxalic acid and α-amino acids. The titration of the carbon dioxide formed can be done with 0.1 or 0.01 N solutions. The interference of atmospheric carbon dioxide is avoided by the use of pentane as a sealing liquid.

L. MAROS, I. MOLNÁR-PERL, M. VAJDA AND E. SCHULEK,
Anal. Chim. Acta, 28 (1963) 179–187

THE NATURE OF EUROPIUM ION IN CARBONATE SOLUTION AND POLAROGRAPHIC DETERMINATION OF MICRO AMOUNTS OF EUROPIUM

The nature of the complex europium carbonate ion in concentrated carbonate solution was studied polarographically. A polarographic method for the determination of micro amounts of europium ion in the presence of diverse ions (and especially lanthanides) was developed.

S. MISUMI AND Y. MASUDA, *Anal. Chim. Acta*, 28 (1963) 188–196

A NEW METHOD FOR THE DETERMINATION OF OXYGEN IN EFFLUENTS FROM THE PHARMACEUTICAL INDUSTRY

(Short Communication, in German)

A. BERKA AND P. HOFMANN, *Anal. Chim. Acta*, 28 (1963) 196–199

THE EFFECT OF FOREIGN IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF BORON WITH METHYLENE BLUE

(Short Communication)

O. B. SKAAR, *Anal. Chim. Acta*, 28 (1963) 200–204.

DETERMINATION OF SULFATE AND SULFUR IN INORGANIC AND ORGANIC MATERIALS

WOLFGANG J. KIRSTEN, KARL-ARNE HANSSON AND S. KJERSTIN NILSSON

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(Received July 25th, 1962)

A generally applicable and not too slow method for the determination of sulfate and sulfur in a wide variety of organic, inorganic and mixed substances was badly needed in these laboratories. Investigation of available methods showed that there is no rapid and convenient method for the direct determination of sulfate in a solution containing a variety of other ions. Further studies led to the development of the methods described below; details of the earlier procedures on which these methods are based are mentioned in the discussion.

THE DETERMINATION OF SULFATE

Sulfate is separated from other substances by a combination of adsorption and ion exchange, and titrated with lead nitrate in a buffered 80% acetone solution using dithizone as indicator.

Apparatus

Chromatographic columns. The columns are shown in Fig. 1.

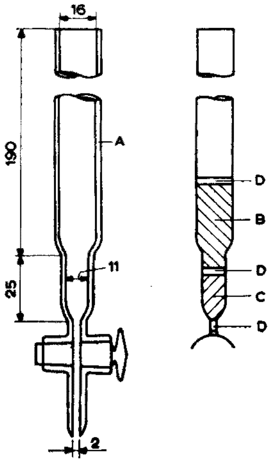

Fig. 1. Column for separation of sulfate. A = Column of borosilicate glass; B = Aluminum oxide, 6 ml; C = Cation-exchange resin, 1.00 g containing 43.7% of water; D = Tightly packed fine-fiber borosilicate (Pyrex) glass wool.

Reagents

Aluminum oxide was prepared by a slight modification of NYDAHL's procedure[1]. Brockmann's aluminum oxide (E. Merck, Darmstadt) is mixed for 1 h at room temperature with 1 *M* hydrochloric acid and washed with water, and the larger particles are allowed to settle. The fines are decanted off until the residue settles in less than 20 sec for a fall height of 10 cm.

Cation-exchange resin. Dowex 50-X8 or 50-W-X8, 50–100 mesh.

All reagents are prepared from analytical reagent grade chemicals.

Nitric acid solutions are prepared from analytical reagent grade acid. If blanks are obtained with the columns, the nitric acid can be purified as follows. A column or a separating funnel with an inner diameter of 50–60 mm is charged with a layer of 200 ml of aluminum oxide, as described above, on a layer of glass wool. The nitric acid is diluted to 3.5 *N* and passed through the column. The first 100 ml are discarded. The acid passes through at a rate of about 1.5 l/h. Weaker solutions are prepared by dilution of this acid. The aluminum oxide is regenerated by washing with sodium hydroxide like the columns described below. This treated acid is used only for the work with the columns.

Lead nitrate (0.02 N standard solution). 3.312 g of lead nitrate (Riedel de Haën) is weighed out accurately, dissolved in water and diluted to 1000 ml.

Dithizone solution. 10 mg of dithizone are dissolved in 50 ml of acetone. The solution is prepared freshly every day.

Alkaline solutions are stored in polyethylene bottles.

Filling and conditioning of columns

The capillary above the stopcock is filled with glass wool, which should not be compressed too tightly. 1.00 g of the ion-exchange resin (water content 43.7% or a corresponding amount if the water content is different) is rinsed into the column with water and packed carefully with a glass rod. A flat layer of 3 mm of glass wool is then packed tightly on the resin; this is best done with a 7 mm glass rod which is cut off flat at the end so that a sharp edge is obtained. Aluminum oxide — sedimented in a graduated cylinder to a volume of 6 ml — is rinsed into the column and allowed to settle. A 3 mm layer of tightly packed glass wool is then added.

The amounts of aluminum oxide and resin are rather critical; if it is desirable to use other quantities, the sorption and elution procedures should be retested.

Before use, new columns are washed with 2 *N* nitric acid, water, 0.5 *N* sodium hydroxide and water, and activated with 30 ml of 3.5 *N* nitric acid and 5 ml of 2 *N* nitric acid.

After every use the columns are filled with water. If they are not required again immediately they can be left thus for long time. Before renewed use they are regenerated with 10 ml of 0.5 *N* sodium hydroxide, 30 ml of 3.5 *N* nitric acid and 5 ml of 2 *N*, 1 *N*, 0.5 *N* nitric acid or 1 *N* perchloric acid, *i.e.* the solution in which the sample is transferred to the column.

It is convenient to mark the columns at levels of 5, 10, 20 and 30 ml above the column filling. This makes it possible to do all washing with wash bottles and still to use the correct volumes. The elution should, however, be made by means of pipets, because it is more important to use accurate volumes in this case.

Procedure

Make the sample solution containing not more than 12 mg of sulfate 0.5 *N* with regard to nitric acid. Transfer to the column with two 5 ml portions of 0.5 *N* nitric acid and wash the column with two 5 and one 10 ml portions of 2 *N* nitric acid and with 5 ml and 10 ml portions of 0.001 *N* nitric acid. Wash the walls of the column with every portion of the wash liquid. Allow each portion to pass into the filling completely before adding the next portion. The capillary power of the aluminum oxide prevents risks of drawing air into the filling. The stopcocks are completely opened; the tightness of the filling is such that a suitable rate of flow — about 2 ml/min with the column filled to half height — is obtained. Elute the sulfate with two 2 ml portions of 0.5 *N* ammonia. When these 4 ml have passed into the filling place a 200 ml Erlenmeyer flask under the column and continue the elution with three 5 ml portions of water.

Add 60 ml of acetone, 0.5 ml of 0.5 *N* ammonia, 0.2 ml of pyridine and 1.0 ml of dithizone solution to the collected 15 ml of eluate and titrate with 0.02 *N* lead nitrate. Add a volume of acetone, 4 times greater than the volume of lead nitrate consumed, to the solution shortly before the end-point, and continue the titration to a permanent bluish-grey colour. One further drop gives a red color.

Other solutions can also be used for the sorption-transfer of the sample and for washing the column. A number of results obtained with different solutions are shown on p. 111 (Table VII).

If the solution contains nitrite or free iodine, 1 ml of 5% w/v hydroxylamine solution is added to 10–15 ml of the sample solution, and the solution is allowed to stand for 2–3 min. Traces of iodine or nitrogen dioxide would otherwise be retained and eluted together with the sulfate, and would oxidize the indicator. It is usually possible in this case to save the analysis by adding more indicator, but the addition of hydroxylamine before the separation is preferable.

THE DETERMINATION OF SULFUR

The samples are decomposed by flask combustion and, depending upon their content of interfering elements, the sulfate formed is titrated either directly[1]— Procedure A — or after evaporation to dryness — Procedure B — or after separation of the sulfate — Procedure C.

Apparatus

Combustion flasks and stoppers as described by SCHÖNIGER[2] or as shown in Fig. 2 b and c. Columns as described above.

Reagents

Ammonium nitrite. Wash Amberlite I.R.A. 400 corresponding to about 150 meq (140 ml) and place in a column of *ca.* 40 mm diameter. Make alkaline with 150 ml of 2 *N* sodium hydroxide and wash with water until neutral. Run in 100 ml of 2 *M* sodium nitrite solution to the column and again wash to a neutral reaction with water. Place a 500 ml brown measuring flask under the column and run in 250 ml of 1 *M* ammonium nitrate to the column, followed by water. Collect the whole effluent until the measuring flask is filled to the mark. Mix the solution. As a control its content of nitrite can be determined[3]. The solution should be about 0.3 *M* with regard to ammonium nitrite and about 0.2 M with regard to ammonium nitrate. It is kept in a refrigerator.

Sodium nitrite. 2.5% $NaNO_2$ in water, kept in a brown bottle in the refrigerator.

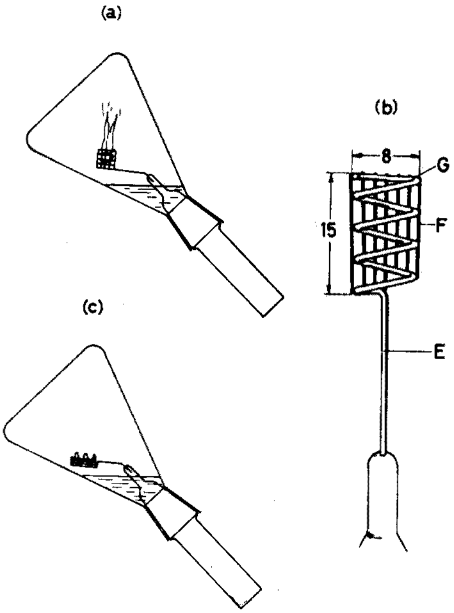

Fig. 2. Combustion arrangements. (a) Combustion with flask and sample holder described by SCHÖNIGER. (b) Improved holder for sample (Diameter of longitudinal platinum wires (F) 0.7 mm; diameter of stem (E) and spiral wire (G) 1.0 mm; joint B14). (c) Use of improved holder.

Procedure A

To be used with substances containing besides sulfur only carbon, hydrogen, oxygen, nitrogen, iodine and moderate amounts (see Table V) of chlorine, bromine and sodium.

Burn the substance in a 300-ml flask containing 0.80 ml of 2 N nitric acid, 5 ml of water and 0.5 ml of ammonium nitrite. Add the nitrite after flushing the flask with oxygen, just before burning the sample. After the combustion shake the flask briefly in order to wet the walls of the flask and the platinum holder, and allow to stand for 1 h for absorption. Rinse the stopper and the neck of the flask with 5 ml of water, remove the stopper and boil the solution for 5 min. Measure the approximate volume of the solution by pouring it into a 20 ml graduated cylinder, then pour it back and wash the cylinder first with water to give a total volume of aqueous solution of 15 ml, and then with 60 ml of acetone. Add 0.4 ml of pyridine and 1 ml of dithizone solution, and titrate the solution with lead nitrate as described above. If the indicator turns partially or completely purple before any lead nitrate has been added, add more indicator until a green colour remains. The titration is then taken to the complete disappearance of the last green tinge.

Procedure B

To be used with substances containing fluorine and/or considerable amounts of chlorine and bromine and moderate amounts (see Table VI) of sodium together with fluorine and/or considerable amounts of chlorine and bromine.

Burn the substance and absorb the combustion products as in procedure A. Transfer the solution to a 50 ml borosilicate glass dish with 3 × 3 ml of 1 *N* nitric acid and evaporate to dryness on a boiling water bath. Dissolve the residue and transfer to a clean flask with a total of 15 ml of water. Add 0.35 ml of 2 *N* nitric acid, 0.2 ml of pyridine, 1 ml of dithizone solution and 60 ml of acetone and titrate the solution as described under procedure A.

Procedure C

To be used with samples containing other metals, phosphorus and with samples of unknown composition.

Burn the sample as described above. Absorb the combustion products in 1 ml of 2 *N* nitric acid, 5 ml of water and 1 ml of sodium nitrite. Add the nitrite after flushing the flask with oxygen. After shaking and absorption for 1 h, rinse the stopper with 5 ml of water and boil the solution for 5 min with the stopper hanging loosely in the flask with a hook of glass between it and the joint of the flask. After cooling, add 3 ml of 3.5 *N* nitric acid and 0.2 ml of 5% w/v hydroxylamine hydrochloride, mix well and transfer to the column with three 5 ml portions of 2 *N* nitric acid. Wash the column with two 5 and one 10 ml portions of 2 *N* nitric acid, and with 5 ml and 10 ml portions of 0.001 *N* nitric acid. Elute and titrate as described under "Determination of sulfate".

If the sample contains both phosphate and fluoride, the latter is removed by evaporation according to procedure B before the transfer to the column.

DISCUSSION

Interfering ions can be removed by the aluminum oxide adsorption method described by NYDAHL AND GUSTAFSSON[4] and by NYDAHL[1] and by the cation-exchange method described by FRITZ AND YAMAMURA[5]. FRITZ, YAMAMURA AND RICHARD[6] have also described a procedure using both methods in succession. This procedure is, of course, rather tedious, and interferences from phosphate and fluoride are not eliminated. Preliminary experiments indicated that it should be possible to simplify the procedure[6] considerably and to remove practically all common ions from the solution; this would make it possible to choose the most suitable conditions for the measurement of the separated sulfate.

The titration

Two titration methods seemed most suitable for the final measurement: the titration with lead nitrate using dithizone as indicator[7–10], and the titration with barium perchlorate using thorin as indicator described by FRITZ AND YAMAMURA[5] and used also by other authors[6,10–12].

Experiments showed that sharp end-points and excellent results were obtained with both methods under suitable conditions. The lead nitrate method required a closer control of the pH for the titration than the barium perchlorate method. On the other hand the visibility of its end-point was found to be so much better, that this method was further investigated.

The titrations were run in such a manner that the concentration of acetone was

80% at the end-point. Experiments showed that the best end-points were obtained when the apparent pH was between 3.7 and 4.1. Lower values of the pH gave indistinct, fading end-points and high results. At higher pH values the reaction near the end-point was too sluggish. The optimum is at about pH 3.9. ARCHER[7] and WHITE[8,9] adjusted the pH of their solutions before the addition of the acetone. For our purposes, this did not appear sufficiently reliable, because the acidity of the acetone solution is determined not only by the pH of the aqueous solution before the addition of the acetone but also by the strength of the acids and bases involved. It appeared most convenient to use a buffer and to determine its effect in the final acetone solution. A suitable buffering system was sought. Fig. 3 shows titration curves of acetic acid, chloroacetic acid, dichloroacetic acid and trichloroacetic acid with ammonia in 80% acetone solution, and of nitric acid with pyridine in the same medium. Dichloroacetic acid–ammonia appeared to be the most suitable buffering system. A series of titrations using this system is shown in Table I. The results were considered satisfactory. The separation procedure was then arranged so that after

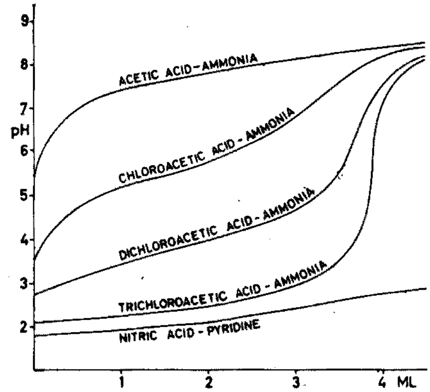

Fig. 3. Buffering curves in 80% acetone. Four ml of about 0.08 *N* solutions of the acids were mixed with 11 ml of water and 60 ml of acetone and titrated with 0.1 *N* ammonia in 80% acetone, except for the nitric acid, which was titrated with 0.1 *N* pyridine in 80% acetone.

TABLE I

TITRATION IN SOLUTION BUFFERED WITH DICHLOROACETIC ACID–AMMONIA

To 20 ml of aqueous solution containing a total of 1.16 meq of dichloroacetic and sulfuric acids (the amount which was found to be eluted from the columns) were added 1.5 ml of 0.5 *N* ammonia and 80 ml of acetone, and the solution was titrated with 0.02 *N* lead nitrate. More acetone was added near the end-point to give a final concentration of 80%.

H_2SO_4 0.0468 *N* taken (ml)	$Pb(NO_3)_2$ 0.0200 *N* (ml)		Error (%)
	Calculated	Found	
0.00	0.00	0.00	0.0
1.25	2.93	2.94	+0.3
2.50	5.85	5.88	+0.5
3.75	8.78	8.79	+0.1
5.00	11.70	11.73	+0.3

the sorption from nitric acid solution, the anions from the column were washed out with dichloroacetic acid before the elution, so that the eluted solution could be expected to contain sulfuric acid and dichloroacetic acid as the only ions. However, dichloroacetic acid in aqueous solution is slowly hydrolyzed and liberates small amounts of chloride. A fairly large amount of acid was needed to wash the column, and all its chloride was adsorbed on the aluminum oxide. This gave such a high concentration of chloride in the final solution that high results and indistinct end-points were obtained. Thus, while dichloroacetic acid was found to be a very suitable buffer for the titration, it could not be used in connection with the separation method used.

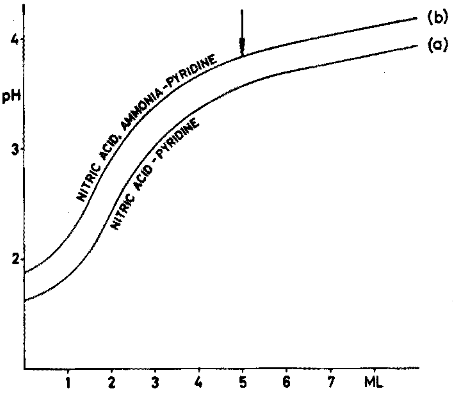

Fig. 4. Titration curves of HNO_3 and $HNO_3 + NH_3$ with pyridine. (a) 9.95 ml of 0.1 *N* nitric acid, 5.05 ml of water and 60 ml of acetone were titrated with 0.5 *N* pyridine in 80% acetone. (b) 9.95 ml of 0.1 *N* nitric acid, 0.5 ml of 0.5 *N* ammonia in 80% acetone, 5.05 ml of water and 60 ml of acetone were titrated with 0.5 *N* pyridine in 80% acetone. The arrow indicates the mixture used in the final analytical method with nitric acid. The amount of titrated acid corresponds to the amount eluted from the columns.

TABLE II

TITRATION IN SOLUTION CONTAINING PYRIDINE AS THE ONLY CATION

To 25 ml of aqueous solution containing a total of 1.08 meq of nitric and sulfuric acids, were added 0.35 ml of pyridine and 100 ml of acetone. The solution was titrated with 0.02 *N* lead nitrate. More acetone was added near the end-point to give a final concentration of 80%.

H_2SO_4 0.0468 N taken (ml)	*$Pb(NO_3)_2$ 0.0200 N (ml)*		*Error (%)*
	Calculated	*Found*	
0.00	0.00	0.00	0.0
0.50	1.17	1.20	+2.6
1.00	2.34	2.38	+1.7
2.00	4.68	4.79	+2.4
4.00	9.36	9.64	+3.0
6.50	15.21	15.67	+3.0
8.50	19.89	20.46	+2.9

Figure 4a shows that a sufficient amount of pyridine added to a nitric acid solution in the medium used gives a suitable pH. A series of titrations was therefore carried out using a solution containing nitric acid in addition to sulfuric acid and pyridine

(Table II). The end-points were found satisfactory, but surprisingly all the results were 2–3% high. It was first thought that this could have been caused by co-precipitation of nitrate. In several experiments the nitric acid was therefore replaced with perchloric acid, trichloroacetic acid and *p*-toluene sulfonic acid, but errors of the same magnitude were obtained. Then it was supposed that the errors might be connected with the absence of cations other than pyridine. In further titrations a part of the pyridine was therefore replaced by ammonia. The results (Table III) became considerably better, and also the end-points were sharper. The results of titrations run with the method finally chosen are given in Table IV. The results are still slightly high but the small errors can easily be avoided by standardizing the solutions of lead nitrate against sulfuric acid.

TABLE III

TITRATION IN SOLUTION CONTAINING PYRIDINE, AMMONIA AND NITRIC ACID

To 22 ml of aqueous solution containing a total of 1.08 meq of acid, were added 3 ml of 0.3 *N* ammonia, 0.05 ml of pyridine and 100 ml of acetone. The solution was titrated with 0.02 *N* lead nitrate. More acetone was added near the end-point to give a final concentration of 80%.

H_2SO_4 0.0468 *N* taken (ml)	$Pb(NO_3)_2$ 0.0200 *N* (ml)		Error (%)
	Calculated	*Found*	
0.00	0.00	0.00	0.0
0.50	1.17	1.17	0.0
1.00	2.34	2.35	+0.4
2.00	4.68	4.69	+0.2
4.00	9.36	9.42	+0.6
6.50	15.21	15.36	+1.0
8.50	19.89	20.12	+1.2

TABLE IV

TITRATION BY THE FINAL METHOD

To 15 ml of aqueous solution containing 0.995 meq of acid, were added 0.5 ml of 0.5 *N* ammonia, 0.2 ml of pyridine and 60 ml of acetone. The solution was titrated with 0.02 *N* lead nitrate. More acetone was added near the end-point to give a final concentration of 80%.

H_2SO_4 0.0499 *N* taken (ml)	$Pb(NO_3)_2$ 0.0200 *N* (ml)		Error (%)
	Calculated	*Found*	
0.00	0.00	0.00	0.0
1.00	2.49	2.51	+0.8
2.00	4.99	5.00	+0.2
3.00	7.48	7.52	+0.5
4.00	9.97	10.00	+0.3

It appears likely that the precipitation of lead sulfate in the absence of cations other than pyridine is not stoichiometric, but that more lead is precipitated. When sufficient ammonia is present this co-precipitation effect is either eliminated or counterbalanced by co-precipitation of ammonium ion. Analyses of the precipitates and other investigations should be made to elucidate the reactions of the titration and to allow certain conclusions, but this went beyond the scope of the present paper.

In procedure A for the sulfur determination, considerable amounts of acidic combustion products can be formed which might affect the pH of the solution to

TABLE V

TITRATIONS CARRIED OUT AS IN PROCEDURE A[a]

SO_4^{2-} taken (mg)	*$Pb(NO_3)_2$ calculated (ml)*	*$Pb(NO_3)_2$ found (ml)*												
		No addition	*Fluoride*	*Chloride*		*Bromide*			*Iodide*	*Sodium*				*Potassium*
			1.9 mg	*3.5 mg*	*7 mg*	*4 mg*	*8 mg*	*16 mg*	*13 mg*	*2.3 mg*	*4.6 mg*	*9.2 mg*	*18.4 mg*	*3.9 mg*
0.000	0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.421	2.52	2.50	2.72	2.53	2.55	2.52	2.51	2.53[b]	2.52	2.52	2.51	2.52	2.48	2.00
7.273	7.57	7.58	7.88	7.60	7.71	7.57	7.62	—[b]	7.56	7.55	7.57	7.53	7.49	7.40
12.116	12.61	12.60	12.94	12.62	12.78	12.62	12.63	—[b]	12.60	12.62	12.58	12.56	12.56	12.46

[a] Fluoride, chloride, bromide and iodide were added as aqueous solutions of HF, HCl, HBr and HI. HF solution was added from a polyethylene container with a polyethylene pipet. Sodium and potassium were added as aqueous solutions of the nitrates.

[b] Indistinct end-points.

be titrated. It therefore appeared desirable to use a larger amount of buffer in this method. In the first tests the amounts of nitric acid, ammonia and pyridine were increased in the same proportions; less distinct end-points were, however, obtained when the amount of ammonia was increased, hence only the amounts of nitric acid and pyridine were increased in later tests. This is, of course, advantageous, because only these compounds give the buffering effect in the solution used. The amount of ammonia must, of course, be sufficient to bind all sulfate as ammonium hydrogen sulfate. Results obtained by the titration methods are given in Tables V and VI.

TABLE VI

TITRATIONS CARRIED OUT AS IN PROCEDURE B

Sulfuric acid and/or water and the reagents used in procedure B were pipetted into a glass dish. The solution was evaporated to dryness, transferred and titrated as described under procedure B. Fluoride, chloride and bromide were added as HF, HCl and HBr as mentioned in Table V.

SO_4^{2-} *taken (mg)*	$Pb(NO_3)_2$ *calculated (ml)*	$Pb(NO_3)_2$ *found (ml)*				
		No addition	*Fluoride*		*Chloride*	*Bromide*
			3.8 mg	*7.6 mg*	*28 mg*	*32 mg*
0.000	0.00	0.00	0.00	0.00	0.00	0.00
7.032	7.32	7.30	7.32	7.30	7.34	7.32
11.719	12.20	12.17	12.16	12.26	12.20	12.18

WHITE[8,9] reports that moderate amounts of chloride do not interfere in the titration, and that interference from all halogens can be avoided by evaporating the solutions to dryness with nitric acid. The titrations reported in Tables V and VI were carried out in order to test the influence of halogens, sodium and potassium. As can be seen from Table V iodine does not interfere at all because it is boiled out already in procedure A, and the amounts of chloride, bromide and sodium that can be tolerated are greater than usually occur in the combustions. Interference from even large amounts of chloride, bromide and fluoride is completely avoided by procedure B. Low results were obtained when the evaporation was carried out with concentrated nitric acid instead of the recommended 1 *N* nitric acid. No formation of nitrite was ever found in the evaporation, and less reliable, frequently low results were obtained when the evaporation was repeated with urea[8]. This operation was therefore omitted.

When samples containing large amounts of halogen were analyzed by the flask combustion procedures A and B (Tables IX and X) the indicator occasionally turned partially or even completely purple before any lead nitrate had been added. This trouble did not occur when the solutions were pipetted out and evaporated as in the experiments reported in Tables V and VI, and it could not be eliminated by evaporation with urea. It did not occur when the solution was run through the column, and it was never worse than that the solution could easily be titrated accurately when more indicator was added. It is probably caused by platinum which is set free from the sample holder by the attack of the burning halogen.

Phosphate and many organic acids, potassium, earths and metals interfere in the titration and must be eliminated on the column.

The titration method has many advantages: the end-point is very sharp and easily discernible and does not fade, and there is ample warning of its approach; moreover, the results are of good accuracy.

The separation

It was first thought that it might be possible to remove all interfering anions and cations by the use of aluminum oxide alone. NYDAHL AND GUSTAFSSON[4] report an experiment which shows that the strength of the adsorption of phosphate on aluminum oxide decreases markedly with increasing acidity of the solution, while that of sulfate increases. This led to the thought that it might be possible to wash the phosphate from the column at a still higher acidity and with an acid which is more strongly adsorbed than perchloric acid, without affecting the sulfate. Experiment showed that phosphate can easily be washed out with 2 *N* nitric acid; sulfate remains in the column but the capacity of the column for sulfate is somewhat de-

TABLE VII

RESULTS OBTAINED WITH DIFFERENT SORPTION AND WASHING SOLUTIONS

The analyses were carried out by the described method, except for the different solutions.

Ions added to column in sorption solution			*2 N HNO_3*		*1 N HNO_3*		*Sorbcd in 0.5 N HNO_3 Washed with 2 N HNO_3*		*1 N $HClO_4$*	
SO_4^{2-} (mg)	*PO_4^{3-} (mg)*	*F^- (mg)*	*SO_4^{2-} found (mg)*	*Dev. (%)*	*SO_4^{2-} found (mg)*	*Dev. (%)*	*SO_4^{2-} found (mg)*	*Dev. (%)*	*SO_4^{2-} found (mg)*	*Dev. (%)*
0.00	—	—	0.00	—	0.00	—	0.00	—	0.00	—
2.39	—	—	2.43	+ 1.6	2.41	+ 0.8			2.38	−0.4
4.79	—	—	4.80	+ 0.2	4.81	+ 0.4	4.81	+0.4	4.78	−0.2
7.19	—	—	7.20	+ 0.1			7.15	−0.6		
9.58	—	—	9.57	− 0.1	9.62	+ 0.4			9.56	−0.2
11.97	—	—	12.00	+ 0.2			11.93	−0.3		
14.37	—	—	14.37	0.0						
16.77	—	—					16.71	−0.3		
19.15	—	—	17.29	− 9.7	19.31	+ 0.8			19.21	+0.2
23.95	—	—			24.27	+ 1.3				
28.73	—	—			28.19	− 1.9			28.96	+0.8
35.91	—	—			32.16	−10.4			35.62	−0.8
47.89		—							46.40	−3.2
0.00	12.0	—	0.00	—	0.00	—	0.00	—	0.00	—
2.39	12.0	—	2.40	+ 0.4	2.43	+ 1.6			2.51	+4.8
4.79	12.0	—	4.80	+ 0.2	4.81	+ 0.4	4.83	+0.8	4.84	+1.0
7.19	12.0	—	7.22	+ 0.4			7.17	−0.3		
9.58	12.0	—	9.61	+ 0.3	9.59	+ 0.2			9.54	−0.4
11.97	12.0	—	12.02	+ 0.4			11.94	−0.3		
14.37	12.0	—	14.41	+ 0.3						
16.77	12.0	—					16.03	−4.4		
0.00	—	4.0	0.00	—						
7.19	—	0.5	7.51	+ 4.5						
7.19	—	1.0	7.67	+ 6.7						
7.19	—	4.0	8.20	+14.2						
0.00	—	4.0	0.00	—	5 ml of a solution containing 4.5% of boric acid and 5% of citric acid added to 15 ml of the sorption solution					
4.79	—	4.0	4.82	+ 0.6						
7.19	—	4.0	7.16	− 0.4						
9.58	—	4.0	9.60	+ 0.2						
11.97	—	4.0	11.98	+ 0.1						
16.77	—	4.0	15.12	− 9.3						
0.00	12.0	4.0	0.00	—						
7.19	12.0	4.0	7.39	+ 2.8						
11.97	12.0	4.0	11.81	− 1.3						
16.77	12.0	4.0	13.29	−20.4						

creased. However, while sulfate could be separated from all common anions and cations except fluoride in this manner, it was found impossible to avoid completely the bleeding of small amounts of aluminum from the column, even when the latter was washed with large amounts of solution at pH 4 before the elution. As aluminum interferes strongly with the titration, it was found necessary to use a small amount of ion-exchange resin like FRITZ *et al.*[6]. The final method was designed so that the sulfate is adsorbed from a solution 0.5 *N* with regard to nitric acid; 2 *N* nitric acid is used to wash out phosphate and other substances from the column. The excess of acid is then washed out with very dilute nitric acid, which also brings the resin into the working condition. Finally the sulfate is eluted with ammonia. Aluminum and ammonia are sorbed by the resin and only sulfuric acid and nitric acid are collected and titrated.

BELCHER AND MACDONALD[13] described a method for the determination of phosphorus in which they used boric and citric acids in order to keep fluoride and silicon compounds in solution during the precipitation of quinoline phosphomolybdate. It appeared interesting to try whether the complexes formed would be strong enough to carry the same fluorine and silica compounds through the column, thus eliminating the interference of fluoride. The experiments were successful as can be seen from Table VII but the method failed when both fluoride and phosphate were present.

Between the analyses the column was originally washed only with 1 *N* ammonia, water and nitric acid. Good results were obtained with new columns with all the types of solutions tested, but after 4–5 analyses, phosphate-containing solutions gave blanks and high results and after some time solutions containing citric acid, etc. also gave erroneous results, whereas solutions containing only sulfate, halides and alkali metals still gave correct results. The error was found to be caused by changes in the properties of the aluminum oxide filling, from which these anions could no longer be washed out quantitatively with 2 *N* nitric acid. The trouble could be eliminated by washing with sodium hydroxide between the analyses. Probably the surface structure of the aluminum oxide is changed during the analyses and the original condition is restored by the washing with alkali. It was first feared that the sodium hydroxide would dissolve much of the aluminum oxide, but experiments showed that only very small amounts of aluminum oxide were dissolved, even when the aluminum oxide was heated in a boiling water bath with 1 *N* sodium hydroxide. Several of our columns have been used for more than 100 runs and still give good service. The washing with 3.5 *N* nitric acid is done in order to remove any aluminum retained in the cation-exchange resin[14].

Other solutions were also tested for the sorption and the washing procedures (Table VII). Some of the solutions might be useful in different cases. The sorption method with 2 *N* nitric acid reported in the first column was used originally and is still used in connection with the sulfur determination described. Correct results were also obtained with this solution in the analysis of many complicated organic mixtures. However, many organic compounds reacted with the strong nitric acid forming nitrogen oxides; usually this caused no great harm when hydroxylamine hydrochloride was added to the solution. It was, however, considered disadvantageous, and therefore the method using sorption with 0.5 *N* nitric acid and washing with 2 *N* nitric acid was worked out. 1 *N* perchloric acid, used by earlier authors, might have been still better for the sorption from this point of view, but it precipitates potassium, which is a common ion in the solutions analyzed in this laboratory, hence nitric acid was considered preferable.

Large volumes of nitric acid are used in the procedure and any impurity of sulfate is retained in the column and causes blanks. Either very pure nitric acid must be used or it must be freed from sulfate by passing it through aluminum oxide. The treated acid contains traces of aluminum and should therefore not be used in the sulfur determination procedures A and B.

Results of tests for interferences with this method are reported in Table VIII. The following compounds did not interfere in experiments carried out under various conditions with sorption in 2 *N* nitric acid: acetic acid, boric acid, citric acid, dichloroacetic acid, molybdic acid, *p*-toluene sulfonic acid, trichloroacetic acid, hydroxylamine hydrochloride, metaphosphoric acid, pyrophosphoric acid. Oxalic acid interfered.

TABLE VIII

TESTS OF SEPARATION AND TITRATION METHOD FOR INTERFERENCE

3 ml of sulfuric acid or water were added to 5 ml of a 1% solution of the compound to be tested. The solution was diluted to 12 ml and 4 ml of 2 *N* nitric acid was added. The solution was transferred to the column with 0.5 *N* nitric acid and the column washed with 2 *N* nitric acid as in the described method. The theoretical result for 3 ml of sulfuric acid is 7.48 ml of 0.02 *N* lead nitrate.

H_2SO_4 added (ml)	*Compound added*	*$Pb(NO_3)_2$ 0.02 N used (ml)*	*Deviation (%)*
0	Dextran	0.00	—
3	Dextran	7.41	−0.9
0	Ethyl alcohol	0.00	—
3	Ethyl alcohol	7.44	−0.5
0	Glycerol	0.00	—
3	Glycerol	7.48	0.0
0	Oxalic acid	>10	very large
3	Oxalic acid	>10	
0	Polyethylene glycol	0.02	—
3	Polyethylene glycol	7.44	−0.5
0	Salicylic acid[a]	0.01	—
3	Salicylic acid[a]	7.48	0.0
0	Sorbitol	0.01	—
3	Sorbitol	7.49	+0.1
0	Starch	0.00	
3	Starch	7.46	−0.3
0	Sucrose	0.03	—
3	Sucrose	7.46	−0.3

[a] 0.1% solution because of low solubility.

The combustion

A considerable number of procedures, flasks and sample-holders for the oxygen flask combustion method have been described[15] and several of them have been tried and used in the authors' laboratories. In the course of several years the following conditions have been found important (*cf.* SCHÖNIGER[15] and MACDONALD[16]). The package containing the sample should have good contact with a suitable mass of platinum; at the beginning of the combustion this mass has a cooling effect, preventing too rapid volatilization of the sample which can cause formation of soot, because insufficient oxygen is admixed with the vapours of the sample. This is especially important when large samples of aromatic substances are burned. In the course of the combustion the platinum is heated almost to white heat, and the glowing platinum helps to burn the last, sometimes refractory particles of the sample.

The shape of the holder should be such that no particles of the sample can drop out before they are burned. The holder described by SCHÖNIGER[2] corresponds very well to these conditions if it is held as shown in Fig. 2a during the combustion, and it is very convenient in use. However, most analysts press together the wings of the holder after inserting the sample, so that the sample is properly held. To insert the next sample the wings have to be opened and this repeated bending causes the holder to break after 20–100 analyses depending upon the care of the analyst. In order to avoid this the holder shown in Fig. 2b was designed; the sample-package is inserted into the spiral-basket without anything being bent. A number of such holders have been tested in one of the authors' laboratories during about 18 months; they give the same performance as the SCHÖNIGER holders but have a considerably longer lifetime. None of them has been broken yet.

When the flask is shaken after the combustion in order to wet all the inner parts for the absorption this should be done in a vertical direction in order to avoid straining of the stem of the platinum holder, which otherwise is broken very rapidly.

Flasks with different sizes of ground-joints were tested; all the analysts preferred the B14 joint to wider joints both for micro- and semimicro-analysis. Its advantages are the greater ease in washing the stopper and flask with small volumes of solution, and the absence of difficulties in removing the stoppers from the flasks after the combustion*.

Volatile substances are burned in polyethylene tubing[17], which was found to be the purest available material for containers. Instead of using the soldering-iron equipment[17] the sample tube can be closed with a small quartz stopper prepared by

TABLE IX

RESULTS OBTAINED WITH PROCEDURE A

Substance[a]	*Weight of sample (mg)*	*Sulfur*		*Deviation (%)*
		Obtained (%)	*Calculated (%)*	
$C_{10}H_{20}N_4S$	21.463	14.03	14.04	−0.01
$C_{16}H_{23}N_5O_3S_2$	14.491	16.15	16.13	+0.02
$C_{16}H_{25}N_5O_2S_2$	14.822	16.83	16.72	+0.11
$C_2H_2N_3SCl$	6.693	23.66	23.65	+0.01
$C_8H_5N_4O_4SCl$	14.833	11.30	11.11	+0.19
$C_{10}H_{21}N_4SCl$	23.002	12.04	12.11	−0.07
$C_{15}H_{12}N_2OSCl_2$	18.163	9.28	9.45	−0.17
$C_{17}H_{17}N_2O_2SCl$	23.501	9.21	9.19	+0.02
$C_{21}H_{17}N_2O_2SCl$	28.994	8.00	8.08	−0.08
$C_6H_5NO_3SI_2$	33.441	7.67	7.54	+0.13
$C_{15}H_{13}N_2O_2SBr$	9.274	8.71	8.78	−0.07
Sodium Dextran sulfate B	13.360	16.80	16.92[b]	

[a] Compounds synthesized in Pharmacia's Research Laboratories.
[b] Mean of analyses reported in Table XI.

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* The flasks and holders are available from Messrs. Rudolph Grave, Pyramidvägen 9, Solna, Sweden.

drawing out and cutting off a thin quartz rod; such stoppers can be used repeatedly. Surprisingly, the analysts in the authors' test laboratory preferred the soldering-iron method, as being easier to handle than the small stoppers. Hygroscopic substances are placed into polyethylene tubing in a gloved dry-box. The tubes are closed with quartz stoppers and weighed outside the box.

TABLE X

RESULTS OBTAINED WITH PROCEDURE B

Substance	*Weight of sample (mg)*	*Sulfur*		*Deviation (%)*
		Obtained (%)	*Calculated (%)*	
Sulfanilic acid	8.498	18.41	18.52	−0.11
	6.838[a]	18.41	18.52	−0.11
	8.000[b]	18.35	18.52	−0.17
$C_{15}H_{12}N_2OSCl_2$	15.664	9.41	9.45	−0.04
	15.302[a]	9.37	9.45	−0.08
	13.666[b]	9.38	9.45	−0.07
$C_{15}H_{13}N_2O_2SBr$	11.208	8.70	8.78	−0.08
	11.834[a]	8.72	8.78	−0.06
	10.764[b]	8.58	8.78	−0.20
$C_6H_5NO_3SI_2$	7.875	7.57	7.54	+0.03
	8.410[a]	7.60	7.54	+0.06
	7.596[a]	7.55	7.54	+0.01

[a] 8.0 mg NaF added.
[b] 12.0 mg of trifluoroacetanilide added.

TABLE XI

RESULTS OBTAINED WITH PROCEDURE C

Substance	*Weight of sample (mg)*	*Sulfur*		*Deviation (%)*
		Found (%)	*Calculated (%)*	
Potassium sulfate	17.357	18.29	18.40	−0.11
Calcium sulfate	14.207	23.74	23.55	+0.19
Sulfanilic acid	13.278	18.42	18.51	−0.09
δ-Phenylthiohydantoic acid	13.429	15.28	15.24	+0.04
Thiourea	5.802	42.11	42.11	0.00
$C_{10}H_{20}N_4S$	20.820	13.94	14.04	−0.08
$C_{16}H_{23}N_5O_3S_2$	18.126	16.11	16.13	−0.02
$C_{16}H_{25}N_5O_2S_2$	16.292	16.72	16.72	0.00
$C_2H_2N_3SCl$	10.271	23.41	23.65	−0.24
$C_8H_4N_4O_4SCl_2$	26.380	10.17	9.92	+0.25
$C_8H_5N_4O_4SCl$	24.325	11.11	11.11	0.00
$C_{10}H_{21}N_4SCl$	20.106	12.15	12.11	+0.04
$C_{15}H_{12}N_2OSCl_2$	20.868	9.36	9.45	−0.09
$C_{17}H_{17}N_2O_2SCl$	26.409	9.14	9.19	−0.05
$C_{21}H_{17}N_2O_2SCl$	33.191	7.94	8.08	−0.14
$C_{15}H_{13}N_2O_2SCl$	10.030	9.01	8.78	+0.23
$C_6H_5NO_3SI_2$	37.038	7.55	7.54	+0.01
Sulfanilic acid + 7 mg NaH_2PO_4	7.483	18.47	18.52	−0.05
$C_6H_5NO_3SI_2$ + 7 mg NaH_2PO_4	10.119	7.79	7.54	+0.25
$C_{17}H_{17}N_2O_2SCl$ + 7 mg NaH_2PO_4	10.383	9.17	9.19	−0.02
$C_{15}H_{13}N_2O_2SBr$ + 7 mg NaH_2PO_4	10.021	8.51	8.78	−0.27

TABLE XI (continued)

Substance	*Weight of sample (mg)*	*Sulfur*		*Deviation (%)*
		Found (%)	*Calculated (%)*	
Sulfanilic acid + 7 mg $Ca_3(PO_4)_2$	10.583	18.21	18.52	−0.31
$C_6H_5NO_3SI_2$ + 7 mg $Ca_3(PO_4)_2$	10.293	7.54	7.54	0.00
$C_{17}H_{17}N_2O_2SCl$ + 7 mg $Ca_3(PO_4)_2$	10.020	9.15	9.19	−0.04
$C_{15}H_{13}N_2O_2SBr$ + 7 mg $Ca_3(PO_4)_2$	10.566	8.74	8.78	−0.04
Sulfanilic acid + 7 mg $(C_6H_5)_3P$	6.745	18.44	18.52	−0.08
$C_6H_5NO_3SI_2$ + 7 mg $(C_6H_5)_3P$	10.631	7.78	7.54	+0.24
$C_{17}H_{17}N_2O_2SCl$ + 7 mg $(C_6H_5)_3P$	9.909	9.06	9.19	−0.13
$C_{15}H_{13}N_2O_2SBr$ + 7 mg $(C_6H_5)_3P$	9.524	8.35	8.78	−0.43
Sulfanilic acid + 7 mg NaH_2PO_4 + 17 mg NaF[a]	10.232	18.39	18.52	−0.12
$C_6H_5NO_3I_2$ + 7 mg NaH_2PO_4 + 17 mg NaF[a]	33.970	7.41	7.54	−0.13
$C_{17}H_{17}N_2O_2SCl$ + 7 mg NaH_2PO_4 + 17 mg NaF[a]	21.756	9.08	9.19	−0.11
$C_{15}H_{13}N_2O_2SBr$ + 7 mg NaH_2PO_4 + 17 mg NaF[a]	22.392	8.76	8.78	−0.02
Sodium Dextran sulfate A	17.40	16.73		
	14.69[b]	16.67		
	12.10[b]	16.77		
Sodium Dextran sulfate B	18.94	16.94		
	13.64	16.90		
	15.68[b]	16.93		
Sodium Dextran sulfate C	17.75	16.98		
	13.40[b]	17.13		
	12.82[b]	17.01		
Sephadex A	30.030	6.76		
	28.773	6.75		
	27.149	6.77		
Sephadex B	45.175	6.03		
	53.567	6.01		
	64.605	6.02		

[a] The samples were evaporated as in procedure B before the transfer to the column with 2 *N* nitric acid.

[b] The samples were not burned. The sulfate was split off by hydrolysis with hydrochloric acid, then the sulfate was separated on the column and titrated as in the other analyses.

For the absorption an aqueous acid solution containing nitrite is used. Nitrite was earlier recommended[18] for the reduction of chlorine, bromine, bromate, chlorate to the halides and for the instant oxidation of sulfite to sulfate. It also oxidizes iodide to iodine and reduces iodate to iodine on heating. It is quickly eliminated by boiling the solution for a short time. It is therefore much more convenient than alkaline hydrogen peroxide. In the cases where alkali ion is not desirable — as in procedures A and B — it is exchanged against ammonia as described above. The solution can be kept in the refrigerator and used for a very long time, at least for 6 months.

Some results of analyses run by procedure A are reported in Table IX, those by method B in Table X and those by procedure C in Table XI.

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SUMMARY

Sulfate is determined by titration with lead nitrate solution in aqueous acetone solutions buffered with nitric acid–pyridine, in presence of dithizone indicator. Sulfate is titrated directly or after separation from interfering ions and other materials on a column containing aluminum oxide and cation-exchange resin. The titration and separation are also applied to determination of sulfur in organic compounds after oxygen flask combustion. Details of the methods are fully discussed.

RÉSUMÉ

Les auteurs ont effectué une étude du dosage des sulfates et du soufre. Ils proposent un titrage des sulfates au moyen de nitrate de plomb, en milieu eau–acétone, en présence de dithizone comme indicateur. Le sulfate peut être dosé directement ou après séparation au moyen d'une colonne contenant de l'oxyde d'aluminium et de l'échangeur de cations. Cette méthode peut également être utilisée lors du dosage du soufre par combustion.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Sulfat durch Titration mit Bleinitratlösung und Dithizon als Indikator. Eine Trennung von störenden Ionen kann mit Aluminiumoxyd und Cationenaustauscherharz erfolgen. Das Verfahren eignet sich auch zur Bestimmung von Schwefel in organischen Verbindungen nach Kolbenverbrennung.

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A RAPID AND PRECISE HETEROMETRIC METHOD FOR THE DETERMINATION OF TRACES OF PHOSPHORIC OR ARSENIC ACID WITH NITRON AND MOLYBDATE

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Over 100 years ago, SONNENSCHEIN[1] first used the phosphomolybdate method for the precipitation of large organic nitrogen-containing bases in nitric acid solutions. He was interested in the separation of alkaloids from the other organic materials. EMBDEN[2] used this reaction for the gravimetric determination of small amounts (1–4 mg) of phosphoric acid in body fluids. DUVAL[3] examined the strychnine compound and showed that the initial precipitate did not correspond to the usually accepted formula but to $P_2O_5 \cdot 33MoO_3$. Quinine was used by VELLUZ AND PESEZ[4] for the detection of submicrogram amounts of phosphoric acid in paper chromatography. WILSON[5] used quinoline for the precipitation of phosphomolybdate, but dissolved the precipitate in excess of sodium hydroxide and back-titrated with hydrochloric acid, using phenolphthalein as indicator. Oxine has also been used by several investigators[6,7]. BRABSON AND EDWARDS[6], who used the oxine phosphomolybdate method for the gravimetric analysis of rocks and alloys, obtained the best results with 5 to 10 mg of P_2O_5.

The true composition of the basic phosphomolybdate precipitate in these procedures depends on the method used and on the washing and drying conditions. The gravimetric method is confusing, hence workers in the last ten years have abandoned the gravimetric method and have used titrimetric methods instead, usually after dissolution of the precipitate in sodium hydroxide[8–10]. Arsenic acid, silicic acid and germanium interfere in these procedures unless prior precautions are taken.

In biological materials and in blood, phosphate is generally determined photometrically.

Although numerous investigations of the various molybdate methods have been published, especially in the analytical field, many problems remain to be solved. In any case, the molybdate compound forms the starting point for all the methods in use. The amount of phosphorus determined fluctuates, according to the method used, between the milligram and microgram ranges. The spectrophotometric molybdenum blue method is satisfactory in the microgram and submicrogram ranges. It is, however, difficult to state with certainty the real error in each case.

As these are all cases of large molecules, it seemed worthwhile to follow the reactions concerned heterometrically, in order to see what conclusions could be drawn from the results.

It was found that nitron, which is stable for a long time if kept in brown bottles, can generally be successfully used for the precipitation of the heteropoly acids.

The theory and application of the heterometric method have been discussed elsewhere[11].

The heterometric behaviour of the different heteropoly acids towards large nitrogen bases and their analytical use in heterometry has already been studied in detail[12]. In the present paper, a method is suggested for the determination of 0.03–0.05 mg of phosphorus within 10–15 min by titration with nitron. The error is usually less than 1%. Foreign anions such as chlorides, nitrates or sulphates, do not interfere even when present in a 100–200-fold molar amount compared to phosphate.

The titration is carried out in mineral acid solution at an optimum concentration of 0.7 N; the results are the same whether hydrochloric or nitric acid is present. The other factors, which are decisive in heterometry for the successful application of the phosphomolybdate method, are quite different from those in gravimetry, titrimetry or photometry, hence the information available for these methods cannot be directly transferred to heterometry. The establishment of the optimum working conditions, *e.g.* the minimum titration time, and the achievement of the maximum sensitivity (maximum optical density) are specific for heterometry and do not require to be considered for the other methods mentioned above. To a certain degree the same is true for the lowest titration error found at the end-point of the titration (first maximum density point). Also the velocity of the formation of phosphomolybdic acid from its components at room temperature at various acid concentrations has not been dealt with previously.

The phosphomolybdic acid reaction was studied by us with a mixture of phosphoric acid and sodium molybdate as well as with the phosphomolybdic acid analytical reagent which is commercially available. Additional information was thus obtained with regard to the essential conditions for the formation and stability of the phosphomolybdic acid. We did not study the compositions of the different phosphomolybdic acids which may be formed under special working conditions. In our case, the compound $P_2O_5 \cdot 24MoO_3$ only was considered.

The heterometric determination of arsenic acid was also examined.

EXPERIMENTAL

The apparatus required has already been described[11].

The chemicals used in this study mostly were "chemically pure" or AnalaR reagents. Special reagents were as follows: $Na_2MoO_4 \cdot 2H_2O$, Na_2HPO_4 (anhydrous), and $Na_2HAsO_4 \cdot 7H_2O$ were Baker Analyzed Reagents. $H_3PO_4 \cdot 12MoO_3 \cdot 24H_2O$ was obtained from Hopkin & Williams Ltd. (analytical reagent).

Nitron (Eastman Organic Chemicals; for chemical purposes). 0.7802 g of nitron and 7 ml of N acetic acid were dissolved in water and made up to 250 ml to give a 0.01 M solution. More dilute solutions were prepared from the stock solution. All solutions were kept in dark brown bottles.

Procedures

(1) Determination of phosphoric acid

10 ml of aqueous solution containing 0.03–0.08 mg of phosphorus (1.5–5 ml of

0.0005 *M* H_3PO_4), 1 ml of 0.1 *M* sodium molybdate and 3.5 ml of 2 *N* hydrochloric acid, were titrated with an aqueous 0.0025 *M* solution of nitron.

Remarks: (a) The hydrochloric acid may be replaced by nitric acid. (b) The analysed solution may contain a 100–200-fold molar excess of the following metals as chlorides, nitrates or sulphates: calcium, barium, magnesium, zinc, manganese, nickel, cobalt (× 50), uranium(VI) (× 10), aluminium, iron, chromium(III) (× 40), cadmium, copper, lead, mercury(II) (× 20), silver, zirconium (× 20), thorium (× 20). Iodide (× 4), silicic acid (× 8), pyrophosphate (× 4) or tartrate (× 40) can also be tolerated.

(2) Determination of arsenic acid

10 ml of aqueous solution containing 0.06–0.16 mg of arsenic (1.5–5 ml of 0.0005 *M* Na_2HAsO_4), 1 ml of 0.1 *M* sodium molybdate and 2 ml of 2 *N* hydrochloric acid, were titrated with an aqueous 0.0025 *M* solution of nitron.

(3) Determination of mixtures of phosphoric and arsenic acids

A rough determination of both acids in one titration was carried out as follows: 10 ml of an aqueous solution of a mixture of both acids, containing about 5–6 ml of 0.0005 *M* acids, 1 ml of 0.1 *M* sodium molybdate and 2 ml of 2 *N* hydrochloric acid, were titrated with an aqueous 0.0025 *M* solution of nitron.

RESULTS AND DISCUSSION

A selection of experiments carried out, their composition and the results obtained are compiled in Tables I and II. Some special experiments are shown in Figs. 1 and 2.

Most of the experiments were carried out with 10 ml of test solution containing a constant amount of phosphoric acid and an approximately 40-fold molar excess of sodium molybdate. The mineral acid concentration in the titrated solutions was studied in detail. From the results given in Table I (exps. 1–10 and 19–24), it can be concluded that the reaction studied was very sensitive to the acid concentration. Thus at 0.3 *N* hydrochloric acid, the end-point occurred at the right place but the maximum density value and consequently the sensitivity were lower than usual, although the titration time was normal. The highest sensitivity combined with a

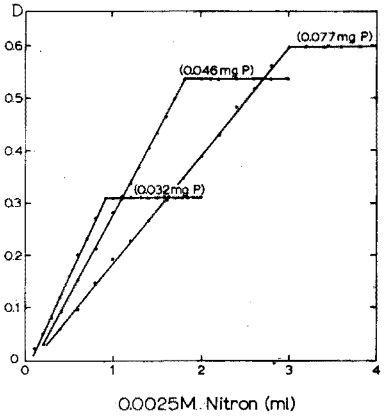

Fig. 1. Titration curves of phosphoric acid containing various amounts of phosphorus. Composition: 1 ml 0.1 *M* Na_2MoO_4 + *a* ml 0.0005 *M* Na_2HPO_4 + 3.5 ml 2 *N* HCl + (5.5-*a*) ml H_2O.

TABLE I

DETERMINATION OF PHOSPHORIC ACID

General composition: *a* ml 0.1 *M* Na_2MoO_4 + *b* ml 0.0005 *M* Na_2HPO_4 + *c* ml *M* HCl + *d* ml supplements + ad 10 ml H_2O + *x* ml 0.0025 *M* nitron ($T = 20°$) (P = H_3PO_4; N = nitron; i = intersection point; h = horizontal maximum density line)

Exp. No.	*Na_2MoO_4 ml*	*Na_2HPO_4 ml*	*HCl ml*	*Supplements*	*Nitron (ml) at*		*Molar ratios* $[P]:[N]$	*Maximum density value*	*Titration time (min)*	*Remarks*
					Intermediate points	*End-point*				
1	1	5	1 ml *M*			i 7.5 h	1 : 7.5	0.77	29	
2	1	5	2 ml *M*		3.4	i 5.2 h	1 : 3.4 → 1 : 5.2	0.47	29	
3	1	5	1.5 ml 2 *M*			i 2.98 h	1 : 3	0.35	17	
4	1	5	2 ml 2 *M*			i 2.98 h	1 : 3	0.32	9	
5	1	5	2.5 ml 2 *M*			i 3.02 h	1 : 3	0.37	10	
6	1	5	3 ml 2 *M*			i 3.05 h	1 : 3	0.47	15	
7	1	5	3.5 ml 2 *M*			i 3.00 h	1 : 3	0.60	15	Linear increase till the max. point
8	1	5	4 ml 2 *M*		2.0	i 3.1 h	1 : 2 → 1 : 3	0.70	16	
9	1	5	2.25 ml 4 *M*		~1.5; 2.8	i 3.4 h	1 : 1 → 1 : 2 → 1:3	0.65	31	
10	1	5	2.5 ml 4 *M*		1.3; 2.7	i 3.4 h		0.58	51	No sure titration
11	1	5	3.5 ml 2 *M*	1 ml 0.1 *M* Na_3-citrate		>5		0.0		
12	1	5	3.5 ml 2 *M*	1 ml 0.1 *M* Na_2-tartrate		3.00	1 : 1 → 1 : 2 → 1:3	0.67	33	
13	1	3	3.5 ml 2 *M*			i 1.84 h		0.53	15	
14	1	1.5	3.5 ml 2 *M*			i 0.90 h		0.33	11	
15	1		2–4 ml 2 *M*			>5		0.0		No ppt.
16	1.25	5	3.5 ml 2 *M*			i 2.97 h		0.48	20	
17	1.5	5	3.5 ml 2 *M*			i 2.98 h		0.41	15	No sure reading
18	2.0	5	3.5 ml 2 *M*			i 2.95 h		0.30	25	
19	1	5		3.5 ml 2 *M* HNO_3	~1.95	i 3.00 h		0.65	12	
20	1	5		2 ml 4 *M* HNO_3	1.8	i 3.00 h[a]		0.67	10	
21	1	5		2.5 ml 4 *M* HNO_3						Slow, no sure titration
22	1			4 ml *M* HNO_3					3	Till 2.5 ml no ppt.
23				4 ml *M* HNO_3		>5		0.0	5	
24	0.5			2 ml *M* $CH_2ClCOOH$		i 5.8 h		0.53	8	No reproducible results

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[a] Slight increase.

TA

DETERMINA

General composition: *a* ml titrated solution + (10
Na_2MoO_4; PMo = phosphomolybdic acid;
h = horizontal maxi

Exp. No.	*Solution titrated*
1	1 ml 0.1 *M* Mo + 1 ml *M* HCl
2	1 ml 0.1 *M* Mo + 2 ml *M* HCl
3	1 ml 0.1 *M* Mo + 3 ml *M* HCl
4	1 ml 0.1 *M* Mo + 1 ml *M* HCl + 5 ml 0.0005 *M* P
5	1 ml 0.1 *M* Mo + 2 ml *M* HCl + 5 ml 0.0005 *M* P
6	2 ml 0.0025 *M* PMo + 2 ml *M* HCl[a]
7	2 ml 0.0025 *M* PMo + 2 ml *M* $CH_2ClCOOH$[a]
7a	2 ml 0.0025 *M* PMo + 2 ml *M* CH_3COOH[a]
8	2 ml 0.0025 *M* PMo + 2 ml *M* HCl + 5 ml 0.01 *M* Na_3-citrate
9	2 ml 0.0025 *M* PMo + 2.5 ml 4 *M* HCl[a]
10	0.5 ml 0.2 *M* Mo + 3.5 ml 2 *M* HCl + 5 ml 0.0005 *M* P + 1 ml waterglass 0.1 *M* (0.1 *M* Na_2
11	0.5 ml 0.2 *M* Mo + 3.5 ml 2 *M* HCl + 5 ml 0.0005 *M* P + 1 ml waterglass 0.02 *M*
12	0.5 ml 0.2 *M* Mo + 3.5 ml 2 *M* HCl + 5 ml 0.0005 *M* P + 1 ml 0.01 *M* KI
13	0.5 ml 0.2 *M* Mo + 3.5 ml 2 *M* HCl + 5 ml 0.0005 *M* P + 1 ml 0.01 *M* $Na_4P_2O_7$
14	1 ml 0.1 *M* Mo + 1 ml *M* HCl + 5 ml 0.0005 *M* As
15	1 ml 0.1 *M* Mo + 2 ml *M* HCl + 5 ml 0.0005 *M* As
16	1 ml 0.1 *M* Mo + 3 ml *M* HCl + 5 ml 0.0005 *M* As
17	1 ml 0.1 *M* Mo + 4 ml *M* HCl + 5 ml 0.0005 *M* As
18	1 ml 0.1 *M* Mo + 5 ml *M* HCl + 5 ml 0.0005 *M* As
19	1 ml 0.1 *M* Mo + 6 ml *M* HCl + 5 ml 0.0005 *M* As
20	1 ml 0.1 *M* Mo + 7 ml *M* HCl + 5 ml 0.0005 *M* As
21	1 ml 0.1 *M* Mo + 3 ml *M* HCl + 6 ml 0.0005 *M* As
22	1 ml 0.1 *M* Mo + 2 ml 2 *M* HCl + 2 ml 0.0005 *M* As + 4 ml 0.0005 *M* P
23	1 ml 0.1 *M* Mo + 2 ml 2 *M* HCl + 3 ml 0.0005 *M* As + 3 ml 0.0005 *M* P
24	1 ml 0.1 *M* Mo + 2 ml 2 *M* HCl + 5 ml 0.0005 *M* As + 1 ml 0.0005 *M* P

[a] 0.005 *M* nitron.

clear and reproducible end-point was obtained at *ca.* 0.7 *N* hydrochloric acid. On further increase of the acid concentration to 0.9–1.0 *N* new undesirable effects were obtained: the readings of the galvanometer and the end-points were displaced. Simultaneously the titration time increased very considerably with the increase in acidity, although the maximum density value remained high. All these effects made titrations at these acid concentrations no longer possible and it was advisable not to work near these critical acid concentrations. Fig. 1 and experiments 7, 13 and 14 of Table I, show the changes in the maximum density values with increasing amounts of phosphorus analysed. The titration sensitivity was high in the region 0.03–0.05 mg of phosphorus (per 10 ml volume). This did not affect the precision of the determination, which was obviously of the same order even if 0.1 mg of phosphorus was analysed.

Influence of acids

No essential differences in the results were found within the acid concentrations

ARSENIC ACID

H_2O + x ml 0.0025 M nitron (T = 20°) (Mo =
$_4$HPO$_4$; As = Na_2HAsO_4; i = intersection point;
nsity line: c = contact point)

Nitron (ml) at		*Calculated molar ratios* $[P]$ *or* $[As]:[N]$	*Maximum density value*	*Titration time (min)*	*Remarks*
Intermediate points	*End-point*				
	~ 5.0		0.70	45	No reliable readings
	> 6.0		>0.60	60	No reliable readings
					Practically no ppt.
	~ 5.0		>0.70	30	No reliable readings
	> 6.0		>0.60	>60	No reliable readings
	i 3.00 h		0.6	7	Linear course till end-point
	i 3.00 h		0.70	11	Linear course till end-point
	i 3.0		0.75	12	Linear course till end-point
					Bad titration (till 1 ml 0.1 density)
					Low density, no end-point
	3.45		0.63	20	
	i 3.00 h		0.60	20	Linear course till end-point
(1.75)	3.05		0.54	19	
1.0; 1.6; c 2.1	i 2.94 h		0.73	20	Not very certain readings
6.1	i 7.75 h		0.80	20	
0.8; 2.45	i 3.85 h		0.70	8	
1.5	i 3.00 h	2 : 3 → 1 : 3	0.68	17	
1.0; 1.83	i 3.0	1 : 1 → ~ 1 : 2 → 1 : 3	0.61	18	
1.2; 2.2	i 2.98	1 : 1 → 1 : 2 → 1 : 3	0.59	42	
					Titration time too long
					Titration time too long
(1.2); 2.1	3.6	1 : 1 → 1 : 2 → 1 : 3	0.80	27	
i 2.3	3.74		0.53	13	
1.7	3.66		0.57	16	
~0.7; 1.55; 2.6	i 3.8		0.79	27	

used, whether hydrochloric or nitric acid was present. Hydrochloric acid was preferred, because less interference would be expected in the presence of foreign salts or other compounds.

Table I shows the following results. Within the range of 0.1 to 0.2 N hydrochloric acid, the solutions containing mixtures of phosphoric and molybdic acids could be titrated with nitron, but no reliable and strictly reproducible galvanometer readings could be obtained (Table I, exps. 1–2). When parallel titrations of molybdic acid solutions in the presence and absence (Table II, exps. 1–5) of phosphoric acid were carried out it seemed as if the phosphoric acid did not participate in these titrations (at least in exp. 1); probably the isopolymolybdate was titrated, giving an insoluble nitron compound. The same thing happened when arsenic acid was substituted for phosphoric acid (see Table II, exps. 14–15). These measurements were not examined further. From Table II, exp. 3, it is clear that this side-reaction with molybdic acid was entirely cancelled in a 0.3 N hydrochloric acid solution. As soon as this occurred, a normal titration of the nitron–phosphomolybdic acid was possible (Table I, exps. 3–7), and the final compound nitron_3–(phosphomolybdic $\text{acid})_1$ was obtained.

The results of parallel titrations of analytical grade phosphomolybdic acid with nitron at low hydrochloric acid concentrations, are interesting. In these experiments the amount of phosphorus remained the same as in the other experiments (see Table II, exps. 6–7a). In contrast to the analogous experiments with mixtures of phosphoric and molybdic acids, entirely normal titrations were obtained independent of the presence of hydrochloric acid or acetic acid. It appears that the velocity of the formation of the phosphomolybdic acid from the components is small in 0.1–0.2 *N* hydrochloric acid solution compared with the velocity of formation of isopolymolybdic acid. In 0.2 *N* hydrochloric acid solution, we may already have a mixed precipitate of both the isopolymolybdic and the heteropoly acids with nitron.

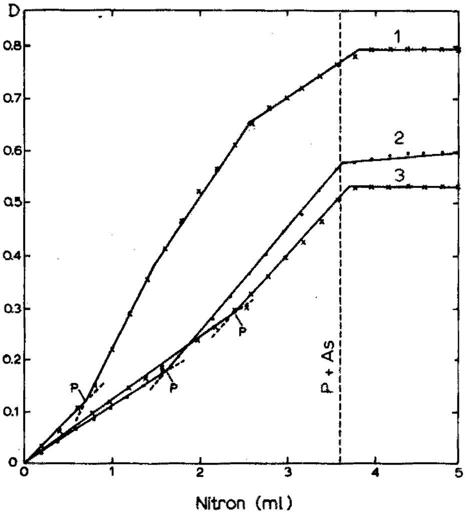

Fig. 2. Titrations of mixtures of phosphoric and arsenic acids. 1. 1 ml 0.1 *M* Na_2MoO_4 + 2 ml 2 *N* HCl + 1 ml 0.0005 *M* Na_2HPO_4 + 5 ml 0.0005 *M* Na_2HAsO_4 + 1 ml H_2O. 2. 1 ml 0.1 *M* Na_2MoO_4 + 2 ml 2 *N* HCl + 3 ml 0.0005 *M* Na_2HPO_4 + 3 ml 0.0005 *M* Na_2HAsO_4 + 1 ml H_2O. 3. 1 ml 0.1 *M* Na_2MoO_4 + 2 ml 2 *N* HCl + 4 ml 0.0005 *M* Na_2HPO_4 + 2 ml 0.0005 *M* Na_2HAsO_4 + 1 ml H_2O.

Influence of foreign salts

The effect of many different salts was tested; no interference was found when the foreign salts were present in the following concentrations (which were mostly not critical):

At 0.2 *M* concentration: $CaCl_2$, $MgCl_2$, $Mg(NO_3)_2$; at 0.1 *M* concentration: $BaCl_2$; at 0.05 *M* concentration: $ZnSO_4$, $Zn(NO_3)_2$, $MnSO_4$, $Ni(NO_3)_2$, $Al_2(SO_4)_3$, $FeCl_3$, $Cd(NO_3)_2$, $CuCl_2$, $Pb(NO_3)_2$ (in HNO_3); at 0.0125 *M* concentration: $CoCl_2$; at 0.01 *M* concentration: $CrCl_3$; at 0.005 *M* concentration: $HgCl_2$ and $Hg(NO_3)_2$ (in HNO_3), $AgNO_3$, $ZrO(NO_3)_2$ and $Th(NO_3)_4$; and at 0.0025 *M* concentration: $UO_2(NO_3)_2$.

Even at the lowest concentrations used, the foreign salt made up a 10–20-fold molar excess over the phosphoric acid analysed. With regard to the effect of anions, the interference of citrate was much greater than that of tartrate, which did not interfere up to 0.01 *M* concentrations. Iodide did not interfere in a 10-fold molar excess, silicic acid in an 8-fold excess, or pyrophosphate in a 4-fold excess.

Influence of excess of molybdate

In almost all our experiments the molybdic acid was in an approximately 40-fold molar excess to the phosphoric acid. Larger excesses of molybdic acid (Table I, exps. 16–18) apparently reduced the maximum density value although the precision of the determination remained unchanged.

Titrations of arsenic acid

Analogously to the experiments with phosphoric acid, some experiments with arsenic acid were also carried out in order to determine the best conditions for such titrations. The compositions and results of some titrations are shown in Table II, exps. 14–24. When only arsenic acid was present it could be titrated as the arsenomolybdate with the same molar sensitivity and precision as phosphoric acid. The optimum hydrochloric acid concentration was different in the two cases (Table II, exps. 16–18). In the case of arsenic acid, less hydrochloric acid was necessary; even at an acidity of 0.5 *N* the titration time was very long, and in 0.6 *N* hydrochloric acid the titration of arsenic acid alone was impossible.

Titrations of mixtures of phosphoric and arsenic acids

When mixtures of the two acids were titrated at the optimum hydrochloric acid concentration for arsenic acid, the highest density values were obtained if the solutions contained mainly arsenic acid (Table II, exp. 24). Two critical points were of analytical value: the first and the last points of the curve. The first point, with the lowest density value, always indicated the amount of phosphoric acid present, while the last point (which coincided with the first maximum density point) corresponded to the sum of the phosphoric and arsenic acids present (Table II, exps. 22–24). Fig. 2 shows the course of such titrations. The titrations of mixtures were not reliable enough and the points were not precise. A further investigation of the optimum working conditions must be carried out.

SUMMARY

The precipitation of phosphomolybdate or arsenomolybdate with nitron was studied by heterometry at various acidities. A rapid and precise heterometric method is presented for the determination of 0.03–0.08 mg of phosphorus (or 0.06–0.16 mg of arsenic). Foreign salts can be tolerated often in 100–200-fold molar amounts. No interference is caused by Ca, Ba, Mg, Zn, Cr^{3+}, Fe, Mn, Co, Ni, Al, U(VI), Cd, Cu, Pb, Hg^{2+}, Ag, Zr or Th. Iodide, silicic acid, tartrate or pyrophosphate can also be tolerated.

The titration time is 10–15 min and the error is usually less than 1%.

RÉSUMÉ

Une méthode hétérométrique, précise et rapide, est décrite pour le dosage de petites quantités de phosphore (0.03–0.08 mg) et d'arsenic (0.06–0.16 mg), sous forme de phospho- et d'arséniomolybdate. On procède par titrage au moyen d'une solution de nitron.

ZUSAMMENFASSUNG

Beschreibung einer heterometrischen Methode zur Bestimmung von Spuren von Phosphor und Arsen in Form ihrer Heteropolysäuren durch Titration mit einer Nitronlösung.

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STUDIES ON COORDINATION POLYMERS

PART II. COORDINATION POLYMERS OF 1,6-DIHYDROXYPHENAZINE*

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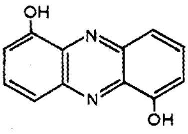
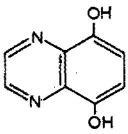
In the preceding paper of this series[1] we described the preparation of the coordination polymers of 8,8'-dihydroxy-5,5'-biquinolyl with six divalent metal ions. In this paper, coordination polymers of 1,6-dihydroxyphenazine (I) with copper(II), zinc(II), nickel(II), cobalt(II) and mercury(II) ions are described.



(I)



(II)

An organic compound very similar to (I) is 5,8-dihydroxyquinoxaline (II) which produces a colored precipitate with many metal ions[2]. The structure of (I) is similar to that of (II) with the exception that (I) has one additional aromatic ring and the hydroxyl groups are widely separated from each other, a desirable criterion for the formation of coordination polymers. Another expected advantage of the use of (I) as the coordinating agent stems from the fact that (I) is less reactive to oxidation than (II) and consequently, coordination polymers of greater thermal stability would be expected with (I) than with (II).

There is no indication in the literature regarding the use of (I) as a coordinating agent for the preparation of polymers or its possible use as an analytical reagent with the following exception. Kidani[3] studied some properties of the copper chelate of (I) and its di-N-oxide in solution by a spectrophotometric method, while Akabori and

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* This paper is a part of the Ph.D. dissertation of A. Alam at Louisiana State University (1962).

NAKAMURA[4] reported that (I) in alcoholic solution produces a colored precipitate with copper(II), silver(I) and lead(II).

Since two oxine functions are present in the structure of (I) it could be assumed that like 8,8′-dihydroxy-5,5′-biquinolyl, (I) will also form coordination polymers of interesting properties.

EXPERIMENTAL

Preparation of 1,6-dihydroxyphenazine

1,6-Dihydroxyphenazine (I) was derived from 1,6-dimethoxyphenazine (III) (prepared following a method described by PACHTER AND KLOETZEL[5]) by refluxing (III) with hydrobromic and glacial acetic acids for 24 h[6]. Golden yellow needles were obtained after two recrystallizations from ethyl acetate. M.p. 274–275° (decomp.). (Calculated for $C_{12}H_8O_2N_2$: C, 67.90%; H, 3.78%; N, 13.20%. Found: C, 67.42, 67.30%; H, 3.78, 3.75%; N, 13.01, 13.18%.)

Preparation of coordination polymers

Preparation of the coordination polymers was performed by the following two methods.

(*1*) An equimolar mixture of (I) and the appropriate metal acetate was refluxed in an alcohol–dimethylformamide (1 : 1) mixture in a nitrogen atmosphere for about 3–4 h to ensure completion of the reaction. The hot reaction mixture was then filtered and the precipitate was treated with boiling water and alcohol, washed with ethyl ether and dried under vacuum over boiling acetone (56°) for 12 h. The dried product was then kept in a desiccator until submitted for analysis.

(*2*) An equimolar mixture of (I) and the metal acetylacetonate was heated at 230–240° in a condensation tube for 3–4 h under vacuum. The reaction mixture was then washed with hot *p*-xylene, water and alcohol in sequence to free it of the starting material. The residue then was washed with ethyl ether and dried under vacuum over boiling acetone for 12 h. The polymer of (I) with copper was prepared by this method.

Experimental procedures

Elemental analysis methods and infrared, X-ray and thermal studies were similar to those described in Part I of this study. Results are reported in Tables I and II.

TABLE I

COMPOSITION OF THE COORDINATION POLYMERS OF 1,6-DIHYDROXYPHENAZINE ON THE BASIS OF STRUCTURE (IV)

Polymer	*Carbon%*		*Hydrogen%*		*Nitrogen%*		*Metal%*	
	Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
Copper	52.65	49.37	2.21	2.51	10.20	9.33	23.19	22.39
Copper[a]	52.65	47.32	2.21	2.55	10.20	8.96	23.19	21.29
Zinc	52.30	47.75	2.20	2.90	10.17	9.06	23.72	24.14
Cobalt	53.54	47.09	2.25	2.83	10.41	9.15	21.90	20.41
Nickel	53.59	47.97	2.25	3.08	10.42	9.05	21.83	19.58
Mercury	35.07	30.23	1.46	1.52	6.87	6.34	48.84	48.07

[a] Polymer prepared by melt polymerization reaction (method 2).

TABLE II

PERCENTAGE WEIGHT LOSS OF COORDINATION POLYMERS OF 1,6-DIHYDROXYPHENAZINE WHEN HEATED IN AIR

Polymer	*Temperature(°)*						
	110	*150*	*175*	*200*	*230*	*260*	*280*
Copper	0.54	0.54	0	1.65	21.30(d)[a]		
Zinc	1.68	1.68	0	0	0.02	4.18	18.27(d)
Cobalt	2.80	0.81	0	0	38.98(d)		
Nickel	2.99	2.35	0	2.99	14.90(d)		
Mercury	0.79	1.56	1.18	25.95(d)			

[a] (d) indicates decomposition of the polymer.

Spot test procedure

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

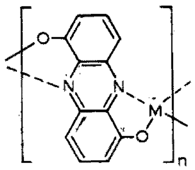
TABLE III

SPOT TEST FOR METAL IONS WITH 1,6-DIHYDROXYPHENAZINE

Metal ion	*Color of precipitate*	*Identification limit in µg*	*Metal ion*	*Color of precipitate*	*Identification limit in µg*
Aluminum(III)	Greenish yellow	>100	Cadmium(II)	Light blue	>100
Gold(III)	Greenish black	10	Cobalt(II)	Bluish purple	30
Zinc(II)	Bluish purple	4	Nickel(II)	Blue	50
Lead(II)	Blue	50	Indium(III)	Blue	100
Copper(II)	Blue	10	Iron(II)	Blue	>100
Mercury(II)	Bluish green	5	Iron (III)	Green	>100
Manganese(II)	Bluish green	>100	Silver(I)	Violet turning black	>100
Gallium(III)	Blue	5			

DISCUSSION

As in the case of 8,8′-dihydroxy-5,5′-biquinolyl, polymerization of (I) with divalent metals would be expected to give polymers of the structure of the type represented as follows:



(IV)

The infrared spectra of all the polymers obtained in this research were in close conformity with the above-postulated structure. In all the cases the infrared spectra of the derived polymers resemble one another more closely than they do the spectrum of (I). However, the spectrum of the copper polymer of (I) deserves some special attention. A strong absorption band at 1455 cm^{-1} which appears in the absorption spectrum of the copper polymer of (I) does not appear in the spectra of the other polymers. This band might correspond either to the strong absorption band at 1484 cm^{-1} or 1445 cm^{-1}

in the spectrum of (I). Similarly a medium absorption band at 1058 cm^{-1} found in the spectrum of the copper polymer of (I) does not appear in any other polymer. Since these peaks do not appear in any other polymer, they may have some analytical potentialities.

Since two oxine functions are present in the structure of (I), the bands due to the vibrations of the $-\mathrm{O}-\mathrm{C}<$ and $-\mathrm{C}=\mathrm{N}-$ bond can be interpreted in the same fashion as in the case of the coordination polymers of 8,8'-dihydroxy-5,5'-biquinolyl. Thus the medium strong absorption band which is observed in the 1125–1135 cm^{-1} region in all the coordination polymers of (I) could be assigned to the $\mathrm{M}-\mathrm{O}-\mathrm{C}<$ bond in the same way as it was attributed to the coordination polymers of 8,8'-dihydroxy-5,5'-biquinolyl[1] or the chelates of 8-hydroxyquinoline[7]. Position of the $-\mathrm{C}=\mathrm{N}-$ vibration of the phenazine ring in (I) could be assigned to both the absorption peaks found in the 1642 cm^{-1} and in the 1530 cm^{-1} region. In the chelated species these bands are shifted to 1592–1610 cm^{-1} and 1518–1520 cm^{-1} respectively.

In the preparation of the polymers of (I) with various divalent metal ions, precipitation was almost immediate when the alcohol : dimethylformamide solution of (I) was added to the appropriate metal acetate solution in alcohol : dimethylformamide. All polymers obtained in this investigation were bluish-black to black powders. The presence of a system of conjugated double bonds in the polymer structure would possibly account for this color.

All polymers were insoluble in the common organic solvents, and most probably were of low molecular weights, since their low solubility would remove them from solution before a high degree of polymerization was reached. The insolubility of these compounds however, prevented a determination of molecular weight by the usual procedures.

An attempt was made to prepare a coordination polymer of (I) with copper acetylacetonate by a melt polymerization technique, with a hope to obtain a coordination polymer of high molecular weight, but such an approach was not successful. This is evident from the results shown in Table I. Much lower values for the elemental analyses were obtained for the coordination polymer of (I) with copper prepared by melt polymerization than for that prepared in solution, which shows the coefficient of polymerization[8] to be low. In the former case it was found to be 9 whereas it was 20 for the latter. This clearly indicates the superiority of the solution reaction polymerization over the melt polymerization technique for the preparation of this particular type of coordination polymer. Thus during this investigation, the method of solution reaction polymerization was employed for the preparation of polymers of (I) with various divalent metal ions.

From Table I, it is evident that only in the case of mercury is the degree of polymerization quite large compared to that observed for the other coordination polymers of (I).

Anomalies in the values of the elemental analyses are possibly due to the fact that mixtures of compounds were formed along with the desired polymer product. However, agreement between calculated and found analysis values for the 1 : 1 compounds can be improved if it is presumed that there is water associated with the polymers. This assumption is reasonable, since metal atoms are present in the polymer chain and water of crystallization is possible. Thus if 0.5 mole of water per metal atom in the polymer chain is considered for the copper compound and 1 mole each for zinc and mercury compounds then the elemental results could be improved greatly for the 1 : 1 compound in these cases. In order to verify this assumption a sample of polymer of (I) with copper was heated under vacuum at 196–200° for 24 h; a weight loss of only 2.85% was observed. The metal content of the dehydrated polymer was found to be 22.78% of copper. Calculations for the 1 : 1 compound with 0.5 mole of water per metal atom in the polymer chain require 3.19% of water. The percentage of copper for the dehydrated compound is 23.19. These values are however, comparable with the values obtained in the thermal degradation of the polymers shown in Table II. In case of nickel and cobalt polymers, two moles of water per metal atom in the polymer chain can be assumed safely because of their maximum coordination number six. This greatly improves the elemental results of these compounds for a 1 : 1 product (Table IV).

TABLE IV

COMPOSITION OF POLYMERS OF 1,6-DIHYDROXYPHENAZINE WITH COBALT AND NICKEL ON THE BASIS OF TWO WATER MOLECULES PER METAL ATOM

Polymer	*Carbon%*		*Hydrogen%*		*Nitrogen%*		*Metal%*	
	Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
Cobalt	47.21	47.09	3.26	2.83	9.11	9.15	19.32	20.41
Nickel	47.26	47.97	3.25	3.08	9.18	9.05	19.26	19.58

The behaviour of these coordination polymers on being heated in air at different temperatures is shown in Table II. It was expected that the coordination polymers would be thermally more stable than the parent organic reagent, but this property was not apparent in any of these coordination polymers. However, the decomposition ranges of these polymers were found to be between 175–240°. From Table II, it appears that the thermal degradation of these polymers depends largely on the nature of the metal present in the polymers. Thus while copper, zinc, cobalt and nickel polymers were found to be stable at 200° for 4 h, the mercury polymer was completely decomposed at this temperature. This may be an indication that at higher temperatures the mercury(II) ion is reduced more rapidly than any of the other above-mentioned ions. Further evidence for this is our failure to prepare a coordination polymer of (I) with silver(I). The product which formed was decomposed very rapidly in the reaction flask, as shown by the color change from violet-green to black. This was further verified from the infrared spectrum of the resulting product.

To test the reliability of the data of Table II, samples of copper and zinc polymers of (I) were heated separately in air at 190° and at 240° respectively for 6 h. Pre- and post-heating infrared spectra were found to be identical in both cases. Thus during this and the previous investigation[1], it was observed that the zinc-containing polymer was most stable. The reason may be that zinc has only one oxidation state and also that the proportion of organic materials in the polymer was found to be minimum.

X-ray examinations of the coordination polymers of (I) showed that the polymers containing cobalt and mercury are amorphous, whereas polymers containing copper, zinc and nickel are crystalline. Fig. 1 shows the X-ray powder diffraction photograph of the polymer of (I) with zinc as an example. The crystalline character of these materials is not, however, obvious from visual inspection of the finely powdered polymers.

Spot tests for the metal ions with alcoholic solutions of (I) show a wide precipitation ability of the reagent in acetic acid–acetate buffer (Table III). But its sensitivity and selectivity are not very impressive for analytical purposes. However, zinc could be detected at a concentration of 4 µg in acetic acid–acetate buffer solution.

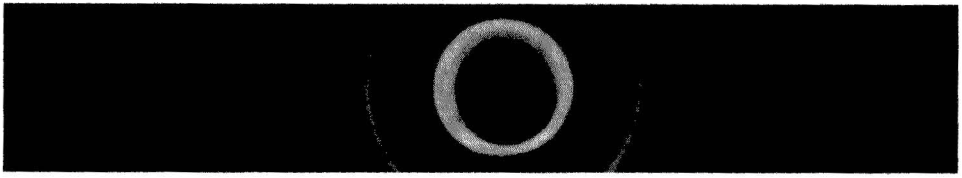


Fig. 1. X-ray powder diffraction photograph of coordination polymers of 1,6-dihydroxyphenazine with zinc.

SUMMARY

Coordination polymers of 1,6-dihydroxyphenazine (I) with Cu(II), Zn(II), Ni(II), Co(II) and Hg(II) were prepared and studied. All the polymers formed were dark blue to black powders, very insoluble in the common solvents, apparently of low molecular weight, and decomposed at temperatures ranging from 200 to 280°. The zinc polymer was the most stable, mercury the least. Infrared studies confirmed the proposed chelation reaction between the metal ion and (I). The polymers of Co and Hg were amorphous, whereas those of Cu, Zn, and Ni were crystalline. When used as a spot test reagent, (I) gave instant color reactions with 15 common ions but neither the sensitivity nor selectivity of the reagent is impressive.

RÉSUMÉ

Une étude a été effectuée sur les polymères de coordination de la dihydroxy-1,6-phénazine avec le cuivre, le nickel, le cobalt et le mercure. Leur coloration va du bleu foncé au noir. Ils sont insolubles dans les solvants courants, et décomposés entre 200 et 280°. Le complexe du zinc est le plus stable, celui du mercure le moins. La dihydroxy-1,6-phénazine donne des réactions colorées avec 15 ions.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Koordinationspolymere von 1,6-Dihydroxyphenazin mit Kupfer, Nickel, Kobalt und Quecksilber. Farbe, Löslichkeit und Zersetzungstemperaturen der Polymere werden angegeben. Das Reagenz gibt Farbreaktionen mit zahlreichen Ionen.

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SYSTEMATIC STUDY OF THE SOLVENT EXTRACTION OF METAL OXINATES

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In recent years a number of investigations concerning the solvent extraction of metal oxinates have been reported but only a few theoretical studies have been made[1-6]. For this reason a systematic study of the extraction of 32 metals with solutions of oxine (8-hydroxyquinoline) in chloroform has been carried out in our laboratory. From these results the extraction constants of metal oxinates and the stability constants of metal complexes with oxalic acid (H_2Oxal), tartaric acid (H_2Tart), hydrocyanic acid (HCN), nitrilotriacetic acid (H_3X), ethylenediaminetetraacetic acid (H_4Y) and 1,2-diaminocyclohexanetetraacetic acid (H_4Z) have been calculated.

THEORY

The solvent extraction of metals by a solution of oxine (HOx) in chloroform can be in general described by the following equation:

$$M^{N+} + (N + r)(HOx)_{org} = (MOx_N(HOx)_r)_{org} + NH^+ \qquad (1)$$

with the equilibrium constant K_0 (extraction constant)

$$K_0 = \frac{[MOx_N(HOx)_r]_{org}[H^+]^N}{[M^{N+}][HOx]_{org}^{N+r}} \qquad (2)$$

where the subscript org denotes the organic phase.

If the metal is present in the aqueous phase exclusively as the metal ion M^{N+}, then

$$K_0 = q_0 \frac{[H^+]^N}{[HOx]_{org}^{N+r}} \qquad (3)$$

where q_0 is the distribution ratio of the metal in the absence of complexing agent.

For the determination of the composition (*e.g.* N and the value of r) and the extraction constants K_0, it is also necessary to find q_0 values at various pH values and at various equilibrium concentrations of oxine.

At pH 4–11 the equilibrium concentration of oxine in the organic phase is practically equal to the initial concentration. If the pH value is outside these limits, the equilibrium concentration of oxine in the organic phase is decreased by dissociation and by the association of hydrogen ions to the oxine molecule.

In Fig. 1 the logarithm of the equilibrium oxine concentration $[HOx]_{org}$ is plotted against pH values (the initial oxine concentration was 0.010 M). The experimental results, determined in the present paper, are in full agreement with the theoretical curve (see Fig. 1) calculated from DYRSSEN's investigations[7].

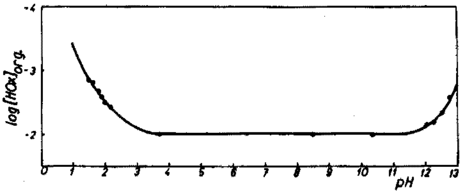

Fig. 1. Effect of pH on the equilibrium oxine concentration in chloroform, $[HOx]_{org}$ (initial oxine concentration, 0.010 M).

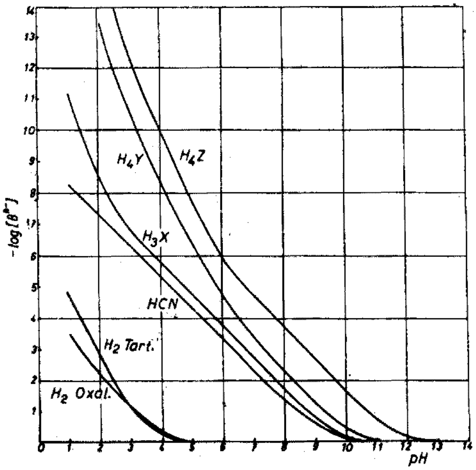

Fig. 2. Effect of pH on equilibrium anion $[B^{n-}]$ concentration (H_2Oxal = oxalic acid; H_2Tart = tartaric acid; HCN = hydrocyanic acid; H_3X = nitrilotriacetic acid; H_4Y = ethylenediaminetetraacetic acid; H_4Z = 1,2-diaminocyclohexanetetraacetic acid).

If the metal is present in the aqueous phase in a hydrolysed form, it is necessary to make hydrolysis corrections for the determination of K_0.

Equation (2) can be rearranged as follows:

$$\log K_0 = \log K_N \cdot Q_N - (N + r) \log q_{HOx} - N \cdot pK_{HOx} \tag{4}$$

where

$$K_N = \frac{[MOx_N(HOx)_r]}{[M^{N+}][Ox^-]^N[HOx]^r} \tag{5}$$

$$Q_N = \frac{[MOx_N(HOx)_r]_{org}}{[MOx_N(HOx)_r]} \tag{6}$$

$$K_{HOx} = \frac{[H^+][Ox^-]}{[HOx]} \tag{7}$$

$$q_{HOx} = \frac{[HOx]_{org}}{[HOx]} \tag{8}$$

From the known extraction constant K_0, from the dissociation constant of oxine ($pK_{HOx} = 9.71$) and from the distribution coefficient of oxine ($\log q_{HOx} = 2.66$) it is possible to calculate from eqn. (4) the two phases stability constant

$$Q_N \cdot K_N = \frac{[MOx_N(HOx)_r]_{org}}{[M^{N+}][Ox^-]^N[HOx]^r}$$

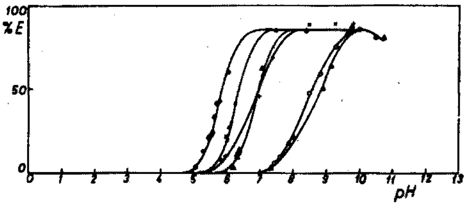

Fig. 3. Effect of pH on extraction of Be^{2+} by 0.100 M oxine in chloroform. ● in the absence of complexing agent, △ in the presence of 0.010 M H_2Oxal, × in the presence of 0.010 M H_2Tart, □ in the presence of 0.010 M HCN, + in the presence of 0.010 M H_3X, ○ in the presence of 0.01 M H_4Y, ▲ in the presence of 0.010 M H_4Z.

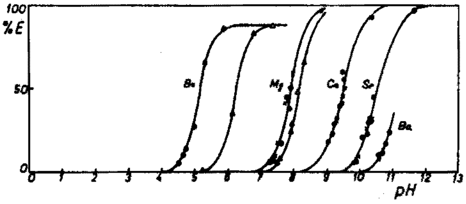

Fig. 4. Effect of pH on extraction of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} by 0.500 M oxine in chloroform (for symbols see Fig. 3).

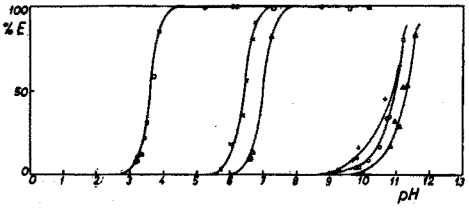

Fig. 5. Effect of pH on extraction of Sc^{3+} by 0.100 M oxine in chloroform (for symbols see Fig. 3).

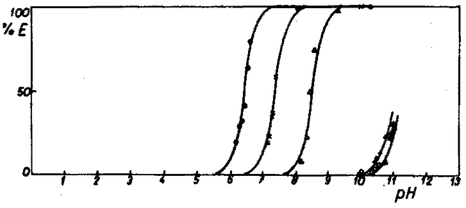

Fig. 6. Effect of pH on extraction of La^{3+} by 0.100 M oxine in chloroform (for symbols see Fig. 3).

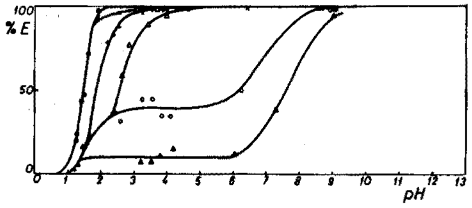

Fig. 7. Effect of pH on extraction of Ti^{4+} by 0.100 M oxine in chloroform (for symbols see Fig. 3).

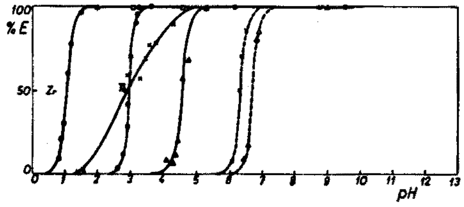

Fig. 8. Effect of pH on extraction of Zr^{4+} and Th^{4+} by 0.100 M oxine in chloroform (for symbols see Fig. 3).

In the presence of a complexing agent H_nB which forms a non-extractable complex $MB_s(OH)_t$, the distribution ratio is generally diminished and the stability of this complex can be calculated from the equation[8]:

$$\frac{q_0}{q} - 1 = \sum_{s=1}\sum_{t=0} K_{s,t}[B^{n-}]^s[OH^-]^t \qquad (9)$$

where q_0 and q are the distribution ratios in the absence and in the presence of complexing agent respectively,

$K_{s,t}$ is the overall stability constant of the metal complex $MB_s(OH)_t$ defined as $K_{s,t} = [MB_s(OH)_t]/[M][B^{n-}]^s[OH^-]^t$, and

B^{n-} is the anion of the complexing agent H_nB.

Equation (9) is valid only for mononuclear complexes; in this case the distribution ratio does not depend on the metal concentration.

Values of q_0 can be calculated for any pH and for any oxine concentration from eqn. (3). For the determination of the stability constant it is also sufficient to find the distribution ratio q at various pH values and at various anion concentrations, $[B^{n-}]$. The last concentration is calculated from the total concentration of complexing agent H_nB and from its dissociation constants. In Fig. 2 is shown the dependence of $\log [B^{n-}]$ on pH value for the complexing agents investigated.

For the calculations the following dissociation constants were used[9]:
oxalic acid: $pK_{H_2Oxal} = 1.25$, $pK_{HOxal^-} = 4.14$
tartaric acid: $pK_{H_2Tart} = 2.88$, $pK_{HTart^-} = 3.94$
hydrocyanic acid: $pK_{HCN} = 9.32$
nitrilotriacetic acid: $pK_{H_3X} = 1.89$, $pK_{H_2X^-} = 2.49$, $pK_{HX^{2-}} = 9.73$
ethylenediaminetetraacetic acid: $pK_{H_4Y} = 1.99$, $pK_{H_3Y^-} = 2.67$,
$pK_{H_2Y^{2-}} = 6.16$, $pK_{HY^{3-}} = 10.26$
1,2-diaminocyclohexanetetraacetic acid: $pK_{H_4Z} = 2.43$, $pK_{H_3Z^-} = 3.52$,
$pK_{H_2Z^{2-}} = 6.12$, $pK_{HZ^{3-}} = 11.70$.

If an insoluble complex M_nB_s is formed, the solubility product S can be calculated from the following equation:

$$\log S = n([MOx_NHOx_r]_{org} - N \cdot pH - \log K_0 - (N + r)[HOx]_{org} + \frac{s}{n} \log [B^{n-}]) \qquad (10)$$

This eqn. (10) is readily obtained by substituting $[M^{N+}]$ from eqn. (2) into the expression for the solubility product.

EXPERIMENTAL

Reagents

All the reagents used were of A.R. purity. Chloroform was purified by washing with concentrated sulphuric acid and concentrated sodium hydroxide solution, followed by distillation. The radioisotopes used were of radiochemical purity.

Procedures

The pH measurements were made with a Radiometer pHM 4b (Copenhagen) equipped with a glass electrode and a saturated calomel electrode as a reference electrode. Spectrophotometric measurements were made on a Zeiss Universal Spectrophotometer. For radiometric measurements an end-window Geiger-Müller counter and a well-type scintillation counter with a NaI(Tl) crystal were used.

Distribution measurements

A solution of oxine in chloroform (5 ml) was shaken on a mechanical shaker with an equal volume of an aqueous phase containing the appropriate metal and complexing agent. The pH was adjusted by addition of potassium hydroxide and perchloric acid, and potassium perchlorate was added to give a constant ionic strength of 0.10 M (except, of course, in experiments below pH 1.2). The aqueous and organic phases were not mutually presaturated before equilibration; volume changes were negligible and were ignored.

After the equilibrium had been reached, the two phases were separated and the concentration of the metal in the organic phase and/or in the aqueous phase was determined spectrophotometrically. The distribution ratio (or the percentage of metal extracted) was then calculated from the known total concentration of metal

($1.0–2.0 \cdot 10^{-4}$ *M*) and from the equilibrium concentration of metal in the aqueous or in the organic phase.

When the radiometric method was used, the distribution ratio was calculated as a ratio of the activity of equal volumes of the organic and aqueous phases.

The analytical methods used in the present work are listed in Table I.

All distribution experiments were carried out at 20°.

Attainment of the extraction equilibrium

The rate of attainment of the extraction equilibrium depends on many factors. Primarily, it depends on the properties of the metal investigated. In the absence of a complexing agent, equilibrium was reached for most of the metals investigated within a few minutes; for nickel(II), palladium(II), molybdenum(VI) and tungsten(VI)

TABLE I

THE ANALYTICAL METHODS USED FOR THE DETERMINATION OF THE DISTRIBUTION RATIO (PERCENTAGE EXTRACTION)

Metal	*Method*
Be	Spectrophotometric as oxinate (380 mμ); spectrophotometric as complex with Eriochrome Cyanine R
Mg	Spectrophotometric as oxinate (380 mμ, 400 mμ)
Ca	Spectrophotometric as oxinate (380 mμ, 400 mμ); radiometric (^{45}Ca)
Sr	Spectrophotometric as oxinate (380 mμ, 400 mμ); radiometric (^{89}Sr)
Ba	Spectrophotometric as oxinate (380 mμ, 400 mμ)
Sc, La, Ti, Zr	Spectrophotometric as oxinate (380 mμ)
Th	Spectrophotometric as oxinate (380 mμ); radiometric (^{234}Th – UX_1)
V	Spectrophotometric as oxinate (550 mμ)
Nb	Spectrophotometric as oxinate (390 mμ)
Cr	Spectrophotometric as oxinate (420 mμ)
Mo	Spectrophotometric as oxinate (380 mμ); radiometric (^{99}Mo)
W	Spectrophotometric as oxinate (380 mμ)
U	Spectrophotometric as oxinate (390 mμ)
Mn	Spectrophotometric as oxinate (395 mμ)
Fe	Spectrophotometric as oxinate (470 mμ, 580 mμ); radiometric (^{59}Fe)
Co	Spectrophotometric as oxinate (400 mμ); radiometric (^{60}Co)
Ni	Spectrophotometric as oxinate (390 mμ)
Pd	Spectrophotometric as oxinate (425 mμ)
Cu	Spectrophotometric as oxinate (400 mμ); radiometric (^{64}Cu)
Ag	Radiometric (^{110}Ag)
Zn, Cd	Spectrophotometric as oxinate (380 mμ); radiometric (^{65}Zn or ^{115}Cd)
Hg	Radiometric (^{203}Hg)
Al	Spectrophotometric as oxinate (390 mμ)
Ga	Spectrophotometric as oxinate (395 mμ); radiometric (^{72}Ga)
In, Tl	Spectrophotometric as oxinate (400 mμ)
Pb	Spectrophotometric as oxinate (400 mμ); radiometric (^{210}Pb – RaD)
Bi	Spectrophotometric as oxinate (390 mμ); radiometric (^{210}Bi – RaE).

the extraction rate is smaller (some hours) and chromium(III) does not react with oxine at room temperature. The achievement of the equilibrium depends also on pH values and on the oxine concentration. In general, it may be said that the rate of the extraction increases with increasing pH values and oxine concentrations.

The presence of tartrate, oxalate and cyanide had little effect on the rate of extraction. The molybdenum(VI)-, tungsten(VI)- and palladium(II)-oxine extractions were the only exceptions. The aminopolycarboxylic acids which formed very stable complexes with the metal investigated were found to reduce substantially the rate of equilibration. The time necessary for reaching equilibrium with bivalent metal ions was some hours; with tri- and tetravalent metal ions it was usually longer. When less stable complexes were formed between the metal ions and the aminopolycarboxylic acid (*e.g.* Be(II), Mo(VI), W(VI), U(VI), V(V), Ag(I)) the presence of the complexing agent had practically no influence on the rate of extraction.

RESULTS AND DISCUSSION

Beryllium

The pH conditions for the extraction of beryllium(II) in the absence and in the presence of the complexing agent investigated are shown in Fig. 3. The extraction equilibrium was reached in all cases within a few minutes. Our results showed that the hydrolysis of beryllium(II) does not occur at pH < 6 under the conditions used, hence eqn. (3) can be used for the determination of K_0. Beryllium is not extracted quantitatively by solutions of oxine in chloroform; the distribution coefficient Q_N is equal to 7. The stability constant of beryllium oxinate, calculated from eqn. (4), is equal to $2 \cdot 10^{14}$.

In the presence of complexing agents the extraction of beryllium occurs in more alkaline regions. The stability constants of beryllium(II) complexes, calculated from eqn. (9), are collected in Table II.

Magnesium, calcium, strontium, barium

The extraction curves of magnesium, calcium, strontium and barium are shown in Fig. 4. Equilibrium was reached for all the systems investigated within a few minutes. For the magnesium–oxine system shaking for only 1 min was used; magnesium oxinate is destroyed on shaking (possibly by formation of insoluble $MgOx_2{\cdot}2H_2O$). The distribution data for the alkaline earths between a 0.1–0.5 *M* solution of oxine in chloroform and the aqueous phase can be explained by assuming the following complexes: $MgOx_2$, $CaOx_2{\cdot}HOx$, $SrOx_2{\cdot}2HOx$ and $BaOx_2{\cdot}2HOx$, in the organic phase. Our results for strontium agree very well with those of DYRSSEN[10]. UMLAND *et al.*[11] found that magnesium, calcium, strontium and barium were extracted as the complexes $MgOx_2$, $CaOx_2$, $SrOx_2{\cdot}HOx$ and $BaOx_2{\cdot}2HOx$ respectively. The different results for calcium and strontium oxinates can readily be explained by the fact that UMLAND does not consider the pH deviations caused by a change of oxine concentration. All the extraction constants calculated are collected in Table II. As was expected, the stability of the metal oxinates decreases with an increase in ionic radius.

Analogous dependence was also observed for tartrate complexes (see Table II). With oxalate, calcium, strontium and barium form insoluble oxalates; solubility products, calculated from eqn. (10), are given in Table II.

TABL

SURVEY OF EXTRACTION CONSTANTS K_0 AND STABILIT

$pH_{1/2}$ – pH value of 50% extraction of the metal inv

c – calc

ppt. – insoluble oxalate is formed (the negative logarithm of the sol

Metal in aq. phase	*Metal oxinate*	*$logK_0$*	*$logK_{NQN}$*	*($pH_{1/2}$)*		*$logK_{MOxal}$*	*$logK_{MOxal2}$*	*$logK_{MOxal}$*
				0.100 M	*0.010 M*			
Ag^+	$AgOxHOx$	−4.51±0.03	10.52	6.51	8.51	<2.0		
Be^{2+}	$BeOx_2$	−9.62±0.04	15.12	5.81	6.81^c	4.12±0.06		
Mg^{2+}	$MgOx_2$	−15.13±0.03	9.61	8.57	9.57^c	2.39±0.05		
Ca^{2+}	$CaOx_2HOx$	−17.89±0.05	9.51	10.38		ppt. (7.9)		
Sr^{2+}	$SrOx_2 2HOx$	−19.71±0.03	10.35	12.06^c		ppt. (6.4)		
Ba^{2+}	$BaOx_2 2HOx$	−20.9 ±0.1	9.2			ppt. (6.0)		
Sc^{3+}	$ScOx_3HOx$	−6.64±0.04	33.13	3.57	4.87			16.28±0.0
La^{3+}	$LaOx_3$	−16.37±0.05	20.74	6.46	7.46			ppt. (25.7)
TiO^{2+}	$TiOOx_2$	+0.9 ±0.1	25.6	1.45			10.7±0.1	
ZrO^{2+}	$ZrOOx_2$	+2.71±0.05	27.45	1.01	1.50			
Th^{4+}	$ThOx_4$	−7.18±0.04	42.30	2.91	3.80^c			
VO_2^+	VO_2Ox	+1.67±0.03	14.04	0.88	1.33	~6.4	~9.0	
H_2MoO_4	MoO_2Ox_2	+9.88±0.05			~0.5	7.37±0.05		
UO_2^{2+}	UO_2OxHOx	−1.60±0.02	24.80	2.60	3.81		11.08±0.03	
Mn^{2+}	$MnOx_2$	−9.32±0.03	15.42	5.66	6.66	3.75±0.05		
Fe^{3+}	$FeOx_3$	+4.11±0.02	41.22	1.00^c	1.50			20.46±0.0
Co^{2+}	$CoOx_2 2HOx$	−2.16±0.02	27.90	3.21	5.08		6.79±0.07	
Ni^{2+}	$NiOx_2$	−2.18±0.03	22.56	2.38	3.16		7.88±0.04	
Pd^{2+}	$PdOx_2$	~+15		<0	<0			
Cu^{2+}	$CuOx_2$	+1.77±0.02	26.51	1.37^c	1.77		10.46±0.07	
Zn^{2+}	$ZnOx_2 2HOx$	−2.41±0.03	27.65	3.30	5.20		7.59±0.05	
Cd^{2+}	$CdOx_2 2HOx$	−5.29±0.02	24.77	4.65	6.65^c	3.71±0.03		
Hg^{2+}	$HgOx_2$(?)	~−3				<4		
Al^{3+}	$AlOx_3$	−5.22±0.04	31.89	2.87^c	3.77			15.60±0.0
Ga^{3+}	$GaOx_3$	+3.72±0.03	48.83	1.07	1.57			17.98±0.0
In^{3+}	$InOx_3$	+0.89±0.03	38.00	1.54^c	2.13			14.7±0.1
Tl^{3+}	$TlOx_3$	~+5.0	42.1		2.05			~16.
Pb^{2+}	$PbOx_2$	−8.04±0.02	16.70	5.04	6.04		6.56±0.04	
Bi^{3+}	$BiOx_3$	−1.2 ±0.1	35.2	2.13				ppt. (35.4)

Owing to the relatively high stability of the complexonates of magnesium, calcium, strontium and barium[9], these metals were practically not extracted by oxine solution from 0.01 *M* ethylenediaminetetraacetic acid or from 0.01 *M* 1,2-diaminocyclohexanetetraacetic acid.

Scandium

Scandium was found to be precipitated by oxine as $ScOx_3 \cdot HOx$ and it was also extracted in this form into chloroform. Although the extraction rate is high (a few minutes) in the absence of complexing agent, the time required to reach equilibrium in the presence of aminopolycarboxylic acids is 10–20 h. With a 0.100 *M* solution of oxine in chloroform, scandium is quantitatively extracted at pH 4.5–10 (see Fig. 5). The extraction constant and stability constant of the scandium(III) complexes investigated are given in Table II. Very good agreement with SCHWARZENBACH's results[9] was found.

NSTANTS K OF METAL ION COMPLEXES DETERMINED

ated by 0.100 M and by 0.010 M oxine solutions.
d value.
.ty product determined by the extraction method is given in brackets).

gK_{MTart}	$\log K_{MTart2}$	$\log K_{MX}$	$\log K_{MX2}$	$\log K_{MY}$	$\log K_{MY(OH)}$	$\log K_{MZ}$	$\log K_{MZ(OH)}$
<2.0		5.16±0.05		7.11±0.06		8.15±0.03	
±0.03		7.11±0.05		9.27±0.03		10.81±0.06	
<2.0							
<2.0							
<2.0							
<2.0							
	12.5 ±0.1		~24.1	~23.0	27.43±0.03	~25.4	~28.0
	6.72±0.05		17.15±0.10	15.3 ±0.2		16.75±0.05	
	9.7 ±0.1	12.3 ±0.1		17.5 ±0.1		19.9 ±0.1	
±0.03							
	9.73±0.05	9.56±0.03					
±0.05		7.36±0.05		12.88±0.05		14.70±0.06	
	11.86±0.05	15.91±0.03	24.61±0.05		34.0 ±0.1		36.6 ±0.1
±0.1		10.81±0.03	14.28±0.05	16.55±0.04		18.92±0.04	
	5.42±0.06	11.54±0.08		18.36±0.06		19.68±0.04	
		13.05±0.01		18.92±0.04		21.59±0.02	
±0.08							
±0.03			15.45±0.04	16.9 ±0.1		~19.0	
<4							
	9.56±0.04	9.5 ±0.1			25.04±0.04		26.61±0.08
	9.76±0.05		25.81±0.04		34.0 ±0.1		35.6 ±0.1
±0.04			24.4		32.0 ±0.1		33.46±0.05
±0.04		11.47±0.04		18.32±0.03		19.5 ±0.1	
	11.3 ±0.1				32.45±0.10		34.55±0.1

Lanthanum

The solvent extraction of lanthanum(III) by oxine solution has been investigated in detail by DYRSSEN[1] using ^{140}La. The present results (Table II) agree well with this work.

From the extraction curves in the presence of tartrate and oxalate (Fig. 6) it was found that lanthanum formed a soluble complex $LaTart_2^-$ ($\log K_2 = 6.72$) with tartrate, and an insoluble complex La_2Oxal_3 ($\log S = -25.7$) with oxalate.

The stability constants of lanthanum(III) complexonates determined from Fig. 6 are in agreement with the values given by SCHWARZENBACH[9].

Titanium

From the distribution data (Fig. 7) it was concluded that titanium(IV) was present at pH 1–2 as the bivalent cation TiO^{2+} and that the extraction occurred mainly according to the reaction:

$$TiO^{2+} + 2\,(HOx)_{org} = (TiOOx_2)_{org} + 2\,H^+$$

with an extraction constant $K_0 = 8$.

The extraction equilibrium was reached even in the presence of complexing agents in 1–2 h.

The extraction curves of titanium(IV) in the presence of oxalate and tartrate ions at pH 1.5–4.0 show that $TiOOxal_2^{2-}$ and $TiOTart_2^{2-}$ complexes are formed with stability constants $5 \cdot 10^{10}$ and $5 \cdot 10^9$ respectively.

The stability constants of the titanyl complexonates are collected in Table II.

Zirconium

The results show that zirconium(IV) is present in the aqueous phase at pH 0.8–1.5 as the bivalent cation ZrO^{2+} or $Zr(OH)_2^{2+}$; this is extracted into the organic phase as the complex $ZrOOx_2$. With 0.10 *M* oxine solution, zirconium(IV) is quantitatively extracted at pH 1.5–4.0. At higher pH values $Zr(OH)_2^{2+}$ hydrolyses[12]: $Zr(OH)_2^{2+} \rightarrow Zr(OH)_4 \rightarrow ZrO(OH)_2 \rightarrow ZrO_2$. The reactivity of the last two species is low and therefore the extraction of zirconium is diminished at these higher pH values.

In the presence of oxalate ions (see Fig. 8) at pH 4–5 a very stable complex, $Zr(Oxal)_4^{4-}$, is formed ($\log K_4 > 26$); the stability of the tartrate complexes is somewhat lower.

In the presence of aminopolycarboxylic acids extraction of zirconium begins at pH values above 8–9.

Thorium

Dyrssen[13] has reported that thorium is extracted in the form $ThOx_4$. The extraction constant determined by Dyrssen agrees well with the present results.

From Fig. 8 it can be seen that oxalate and tartrate form very stable complexes $Th(Oxal)_4^{4-}$ and $Th(Tart)_3^{2-}$ with $\log K_4 = 23.6$ and $\log K_3 = 20.0$ respectively. The stability constant of the thorium(IV)–oxalate complex determined by Bose and Chowdhury[14] is a little higher ($\log K_4 = 24.48$). In the presence of nitrilotriacetic acid, ethylenediaminetetraacetic acid and 1,2-diaminocyclohexanetetraacetic acid, extraction of thorium starts above pH 7 and above pH 9 respectively.

Vanadium

The distribution data indicated that vanadium(V) is present at pH 1.0–1.5 as the monovalent cation VO_2^+ which forms a 1:1 complex with oxine. The extraction equilibrium was reached even in the presence of tartrate or 1,2-diaminocyclohexanetetraacetate within a few minutes; the presence of oxalate, nitrilotriacetate and ethylenediaminetetraacetate reduced not only the rate of equilibration but also the amount of vanadium extracted.

Vanadium(V) is quantitatively extracted by a 0.100 *M* solution of oxine in chloroform at pH 2–6. Above pH 9 vanadium(V) is not extracted owing to formation of VO_3^-.

Niobium

The extraction of niobium(V) by oxine solutions has already been investigated by

ALIMARIN[15,16] using ^{95}Nb, and by MOTOJIMA AND HASHITANI[5,17] using a spectrophotometric method.

In the present work only a few experiments were carried out. It was found that niobium(V) could be extracted in the presence of all the complexing agents investigated. The most reproducible results were obtained in the extraction from oxalate solution.

Chromium

Chromium(III) does not react with oxine at room temperature and therefore is not extracted at any pH value by 0.01–0.10 *M* oxine solution. Extractable chromium(III) oxinate is formed only by heating.

Molybdenum

The extraction of molybdenum(VI) has been studied with 0.0004–0.0100 *M* oxine solutions in chloroform at pH 1–2. At these pH values molybdenum is present predominantly as H_2MoO_4 [18] and the extraction of molybdenum can be expressed by the following equation:

$$H_2MoO_4 + 2\,(HOx)_{org} = (MoO_2Ox_2)_{org} + 2\,H_2O$$

with the equilibrium constant:

$$K_0 = \frac{[MoO_2Ox_2]_{org}}{[H_2MoO_4]\,[HOx]_{org}^2} = q_0 \cdot \frac{1}{[HOx]_{org}^2} = 7.6 \cdot 10^9$$

The extraction of molybdenum(VI) does not, however, depend on pH but only on the oxine concentration. At higher pH values the equilibrium concentration of H_2MoO_4 is decreased by dissociation and therefore the amount of molybdenum(VI) extracted is also decreased (see Fig. 9). The extraction constant calculated from the distribution data at pH 6–7, corrected for the dissociation and polymerisation[18] of H_2MoO_4, agrees with the extraction constant determined at low pH values.

The extraction equilibrium was attained at high pH values and at high oxine concentrations within a few minutes; at low pH values and oxine concentrations (especially when tartrate or oxalate was present) the extraction rate was smaller (several hours). The presence of aminopolycarboxylic acids did not reduce either the rate of extraction or the amount of molybdenum extracted (see Fig. 9).

The influence of oxalate and tartrate ions was studied in some detail. From these experiments it was concluded that at pH 1.5–6.0 and at various oxalate or tartrate concentrations only 1 : 1 complexes are formed (probably MoO_3Oxal^{2-} or MoO_3Tart^{2-}) with the stability constants

$$\frac{[Mo(VI) - oxalate]}{[H_2MoO_4][Oxal^{2-}]} = 2.35 \cdot 10^7 \text{ and } \frac{[Mo(VI) - tartrate]}{[H_2MoO_4][Tart^{2-}]} = 4.6 \cdot 10^7 .$$

The stability constant of molybdenum(VI) oxalate determined from YATSIMIRSKII's data[20] ($3 \cdot 10^7$) agrees quite well with our results.

Tungsten

In the absence of complexing agents the distribution data of tungsten(VI) are not reproducible (probably insoluble polytungstic acids are formed in the aqueous phase).

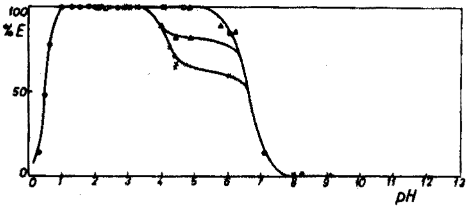

Fig. 9. Effect of pH on extraction of H_2MoO_4 by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

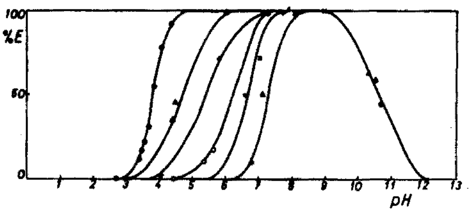

Fig. 10. Effect of pH on extraction of UO_2^{2+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

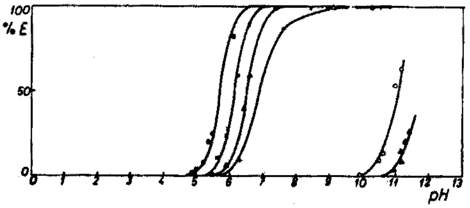

Fig. 11. Effect of pH on extraction of Mn^{2+} by 0.100 *M* oxine in chloroform (for symbols see Fig. 3).

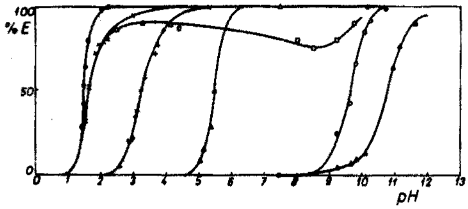

Fig. 12. Effect of pH on extraction of Fe^{3+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

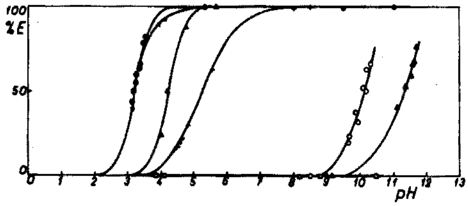

Fig. 13. Effect of pH on extraction of Co^{2+} by 0.100 *M* oxine in chloroform (for symbols see Fig. 3).

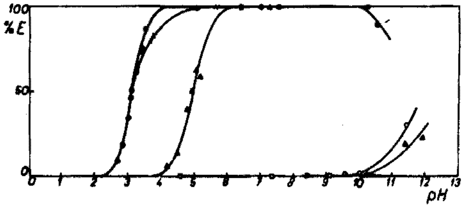

Fig. 14. Effect of pH on extraction of Ni^{2+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

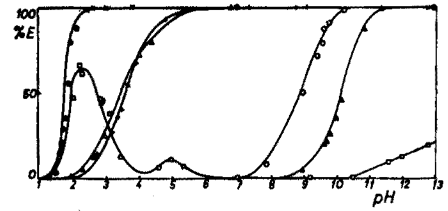

Fig. 15. Effect of pH on extraction of Cu^{2+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

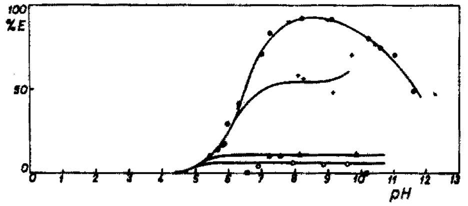

Fig. 16. Effect of pH on extraction of Ag^+ by 0.100 *M* oxine in chloroform (for symbols see Fig. 3).

In the presence of the aminopolycarboxylic acids investigated (0.01 *M*), tungsten is quantitatively extracted by 0.010 *M* oxine solution at pH 2.5–3.5. The extraction equilibrium was reached in 1 h. Oxalate and especially tartrate ions were found to reduce the extraction of tungsten(VI) oxinate.

Uranium

The solvent extraction of uranium(VI) by 0.010 *M* oxine in chloroform is shown in

Fig. 10. From the distribution data determined at various oxine concentrations, it was concluded that uranium(VI) is extracted into the organic phase as the complex, UO_2Ox_2HOx. The present results agree very well with those of DYRSSEN[1].

The stability constants of the uranyl complexes formed with the complexing agents investigated were determined in previous work[21]. The theoretical extraction curves calculated from eqn. (9) agree very well with some experiments carried out in the present work.

The extraction equilibrium was reached even in the presence of complexing agents within a few minutes.

Manganese

Manganese(II) can be completely extracted by 0.100 *M* oxine in chloroform in the pH range 6.5–11 (Fig. 11). At higher pH values hydroxylamine must be added to prevent the oxidation of manganese(II); manganese(III) oxinate has a red-violet colour.

The stability constants of the manganese(II) complexes with the complexing agents investigated are collected in Table II. Good agreement with previous literature data[9] has been achieved for the oxalate and nitrilotriacetate complexes. The stability constants for the MnY^{2-} and MnZ^{2-} complexes determined in the present work, are in better agreement with IRVING–ROSSOTTI's theory[22] than the constants determined by SCHWARZENBACH.

Iron

The pH conditions for the extraction of iron(III) are shown in Fig. 12. The results showed that iron(III) forms very stable complexes with oxalate ions ($\log K_3 = 20.46$) and with tartrate ions ($\log K_2 = 11.86$). For the iron(III)–oxalate complex the following values for $\log K_3$ are given in the literature[9]: 17.96, 20.2, 21.6 and 23.9.

Nitrilotriacetic acid (0.010 *M*) forms a complex FeX with iron(III) below pH 3; at pH 3–4 FeX_2^{3-} is formed and above pH 4 hydroxo complexes are formed. Ethylenediaminetetraacetic acid and 1,2-diaminocyclohexanetetraacetic acid form above pH 9 hydroxo complexes FeY(OH) and FeZ(OH) ($\log K_{1\cdot 1} = 34.0$ and 36.6 respectively). The stability constant of FeY(OH) given by SCHWARZENBACH is lower ($\log K_{1\cdot 1} = 31.6$).

Distribution data in the presence of cyanide showed that at pH 1–9 a neutral complex $Fe(CN)_3$ is probably formed ($\log K_3 \sim 31$). No evidence of the presence of $Fe(CN)_6^{3-}$ was obtained in these extraction experiments or in ion-exchange studies.

Cobalt

The extraction of cobalt(II) by oxine solution (0.010–0.100 *M*) can be expressed by the following equation:

$$Co^{2+} + 4\,(HOx)_{org} = (CoOx_2 2HOx)_{org} + 2\,H^+$$

with the extraction constant $K_0 = 7.2 \cdot 10^{-3}$.

The composition and stability constants determined from the extraction curves in the presence of the complexing agents (Fig. 13) agree in general with earlier literature data[9].

Nickel

The extraction equilibrium of nickel(II) was reached at low pH values and at low oxine concentration after several hours; in the presence of aminopolycarboxylic acids several days were needed. At higher pH values the equilibrium was reached more rapidly.

The extraction constant and stability constants determined in the present work are given in Table II.

Distribution data in the presence of cyanide (Fig. 14) show that in the aqueous phase insoluble $Ni(CN)_2$ is formed ($\log S = -23.2$).

Palladium

It was found that palladium(II) is extracted quantitatively by 0.010 *M* oxine in chloroform at pH 0–10; it is therefore impossible to use eqn. (3) for the determination of K_0. In the presence of chloride and bromide ions, which form very stable complexes with palladium(II), the distribution ratio is decreased and the K_0 value can be calculated from eqn. (9) with the use of the stability constants of $PdCl_n^{2-n}$ and $PdBr_n^{2-n}$ complexes given by SHUKAREV *et al.*[23] and by LATIMER[24].

The extraction equilibrium was reached at low pH values after a few hours, and at higher pH values within a few minutes. The presence of aminopolycarboxylic acids was found to reduce the rate of extraction and the amount of palladium extracted.

Copper

The extraction curves of copper(II) with 0.010 *M* oxine in chloroform are shown in Fig. 15. The stability constants of the complexes investigated (Table II) are in good agreement with the literature data[9]. In the presence of cyanide ions, partial reduction of copper(II) occurs and therefore the extraction of copper(II) is decreased.

Silver

Systematic studies of the solvent extraction of silver(I) oxinate have been carried out by SCHWEITZER AND BRAMLITT[2]. From this work it may be concluded that silver(I) is extracted into the chloroform phase as a complex AgOxHOx. Our results agree well with this earlier work.

For the determination of the distribution ratio only the radiometric method can be used; the spectrophotometric method was unsuitable because of the reduction of silver ions and because of the adsorption of silver ions on glass vessels.

Oxalate and tartrate ions did not affect the extraction of silver(I). Aminopolycarboxylic acids decreased the extent of the extraction, and in the presence of cyanide silver(I) was not extracted by oxine solution (see Fig. 16).

Zinc

From the distribution data it was concluded that zinc(II) was extracted into the organic phase as the complex $ZnOx_2 2HOx$. The extraction equilibrium was reached after several minutes, but the zinc(II)–oxinate complex was quickly destroyed at higher pH values on shaking (probably insoluble $ZnOx_2 2H_2O$ was formed).

Quantitative extraction of zinc(II) by 0.100 *M* oxine solution occurs at pH 4–5.

Cadmium

Cadmium(II) is extracted into chloroform as the complex $CdOx_2 2HOx$. At high pH values and at small oxine concentrations (< 0.020 *M*) the complex is destroyed on shaking.

The extraction constant and stability constants of the cadmium(II) complexes calculated from Fig. 17 are collected in Table II.

From the distribution data in the presence of cyanide, it was concluded that above pH 9 a complex $Cd(CN)_4^{2-}$ is formed (log $K_4 = 18.65 \pm 0.15$).

Mercury

Mercury(II) begins to be extracted by 0.100 *M* oxine in chloroform at a pH of

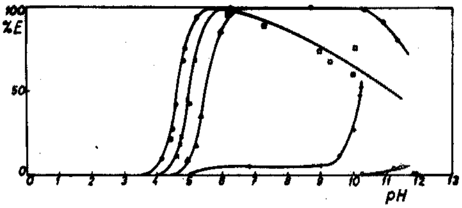

Fig. 17. Effect of pH on extraction of Cd^{2+} by 0.100 *M* oxine in chloroform (for symbols see Fig. 3).

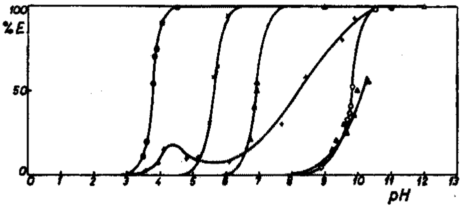

Fig. 18. Effect of pH on extraction of Al^{3+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

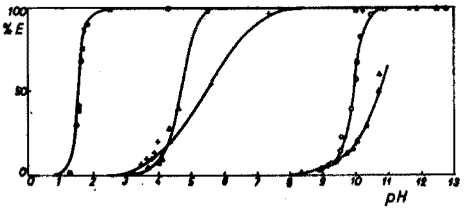

Fig. 19. Effect of pH on extraction of Ga^{3+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

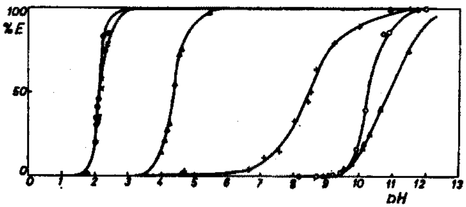

Fig. 20. Effect of pH on extraction of In^{3+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

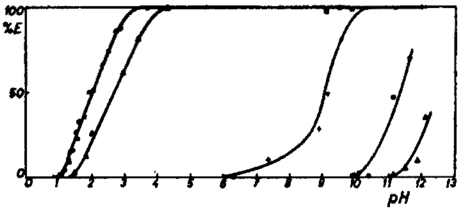

Fig. 21. Effect of pH on extraction of Tl^{3+} by 0.010 *M* oxine in chloroform (for symbols see Fig. 3).

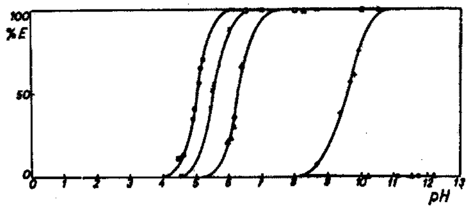

Fig. 22. Effect of pH on extraction of Pb^{2+} by 0.100 *M* oxine in chloroform (for symbols see Fig. 3).

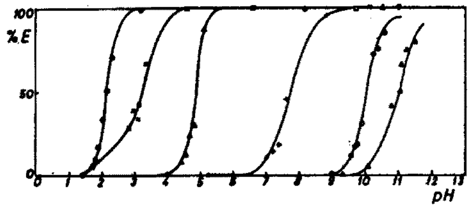

Fig. 23. Effect of pH on extraction of Bi^{3+} by 0.100 *M* oxine in chloroform (for symbols see Fig. 3).

approximately 3.5. In this region mercury(II) hydrolyses[18]: $Hg^{2+} \rightarrow Hg(OH)_2 \rightarrow HgO$ and therefore the extraction of mercury(II) is incomplete. The presence of oxalate and tartrate does not prevent the hydrolysis. In the presence of the aminopolycarboxylic acids or cyanide, mercury(II) is not extracted.

Aluminium

The pH conditions for the extraction of aluminium(III) are shown in Fig. 18. From the distribution data it was concluded that aluminium(III) forms with oxalate and tartrate stable complexes $AlOxal_3^{3-}$ ($\log K_3 = 15.6$) and $AlTart_2^-$ ($\log K_2 = 9.56$).

Below pH 4 aluminium(III) forms with nitrilotriacetic acid a complex AlX ($\log K_1 = 9.5$); at higher pH values the complexes AlX(OH) and AlX_2 are formed. Above pH 9 aluminium(III) forms with ethylenediaminetetraacetic acid and with 1,2-diaminocyclohexanetetraacetic acid, hydroxo complexes AlY(OH) and AlZ(OH) ($\log K_{1.1} = 25.04$ and 26.61 respectively). SCHWARZENBACH[9] found for these complexes the values $\log K_{1.1} = 24.24$ and 24.05 respectively.

Gallium

The results obtained for the extraction of gallium(III) by 0.010 M oxine in chloroform are shown in Fig. 19.

Gallium forms with nitrilotriacetic acid (0.010 M) at pH 3–4 a complex GaX_2; at higher pH values hydroxo complexes are formed.

From the distribution data obtained above pH 9 it was concluded that gallium(III) forms with ethylenediaminetetraacetic acid and with 1,2-diaminocyclohexanetetraacetic acid, the hydroxo complexes GaY(OH) and GaZ(OH) ($\log K_{1.1} = 34.0$ and 35.6 respectively). The stability constants for GaY and GaZ given by SCHWARZENBACH[9] ($\log K_1 = 20.27$ and 22.91 respectively) seem to be too low in comparison with our results.

Indium

The distribution data for indium(III) determined in the present work (see Fig. 20) are in good agreement with the results of SCHWEITZER AND COE[3]. Indium forms with tartrate at pH 2–3 the complex $InTart^+$ (at higher pH $InTart_2^-$ is probably also formed); with oxalate, $InOxal_3^{3-}$ is formed.

Our results show that indium(III) complexonates are less stable (see Table II) than the corresponding gallium(III) complexes.

Thallium

The distribution data showed (Fig. 21) that thallium(III) is present in a hydrolysed form above pH 1.3. For the determination of K_0 the hydrolysis corrections[18] were taken into account. In the presence of chloride ions (0.10 M) thallium(III) is not hydrolysed.

The presence of tartrate or cyanide has no influence on the thallium(III) extraction. Oxalate was found to form the very stable complex, $TlOxal_3^{3-}$, at pH 1.5–4.0. Very stable complexes are also formed between thallium(III) and aminopolycarboxylic acids. The stability constants of these complexes were not determined because of the slow extraction rate and the low stability of thallium(III) oxinate to light[5].

Lead

The extraction curves of lead(II) are shown in Fig. 22. The extraction constants and stability constants of the lead(II) complexes investigated are collected in Table II.

Bismuth

The extraction curves (Fig. 23) show that bismuth(III) is present in a hydrolysed form above pH 1.5. The extraction constant was calculated from the distribution data below pH 1.5 by direct use of eqn. (3); for the distribution data obtained above pH 1.5 hydrolysis corrections were made.

Tartrate forms a soluble complex, $BiTart_2^-$, with bismuth(III); oxalate forms insoluble Bi_2Oxal_3 ($\log S = -35.4$).

Analytical applications

The present work shows that oxine forms extractable complexes with all the metals investigated. Chromium(III) oxinate is formed only on heating and chromium can readily be separated from the other metals.

Solutions of metal oxinates have absorption maxima at 380–420 mμ and therefore the spectrophotometric method can be used for the determination of all the metals investigated (with the exception of silver and mercury). Iron(III) oxinate and vanadium(V) oxinate absorb strongly also at 580 mμ and 550 mμ respectively. At these wavelengths the other investigated oxinates do not absorb. Iron(III) can therefore be determined very selectively by measuring the absorbancy at 580 mμ after extraction with oxine solution from an aqueous phase with a pH value higher than 9 (vanadium(V) is not extracted). After this separation of iron(III), vanadium(V) can be selectively determined by extraction from the aqueous phase after adjustment to pH 2–6. A selective determination of vanadium(V) can be carried out by extraction from 0.01 *M* 1,2-diaminocyclohexanetetraacetic acid solution at pH 2–6, the absorbancy being measured at 550 mμ.

From the extraction constants determined in the present work it is possible to find the best conditions for the separation of many metals. The separation factor (F) is as follows:

$$F = \frac{q'_0}{q''_0} = \frac{K'_0\,[\mathrm{HOx}]_{\mathrm{org}}^{(N'+r')-(N''+r'')}}{K''_0[\mathrm{H}^+]^{N'-N''}} \tag{11}$$

where q'_0 and q''_0 are the distribution ratios of the metals M′ and M″ respectively.

It is evident that the metal oxinate with the higher K_0 value can be selectively separated from all other metal oxinates with lower K_0 values. Thus, for example, at pH 0 only palladium is extracted by 0.01 *M* oxine solution, and at pH 1 molybdenum(VI) is extracted (palladium and, to some extent, tungsten and vanadium interfere).

Selective separations can also be obtained by addition of a complexing agent which forms non-extractable complexes with interfering ions. In this case:

$$F = \frac{q'}{q''} = \frac{q'_0(1 + K''_N[\mathrm{B}^{n-}]^N)}{q''_0(1 + K'_N[\mathrm{B}^{n-}]^N)} \tag{12}$$

where K'_N and K''_N are the stability constants of the complexes $M'B_N$ and $M''B_N$ respectively.

The results given in Table II show that in the presence of 1,2-diaminocyclohexanetetraacetic acid at pH 1–2, only molybdenum(VI), tungsten(VI), vanadium(V) and palladium(II) are extracted by 0.010 *M* oxine solution, and that at pH 9 only uranium(VI) is extracted; beryllium(II), titanium(IV) and niobium(V) interfere slightly. With the utilisation of stability constants of other complexing agents (see [9]) many other selective separations can be carried out.

The values of the extraction constants and stability constants determined in the present work may also be used for the determination of traces of metals by means of isotopic dilution analysis by extraction[25] or ion exchange[26].

CONCLUSIONS

From the distribution data obtained for the metals investigated, the equilibrium constant (extraction constant) of the following reaction has been determined:

$$M^{N+} + (N + r)(HOx)_{org} = (MOx_N(HOx)_r)_{org} + NH^+$$

In the case of Be^{2+}, Mg^{2+}, La^{3+}, TiO^{2+}, ZrO^{2+}, Th^{4+}, VO_2^+, Mn^{2+}, Fe^{3+}, Pd^{2+}, Cu^{2+}, Al^{3+}, Ga^{3+}, In^{3+} and Pb^{2+}, $r = 0$; for Ca^{2+}, Sc^{3+} and UO_2^{2+}, $r = 1$; and for Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+} and Co^{2+}, $r = 2$. H_2MoO_4 is extracted as MoO_2Ox_2.

The extractability of the metal ions by a solution of oxine in chloroform decreases in the following order: Pd^{2+}, H_2MoO_4, (W(VI)), VO_2^+, Tl^{3+}, Fe^{3+}, ZrO^{2+}, Ga^{3+}, Cu^{2+}, TiO^{2+}, In^{3+}, Bi^{3+}, Ni^{2+}, UO_2^{2+}, Al^{3+}, Th^{4+}, (Hg^{2+}), Co^{2+}, Zn^{2+}, Sc^{3+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Be^{2+}, La^{3+}, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}.

Oxalate ions were found to form with silver(I) only a weak complex; with bivalent cations complexes of the type MOxal (Be^{2+}, Mn^{2+}, Cd^{2+}, Mg^{2+}) or $MOxal_2^{2-}$ (UO_2^{2+}, TiO^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}) are formed. Trivalent cations form very stable complexes $MOxal_3^{3-}$ (Fe^{3+}, Ga^{3+}, Tl^{3+}, Sc^{3+}, Al^{3+}, In^{3+}) and tetravalent cations form complexes $MOxal_4^{4-}$ (Zr^{4+}, Th^{4+}). Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+} and Bi^{3+} form insoluble oxalates. Very stable complexes are also formed between H_2MoO_4 or VO_2^{2+} and oxalate.

Tartrate complexes are in general less stable than oxalate ones. Molybdenum(VI) and tungsten(VI) tartrates are the only exceptions.

Nitrilotriacetic acid (H_3X) forms complexes of the type MX and MX_2 with metal ions. The formation of hydroxo complexes of bivalent metal ions was not observed, but trivalent metal ions form hydroxo complexes even in neutral medium (Sc^{3+} and La^{3+} complexes are the exceptions).

Ethylenediaminetetraacetic acid (H_4Y) and 1,2-diaminocyclohexanetetraacetic acid (H_4Z) form complexes of the type MY and MZ respectively with the metal ions investigated. The formation of hydroxo complexes of bivalent metal ions was again not observed. Trivalent and probably also tetravalent metal ions form hydroxo complexes, MY(OH) and MZ(OH), at higher pH values; their stability is decreased in the following order: Tl^{3+}, Fe^{3+}, Ga^{3+}, Bi^{3+}, In^{3+}, Sc^{3+} and Al^{3+}. Uranyl ions form hydrogen complexes, UO_2HY^- and UO_2HZ^-, with H_4Y and with H_4Z respectively[21]. In all cases the stability of the metal complexes with H_4Z is higher than the stability of the corresponding metal complexes with H_4Y. The uranyl and possibly the vanadyl complexes are the only exceptions.

The author wishes to thank Mrs. V. URBANOVA for her technical assistance.

SUMMARY

The extraction of 32 metals (Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, V, Nb, Cr, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Al, Ga, In, Tl, Pb and Bi) with oxine solution has been studied. The effects of pH, oxine concentration and water-soluble complexing agents (oxalic acid, tartaric acid, hydrocyanic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid and 1,2-diaminocyclohexanetetraacetic acid) have been investigated. From these results the extraction constants and stability constants of the metal complexes with the various complexing agents investigated have been calculated.

RÉSUMÉ

L'auteur a effectué une étude sur l'extraction de 32 métaux, au moyen d'oxine. L'influence de divers facteurs (pH, concentration, agents complexants) a été examinée. Les constantes d'extraction et de stabilité ont été déterminées.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten von 32 Metallen bei der Extraktion mit Oxinlösung unter Berücksichtigung des Einflusses von pH und anderer Faktoren. Extraktions- und Stabilitätskonstanten mit verschiedenen Komplexbildnern werden angegeben.

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COLORIMETRIC DETERMINATION OF LIGANDS BY THE EFFECT OF THEIR COBALT(II) COMPLEXES ON REDOX INDICATORS*

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In a previous publication[1], a novel colorimetric method for the determination of ligands based on the change in oxidation potential that occurs on coordination was elucidated. The method described depends on the color produced upon oxidation of a redox indicator such as *o*-dianisidine by a cobalt(III) complex. It was pointed out, however, that ethylenediamine and cyanide which form cobalt(II) complexes that are particularly good reducing agents[2,3] could not be determined by the method.

In this paper, ethylenediamine and cyanide are determined by the ability of their cobalt(II) complexes to reduce a tetrazolium salt to the colored formazan.

EXPERIMENTAL

Reagents

Cobaltous chloride solution. A 0.2% stock solution was prepared by dissolving 2 g of cobaltous chloride hexahydrate in 1 l of distilled water. This solution was used for the determination of cyanide. It was diluted to 0.1% for the determination of ethylenediamine.

Tetrazolium salt solution. 3-*p*-Iodophenyl-2-*p*-nitrophenyltetrazolium chloride (INT) was dissolved in 100 ml of distilled water with the aid of heat and then filtered. The solution was stored at 0° in an amber bottle.

Gelatin solution. A 5% gelatin stock solution was prepared by dissolving 5 g of gelatin in 100 ml of distilled water with heating and stirring. This solution was stored as a gel at 0° in an amber bottle and liquified before use by warming. A 1% solution prepared from the gelatin stock solution was mixed with 2 parts of INT solution to give the gelatin–INT reagent used in the assay.

TRIS buffer solution. 1 *M*, pH 10.5. Tris(hydroxymethyl)aminomethane (121.13 g) was dissolved in 800 ml of water. The pH was adjusted to 10.5 with 6 *N* hydrochloric acid. The solution was then diluted to 1 l.

Apparatus

Colorimetric measurements were made with a Klett-Summerson Colorimeter using

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a No. 50 filter. The colorimeter was standardized before each series of readings so that a sealed Klett tube containing copper nitrate solution read 132 Klett units *vs.* distilled water.

Spectrophotometry was performed with a Bausch & Lomb Spectronic 505 Recording Spectrophotometer.

All pH measurements were made with a Beckman Model G pH meter using glass electrodes.

B-D Cornwall Automatic pipettes were used to deliver reagents.

Procedures

Determination of ethylenediamine. A standard curve was prepared by using known concentrations of ethylenediamine in distilled water in the range from 25 to 200 μg/ml. To 1 ml of the sample solution in a Klett tube was added 1 ml of the 0.1% cobaltous chloride reagent, 1.5 ml of the gelatin–INT reagent, and 1 ml of the TRIS buffer solution. The tubes were immersed in a shaking water bath at 60° for 30 min and read in a Klett-Summerson Colorimeter using a No. 50 filter.

Determination of cyanide. A standard curve was prepared by using known concentrations of cyanide from 100 to 400 μg/ml of water. To 1 ml of the sample solution in a Klett tube was added 1.5 ml of gelatin–INT reagent, 1 ml of 0.2% cobaltous chloride solution and 1 ml of TRIS buffer solution. After standing for 10 min, the tubes were read in a Klett-Summerson Colorimeter using a No. 50 filter.

RESULTS

Wavelength

The absorption spectrum of the formazan obtained upon the reduction of INT by the cobalt(II) ethylenediamine complex, the cobalt(II) cyanide complex or sodium sulfide was studied at pH 9.8 from 330 to 630 mμ (Fig. 1). An absorption maximum in this range occurred at 502 mμ.

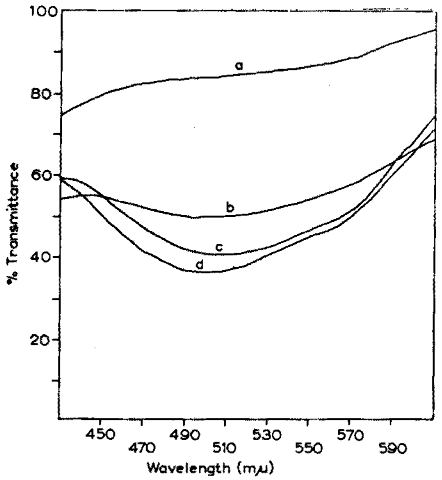

Fig. 1. Visible absorption spectra at pH 9.8. a. Reagent blank: $CoCl_2$, TRIS, INT–gelatin, b. Formazan from reduction of INT by Co(II)–cyanide complex, c. Formazan from reduction of INT by Co(II)–*en* complex, d. Formazan from reduction of INT by Na_2S.

Effect of order of addition of reagents

In order to achieve maximum color intensity, INT had to be present before the formation of the cobalt cyanide or cobalt ethylenediamine complex. This was necessary because the cobalt(II) complexes concerned were found to undergo oxidation slowly on standing in the absence of INT (Fig. 2). Hence the amount of INT reduced by a given quantity of cobalt(II) complex was dependent on the time elapsed before the addition of the INT (Table I).

The only reagents that could be combined were gelatin and INT.

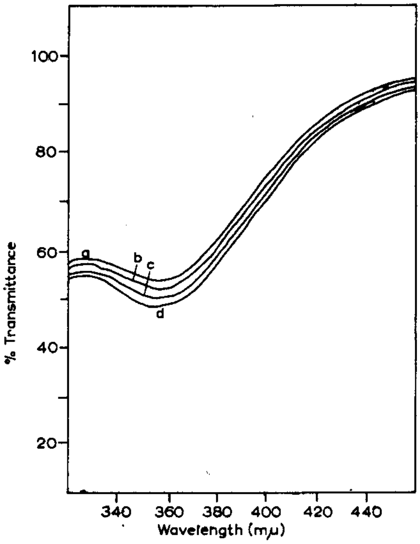

Fig. 2. Oxidation of Co(II)-*en* complex on standing in air. a. 10 min, b. 20 min, c. 30 min, d. 40 min.

TABLE I

EFFECT OF ADDITION OF INT AFTER FORMATION OF Co(II)-*en* COMPLEX ON ESTIMATION OF 100 μg OF *en*

Time elapsed before addition of INT (min)	*Net Klett units*
0	235
10	197
20	180
30	165

Effect of concentration of reagents

For the ethylenediamine concentrations of interest, 0.1% cobaltous chloride solution gave the best results over the entire range. However, for concentrations of ethylenediamine of less than 100 μg/ml, 0.0625% cobaltous chloride solution gave satisfactory results.

For cyanide concentrations of up to 400 μg/ml, best results were obtained using a 0.2% cobaltous chloride solution (Table II).

It was determined early in this work that an excess of INT was necessary for greatest sensitivity. The minimum concentration which gave suitable sensitivity and blanks was a 0.4% solution. Lower concentrations of INT gave less sensitivity and less linear results (Fig. 3).

TABLE II

EFFECT OF VARYING CONCENTRATION OF COBALTOUS CHLORIDE ON CYANIDE DETERMINATION

Cyanide concn. (μg/ml)	*% Cobalt solution (net Klett units)*		
	0.1%	*0.2%*	*0.4%*
100	0	10	—6
200	35	203	120
300	89	435	375
400	167	775	400

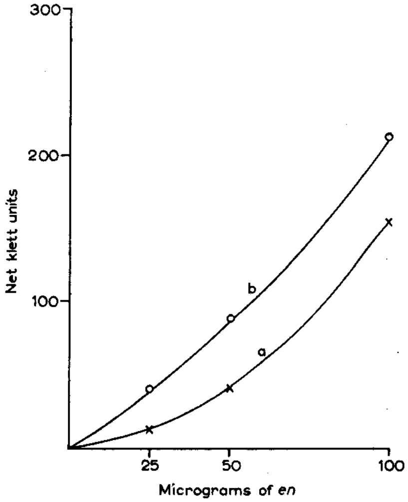

Fig. 3. Effect of varying INT concentration on determination of *en*. a. 0.2% INT, b. 0.4% INT.

Rate of reaction

For any given concentration of ethylenediamine in this reaction, color intensity is dependent on time. Preliminary studies showed that by heating at 80° for 30 min,

TABLE III

EFFECT OF INCREASING pH ON CYANIDE DETERMINATION

Cyanide concn. (μg/ml)	*pH*	*Net Klett units*
100	10.01	—8
	10.45	4
200	9.96	88
	10.54	95
300	10.05	277
	10.60	286
400	10.01	402
	10.58	386

the color reached maximum intensity and the results were quite linear. However, by heating at 60° for 30 min more reproducible results were obtained.

Since the cyanide and ethylenediamine solutions are basic, the effect of pH on the color reaction was tested. However, the basic ethylenediamine and sodium cyanide sample solutions did not change the pH of the buffered reaction mixture under the conditions of the analysis. Moreover, when the pH of the reaction mixture was intentionally changed by the addition of sufficient 0.02 *N* alkali, the net sample readings were not substantially increased (Table III).

The TRIS buffer (1 *M*, pH 10.5) brought the reaction mixture to pH 9.8. This pH was desirable since INT is more readily reduced at an elevated pH. The TRIS also complexed the cobalt and kept it from precipitating as the hydroxide.

Conformity to Beer's law

The standard curves obtained for the determination of ethylenediamine followed Beer's law in the region 0 to 100 μg/ml (Table IV). From 50 to 200 μg/ml, a negative deviation was observed but the curve was still useful for analysis.

The standard curve obtained for the determination of cyanide was useful in the range of 200–400 μg/ml and exhibited a positive deviation (Table V).

TABLE IV

STANDARD CURVE FOR DETERMINATION OF ETHYLENEDIAMINE

Concentration (μg/ml)	*Mean values ($n = 6$)*	*Standard deviation*
25	62.7	0.36
50	126.3	6.99
100	243.0	10.81

TABLE V

STANDARD CURVE FOR DETERMINATION OF CYANIDE

Concentration (μg/ml)	*Net Klett units*[a]
200	203, 222
300	435, 470
400	775, 780

[a] Replicate determinations on the same standard solutions.

DISCUSSION

The mechanism of this reaction is perhaps best considered a redox reaction of the electron-transfer type[4–6].

Cesium ion, known for its ability to facilitate electron transfer[5,7,8], was found to accelerate the reduction of INT by the cobaltous cyanide complex as it does the reduction of water to hydrogen[7].

Phenazine methosulfate (PMS) which can act as an electron carrier to tetrazolium salts[9], increased the rate of color development in the determination of ethylenediamine; it permitted the reaction to proceed with sufficient color development at pH 9 rather than 9.8. When PMS was used it was noted that the time at which ethylenediamine gave maximum color was dependent on the concentration of ethylenediamine. The instability of solutions of PMS however, precluded its use in this method.

Ammonia and amines such as pyridine, aniline, 2-aminodimethylamine and 2-aminodiethylamine could not be determined by this procedure.

From the stability constants of the cobalt ethylenediaminetetraacetic (EDTA) complexes it might be expected that EDTA could be determined by this procedure. The cobalt(II)-EDTA complex however, was found incapable of reducing INT under the conditions of our method. This could be related to the fact that electron transfer between cobalt(II) and cobalt(III) proceeds more rapidly when the surrounding ligand is ethylenediamine (high crystal field strength) than with EDTA (medium crystal field strength)[10].

SUMMARY

Coordination of cobalt(II) with ligands facilitates oxidation to the trivalent state by an oxidizing agent such as 3-*p*-iodophenyl-2-*p*-nitrophenyl tetrazolium chloride (INT). Since the formazan produced by the reduction of the tetrazolium chloride is highly colored, a sensitive measure of the amount of ligand (ethylenediamine or cyanide) present is obtained.

RÉSUMÉ

Les auteurs proposent une méthode de dosage colorimétrique de complexants (éthylènediamine, cyanure) basée sur l'effet de leurs complexes de cobalt sur les indicateurs redox, tel que le chlorure de *p*-iodophényl-2-*p*-nitrophényltétrazolium. Le produit de réduction obtenu est très coloré.

ZUSAMMENFASSUNG

Die Oxydation von Kobalt-(II) zu Kobalt-(III) mit *z.B.* 3-*p*-Iodophenyl-2-*p*-nitrophenyl-tetrazoliumchlorid (INT) wird durch Komplexierung des Kobalts erleichtert. Da das hierbei gebildete Formazan stark gefärbt ist, lässt sich diese Reaktion zur Bestimmung des Komplexbildners (Aethylendiamin oder Cyanid) anwenden.

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SPECTROPHOTOFLUORIMETRIC DETERMINATION OF FORMALDEHYDE AND ACROLEIN WITH J-ACID

COMPARISON WITH OTHER METHODS

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In this paper some extremely sensitive procedures for the detection and determination of formaldehyde and acrolein are introduced. The advantages and disadvantages of these procedures are discussed. This multiplicity of methods makes possible the selection of a method with the optimum advantages for the analysis of a particular mixture.

Six important factors that must be considered in formaldehyde analysis are simplicity of application, precision, color stability, selectivity, sensitivity, and compliance with Beer's law. The sensitivity of a spectrophotometric method depends upon the molar absorptivity and the dilution factor. The three main types of interferences are (*1*) compounds that give spectra somewhat similar to that obtained with formaldehyde, (*2*) compounds that react with the reagent, and (*3*) compounds that react with the formaldehyde.

For the determination of acrolein the most selective method is the 4-hexylresorcinol procedure[1,2]. This method has been thoroughly investigated with respect to interferences and has been applied to atmospheric and auto exhaust analyses[2]. The main interferences are malonaldehyde and compounds that form malonaldehyde and acrolein under the conditions of the test[3].

EXPERIMENTAL

Reagents

1-Ethylquinaldinium iodide (Distillation Products, Inc.) was recrystallized from water to a constant melting point. 6-Amino-1-naphthol-3-sulfonic acid or J-Acid (K and K Laboratories, Inc., Jamaica, N.Y.) was washed with boiling dimethylformamide and then with acetone, dissolved in hot aqueous alkali, treated with charcoal, filtered hot and precipitated with hydrochloric acid, filtered, and finally washed with acetone.

Apparatus

A Cary Model 14 recording spectrophotometer with 10-mm light-path cells was used for absorption spectral measurements; an Aminco-Bowman spectrophotofluorimeter with 0.3- and 1-ml cells was used for fluorimetric measurements. All excitation and emission wave-length maxima were uncorrected.

Microestimation of formaldehyde with J-Acid

To 0.1 ml of aqueous test solution was added 0.25 ml of 0.01% J-Acid in concentrated sulfuric acid. The mixture was heated at 100° for 5 min and then allowed to come to room temperature. In the presence of formaldehyde, excitation wave-length maxima are obtained at 470, 380, 315, and 270 mμ, with decreasing intensity; the emission wave-length maximum is 522 mμ (Fig. 1). For the estimation the instrument is set at the excitation wave-length maximum of 470 mμ and read at the emission wave-length maximum. The lower limit of estimation is about 0.0005 μg. The presence of formaldehyde in more concentrated solutions can be confirmed

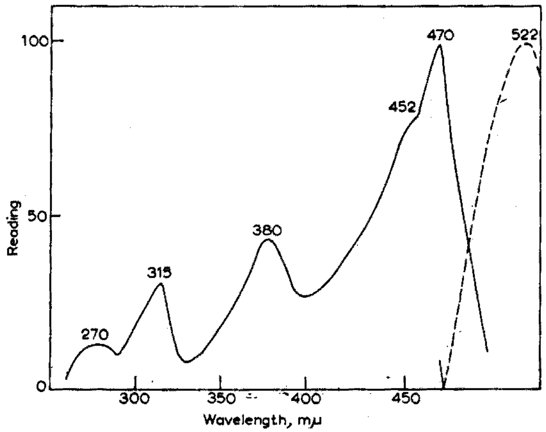


Fig. 1. Formaldehyde ($3 \cdot 10^{-6}$ M final concentration). Meter multiplier = 0.03. Excitation spectrum obtained with J-Acid at emission λ max 522 mμ (———). Emission spectra obtained at excitation λ max 470 mμ (- - -).

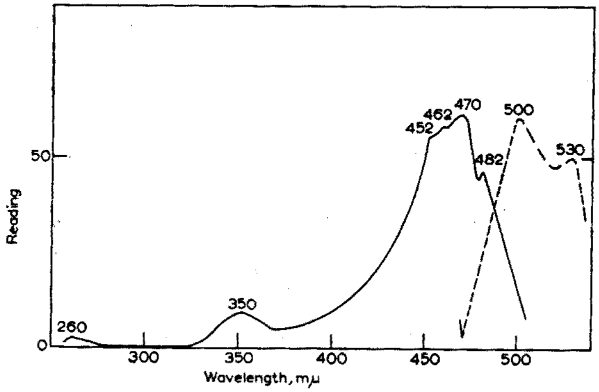


Fig. 2. Acrolein ($3 \cdot 10^{-6}$ M final concentration). Meter multiplier = 0.01. Excitation spectrum obtained with J-Acid at emission λ max 500 mμ (———). Emission spectrum obtained at excitation λ max 470 mμ (- - -).

further by overlaying the sulfuric acid solution with water. A blue ring indicates the presence of formaldehyde.

Microestimation of acrolein with J-Acid

To 0.1 ml of aqueous test solution was added 0.1 ml of 0.07% J-Acid in concentrated sulfuric acid. The mixed solution was heated at 100° for 30 min in a 0.3-ml, 6 × 40-mm cell. It was allowed to come to room temperature and then 0.1 ml of water was added. The excitation and emission spectra obtained in the presence of acrolein are shown in Fig. 2. With the instrument set at the excitation wave-length maximum of 470 mμ, a reading was taken at the emission wave-length maximum of 500 mμ. The lower limit of estimation is about 0.01 μg. The presence of fairly large amounts of formaldehyde is shown by a blue color.

Spectrophotofluorimetric determination of formaldehyde

To 2 ml of aqueous test solution was added 5 ml of 0.01% J-Acid in sulfuric acid. The mixture was allowed to stand until it reached room temperature (about 15 min). The mixture was diluted to 10 ml with concentrated sulfuric acid and cooled under the tap at the same time. With the instrument set at the excitation wave-length maximum of 470 mμ, a reading was taken at the emission wave-length maximum of 522 mμ.

Spectrophotofluorimetric determination of acrolein

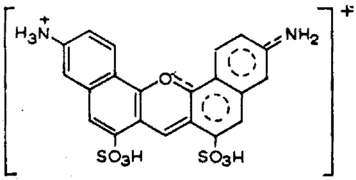
To 2 ml of aqueous test solution was added 3 ml of 0.07% J-Acid in sulfuric acid. The homogeneous mixture was allowed to stand until it cooled to room temperature and was then diluted to 10 ml with water while cooling in an ice bath. With the instrument set at the excitation wave-length maximum of 470 mμ, a reading was taken at the emission wave-length maximum of 500 mμ. The presence of interfering amounts of formaldehyde is shown by a blue color.

Determination of formaldehyde with 1-ethylquinaldinium iodide

To 1 ml of the aqueous test solution was added 1 ml of an aqueous solution containing 1.5% 1-ethylquinaldinium iodide. After the addition of 0.1 ml of 10% aqueous tetraethylammonium hydroxide, the mixture was heated on the water bath for 60 min, cooled, and then diluted to 10 ml with alcohol. In the presence of formaldehyde, absorption bands are found at 564 and 608 mμ. The absorbance is read at the stronger 608-mμ band.

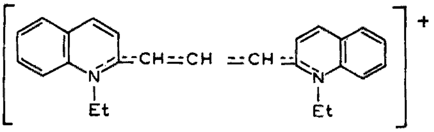
Mechanism of reactions

The reaction of formaldehyde with J-Acid to give a blue dibenzoxanthylium dye with a green-yellow fluorescence and a yellow color in sulfuric acid has been described[4]. The fluorescent chromogen probably has the following structure:



The structure of the chromogen(s) formed in the analysis for acrolein is not known.

The chromogen formed from the determination of formaldehyde with 1-ethylquinaldinium iodide has the structure:



The pure dye in methyl cellosolve solution has molar absorptivities of 210,000 and 94,000 at 610 and 565 mμ, respectively. In the identical solvent mixture used in the determination of formaldehyde with 1-ethylquinaldinium iodide, molar absorptivities of 210,000 and 93,000 were obtained at 608 and 564 mμ, respectively. Since a molar absorptivity of approximately 70,000 is obtained at 608 mμ in the determination of formaldehyde, the method can be improved further.

DISCUSSION

In any determination of formaldehyde or acrolein a standard should be run daily. Unless otherwise stated all data are for macro procedures.

Spectrophotofluorimetric determination of formaldehyde

Variables in the recommended procedure were investigated. Optimum results were obtained with 0.01 to 0.05% J-Acid. Higher percentages gave blanks with greater background absorption and fluorescence. If the samples were kept cool during the mixing of the first two solutions, lower values were obtained. Heating a mixture of the test solution and the reagent on the water bath did not improve results enough to warrant this extra step. Adding a decreasing volume of the same weight of J-Acid did not improve results. If with this decreased volume of reagent solution an increasing percentage of water was used in the diluting solvent, then the intensities decreased with this change. At 20% water the results were optimum, and at 30% water the values decreased slightly. From 40 to 50% water the decrease was sharp; the decrease continued gradually until at 70% fluorescence was negligible. At this stage practically all the yellow fluorescent dication had been converted to the blue cation.

The excitation and emission intensities were stable for at least 2 h. With amounts of formaldehyde larger than 2 μg, quenching effects depressed the values.

The procedures for the estimation and determination of formaldehyde suffer from the same interferences found with the chromotropic acid method[5,6]. These are formaldehyde-releasing compounds and acrolein. In the spectrophotofluorimetric determination of formaldehyde with J-Acid, ratios of acrolein to formaldehyde as high as 4 to 1 by weight can be tolerated, whereas ratios of 7 to 1 through 17 to 1 give intensity values that are about 25% higher than those obtained with the same concentration of formaldehyde alone. The following compounds gave negative results: methanol, ethanol, allyl alcohol, glycerol, acetone, 1,3-dihydroxyacetone, 2-butanone, 3-pentanone, biacetyl, acetaldehyde, chloral, propionaldehyde, glycolaldehyde, crotonaldehyde, glutaraldehyde, furfural, and glyoxylic acid. Large amounts of pyruvaldehyde and methacrolein and very large amounts of methanol give positive results.

Determination of formaldehyde with 1-ethylquinaldinium iodide

1-Alkylquinaldinium and lepidinium salts can also be used to determine formaldehyde spectrophotometrically. For example, 1-ethylquinaldinium iodide reacts with formaldehyde to give the trimethine dye absorbing at 608 mμ with $\varepsilon \sim 73{,}000$. With improvement this method could be approximately three times as sensitive with much better selectivity and precision. Other aliphatic aldehydes react to give one-fiftieth to one-fifth the intensity obtained with an equivalent amount of formaldehyde.

Spectrophotofluorimetric determination of acrolein

Variables in the recommended procedure were investigated. Optimum results were obtained with about 0.01 to 0.08% J-Acid. A concentration of 0.07% was chosen because the excitation spectra were more reproducible at this concentration than at the lower concentrations.

External heat was not needed to obtain good results except in the micro procedure where 30 min of heating on the water bath was required for optimum results. With the 30-min heating period the intensity was increased to almost 20 times that obtained with no external heating.

The excitation and emission intensities were stable for at least 1.5 h. For 21 determinations a percent deviation of 1.40 was obtained. A straightline relationship between readings and concentration was obtained from 0.25 to about 7 μg of acrolein.

The analysis for acrolein was performed with a solvent mixture containing about 70% water. The intensities were about as high as in solvent mixtures having lower concentrations of water. In 70% water, however, the formaldehyde chromogen becomes virtually non-fluorescent in the 500-mμ region. Its presence is then shown by a blue-colored solution. Although acrolein can be detected in the presence of a very large amount of formaldehyde, the presence of formaldehyde in greater than equivalent amounts interferes with the determination (Table I).

TABLE I

DETERMINATION OF ACROLEIN (1.68 μg) IN THE PRESENCE OF FORMALDEHYDE

Formaldehyde (μg)	*Excitation at λ 470 mμ Read at emiss. λ 500 mμ*	*Emission at λ 500 mμ Read at excit. λ 470 mμ*
0	0.60	0.60
0.45	0.60	0.60
1.8	0.59	0.59
4.5	0.43	0.43
8.1	0.31	0.31
90	~0.02	~0.02

Other interferences are methacrolein and crotonaldehyde, whose intensity in the procedure is about 1% that of acrolein. Although these aldehydes were distilled for these tests, their weak activity may have been due to impurities.

The following compounds gave negative results: acetaldehyde, propionaldehyde,

TABLE II

COMPARISON OF METHODS FOR THE DETERMINATION OF FORMALDEHYDE

Reagent	*Ref.*	*λ max*	*ε · 10⁻³*	*Beer's law range (μg)*[a]	*Dilution factor*[b]	*Sensitivity*[c]	*Precision (% deviation)*[d]	*Color stability (min)*	*Interferences*
o-Aminobenzaldehyde	9	440	2.5	12–120	2.5	1.0	—	—	Aliphatic aldehydes
Schiff	10	550	3.5	—	5	0.7	0.021	~30	—
Chromotropic acid	5,8	578	15.7	2.0–40	10	1.57	—	>24 h	Formaldehyde-yielding compounds
J-Acid (dication)	6	468	21.0	1.5–32	5	4.2	1.86	>24 h	Formaldehyde-yielding compounds
HBT + NBD	11	610	24	—	10	2.4	—	—	All aldehydes
J-Acid (monocation)	6	612	34	0.88–15	12.5	2.7	1.46	10	Formaldehyde-yielding compounds
Phenylhydrazine	12,13	520	34.2	0.88–15	25	1.4	—	15	—
HBT	14	582	48.0	0.62–12.5	10	4.8	1.78	20	Water-soluble aliphatic aldehydes give molar absorptivities of about 1800
					20	2.4			
Phenyl J-Acid	6	660	51.4	0.56–13	12.5	4.1	2.22	>24 h	Formaldehyde-yielding compounds
MBTH	7	670	65.0	0.5–9.2	10	6.5	0.40	>40	Water-soluble aliphatic aldehydes, aromatic amines, imino heterocyclic compounds
					20	3.25			
1-Ethylquinaldinium iodide	–	608	~73[e]	0.40–8.2	10	7.3	15	30	Other aliphatic aldehydes give molar absorptivities of about 1500 to 15000
		Excit. λ max	*Emiss. λ max*						
J-Acid Fluor.	–	470	520	0.01–2	—	—	8.8	>120	Formaldehyde-yielding compounds, acrolein

[a] Beer's law is not obeyed in Schiff and 1-ethylquinaldinium procedures. The Beer's law range is based on 10 ml final volume; lower limits for this range are taken at an absorbance of 0.1.

[b] Dilution factor is the proportion of final volume to test solution volume.

[c] $\text{Sensitivity} = \dfrac{\varepsilon \cdot 10^{-3}}{\text{Dilution factor}}$

[d] For each reagent the percent deviation is given for 10 to 12 determinations.

[e] For 9.9 μg of formaldehyde.

chloral, glyoxal, glutaraldehyde, acetone, 1,3-dihydroxyacetone, butanone, 3-pentanone, biacetyl, glyoxylic acid, glycolic acid, methanol, ethanol, allyl alcohol, and glycerol. Trioxane and piperonal gave light-blue colors.

Comparison of methods for the determination of acrolein shows that the 4-hexylresorcinol method is more selective and the fluorimetric method more sensitive.

Comparison of methods for the determination of formaldehyde

Twelve methods for the determination of formaldehyde are compared critically in Table II.

The simplest procedures for the determination of formaldehyde are the chromotropic acid, J-Acid dicationic, and the J-Acid spectrophotometric methods. These methods involve the fewest steps and require no external heating. The Schiff test is probably the most complicated and the most studied of all the procedures.

When the dilution factors of the various formaldehyde methods are equivalent, the 3-methyl-2-benzothiazolone hydrazone (MBTH)[7] and the quinaldinium procedures are the two most sensitive spectrophotometric methods. In the analysis of a gas for formaldehyde by passage of the gas through a sulfuric acid solution of chromotropic acid followed by a measurement of the absorbance[8], a dilution factor very close to 1 can be obtained. Such a method is then much more sensitive than comparable methods with dilution factors of about 10. Dilution factors of some of the other methods could also be improved in a similar fashion.

The J-Acid spectrophotofluorimetric method is by far the most sensitive method. With present instrumentation, however, standards must be run with each series of determinations and care must be exercised in using the instrument, *i.e.*, several readings should be taken on each solution, the instrument and cells should be kept free of dust, etc.

A comparison of the selectivities of the MBTH, HBT, J-Acid, phenyl J-Acid, and chromotropic acid methods shows that (*1*) MBTH gives positive results with many aliphatic aldehydes, (*2*) HBT gives positive results with aliphatic aldehydes but to about one-twentieth the intensity obtained with formaldehyde, (*3*) J-Acid, phenyl J-Acid, and chromotropic acid give positive results with formaldehyde-releasing compounds such as glyoxal, biacetyl, glyoxylic acid, glycolic acid, dextrose, piperonal, piperonylic acid, and anisyl alcohol[6], but give negative results with aliphatic aldehydes and many other types of compounds[6,8].

Many of the advantages and disadvantages of the procedures are enumerated in Table II. A more thorough understanding of these factors can be obtained by an examination of the original papers. The final determinant of whether any of these methods is superior for some particular problem is to try the method or some modification of it in the laboratory.

SUMMARY

Highly sensitive spectrophotofluorimetric methods for the determination and estimation of formaldehyde and acrolein have been described. Formaldehyde and acrolein can be estimated in amounts as low as 0.0005 μg formaldehyde and 0.01 μg acrolein. Quinaldinium salts have been shown to have high sensitivity for the spectrophotometric determination of formaldehyde. The procedure in which these salts are used has a high potentiality for further improvement. Twelve different methods for the determination of formaldehyde have been compared.

RÉSUMÉ

Des méthodes spectrophotofluorimétriques extrêmement sensibles sont décrites pour le dosage du formaldéhyde (0.0005 μg) et de l'acroléine (0.01 μg). Les sels de quinaldinium ont montré une grande sensibilité pour le dosage spectrophotométrique du formaldéhyde.

ZUSAMMENFASSUNG

Beschreibung von hochempfindlichen spektrofluorimetrischen Methoden zur Bestimmung von Formaldehyd und Acrolein durch Reaktion mit Chinaldinsalzen. Die Methode wird mit anderen Methoden zur Bestimmung von Formaldehyd verglichen.

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THE USE OF THE MASS SPECTROMETER FOR THE QUANTITATIVE ANALYSES OF MIXTURES OF AMINO ACIDS*

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The use of the mass spectrometer for quantitative assays of mixtures of amino acids has been reported by BIEMANN AND VETTER[1]. Their procedure requires the uniform conversion of the amino acids in a mixture to the ethyl esters and subsequent mass spectrometric analysis of the mixture of esters using an externally heated inlet system. The esterification is necessary because of the inherent experimental difficulty encountered when attempts are made to obtain the mass spectra of relatively low vapor pressure, unstable compounds such as the amino acids[2,3]. However, it is possible to overcome the experimental difficulties and to obtain a unique and reproducible mass spectrum of each individual amino acid by charging a crucible with the pure acid and then placing the crucible directly into the ionization chamber of the mass spectrometer**. The spectra of mixtures can be determined in the same manner used for the individual pure acids.

Mixtures of the amino acids were studied with the intention of establishing an instrumental method of quantitatively assaying amino acids. A method which is solely instrumental, *i.e.* free of any chemical treatment of the acid mixture, necessitates free sublimation from the surface of the mixture containing the amino acids. The aliphatic amino acids were chosen for the initial study because these acids are similar in structure and contain identical functional groups. Consequently, these acids should exhibit close to ideal vapor pressure behavior upon evaporation from the surface of a solid mixture. The possible extension of the method to include amino acids other than the aliphatic type is reported.

EXPERIMENTAL

A General Electric analytical mass spectrometer, modified to include a crucible ion source, was employed to obtain the data from which the results reported here were calculated. The energy of the ionizing electrons is adjustable but the spectra were taken using 75 V electrons. The mass spectra of the mixtures of the amino acids were obtained using the crucible source and instrumental conditions identical to those which were used to secure the spectra of the individual acids.

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* Contribution No. 1190. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

** Details of this experimental procedure are to be published elsewhere.

Synthetic mixtures were prepared by dissolving accurately weighed portions of the various acids in 1.5 ml of distilled water. The solution was then placed into a vacuum desiccator which was evacuated rapidly so that the solution froze. Evacuation continued until all the water was removed by sublimation. This procedure insured intimate blending of the crystal mixture even though a factor of six exists in the comparative solubilities of the acids reported here. Ball-milling the crystal mixture to a uniform fine powder further mixed the acids. The milling was done by placing 75 to 100 stainless steel ball-bearings (0.095 in. diameter) in a 10-ml vial which contained the dried acid mixture. The vial was rotated in a horizontal position at a speed sufficient to cause rapid tumbling of the bearings but not so fast as to cause the bearings to be held against the walls of the vial by the centrifugal force developed. In some instances, the analytical results with and without ball-milling compare favorably and the necessity of the ball-milling procedure is currently subject to question.

PROCEDURES AND RESULTS

It is necessary to normalize the raw data obtained from the mass spectrometer due primarily to the differences in the cross-sections for ionization, and the intensities of the parent-minus-carboxyl, $(\text{P–COOH})^+$, ion currents which are used to indicate the amount of each acid present in a mixture. Isoleucine was chosen as an internal standard to establish the sensitivity of the mass spectrometer for each of the amino acids – glycine, alanine, α-amino-*n*-butyric acid, and valine. Isoleucine was the common component in a series of five two-component mixtures, each containing one of the acids mentioned above. The mixtures were prepared in approximately a 50/50 mole ratio and each mixture was assayed mass spectrometrically. The raw data were corrected for any interference at the $(\text{P–COOH})^+$ masses of the two acids by the solution of two simultaneous equations. The sensitivity of isoleucine was arbitrarily set at 1.00 and the sensitivity of the other acid in the mixture was calculated using the known composition of the mixtures expressed in mole fractions (N) and the ratio of the $(\text{P–COOH})^+$ ion currents. Equation 1 illustrates a sample calculation for the sensitivity of glycine, (S_{gly}).

$$S_{\text{gly}} = \frac{(\text{P–COOH})^+ \text{ from gly} \cdot \text{known } N_{\text{iso}}}{(\text{P–COOH})^+ \text{ from iso} \cdot \text{known } N_{\text{gly}}}$$

The experimentally determined sensitivities which were obtained in this manner are tabulated in Table I along with the raw mass spectral data. The normalized spectra are listed in Table II. Values given were calculated by multiplying the mass spectral

TABLE I

RAW DATA MASS SPECTRAL PATTERNS

Mass	*Gly*	*Ala*	*But*	*Val*	*Isoleu*
30	100.00	1.18	16.16	12.30	37.05
44	2.65	100.00	0.39	2.19	10.97
58	0.00	0.04	100.00	3.67	5.67
72	0.00	0.12	0.17	100.00	0.49
86	0.00	0.00	0.11	0.03	100.00
S	0.880	0.873	0.889	0.965	1.000

pattern of each acid given in Table I by its sensitivity. With the use of the normalized spectral patterns and the observed raw data it is possible to set up simultaneous equations which enable one to calculate the composition of a mixture containing any combination of the listed acids.

TABLE II

NORMALIZED MASS SPECTRAL PATTERNS

Mass	*Gly*	*Ala*	*But*	*Val*	*Isoleu*
30	88.03	1.03	14.36	11.87	37.05
44	2.33	87.26	3.01	2.11	10.97
58	0.00	0.03	88.89	3.54	5.67
72	0.00	0.10	0.15	96.53	0.49
86	0.00	0.00	0.10	0.04	100.00

The applicability of the sensitivity for each acid through a reasonable composition range with isoleucine was checked with mixtures above and below 50 mole per cent isoleucine. These results are given in the first part of Table III. Additional checks on the reliability of the sensitivities were made by analyzing other two-component mixtures of glycine, alanine, α-amino-*n*-butyric acid, and valine.

When mixtures contain more than two components, the data should be taken in a manner similar to the following approach for best results. Only ion currents corresponding to the $(P\text{–}COOH)^+$ fragments of the acids known to be present in a mixture should be observed. Any pair of these ion currents can be successively focused on the ion collector by use of the manual magnetic scan control of the instrument. With a minimum of practice the time required to do this in the mass range 30 to 86 is less than 5 sec. The intensity of a particular $(P\text{–}COOH)^+$ ion current should be chosen as unity and a proportional intensity should be calculated for each of the other $(P\text{–}COOH)^+$ ion currents. These numbers (which are proportional to the observed ion currents but include interference currents) and the normalized fragmentation patterns are then used in setting up the necessary simultaneous equations. The solution of these equations yields numbers which are proportional to the $(P\text{–}COOH)^+$ ion currents which are corrected for differences in sensitivity and are free from any interference currents. The composition of the solid mixture is then readily computed using these proportional numbers.

The manual method of taking the data results in considerable time saving compared to the usual automatic scanning of the spectra and it eliminates much of the error caused by any changing ion intensities during the time it would ordinarily be necessary to complete the automatic scan.

Instrument time required to record enough data for a statistical treatment with a five-component mixture is less than 15 min. The increase in time with mixtures of more components should be small since it would be necessary to read only one additional ion current for each additional component. However, the time required to evacuate the instrument to a safe operating level and the bake-out of the ion chamber between samples, make it possible to run, on a routine basis, only two mixtures per 8-h day with the present instrumental setup. Suitable refinements however in the analyzer vacuum system could lead to more efficient use of instrument time and it is conceivable that four or five mixtures could be assayed in an ordinary 8-h day.

Comparisons of the known and observed compositions of some three-, four-, and five-component mixtures are given in Table III.

TABLE III

MIXTURE ANALYSES

Mixture no.	*Components*	*Known composition (mole %)*	*Observed composition (mole %)*
1	iso-gly	71.8 ± 0.7 gly	71.9 ± 1.9
2	iso-gly	40.0 ± 0.5 gly	39.1 ± 0.4
3	iso-ala	90.7 ± 0.4 ala	89.6 ± 0.7
4	iso-ala	33.9 ± 0.3 ala	34.2 ± 0.2
5	iso-but	66.3 ± 0.6 but	67.0 ± 0.9
6	iso-val	81.5 ± 0.5 val	82.0 ± 0.5
7	iso-val	35.7 ± 0.3 val	36.1 ± 0.5
8[a]	ala-gly	46.3 ± 0.3 gly	46.2 ± 0.1
9[a]	val-gly	49.4 ± 0.4 gly	52.3 ± 0.8
10[a]	val-ala	49.3 ± 0.4 ala	54.3 ± 0.5
11	ala-but	61.8 ± 0.6 but	60.3 ± 0.5
12[a]	ala	30.3 ± 0.3	30.8 ± 0.9
	iso	17.6 ± 0.2	14.8 ± 1.5
	val	52.2 ± 0.5	54.4 ± 0.5
13[a]	gly	56.8 ± 0.4	56.1 ± 0.6
	ala	26.9 ± 0.3	28.0 ± 0.4
	iso	16.3 ± 0.2	16.0 ± 0.3
14[a]	gly	28.0 ± 0.2	28.2 ± 0.3
	ala	24.0 ± 0.3	23.2 ± 1.3
	val	25.8 ± 0.2	25.8 ± 0.2
	iso	22.1 ± 0.2	22.8 ± 0.8
15[a]	gly	28.1 ± 0.2	28.8 ± 0.3
	ala	34.1 ± 0.3	35.4 ± 0.4
	but	23.8 ± 0.2	23.5 ± 0.3
	iso	14.0 ± 0.2	12.3 ± 0.7
16[a]	gly	25.5 ± 0.2	25.0 ± 0.6
	ala	29.8 ± 0.2	30.2 ± 0.6
	but	10.6 ± 0.2	11.3 ± 0.2
	val	19.8 ± 0.2	19.6 ± 0.6
	iso	14.3 ± 0.2	13.9 ± 0.7

[a] The observed results on these mixtures represent the average deviations of two sets of data from the solid mixtures obtained from the same standard solution. (All the results demonstrate the limits of reproducibility of the ion currents over a 1-h period.)

DISCUSSION

Some of the observed compositions listed in Table III were calculated using fragmentation patterns which had been established five months prior to the time the mixture data were taken. Small changes in the source conditions which affect the ionization and fragmentation processes could account for part of the discrepancies between the observed and known compositions. On a routine basis, the accuracy of the results could be improved by running calibrating mixtures at frequent intervals in a manner following the practice employed in the assay of hydrocarbon mixtures.

The reason for the poor results with many of the mixtures containing valine can be attributed to improper mixing. Valine has a physical form which is flakier than the other amino acids. This characteristic may have caused sublimation from the surface of the acid mixture which is not representative of the composition of the bulk of the mixture. Thus some question exists regarding the consistent applicability of valine to the freezing out and ball-milling procedures.

Attempts to use the low voltage technique originally described by FIELD AND HASTINGS[4] for quantitative assays were only moderately successful because instrumental sensitivity was low. Thus it was necessary to raise the temperature of the ion chamber to increase the ion currents at the $(P\text{–}COOH)^+$ masses. These ion currents, however, were unstable and a high proportion of the data had to be rejected due to changes in the ion intensities which occurred during the time required to successively focus any two ion currents. This high rejection rate of the observed data makes the use of the low voltage technique unsatisfactory.

No attempts were made to facilitate the use of the technique by improving the sensitivity and ion current stability of the General Electric instrument. However, the increase in accuracy and shortening of computational time, which are the desirable aspects of the use of the low-voltage technique, warrant possible future improvements in the instrument.

The mass spectrometric method of analysis described here has been checked with a representative number of acids and should be applicable to all other aliphatic amino acids as well as methionine, proline, and phenylalanine. The very nature of the method (free sublimation from the surface of a solid mixture in the source region) prevents the extension of the method to include more complex acids such as tryptophan, serine, aspartic acid, cystine, etc., since these acids have vapor pressures which are low relative to those of the aliphatic amino acids. Hence complex acids cannot be detected or analyzed to any high degree of sensitivity in mixtures which contain the aliphatic amino acids.

The method could be well applied to other organic compounds of limited stability and low vapor pressure. In view of the excellent behavior of mixtures of the series of aliphatic amino acids reported here, reasonable accuracy might be expected with mixtures of organic solids which are quite dissimilar in structure but have similar vapor pressures and even solid mixtures of inorganic compounds which are in the proper vapor pressure range.

The data tabulated in Table IV show the intensity of the $(P\text{–}COOH)^+$ ion currents relative to the total ion intensity, and the experimentally determined sensitivities of the aliphatic amino acids. The fragmentation data suggest that the mass spectrometer is least sensitive to isoleucine and progressively more sensitive as the amino

TABLE IV

INTENSITY OF THE $(P\text{–}COOH)^+$ FRAGMENTS RELATIVE TO THE TOTAL ION INTENSITY

	% of total	*Sensitivity*
gly	68	0.880
ala	49	0.873
but	33	0.889
val	28	0.965
isoleu	21	1.000

acid molecular structure becomes less bulky. However, a wide discrepancy exists between the experimentally determined sensitivities and the relative intensities of the $(P\text{-}COOH)^+$ fragments. Evidently the observed large difference in the intensity of the $(P\text{–}COOH)^+$ ion fragment which is used to measure the amount of the vapor present in the ion-source region is balanced by other factors such as the cross-sections for ionization, gas flow, and the vapor pressures. Of these effects those due to vapor pressures and gas flow are small. However, the ionization cross-section effect is quite large since the cross-section is a constitutive property[5] which causes a uniform and rapid increase in sensitivity from glycine to isoleucine.

The authors thank G. FLESCH for helpful suggestions regarding the calculations.

SUMMARY

The quantitative analysis of a low vapor pressure unstable solid mixture of amino acids is possible by putting the solid mixture in a crucible which is then placed directly into the ionization chamber of a mass spectrometer. Relative sensitivities for the various acids in a mixture can be established by the proper use of a particular amino acid as an internal calibrating standard. The success of the method depends upon: (1) the reproducibility of the mass spectra of the pure components, (2) the ideal vapor pressure behavior of the solid mixture, (3) the preparation of an intimate solid mixture by rapid freezing of the water solution of the acids with subsequent vacuum sublimation of the ice and ball-milling the dried mixture.

RÉSUMÉ

Les auteurs décrivent une méthode utilisant le spectromètre de masse pour l'analyse quantitative de mélanges d'acides aminés. La réussite de la méthode dépend: (1) de la reproductibilité des spectres de masse des composants purs, (2) du comportement du mélange solide (tension de vapeur), et (3) de la préparation de l'échantillon.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Analyse von Gemischen von Aminosäuren mit Hilfe des Massenspektrographen. Die Brauchbarkeit der Methode hängt ab: (1) von der Reproduzierbarkeit der Massenspektren der Komponenten, (2) vom Dampfdruckverhalten der festen Mischung, und (3) von der Homogenität des Gemisches der festen Substanzen.

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FURTHER OBSERVATIONS IN ATOMIC ABSORPTION SPECTROSCOPY

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During the course of studying the phenomenon of atomic absorption spectroscopy, several interesting and pertinent observations were made. These are outlined below.

The mechanism of metal atom production in flames

A basic prerequisite for the understanding of atomic absorption is the understanding of the mechanism by which metal atoms are produced in flames. This is a key to the understanding of the reasons why some metals are detectable by atomic absorption in flames while others are not, and of the effect of different solvents on the absorption signal. A suggested mechanism is shown in Table I.

TABLE I

MECHANISM OF METAL ATOM REDUCTION IN FLAMES

Part of flame	*Physical form of sample*	*Reaction*	*Factors controlling reaction*
Outer mantle	Oxide	Equilibrium with metal atoms	Flame composition, stability of oxide
↑	↑		$M + O_2 \overset{K_{eq}}{\rightleftharpoons} Mox$
Reaction zone	Atoms	Oxidation	Flame composition, stability of oxide
↑	↑		
Inner cone	Solid particles	Disintegration to atoms	Flame temperature, anion
↑	↑		
Base	Droplets	Evaporation	Droplet size, solvent, flame temperature, feed rate

The population of atoms at any point in the flame is probably dependent on the reactivity of the metal itself. A flame profile is a plot of atomic absorption by a given metal *vs.* height above the base of the flame. Typical flame profiles are shown in Fig. 1.

The lower part of the profile is controlled by the production of atoms. It is therefore dependent on vaporization and the reduction step. The upper part of the profile is controlled by the rate of loss of atoms — probably by oxidation — and should be

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a function of the reaction $M + O_2 \overset{K_{eq}}{\rightleftharpoons} Mox$. Hence, there should be a relationship between the position of maximum absorption in the flame and the oxide stability.

To check this, stabilities were calculated by extrapolating ΔF (free energy) up to 3000°K which is the approximate temperature of the oxy-hydrogen flame. The equilibrium constant was calculated from the relationship $K_{eq} = e^{-\Delta F/RT}$ where K_{eq} is the equilibrium constant, ΔF is the free energy change, R the universal gas constant in calories and T the absolute temperature. Although the values for ΔF are not exact because of lack of thermodynamic data describing possible phase changes, they are of the right relative order. A comparison of values is shown in Table II. This shows a close correlation between oxide stability and the position of the absorption maximum in the flame. Of course it will be appreciated that the position of the maximum will also be affected by flame temperature and the composition of the flame, *i.e.* if the flame is oxidizing (excess oxygen) or reducing (excess hydrogen).

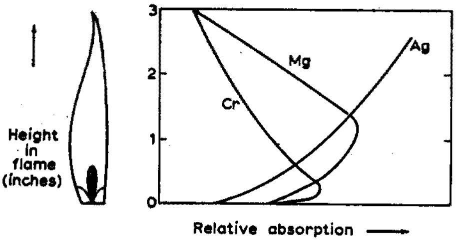

Fig. 1. Flame profile.

Metal	*Maximum absorption*	*Stability of oxide*
Cr	Low	High
Mg	Middle	Medium
Ag	High	Low

TABLE II

ORDER OF OXIDE STABILITY

Oxide stability	*Predicted from flame profiles*	*Calculated from ΔF values*	K_{eq}
Least stable	Cd ⟩ Same order	Cd	$10^{-4.1}$
	Ag	Ag	$10^{-2.7}$
	Tl	Tl	$10^{1.5}$
↓	Mg	Mg	$10^{1.9}$
Most stable	Cr	Cr	$10^{5.9}$

The enhancement of the absorption signal by organic solvents and organo-metallic compounds

In organic solutions, the absorption signal varies with the type of solvent but usually is equal to or greater than the absorption signal from an analogous aqueous solution. This enhancement has been attributed to a more efficient production of atoms from organic solutions and to the increased flame temperature. This increase in efficiency of atom production may be divided into two aspects: (*1*) easier combustion of organic solvents than water, and (*2*) easier chemical release of atoms from an organic addend than from an inorganic salt.

A brief study has been made to determine the effect of easier chemical release of atoms in a flame, *e.g.* from an organic addend. Results are shown in Table III.

TABLE III

EFFECT OF EASIER CHEMICAL RELEASE OF ATOMS IN A FLAME

All solutions contained 10 p.p.m. chromium except where indicated

Solute	*Solvent*	*Signal $I_0 - I_1$*
Sodium chromate	Water	16.5
Chromic nitrate	Water	16.0
Chromic nitrate	Ethanol	20.5
Chromium naphthenate	Ethanol	26.5
Sodium chromate (4 p.p.m. only)	Ethanol–Benzene (50 : 50)	9.5
Chromium naphthenate	Ethanol–Benzene (50 : 50)	33
Chromium naphthenate	Benzene	39
Chromium naphthenate	Ethanol	27

The results indicate that when organo-metallic solutions are used, a greater absorption signal is obtained. This supports the thesis that the population of metal atoms in a given flame is increased both by using organic solvents and by the use of organo-metallic compounds. These results indicate that the organo-metallic compounds in organic solutions would give the most absorption and that inorganic-aqueous solutions would give the smallest sensitivity. If, therefore, maximum sensitivity is required, the metal should be in an organic solvent and in the form of an easily decomposed organo-metallic compound.

Hydroxyl absorption bands in atomic absorption spectroscopy

In the course of scanning the spectra of various metals to determine the wavelengths at which atomic absorption occurs, certain metal emission lines were found to be partially absorbed by the flame alone. At first, it was thought that this absorption might be due to traces of copper, platinum, osmium or iridium from the burner that had contaminated the flame. However, no additional absorption was observed

TABLE IV

ABSORPTION OF COPPER 2824 Å LINE BY VARIOUS FLAMES

Light path through flame	*Absorption ($I_0 - I_1$)*			*Amplifier noise level*
	Flame alone	*Organic solvent in flame*	*Aqueous solvent in flame*	
Oxy-hydrogen flame				
High	64	54	56	2
Middle	60	38	56	2
Low	40	25	39	2
Oxy-cyanogen flame				
High	15	42	—	2
Middle	12	27	34	5
Low	2	14	—	4

when solutions of these metals were introduced into the flame. Further investigations gave the results tabulated in Table IV.

It was found that organic solvents significantly decreased the absorption by the oxy-hydrogen flame while aqueous solutions only slightly decreased the absorption. This effect was a function of the solvent, although the presence of a metal ion in the solvent usually resulted in a lower noise level and a stabilization of signal. The oxy-cyanogen flame absorbed at least 25% less than the oxy-hydrogen flame. In the oxy-cyanogen flame both organic and aqueous solvents caused additional absorption.

These rather diverse observations can all be explained by assuming that hydroxyl radicals are produced in the flame, generating absorption bands. When an aqueous solution is aspirated into the oxy-hydrogen flame, the rate of production of hydroxyl radicals is only slightly decreased due to the slight lowering of the flame temperature. Although an organic solvent increases the flame temperature slightly, the rate of production of hydroxyl radicals must be decreased to agree with the observations. Simon[1] found the rate constant k for the combustion reaction of various hydrocarbon flames, with the exception of C_2H_4, to be $1.4 \pm 0.1 \cdot 10^{11}$ cm^3 mole^{-1} sec^{-1} while Tanford and Pease[2] have calculated a value of $3.9 \cdot 10^{11}$ cm^3 mole^{-1} sec^{-1} for a hydrogen flame. Since these values can be roughly correlated to the rate of hydroxyl radical production, they suggest a decreased rate in the presence of an organic solvent.

An oxy-cyanogen flame would also be expected to contain hydroxyl radicals because both the cyanogen and the oxygen contain some water vapor, but the concentration should be less than in the oxy-hydrogen flame. When an organic solvent or an aqueous solution is aspirated into the oxy-cyanogen flame the hydroxyl radical concentration should increase which would lead to the observed increase in absorption. This hydroxyl radical assumption also explains the variation in absorption with the height of the light path through the flame.

To determine the limits of these hydroxyl absorption bands, the spectrum from a hydrogen discharge lamp was scanned with and without the flame in the light path. Absorption regions were observed between the wavelengths 2800–2860 Å and 3060–3200 Å. These regions correspond to those at which hydroxyl emission bands occur[3]. It has been reported by Herzberg[4] that both excited and ground state hydroxyl radicals are present in the combustion of an oxy-hydrogen flame. These

TABLE V

SPECTRAL LINES ABSORBED AND NOT ABSORBED BY HYDROXYL ABSORPTION BAND IN FLAMES
2800–2860 Å
3060–3200 Å

Absorbed by flame		*Not absorbed by flame*	
Hollow cathode	*A*	*Hollow cathode*	*A*
Pb	2802 - Slight absorption	Pt Pb and Ta	2818
Cu	2824		2823
Pt	2830		2840
Pb	2833 - Slight absorption		2851
Pt	3065		3058
Ta	3103		3094
Pb	3175		3118
			3174
			3176
			3180

observations seem to corroborate the theory that the observed absorption is due to the hydroxyl radicals in the flame.

The absorption spectrum of hydroxyl radicals was first observed by Bonhoeffer and Reichardt[5] in thermally dissociated water vapor at temperatures up to 1600°C. Further attempts to observe similar absorption in electric discharge tubes and in chemical reactions led to failure until 1934 when Oldenberg[6] observed hydroxyl absorption bands in electric discharge tubes by using a spectrograph with a twenty-one foot grating. This work extends the observation of hydroxyl absorption bands during the chemical reaction of combustion up to temperatures near 5000°C.

The hydroxyl absorption bands have been observed to differ from the emission bands in intensity and occurrence of band heads as was described by Oldenberg[6]. A continuum of absorption is not observed and thus all metal emission lines in the regions of absorption are not absorbed. For instance, the 3065 Å Pt and 3103 Å Ta lines are partially absorbed but the Ta 3049 Å and Ta 3118 Å lines show no absorption. Table V tabulates the lines investigated which do or do not show absorption in the hydroxyl absorption band region.

The existence of the hydroxyl absorption bands does have a practical effect on atomic absorption. Since, in an oxy-hydrogen flame, organic solvents decrease the flame absorption in the hydroxyl absorption band region it would be predicted that an organic solution of a metal whose emission line is partially absorbed in this region would give a smaller total absorption signal than that obtained from an equal concentration of the metal in an aqueous solution. This is confirmed by experiment as is shown by the following data:

Absorption of the Pt 2830 Å line	
500 p.p.m. Pt in 2% HCl	10 units
500 p.p.m. Pt in C_2H_5OH–2% HCl (50 : 50)	4 units
Absorption of the Pt 3065 Å line	
500 p.p.m. in 2% HCl	22 units
500 p.p.m. in C_2H_5OH–2% HCl (50 : 50)	10 units

It is worth noting that methanol decreases the absorption to about 66% of that obtained from hydrocarbon solvents. The lead 2802 Å and 2833 Å absorption lines give similar results.

It would be expected that this solvent effect could be eliminated by subtracting the absorption due to a blank (solvent only) from the total absorption signal. However, it has been found that this is not the case. A smaller signal is still obtained with organic solvents than with aqueous ones. Evidently, the two processes, the absorption due to the metal atoms and the decreased absorption due to the organic solvent, cannot be considered separately.

A calibration curve (absorption signal *vs.* concentration) was made for the 50% organic solution of platinum at the 3065 Å line in which the absorption signal was corrected for flame absorption but not for decreased absorption due to solvent. The resultant calibration curve was linear. This indicates that although the limits of detection are lowered in the organic solvent, the validity of the quantitative method is not affected.

In the oxy-cyanogen flame the absorption signal of lines such as the 3065 Å platinum line is enhanced more by organic than by aqueous solvents as would be predicted. This trend is the same as that for metal absorption lines outside the hydroxyl absorption band region.

From a practical viewpoint, the effect on atomic absorption is only important when determinations are made in the oxy-hydrogen flame and when the line of any one element which is most sensitive to absorption coincides with a strong absorption band in the hydroxyl absorption band region.

From the group Ba, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Hg, Ni, Pd, Pt, K, Rh, Ag, Na, Sr, Sn, and Zn, only Pb, Mg, Mn, and Sn have their wavelengths, which are most sensitive to absorption, occurring in the hydroxyl absorption band region. The 2852 Å magnesium line is unaffected and the enhancement of signal by an organic solvent in any oxy-hydrogen flame is observed as usual. However, the 2833 Å lead line is subject to flame absorption and organic solvents reduce the signal in oxy-hydrogen flames as is pointed out above. Hence, the greatest sensitivity for the atomic absorption determination of lead in oxy-hydrogen flames may be realized in aqueous rather than organic solutions. Quantitative validity is still retained in the organic solutions as is shown by the linearity of the calibration curve. The presence of hydroxyl absorption bands also explains some incongruities found in the theory of absorption signal enhancement by organic solvents[7] at wavelengths found in the hydroxyl absorption band region.

The authors wish to thank Humble Oil and Refining Company for permission to publish this article.

SUMMARY

Three observations have been made pertinent to atomic absorption spectroscopy. With a flame atomizer, it is shown that (*1*) the absorption profile is controlled by metal oxide formation, (*2*) organo-metallic compounds give rise to greater absorption than metal salts, and (*3*) absorption by hydroxyl bands affects the apparent metal absorption in certain spectral regions.

RÉSUMÉ

Exposé de quelques remarques concernant l'absorption atomique:
(*1*) Le profil d'absorption est contrôlé par la formation d'oxyde métallique.
(*2*) L'absorption des composés organo-métalliques est plus grande que celle des sels métalliques.
(*3*) L'absorption, dans certaines régions spectrales, peut être affectée par les hydroxyles.

ZUSAMMENFASSUNG

Bei der Anwendung eines Flammenzerstäubers bei der atomaren Absorptionsspektroskopie wurde festgestellt, dass
(*1*) das Absorptionsprofil durch die Bildung von Metalloxyd bestimmt wird,
(*2*) Organometallverbindungen stärkere Absorption zeigen als Metallsalze,
(*3*) die Absorption in gewissen Spektralbereichen durch Hydroxyle beeinflusst wird.

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THE DETERMINATION OF PERIODATE BY INFRARED SPECTROSCOPY

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The infrared technique has been used for the systematic identification of polyatomic anions[1] and for the determination of pertechnetate and perrhenate ions[2]. In the literature, few methods are known for the determination or identification of periodate ion on a microgram scale. The classical methods for determining periodate are slow and tedious and the presence of iodate, bromate, chlorate and perchlorate with periodate adds complexity to the methods. Tetraphenylarsonium chloride is a known reagent for precipitating periodate, perrhenate, and a large number of similar anions[3]. Unfortunately, no gravimetric method with this reagent is possible unless methods of separation for other ions are used.

This paper describes the determination of periodate by infrared spectroscopy with separation from other anions. The advantages in using tetraphenylarsonium chloride have been discussed in earlier work[1,2].

EXPERIMENTAL

Reagents and apparatus

The spectra were recorded on a Perkin-Elmer infrared spectrophotometer, "Infracord" Model 137. Potassium bromide discs were prepared with a Perkin-Elmer die using an "Apex" hydraulic press with a 10-ton capacity on a ram of 2.1/8 inch diameter. The complete potassium bromide disc is fixed on the "Infracord" with a simple holder. Before use, the potassium bromide which is of analytical grade, was ground in a mortar to pass a cloth of 100 mesh and dried at 150° for 24 h. The tetraphenylarsonium chloride (L. Light & Co. Ltd.) was used as a 5% aqueous solution. All other reagents and chemicals were of AnalaR grade. The potassium periodate standard solution contained 500 μg IO_4^- per ml. Potassium perchlorate was used as an aqueous solution containing 5 mg per ml.

Procedure

To a solution of periodate containing 100–1000 μg in a volume of not more than 10 ml, add 2 ml of perchlorate solution as a carrier, 2 drops of concentrated hydrochloric acid, about 1.2 g of sodium chloride and a measured excess of tetraphenylarsonium chloride solution. Stir the solution vigorously for several minutes to improve precipitation. Allow to stand in an ice-bath for nearly 2 h. Filter on a weighed microsintered crucible. Wash the precipitate with an ice-cold saturated solution of sodium chloride, then once with ice-cold water. Dry the precipitate at 105° to constant weight. Break up any lumps with the aid of a microspatula, and weigh accurately about 2 mg together with about 298 mg of powdered potassium bromide to form a mixture of exactly 300 mg. Place the mixture in a mortar and mix. Grind for 10 min. Transfer the mixture to the die. Since the mixture is homogeneous, it need not be transferred quantitatively. Assemble the die and apply the vacuum for 2 min, then while under vacuum, apply gradually a pressure of 10 tons for 5 min. Fix the disc in the holder and scan the spectra from 10.5–12.0 μ using a pure potassium bromide disc of the same weight in the reference beam. Draw a base-line on the chart between 11.5 and 12.0 μ. Determine I_0 and I_t, and calculate the absorbance in the normal way. Correct the absorbance to a 300 mg basis, *i.e.* multiply by $300/W$, where W is the actual weight of the disc. Calculate the concentration of periodate from a calibration curve, prepared according to the above procedure (Fig. 1).

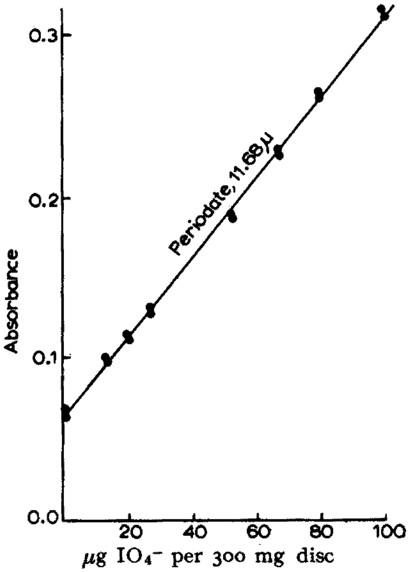

Fig. 1. Plot of absorbance of IO_4^-.

RESULTS AND DISCUSSION

The periodate ion in the tetraphenylarsonium complex (TPAC) exhibits a strong and sharp absorption band at 11.68 μ. In fact, it is the centre of 2 close and overlapping bands at 11.64 and 11.72 μ. These 2 bands appear only at high concentration of periodate ion[1].

In this method, perchlorate was used as a carrier. Tetraphenylarsonium perchlorate exhibits a very weak absorption band at 11.7 μ and when about 2 mg of a mixture of tetraphenylarsonium perchlorate was mixed with about 300 mg of potassium bromide, the perchlorate band at 11.7 μ showed an absorbance value of about 0.06 units (Fig. 1).

Anions which form precipitates with TPAC but which do not show interfering bands at 11.7 μ are permanganate, pertechnetate, perrhenate, persulphate and chlorate. The presence of large quantities of these ions tends to dilute the periodate.

Interference by molybdate and tungstate can be eliminated by adding excess of citrate ion. Dichromate must be reduced with ferrous sulphate in acid solution. The presence of chloro-complexes of mercury, zinc, cadmium and tin, although they form precipitates with TPAC, does not cause interference at 11.7 μ, but excessive amounts of these ions act as diluents to periodate. A number of "unknowns" containing periodate ion in the presence of a number of other anions were analysed. The results are shown in Table I.

TABLE I

DETERMINATION OF IO_4^- IN THE PRESENCE OF OTHER IONS

Sample No.	*Periodate (µg)*		*% Error*	*Other anions present*	*mg*
	Given	*Found*			
1	400	390	− 2.5	—	—
2	200	206	+ 3.0	Iodate	5.0
3	200	207	+ 3.5	Chlorate	10.0
4	200	207	+ 3.5	Bromate	8.3

SUMMARY

An infrared method has been developed to determine periodate on the microgram scale. Periodate is precipitated in slightly acid solution with tetraphenylarsonium chloride and in presence of perchlorate as carrier. The precipitate is mixed with powdered potassium bromide and pressed into a disc. The base-line absorbance of the periodate band at 11.68 μ is calculated in order to find the concentration of periodate from a calibration curve. No interference is caused by perchlorate, permanganate, perrhenate, chlorate, iodate or bromate.

RÉSUMÉ

Une méthode par spectrophotométrie infra-rouge est décrite pour le microdosage des periodates par précipitation en solution légèrement acide au moyen de chlorure de tétraphénylarsonium et en présence de perchlorate.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Mikromengen von Periodat durch IR-Spektroskopie nach Fällung mit Tetraphenylarsoniumchlorid.

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DIE ANALYTISCHE ANWENDUNG DER KOHLENDIOXYDDESTILLATION

III. UNTERSUCHUNG VON DEKARBOXYLIERUNGSREAKTIONEN IN WÄSSRIGER LÖSUNG

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Die Bestimmung des im Laufe von Dekarboxylierungsreaktionen gebildeten Kohlendioxyds ermöglicht die selektive Feststellung der Menge mehrerer Karbonsäuren. In einigen Fällen spielt sich die Dekarboxylierung in wässrigen Lösungen spontan ab, in anderen Fällen lassen sich die Karbonsäuren so oxydieren, dass nur aus der Karboxylgruppe Kohlendioxyd gebildet wird. Für die Dekarboxylierung und die Bestimmung des bei dieser gebildeten Kohlendioxyds sind zahlreiche Methoden bekannt geworden[1]. In vorliegender Arbeit soll über die Ergebnisse unserer Untersuchungen über Dekarboxylierungsreaktionen unter Anwendung unseres bereits früher beschriebenen Verfahrens zur Bestimmung von Kohlendioxyd berichtet werden[2-4].

Das Verfahren ermöglicht die rasche und genaue Bestimmung des im Laufe von Dekarboxylierungsreaktionen gebildeten Kohlendioxyds im 0.1 und 0.01 *N* Massstabe.

Im ersten Teil unserer Untersuchungen befassten wir uns mit der Bestimmung von Karbonsäuren, die bereits beim Kochen der wässrigen Lösung Kohlendioxyd abspalten. Hierzu gehören die Acetondikarbonsäure, die Acetessigsäure (Acetessigester) sowie die substituierten Malonsäure bzw. Cyanessigsäure-Derivate. Ein ähnliches Verhalten zeigt auch die *p*-Aminosalizylsäure[5]. Die Frage war, unter welchen Bedingungen die Dekarboxylierung in verdünnten Lösungen quantitativ vor sich geht.

Die Bestimmung der Acetondikarbonsäure wurde im Zusammenhange mit einem technischen Problem näher untersucht. Erfahrungsgemäss findet bei dieser Verbindung auch in kristallinem Zustande schon bei Raumtemperatur eine allmähliche Zersetzung statt:

$$\mathrm{HOOC{-}CH_2{-}CO{-}CH_2{-}COOH} \rightarrow 2\ \mathrm{CO_2} + \mathrm{CH_3COCH_3} \quad (1)$$

Die jodometrische Titration des im Laufe der Dekarboxylierung gebildeten und abgetrennten Acetons ermöglicht die selektive Bestimmung der Acetondikarbonsäure bzw. der Citronensäure[6]. Da die zersetzte Acetondikarbonsäure jedoch etwas Aceton zurückhält, ist bei deren Bestimmung über das Kohlendioxyd ein genaueres Ergebnis (Tabelle I) zu erwarten.

Praktisch lässt sich diese Bestimmung unter Verwendung der früher beschriebenen Apparatur äusserst einfach durchführen (Abb. 1, Mitt. II[3]). Man gibt die zu untersuchen Acetondikarbonsäure-Lösung durch den Hahntrichter in kleinen Anteilen in den Destillationskolben, der verdünnte CO_2-freie Säure enthält und destilliert das

TABELLE I

BESTIMMUNG DER ACETONDIKARBONSÄURE ÜBER DAS BEI DER DEKARBOXYLIERUNG GEBILDETE KOHLENDIOXYD

Einwaage Acetodikarbonsäure (g/100 ml)	*Einwaage Stammlösung (ml)*	*Verbrauch 0.1 N $Ba(OH)_2$-Lösung (ml)*		*Gefunden Acetondikarbonsäure*	
		einzeln	*mittel*	*(mg)*	*(%)*
0.1845	10.06	5.07 5.07	5.07	18.52	99.7
	5.04	2.54 2.53	2.54	9.28	99.7
	2.01	1.02 1.01	1.01	3.69	99.5

TABELLE II

BESTIMMUNG VON ACETESSIGESTER ÜBER DAS BEI DER HYDROLYSE UND DEKARBOXYLIERUNG GEBILDETE KOHLENDIOXYD

Einwaage Acetessigester (g/100 ml)	*Einwaage Stammlösung (ml)*	*Verbrauch 0.1 N $Ba(OH)_2$-Lösung (ml)*		*Gefunden Acetessigester*	
		einzeln	*mittel*	*(mg)*	*(%)*
0.6431	10.00	9.70 9.70	9.70	63.05	98.0
	5.04	4.87 4.93	4.90	31.88	98.4
	2.01	1.95 1.94	1.95	12.69	98.2

TABELLE III

Verbindung	*Dekarboxylierung in % nach Hydrolyse Hydrolysedauer*	
	60 Min	*120 Min*
Cyklohexenylcyanessigester	55.1	59.3
Cyklohexenyläthylcyanessigester	36.4	51.3
Cyklohexenylbutylcyanessigester	59.3	82.4
Diäthylmalonsäurediäthylester	11.7	
Äthylbutylmalonsäurediäthylester	5.38	

Kohlendioxyd in eine Bariumhydroxydlösung deren Überschuss anschliessend titriert wird.

Bei der Zersetzung des Acetessigesters bzw. der Substituierten Malonester und Cyanessigester geht der Dekarboxylierung eine Hydrolyse des Esters voraus. Mit befriedigender Geschwindigkeit spielt sich die Hydrolyse jedoch nur in alkalischen Lösungen ab. Hierzu muss eine Karbonatfreie Lauge verwendet werden und es ist darauf zu achten, dass die Lauge keine Kohlensäure aus der Luft aufnehmen kann.

Unseren Erfahrungen nach weist unter den allgemein üblichen sogenannten „karbonatfreien" Laugen die entsprechend gelagerte Bariumhydroxydlösung die geringste Karbonat-Verunreinigung auf.

Die Bestimmung des sich im Zusammenhange mit der Hydrolyse der Ester infolge von Dekarboxylierung bildenden Kohlendioxyds erfolgt nach der im Versuchsteil beschriebenen Vorschrift. Die Bestimmung des Acetessigesters lässt sich nach dieser Methode mit grosser Genauigkeit durchführen (Tabelle II). Unter den angewandten experimentellen Bedingungen tritt die Dekarboxylierung nur bei einigen Estern der Malonsäure und Cyanessigsäure bzw. deren substituierten Derivaten ein (Tabelle III). In 2–50%iger Schwefelsäurelösung erleidet die Malonsäure keine spontane Dekarboxylierung. Eine quantitative Dekarboxylierung konnte aus der Reihe der untersuchten substituierten Malonsäure- bzw. Cyanessigsäure-Derivate nur im Falle des Phenyläthylcyanessigsäureäthylesters festgestellt werden; die Bestimmung dieser Verbindung ist unter den oben beschriebenen Versuchsbedingungen durchführbar (Tabelle IV).

Unter ähnlichen Bedingungen lassen sich auch die Kohlensäureester bestimmen. Die starke Flüchtigkeit dieser Verbindungen macht es jedoch notwendig, die Hydrolysebedingungen peinlichst genau einzuhalten. Man hydrolysiert diese Verbin-

TABELLE IV

BESTIMMUNG DES PHENYLÄTHYLCYANESSIGSÄUREÄTHYLESTERS ÜBER DAS BEI DER DEKARBOXYLIERUNG GEBILDETE KOHLENDIOXYD

Einwaage Phenyläthylcyanessigsäureäthylester (g/100 ml)	*Einwaage Stammlösung (ml)*	*Verbrauch 0.1 N $Ba(OH)_2$-Lösung (ml)*		*Gefunden Phenyläthylcyanessigsäureäthylester*	
		einzeln	*mittel*	*(mg)*	*(%)*
0.9740	10.05	8.97 8.98 9.00	8.97	97.5	99.6
	4.99	4.44 4.45 4.47	4.45	48.3	99.1
	2.01	1.80 1.79 1.78	1.79	19.4	99.3

TABELLE V

BESTIMMUNG DES DIÄTHYLKARBONATS ÜBER DAS BEI DER HYDROLYSE GEBILDETE KOHLENDIOXYD

Einwaage Diäthylkarbonat (g/100 ml)	*Einwaage Stammlösung (ml)*	*Verbrauch 0.1 N $Ba(OH)_2$-Lösung (ml)*		*Gefunden Diäthylkarbonat*	
		einzeln	*mittel*	*(mg)*	*(%)*
0.6331	10.05	10.74 10.76	10.75	63.5	99.8
	5.03	5.39 5.40	5.39	31.8	100.0

dungen auf dem Wasserbade unter dem Rückflusskühler längere Zeit hindurch und isoliert das im Laufe der Reaktion gebildete Kohlendioxyd aus dem Bariumkarbonat nach Ansäuern der Lösung durch Destillation (Tabelle V).

Das Problem der Bestimmung des Phenyläthylcyanessigsäureäthylesters und Kohlensäurediäthylesters nebeneinander, ergab sich im Zusammenhange mit einer konkreten präparativen Aufgabe. Die Bestimmung wurde durch die Tatsache ermöglicht, dass sich der Kohlensäurediäthylester aus äthanolischer Lösung in Gegenwart des Phenyläthylcyanessigsäureesters von diesem durch Destillation quantitativ trennen lässt. Die isolierten Komponenten wurden dann nach Hydrolyse mit Bariumhydroxyd mit Hilfe unserer Destillationsmethode über das Kohlendioxyd bestimmt.

Einige Methoden zur Bestimmung von Karbonsäuren über das bei der oxydativen Dekarboxylierung gebildete Kohlendioxyd wurden in unseren früheren Mitteilungen bereits eingehend beschrieben, namentlich die Bestimmung der Ameisensäure durch Oxydation mit Quecksilber(II)chlorid[3], der Oxalsäure mit Permanganat[2] sowie der Aldonsäuren und Zuckerdikarbonsäuren mit Perjodat[7]. Ein Zwischenprodukt bei der Oxydation der Aldonsäuren und Zuckerdikarbonsäuren mit Perjodat ist die Glyoxylsäure, die in schwach saurem oder schwach alkalischem Medium mit Perjodat gemäss der folgenden Gleichung reagiert:

$$\mathrm{CHO{-}COOH} + \mathrm{JO_4^-} \rightarrow \mathrm{HCOOH} + \mathrm{CO_2} + \mathrm{JO_3^-} \qquad (2)$$

Die Glyoxylsäure ist ein charakteristisches Intermediärprodukt bei der Oxydation der Gruppen —CHOH—CHOH—COOH sowie —CHOH—$\mathrm{CHNH_2}$—COOH mit Perjodat. Die Messung der Glyoxylsäure über das Kohlendioxyd ermöglicht eine selektive Bestimmung jener Verbindungen, die diese Gruppen enthalten. Bei diesen Bestimmungen muss jedoch berücksichtigt werden, dass die Oxydation nur in der Kälte durchgeführt werden kann, da durch das Perjodat bei höherer Temperatur auch die in der Reaktion gebildete Ameisensäure und das Formaldehyd unter Bildung von Kohlendioxyd oxydiert wird. Genaue Beschreibung sowie Einzelheiten dieses Verfahrens wurden in unserer Mitteilung „Bestimmung der Aldonsäuren und Zuckerdikarbonsäuren nebeneinander" beschrieben[7]. Diese Methode ist ohne Abänderung z.B. zur Bestimmung der Weinsäure, des Serins und Threonins geeignet. Die Ergebnisse der Bestimmung der Glyoxylsäure sind in Tabelle VI zusammengefasst.

TABELLE VI

BESTIMMUNG DER GLYOXYLSÄURE ÜBER DAS BEI DER OXYDATION MIT PERJODAT GEBILDETE KOHLENDIOXYD

Einwaage Glyoxylsäure ($HOOC{-}CHO \cdot H_2O$) *(g/100 ml)*	*Einwaage Stammlösung(ml)*	*Verbrauch 0.05 N* $Ba(OH)_2$*-Lösung (ml)*		*Gefunden Glyoxylsäure*	
		einzeln	*mittel*	*(mg)*	*(%)*
0.2392	10.05	10.78 10.78	10.78	24.80	100.8
	5.03	5.40 5.38	5.39	14.90	100.2
	2.01	2.16 2.17	2.16	4.97	100.9

Zur Bestimmung des bei der Oxydation der Aminosäuren mit Ninhydrin gebildete Kohlendioxyds schlugen VAN SLYKE *et al.*[8,9] eine gasvolumetrische bzw. titrimetrische Methode vor. Das im Laufe dieser Reaktion gebildete Kohlendioxyd kann aber auch durch „blasenfreie Destillation" sehr einfach isoliert und bestimmt werden. Leider führten diese Bestimmungen nicht in jedem Falle zu einem befriedigenden Ergebnis (Tabellen VII und VIII). Die Bestimmung der Aminosäuren wurde im 0.1 und 0.01 *N* Massstabe durchgeführt.

TABELLE VII

BESTIMMUNG EINIGER AMINOSÄUREN ÜBER DAS BEI DER OXYDATION MIT NINHYDRIN GEBILDETE KOHLENDIOXYD

Aminosäure	*pH 2–3 (%)*	*pH 4–5 (%)*	*Aminosäure*	*pH 2–3 (%)*	*pH 4–5 (%)*
Glycin	94.7	97.7	Tyrosin	100.1	100.1
Alanin	98.3	98.3	Glutaminsäure	97.8	102.8
Leucin	99.7	99.7	Lysin	96.9	102.8
Serin	96.1	97.0	Arginin	83.8	83.8
Methionin	100.1	100.1	Histidin	100.8	102.8
Phenylalanin	98.5	98.5			

TABELLE VIII

BESTIMMUNG DES ALANINS ÜBER DAS BEI DER OXYDATION MIT NINHYDRIN GEBILDETE KOHLENDIOXYD

Einwaage Alanin (g/500.00 ml)	*Einwaage Stammlösung (ml)*	*Verbrauch $Ba(OH)_2$-Lösung (ml)*		*Gefunden Alanin*	
		einzeln	*mittel*	*(mg)*	*(%)*
			0.01 *N*		
0.2283	10.05	10.05 10.02	10.04	4.47	97.5
	5.01	5.04 5.02	5.03	2.24	97.9
	2.01	2.01 2.00	2.01	0.89	97.5
			0.1 *N*		
1.0850	20.00	9.57 9.58 9.58	9.58	42.77	98.5
	10.02	4.80 4.78 4.81	4.80	21.38	98.3
	5.03	2.42 2.41 2.41	2.41	10.73	98.3

BESCHREIBUNG DER VERFAHREN

Reagenzien

0.1 N bzw. 0.01 N Bariumhydroxydlösung (mit 5% Bariumchlorid-Zusatz). Die Messlösungen werden unter einer 0.5 cm dicken Pentan-Sperrschicht auf die übliche Weise in automatischen Büretten aufbewahrt.

0.3%ige, alkoholische Thymolblau-Indikatorlösung.

Bimsstein. Korngrösse 1–2 mm.

Ausgekochtes, destilliertes Wasser. 1–1.5 Liter destilliertes Wasser werden in Gegenwart von 10–15 Körnchen Bimsstein 25–30 Minuten hindurch – berechnet vom Siedebeginn — lebhaft gekocht, ohne Schütteln abgekühlt und in einer Flasche mit eingeschliffenem Glasstopfen aufbewahrt (täglich frisch herzustellen).

Bestimmung der Acetondikarbonsäure über das bei der Dekarboxylierung gebildete Kohlendioxyd

0.3–0.4 g Acetondikarbonsäure werden in ausgekochtem destilliertem Wasser gelöst, in einen 100 ml-Messkolben gespült und das Volumen bis zur Marke aufgefüllt.

Das Auslaufrohr des Hahntrichters des Destillationsapparats wird mit ausgekochtem destilliertem Wasser blasenfrei aufgefüllt (man saugt das Wasser von unten auf und verschliesst den Hahn). In einen 100 ml-Destillationskolben gibt man 5 ml 10%ige Schwefelsäure, 10–15 Körnchen Bimsstein und destilliertes Wasser bis auf ein Volumen von ungefähr 30–40 ml. Der Apparat wird zusammengesetzt und die Heizung eingeschaltet. Für eine Beschreibung des Heizkörpers siehe die erste Mitteilung dieser Serie[2]. Durch entsprechende Einstellung des Schiebewiderstandes wird ein lebhaftes, gleichmässiges Sieden herbeigeführt. Durch den Kühlmantel strömt kein Wasser, der Mantel ist leer. Es wird nun der Vorlagekolben vorbereitet: Ein 100 ml fassender Erlenmeyer-Schliffkolben wird mit ausgekochtem destilliertem Wasser einige Male ausgespült und dann mit 5 ml Pentan und nachfolgend mit 15.00 ml 0.1 *N* Bariumhydroxydlösung beschickt. Die an der Innenwand des Kolbens haftende Bariumhydroxydlösung wird mit 5–10 ml ausgekochtem destilliertem Wasser unter das Pentan gespült. Man lässt aus dem Ausflussrohr des Kühlers zunächst 2–3 Minuten lang einen lebhaften Wasserdampfstrom entweichen und schaltet dann erst das Kühlwasser bei geöffneten unteren und geschlossenen oberen Hähnen ein. Bei diesem ersten Kühlungsgrad wird der Vorlagekolben mit Hilfe eines doppelt durchbohrten Korken so am Auslaufrohr des Kühlers befestigt, dass das Ende des Rohres am Boden des Kolbens anliegt. In den Kelchtrichter bringt man gleichzeitig einen mit Bariumhydroxydlösung angefeuchteten Wattebausch. Der mittlere Hahn des Kühlers wird hierauf geöffnet und der untere verschlossen. Infolge der intensiveren Kühlung steigt das Niveau der Bariumhydroxydlösung im Kühlerrohr höher auf. Ein Anteil von 10.00 ml der vorbereiteten Acetondikarbonsäure-Lösung wird in den Hahntrichter pipettiert und in kleinen Anteilen (0.3–0.5 ml) in die lebhaft siedende Schwefelsäure einlaufen lassen. Nach jeder zugegebenen Portion wird das Niveau der Bariumhydroxydlösung im Kühler beobachtet und die Geschwindigkeit der Zugabe so eingestellt, dass das Niveau der Bariumhydroxydlösung im Kühlerrohr immer unter dem Niveau des Wassers im Kühlmantel bleibt. Man achte auch darauf, dass bei Zugabe des letzten Anteiles das Rohr des Hahntrichters nicht leer läuft und Luft in den Destillationskolben gelangt. Nach beendeter Zugabe der Lösung wird der

Hahntrichter mit 10 ml und noch zweimal mit je 5 ml ausgekochtem destilliertem Wasser nachgespült. Das Spülwasser lässt man gleichfalls in kleinen Portionen in den Kolben einlaufen. Die dritte Kühlstufe wird eingeschaltet, wenn das Niveau der Bariumhydroxydlösung im Kühlerrohr stark zu sinken beginnt. (Die Lösung darf höchstens bis zum verjüngten Ausflussrohr des Kühlers sinken.) Das Niveau der Bariumhydroxydlösung kann auch durch Reduzieren der Heizung erhöht werden; bei richtig geführter Destillation wird dies jedoch in der Regel nicht notwendig sein.

Während der Destillation hebt und senkt sich das Niveau der Bariumhydroxydlösung dauernd. Diese Tatsache fördert die rasche Vermischung des kohlendioxydhaltigen Wassers und der Bariumhydroxydlösung im Kühlerrohr. Mit dem Fortschreiten der Absorption des Kohlendioxyds steigt das Niveau der Bariumhydroxydlösung im Laufe der Destillation im Kühler dauernd höher, um dann bei einer bestimmten Höhe stehen zu bleiben. Nach 25–30 Minuten (diese Zeit genügt zur Dekarboxylierung der Acetondikarbonsäure und zur Absorption des Kohlendioxyds) geht man wieder auf die erste Kühlstufe über. Zu diesem Zweck wird der untere Hahn des Kühlers geöffnet und das Ende des an den oberen Hahn angeschlossenen Ableitungsschlauches auf ein höheres Niveau gebracht um den freien Rücklauf des Kühlwassers zu sichern. Auf diese Weise wird die karbonathaltige Bariumhydroxydlösung aus dem Kühler verdrängt. Der Vorlagekolben wird nun mitsamt des doppelt durchbohrten Korken am Ausflussrohr des Kühlers so weit nach unten gezogen, dass das Kühlerrohr über der Flüssigkeitsoberfläche zu stehen kommt. Die Destillation wird noch 2–3 Minuten weiter fortgesetzt um das Kühlerrohr auszuspülen; dann wird die Heizung abgeschaltet. Man nimmt den Vorlagekolben vom Ausflussrohr des Kühlers ab und titriert die Lösung in Gegenwart von 10 Tropfen Thymolblau-Indikatorlösung mit 0.1 N Salzsäure. Während der Titration wird die Messlösung unter lebhaftem Schütteln tropfenweise zugegeben. In der Nähe des Endpunktes (die blaue Farbe wird hier bereits blass) wird der Kolben verschlossen und energisch durchgeschüttelt. Bis zur Erreichung des Endpunktes wird dies noch einige Male wiederholt. Beim Titrationsendpunkt ist die Farbe der Lösung grün. Bei dieser Bestimmung ist es nicht notwendig, eine Destillation mit einer blinden Probe durchzuführen. Das während der Destillation und Titration in das System gelangende Kohlendioxyd der Luft ist mengenmässig kleiner als der Tropfen-Fehler (0.03 ml 0.1 N Bariumhydroxydlösung). Parallel mit der Titration werden 15.00 ml mit Pentan überschichtete Bariumhydroxydlösung titriert und der gefundene Blindwert bei der Berechnung berücksichtigt.

1 ml 0.1 N Salzsäure entspricht 3.65 mg Acetondikarbonsäure.

Bestimmung des Acetessigesters, Phenyläthylcyanessigsäureesters und des Diäthylkarbonats über das bei der Hydrolyse und Dekarboxylierung gebildete Kohlendioxyd

0.6–0.7 g Acetessigester, 1.0–1.2 g Phenyläthylcyanessigsäureäthylester, bzw. 0.6–0.7 g Diäthylkarbonat werden in ausgekochtem destilliertem Wasser (bei Acetessigester) bzw. in mit 1–2 Tropfen 10%ige Schwefelsäure ausgekochtem Äthanol gelöst (bei Phenyläthylcyanessigsäureester und Diäthylkarbonat), in einen 100 ml-Messkolben gespült und das Volumen bis zur Marke ergänzt. Der 150 ml fassende Destillationskolben wird mit ausgekochtem destilliertem Wasser einige Male ausgespült und mit 5 ml Pentan und 20 ml 0.1 N Bariumhydroxydlösung aus der automatischen Bürette beschickt. 10.00 ml der vorbereiteten Lösung werden in den Destillationskolben pipettiert und nach Zugabe von 10–15 Körnchen Bimsstein das Volumen mit ausgekochtem destilliertem Wasser auf 50–60 ml ergänzt. Zur Hydrolyse des Diäthylkarbonats wird der mit einem Rückflusskühler versehene Kolben in ein kochendes Wasserbad gestellt. Die Hydrolyse ist beim Diäthylkarbonat und Acetessigester nach 30–40 Minuten, beim Phenyläthylcyanessigsäureester nach 60 Minuten beendet. Bei der im Destillationsapparat durchgeführten Hydrolyse wird die Lösung allmählich erwärmt, die Flüssigkeit soll nur während der letzten 5–10 Minuten der Hydrolyse sieden. Nach der Hydrolyse wird die Lösung im Destillationsapparat bei leerem Kühler lebhaft gekocht. Nachdem am Ausflussrohr des Kühlers bereits ein lebhafter Wasserdampfstrom austritt, wird die schwächste Kühlstufe eingeschaltet und der mit 15.00 ml Bariumhydroxydlösung (mit Pentan überschichtet) beschickte Vorlagekolben am Kühlerrohr befestigt. Im weiteren wird die Destillation des Kohlendioxyds nach der oben bereits beschriebenen Methode durchgeführt. Die niederschlaghaltige Lösung wird aus dem Hahntrichter mit 2%iger Salzsäure angesäuert; nach Einsetzen der Kohlendioxyd-Entwicklung werden kleinere Säure-Portionen in die Lösung getropft (das Ansäuern kann auch mit 1–2 Tropfen Methylrot kontrolliert werden). Man vermeide eine zu grosse Säuremenge auf einmal zuzugeben, da sich sonst der Niederschlag vollständig auflöst, und die Lösung in den Kühler überschäumen bzw. die plötzlich in Freiheit gesetzte grosse Kohlendioxydmenge durch die Vorlagelösung hindurchperlen kann.

Nach vollständiger Auflösung des Niederschlages wird noch 15–20 Minuten hindurch destilliert, dann verdrängt man die karbonathaltige Bariumhydroxydlösung durch Reduzierung der Kühlung aus dem Kühlerrohr.

Nach Abnahme des Vorlagekolbens wird dessen Inhalt auf die bereits beschriebene Weise titriert.

1 ml 0.1 *N* Salzsäure entspricht 6.50 mg Acetessigester bzw. 10.86 mg Phenyläthylcyanessigsäureäthylester bzw. 5.90 mg Diäthylkarbonat.

Aminosäurebestimmung über das bei der Oxydation mit Ninhydrin gebildete Kohlendioxyd

Zur Bestimmung der Aminosäure werden 0.1 *N* bzw. 0.01 *N* Stammlösungen hergestellt (Äquivalentgewicht = Molekulargewicht/2). Man stellt die Lösung mit ausgekochtem destilliertem Wasser her oder befreit sie durch Kochen vom Kohlendioxyd.

In den 150 ml fassenden Destillationskolben füllt man 3 ml 2%ige Kaliumcitrat- und 9 ml 2%ige Citronensäurelösung (pH 2–3) sowie 0.20–0.40 g krist. Ninhydrin und ergänzt das Lösungsvolumen nach Zugabe von 10–15 Körnchen Bimsstein mit destilliertem Wasser auf 30–40 ml. (Für die Bestimmungen in Lösungen bei pH 4.5 werden je 6 ml Citrat–Citronensäure Puffer verwendet.) Nach Entlüftung des Apparats durch 10–15 Minuten langes Kochen wird der Vorlagekolben — der 15.00 ml 0.1 *N* bzw. 0.01 *N* mit 5 ml Pentan überschichtete Bariumhydroxydlösung enthält — auf die bekannte Weise am Kühlerrohr angebracht.

Bei Bestimmungen im 0.01 *N* Massstabe wird das Volumen von 50 ml am Vorlagekolben markiert. Man lässt die Bariumhydroxydlösung durch Verstärkung der Kühlung im Inneren des Kühlerrohres aufsteigen und einen 10.00 ml betragenden Anteil der vorbereiteten Aminosäure-Lösung in kleinen Portionen in den lebhaft siedenden Kolbeninhalt einlaufen. Der Hahntrichter wird mit 10 ml und zweimal mit je 5 ml ausgekochtem destilliertem Wasser nachgespült. Nach 30 Minuten langem Kochen wird die Bariumhydroxydlösung durch Verminderung der Kühlung aus dem Kühler verdrängt, und der Vorlagekolben tiefer gezogen. Zum Ausspülen des Kühlerrohres wird noch 2–3 Minuten weiter destilliert.

Bei Bestimmungen im 0.01 *N* Massstabe wird der Inhalt des Vorlagekolbens mit ausgekochtem destilliertem Wasser auf 50 ml ergänzt. Die niederschlaghaltige Lösung wird nach Zugabe von 10 Tropfen Thymolblau-Indikatorlösung unter lebhaftem Rühren mit 0.1 *N* bzw. 0.01 *N* Salzsäure bis zum Farbumschlag auf grün titriert.

Parallel führt man unter Verwendung sämtlicher Reagenzien eine blinde Destillation bzw. Titration durch und rechnet mit der Differenz zwischen den beiden Verbrauchswerten.

ZUSAMMENFASSUNG

Die auf der blasenfreien Destillation beruhende Kohlendioxyd-Bestimmungsmethode eignet sich zur Bestimmung von Karbonsäuren, die beim Kochen ihrer wässrigen Lösung spontan oder mit Oxydationsmittel Kohlendioxyd abspalten. Mit spontaner Dekarboxylierung kann die Acetondikarbonsäure und *p*-Aminosalizylsäure bestimmt werden. Beim Acetessigester, Phenyläthylcyanessigsäureäthylester und bei den Kohlensäureestern muss eine Hydrolyse vorausgehen. Mit oxydativer Dekarboxylierung können bestimmt werden: Glyoxylsäure, die Aldonsäuren und Zuckerdikarbonsäuren (Oxydation mit Perjodat), die Ameisensäure (Oxydation mit Quecksilber(II)chlorid), die Oxalsäure (Oxydation mit Permanganat) und die α-Aminosäuren (Oxydation mit Ninhydrin). Die Isolation und titrimetrische Bestimmung des bei diesen Reaktionen gebildeten Kohlendioxyds lässt sich im 0.1 *N* und 0.01 *N* Massstabe durchführen. Die störende Wirkung des Kohlendioxydgehaltes der Luft kann durch Anwendung von Pentan als Sperrflüssigkeit ausgeschaltet werden.

SUMMARY

Carboxylic acids which decompose spontaneously on boiling or by oxidation in aqueous solutions can be determined by titration of the carbon dioxide formed after distillation as described previously. Acetonedicarboxylic acid and *p*-aminosalicylic acid are determined by spontaneous decarboxylation. Hydrolysis must precede the determination for acetoacetic ester, phenylethylcyanoacetic ethyl ester and for carbonic acid esters. Oxidative decarboxylation allows determinations of glyoxylic acid, aldonic acids, sugar dicarboxylic acids, formic acid, oxalic acid and α-amino acids. The titration of the carbon dioxide formed can be done with 0.1 or 0.01 *N* solutions. The interference of atmospheric carbon dioxide is avoided by the use of pentane as a sealing liquid.

RÉSUMÉ

Les acides carboxyliques se décomposant par ébullition ou par oxydation, en solution aqueuse, peuvent être dosés par titrage de l'anhydride carbonique formé par distillation. L'anhydride carbonique qui se dégage est recueilli dans une solution d'hydroxyde de baryum, recouverte de pentane, pour éviter l'influence néfaste de l'anhydride carbonique atmosphérique. On titre finalement par l'acide chlorhydrique.

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THE NATURE OF EUROPIUM ION IN CARBONATE SOLUTION AND POLAROGRAPHIC DETERMINATION OF MICRO AMOUNTS OF EUROPIUM

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The nature of the complex europium carbonate ion in concentrated carbonate solution has been studied polarographically and its existence has been proved by means of anion-exchange resins in the carbonate form[1]. In the present work, the effects of pH and carbonate ion concentration on the reduction wave and electrode reaction were studied in detail. The electrode reaction was always irreversible and consisted of a one-electron change. From the slope of $d(E_{1/2})_c/d \log(CO_3^{2-})$ (or $d(E_{1/2})_c/d \log a_{\pm}$), the coordination number for carbonate was found to be one; the existence of $Eu(CO_3)^+$ ion at a pH above 10.0 was presumed from the electrode reaction and europium(II) carbonate as the basic salt was assumed to be precipitated on the mercury electrode after reduction.

On this basis, a polarographic method for the determination of micro amounts of europium ion in the presence of other diverse ions and rare earth ions was developed. Europium could be determined even in presence of the complex cerium carbonate ion. Under the optimum conditions europium in the range $2 \cdot 10^{-4}$ M to $2 \cdot 10^{-3}$ M could be determined successfully in mixtures of rare earth oxides.

EXPERIMENTAL

Apparatus

Yanagimoto's photographic polarograph PEL-model 3 Type and a pen recorder were used to record the current–voltage curves. All cathode potentials were corrected and referred to the saturated calomel electrode (S.C.E.) prepared by the method of HUME AND HARRIS[2]. The sensitivity of the automatic recorder was 0.04 μA/mm. The capillary used had an m value of 0.680 mg/sec and a drop-time of 3.20 sec at the potential of -1.83 V *vs.* S.C.E. when measured in an oxygen-free 1.5 M carbonate solution at an effective height of mercury of 67.61 cm. The value of the capillary constant $m^{2/3}t^{1/6}$ was about 0.938. The pH was measured with a Hitachi glass electrode pH meter model EHM-1. All experiments were carried out in a thermostat at $25.0 \pm 0.1°$. The value of the half-wave potential was obtained by wave analysis of logarithmic plots, and that of the diffusion current by compensation of residual current.

Chemicals

Europium stock solution was prepared by dissolving pure europium perchlorate made from pure oxide (purity more than 99.99%), in distilled water and was standardized gravimetrically. The concentration of europium(III) was $1.05 \cdot 10^{-2}$ M. The carbonate–bicarbonate buffer solutions in the pH range 8.5 to 10.5 were prepared from 2 M potassium carbonate and 2 M potassium bicarbonate solutions; these salts were guaranteed pure-grade reagents and the stock solutions were standardized by the method of WINKLER AND WARDER[3]. The stock solutions were filtered before use.

Other chemicals used were of analytical reagent grade. Nitrogen gas was purified by passing it through a pyrogallol solution before use.

Other rare earth oxides used were also highly pure spectroscopically, the purity of each oxide being more than 99.99%.

Procedure

An appropriate amount of the europium stock solution was diluted to the required concentration of europium ion. At the same time carbonate solution as supporting electrolyte was added to give a final concentration of 0.2–1.8 M and the pH was adjusted with buffer solution to the required value of 9.0–11.0. The total volume of the solution was always adjusted to 10 ml with distilled water. The concentration of europium ion was varied in the range from 0.2 mM to 2.7 mM per liter. Dissolved oxygen was removed by passing purified nitrogen gas through the solution at least for 30 min. An appropriate quantity of this solution was taken and a polarogram was recorded at 25.0° ± 0.1°.

RESULTS AND DISCUSSION

A polarogram of the complex europium carbonate ion in presence of a large excess of carbonate ion is shown in Fig. 1. The complex europium carbonate ion shows a single reduction wave; the half-wave potential is more negative than that of the reduction wave of the aquo single europium ion. From Fig. 1 the half-wave potential of the complex carbonate ion is −1.739 V *vs.* S.C.E., whereas that of the single europium ion is known to be −0.762 V *vs.* S.C.E.[4]. Except for cerium, no other rare earth ions

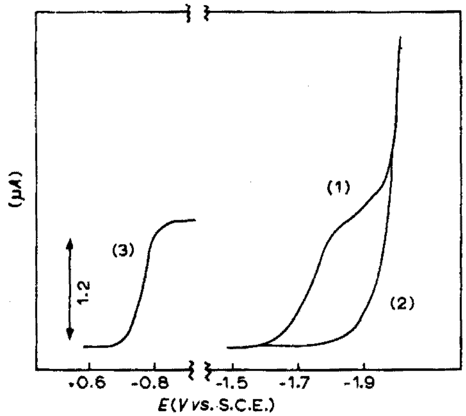

Fig. 1. Reduction wave of the complex europium carbonate ion. (1) Eu^{3+} ion: 1.05 mM in 1.53 M carbonate medium, pH = 10.1; (2) Residual current: 1.53 M carbonate solution, pH = 10.1; (3) Eu^{3+} ion: 1.10 mM in 0.1 M LiCl medium, pH = 3.05.

give reduction waves in the presence of a large excess of carbonate. The half-wave potential of the complex cerium(IV) carbonate ion is −0.124 V *vs.* S.C.E.[5].

Accordingly, the wave obtained for the complex europium carbonate ion is quite characteristic.

Dependence of the limiting current on the pressure on the dropping mercury electrode and the influence of temperature on the limiting current and half-wave potential

The relationship between the limiting current and the height of the mercury column is shown in Table I.

TABLE I

DEPENDENCE OF LIMITING CURRENT ON THE HEIGHT OF MERCURY COLUMN

(1.05 mM Eu^{3+} in 1.53 M total carbonate medium)

h_{corr} (cm)	i_l (μA)	$i_l/\sqrt{h_{corr}}$
47.61	1.12	0.162
57.75	1.24	0.163
67.61	1.36	0.165

As the limiting current is proportional to the square root of the height of the mercury column, the limiting current is diffusion-controlled. The temperature coefficients of the half-wave potential and of the diffusion current from 20° to 30° are 0.6 mV/degree and 1.81%/degree respectively; the values agree well with the theoretical values in the case of a diffusion-controlled process.

Irreversibility of the reduction wave

From the standpoint of absolute reaction rate theory, the current–potential curve for an irreversible reduction wave of a complex ion is given by equation (1).

$$E = (E_{1/2})_c - \frac{RT}{\alpha n F} \ln \frac{i}{i_d - i} \qquad 0 < \alpha < 1 \qquad (1)$$

From wave analyses of polarograms of the complex europium carbonate ion obtained under defined conditions, the mean value of the reciprocal slope was found to be 76 mV if the pH was varied at a constant total concentration of 1.80 M carbonate, and 70 mV if the total carbonate concentration was varied at a constant pH of 10.1. The mean values of αn were therefore 0.777 and 0.792 respectively.

It was found that the electrode reaction was irreversible and involved a one-electron change.

Effect of pH on the reduction wave

Polarograms were recorded with 1.05 mM europium in 1.80 M total carbonate solution at various pH values from 9.0 to 11.0. It was necessary to keep the ionic strength of every sample solution strictly constant during the variation of pH. The half-wave potential shifted to the more negative side with increase of pH from 9.0 to 11.0 and, especially at pH values between 9.0 and 9.9, the shift of half-wave potential was very large; a break-point at pH about 9.9 was observed. In this pH range, it was supposed that bicarbonate ion dissociated rapidly to carbonate ion. Above pH 9.9, the shift of half-wave potential was very small and the stability of the complex europium carbonate ion in presence of a large excess of carbonate became almost constant. Thus:

$$\mathrm{pH} > 9.9 \qquad \frac{\mathrm{d}(E_{1/2})_c}{\mathrm{dpH}} = 0.024\ \mathrm{V}$$

$$9.9 > \mathrm{pH} > 9.0 \qquad \frac{\mathrm{d}(E_{1/2})_c}{\mathrm{dpH}} = -0.260\ \mathrm{V}$$

$$(\mu = 5.4)$$

It was observed that above pH 9.9 the electrode reaction was almost independent of pH.

The diffusion current was almost constant (1.364 μA) at the same concentration of europium ion (1.05 mM) in the pH range 9.3–10.3. Above pH 10.3, formation of a complex hydroxycarbonate ion would probably take place. The diffusion current constant was also constant (1.397) in the pH range 9.3–10.3.

Therefore, for determination of europium ion pH 10.1 was considered to be most suitable.

Effect of total carbonate concentration on the reduction wave

Polarograms were recorded with 1.05 mM europium ion in the presence of 0.8–1.8 M carbonate medium. As the concentration of total carbonate was so high, it was necessary to use activity instead of concentration and to take into account the liquid junction potentials. With the activity coefficients of potassium carbonate[6], calculations were made by referring to the descriptions of HARNED AND OWEN[7]. The liquid junction potentials for the potassium carbonate solutions were within the limits of experimental error, hence the measured values of the half-wave potential were not corrected. Since it was impossible to determine an individual value for the activity of

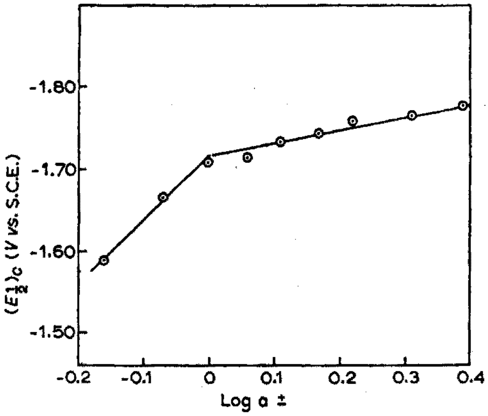

Fig. 2. Effect of the mean activities of carbonate ion on half-wave potential. Eu^{3+} ion: 1.05 mM, 10.0 < pH < 10.2.

carbonate ($a_{CO_3^{2-}}$), the mean ion activities $a_\pm$ were used in the calculation of the slope of the line, $(E_{1/2})_c$ *vs.* log $a_\pm$.

Because of the present lack of data for the activity coefficients in the mixed solutions, an almost complete dissociation of bicarbonate added as buffer had to be assumed.

As shown in Fig. 2, the half-wave potential of the reduction wave shifted to more negative potentials with increasing mean activities of total carbonate ion at a constant pH. However, it was observed that at total carbonate concentrations above 1.17 *M*, which corresponds to −0.008 of log $a_\pm$ in Fig. 2, the shift of half-wave potential decreased markedly. It is interesting to note that although the ionic strength of the solution increased as the proportion of the total carbonate increased, the shift in the half-wave potential decreased.

The slope of the tangent $(E_{1/2})_c$ *vs.* log $a_\pm$ had a value of −162 mV *vs.* S.C.E. at a pH 10.1 and an experimental equation for the half-wave potential (*vs.* S.C.E.) obtained from the curve was given by

$$(E_{1/2})_c = -1.714 - 0.162 \log a_\pm \qquad (1.17\ M < [CO_3^{2-}])$$

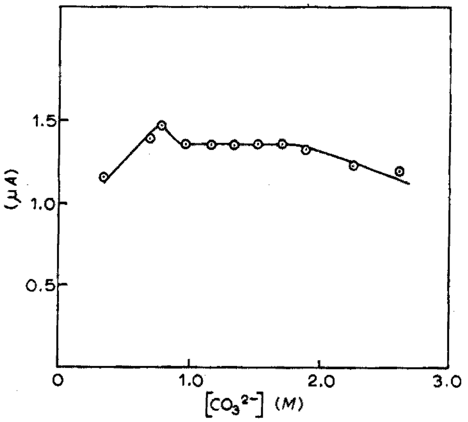

Fig. 3. Effect of concentration of total carbonate ion on diffusion current. Eu^{3+} ion: 1.05 m*M*, 10.0 < pH < 10.2.

As shown in Fig. 3, the diffusion current increased as the total carbonate concentration increased from 0.2 to 0.8 *M*; from 1.0 to 1.8 *M* a constant and reproducible diffusion current was obtained at pH 10.1, whereas above 1.8 *M*, the diffusion current began to decrease slightly. This variation in the diffusion current was probably due to the varying viscosity, *i.e.* varying diffusion coefficient. The constant reproducible diffusion current obtained at a total carbonate concentration of 1.0 – 1.8 *M* is considered to be due to the stable complex carbonate ion. In this range, the diffusion current constant also had a constant value (1.393) and these conditions were therefore applied to the determination of europium ion.

The electrode reaction of the complex europium carbonate ion above pH 9.9, being independent of hydroxide, takes place according to the following scheme,

$$\mathrm{Eu(CO_3)_N}^{(3+-2N)} \rightleftharpoons \mathrm{Eu(CO_3)_p}^{(3+-2p)} + (N-p)\mathrm{CO_3}^{2-}$$

$$\mathrm{Eu(CO_3)_p}^{(3+-2p)} + ne \rightarrow \mathrm{Eu(CO_3)_p}^{(3+-n-2p)} \qquad (2)$$

where N is the maximum number of carbonate ions attached to europium ion, p the number of carbonate ions attached to europium ion in the vicinity of the electrode surface, and n the number of electrons associated with the electrode reaction.

As the electrode reaction of the complex europium carbonate ion is irreversible, the equation for the current-potential curve (1) due to the irreversible reduction of a complex ion is applicable and the half-wave potential $(E_{1/2})_c$ is given by equation (3):

$$(E_{1/2})_c = 2.3\frac{RT}{\alpha nF}\left\{\log\frac{(k^\circ{}_f)_B f_N}{\sqrt{D_N}} + \tfrac{1}{2}\log\tau - 0.053 - \log(\bar{i}_l/\bar{i}_d) - (N-p)\log(f_x C_x)\right\} \quad (3)$$

which was derived by MATSUDA AND AYABE[8], where α is the transfer coefficient, $(k^\circ{}_f)_B$ the forward (reduction) rate constant of the electron transfer process at the potential of the normal hydrogen potential, D_N the diffusion coefficient of the complex metal ion $Eu(CO_3)_N{}^{(3^+-2N)}$ in the solution, τ the drop time, $\bar{i}_d$ the diffusion current, $\bar{i}_l$ the limiting current, C_x the concentration of the carbonate complexing agent, and f_x the activity coefficient of carbonate.

From the equation (3), a plot of $-(E_{1/2})_c - 2.3(RT/\alpha nF)\log(\bar{i}_l/\bar{i}_d)$ *vs.* $\log(f_x C_x)$ should produce a straight line with a slope equal to $(N-p)2.3(RT/\alpha nF)$ $(= 59(N-p)/\alpha n$ mV at 25°). If the limiting current is completely diffusion-controlled and $\bar{i}_l$ is equal to $\bar{i}_d$, the value of the tangent for the half-wave potential *vs.* logarithm of the mean activities is given by

$$d(E_{1/2})_c/d\log(f_x C_x) = d(E_{1/2})_c/d\log a_\pm = -(N-p)\,0.0591/\alpha n$$

Therefore, as the electrode reaction of the complex europium carbonate ion is irreversible with a one-electron change ($n = 1$) and the limiting current is diffusion-controlled, $(N-p)$ was calculated to be about 2, using the observed value 0.792 of αn from the reciprocal slope of the log-plot at a pH between 10 and 10.5 ($N-p = 2.3 \approx 2$).

On the assumption that $N = 3$ (the coordination number of europium(III) is assumed to be 6) for example, the species $(EuCO_3)^+$ would participate in the electron-transfer process, the transfer coefficient being equal to 0.792.

The value of the forward rate constant of the electron-transfer process $(k^\circ{}_f)_B$ was calculated for a total carbonate concentration of 1.52 M with the value of the half-wave potential −1.732 V *vs.* S.C.E. (−1.486 V *vs.* N.H.E.), the diffusion coefficient of the complex europium carbonate ion D_N: $5.29\cdot10^{-6}$ cm sec^{-1}, and 3.2 sec for the drop-time, provided that $f_N = f_x = 1$. The calculated value was

$$\log(k^\circ{}_f)_B = -22.5 \; (k^\circ{}_f \text{ cm/sec})$$

The electrode reactions at pH values below 10.0 were very difficult to discern because of pH dependence.

Effect of gelatin on the reduction wave

In the polarogram of the complex europium carbonate ion, no wave maximum occurred, hence it was unnecessary to add gelatin throughout these experiments. However, it was observed that increasing the gelatin concentration from 0.002% to 0.1% in a solution containing 1.05 mM europium(III) and 1.53 M carbonate, caused the reduction wave to shift to more negative potentials; its height decreased and it finally disappeared.

Effect of concentration of europium(III) on the reduction wave

As a constant and reproducible diffusion current was obtained in a 1.53 M total carbonate medium at pH 10.1, under these optimum conditions polarograms were recorded over the range $2 \cdot 10^{-4}$ M to $2 \cdot 10^{-3}$ M europium(III). In further tests, sodium malonate solution was added as an auxiliary complexing agent in a final concentration of 0.2 M to the sample solutions, and polarograms were recorded over the range $2 \cdot 10^{-4}$ M to $3.1 \cdot 10^{-3}$ M europium(III) under the conditions mentioned above. The diffusion current was proportional to the concentration of europium(III) and reproducible; a linear relationship was obtained in the range $2 \cdot 10^{-4}$ M to $2 \cdot 10^{-3}$ M europium(III). The half-wave potential was almost constant. It was therefore possible to determine europium over the range mentioned.

By the method of standard addition[9], an unknown concentration of europium was determined. From the increase in height of the reduction wave caused by the known addition of europium ion, the original concentration X of the unknown europium ion is given by

$$X = \frac{nch}{m(H - h)}$$

where n is the volume of standard solution added, c the concentration of the standard solution, m the total volume, and H and h are the heights of the waves obtained with and without an addition of the standard solution. To each 0.5 mM europium solution a different volume of 1.05 mM standard europium solution was added. The values of the concentrations of europium ion found were in good agreement with the europium taken. The error was within ±3%.

Effect of diverse ions

In the presence of diverse ions, polarograms were recorded with 1.05 mM europium ion in 1.53 M carbonate solution at pH 10.1.

TABLE II

EFFECT OF DIVERSE IONS

(1.05 mM Eu^{3+} ion in 1.53 M total carbonate medium. pH: 10.1. $(i_d)_e$: 1.36 μA. $(E_{1/2})_e$: -1.730 V *vs.* S.C.E.)

Ion added	*Concentration (mM)*	*Half-wave potential of europium(III) (V vs. S.C.E.)*	*Half-wave potential of ion added (V vs. S.C.E.)*	*Diffusion current of europium(III) (μA)*	*Diffusion current of ion added (μA)*
Tl^+	1.00	-1.743	-0.510	1.36	—
Be^{2+}	1.00	-1.726	—	1.36	—
Cu^{2+}	1.13	-1.748	-0.315	1.36	7.80
Zn^{2+}	1.00	-1.738	-1.445	1.36	2.76
Pb^{2+}	1.00	—	-0.885	—	2.82
Fe^{3+}	1.02	Unmeasurable	-0.570 -1.730	—	1.80 3.84
Al^{3+}	1.00	-1.730	—	1.36	—
UO_2^{2+}	1.21	—	-0.930	—	2.88
Th^{4+}	1.00	—	—	—	—
VO_3^-	1.00	-1.805	-1.045 -1.645	1.12	1.64 1.68
MoO_4^{2-}	1.00	—	-1.827	—	Maximum wave

As shown in Table II, beryllium, zinc, aluminium, thallium(I) and copper(II) did not interfere. Uranyl ion decreased the diffusion current of europium ion; thorium(IV), lead(II) and molybdate suppressed the reduction wave of europium(III). Vanadate also interfered, the half-wave potential of europium(III) being shifted to the negative side and the diffusion current decreased. Iron(III) interfered, because its second wave overlapped with the reduction wave of the complex europium carbonate ion.

Except for cerium(IV), all the lanthanides, yttrium and scandium were found not to interfere.

The determination of europium in the presence of cerium(III), which was oxidized gradually by oxygen in the carbonate solution to cerium(IV) was therefore studied. Without removal of oxygen from the solution, polarograms were recorded for 1.02 m*M* europium(III) in carbonate solutions containing concentrations of cerium(III) from 2 m*M* to 13 m*M*. Up to 4.46 m*M* of cerium(III) had no effect on the diffusion current (the half-wave potential of the complex ceric carbonate ion was −0.124 V *vs.* S.C.E.), but at higher concentrations a cerium salt began to precipitate; adsorption of the complex europium ion on this precipitate caused the diffusion current to decrease with increase of cerium(III) concentration. Moreover, because of the simultaneous decrease in the total carbonate concentration in solution, the half-wave potential seemed to shift very slightly to the positive side. In further tests, dissolved oxygen was removed by passing nitrogen gas through the carbonate solution containing 1.02 m*M* europium ion and concentrations of cerium(III) from 0 to 18 m*M*, and polarograms were recorded at potentials from −1.3 V to −2.0 V *vs.* S.C.E. With increasing concentrations of cerium(III), the half-wave potential of the complex europium carbonate ion shifted to the more positive side and the electrode reaction gradually became reversible. When oxygen was removed from the solution, the diffusion current remained constant in presence of up to 9 m*M* cerium(III). Above this concentration, precipitation of cerium salt and adsorption of the complex europium ion again occurred, so that the diffusion current decreased. Consequently, when oxygen was removed from the solution, cerium(III) could be tolerated up to a limit of 9 m*M*.

As an example of the possible application of this method, determinations of europium in the presence of other lanthanides (except promethium) were carried out. Pure lanthanide oxides (14 different oxides from lanthanum oxide to lutetium oxide which were all specially purified with ion-exchange resins and had purities of more than 99.9% spectroscopically) were weighed precisely (CeO_2: 67.0 mg, each of other 13 rare earth oxides: 13.0 mg, total weight = 235.5 mg). The oxides were mixed well, converted to perchlorates and dissolved in a measuring flask with distilled water. The total volume was made up to 25 ml. One ml of this stock solution was taken and under the optimum conditions, europium was determined polarographically. The concentration of europium was found to be 0.28 m*M*, which agreed well with the original concentration of 0.29 m*M* europium in 1.53 *M* total carbonate medium at pH 10.1

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SUMMARY

The nature of the complex europium carbonate ion in concentrated carbonate solution was studied polarographically. A polarographic method for the determination of micro amounts of europium ion in the presence of diverse ions (and especially lanthanides) was developed.

RÉSUMÉ

Une étude polarographique a été effectuée sur la nature du carbonate complexe d'europium. Une méthode par polarographie a été mise au point pour le dosage de traces d'europium en présence de divers ions et spécialement des lanthanides.

ZUSAMMENFASSUNG

Beschreibung einer polarographischen Untersuchung über die Natur der komplexen Karbonate des Europiums und Anwendung der Methode zur Bestimmung des Europiums neben anderen Ionen, besonders Lanthaniden.

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Short Communications

Eine neue Methode der Sauerstoffbestimmung in Abwässern der pharmazeutischen Industrie

Der Sauerstoffgehalt von Oberflächen- und Abwässern wird gewöhnlich nach der Winkler-Methode bestimmt[1]. Abwässer aus der chemisch-pharmazeutischen Industrie enthalten jedoch oft organische Stoffe, die mit freiem Jod reagieren und dadurch die Anwendung der Winkler-Methode unmöglich machen. Die neue Methode, die nachstehend beschrieben wird, beruht auf der Bindung des Sauerstoffs in Form von Mangan-III-Hydroxyd (ähnlich wie bei der Winkler-Methode) und der direkten Titration der höheren Oxydationsstufen des Mangans mit einer Hydrochinonlösung. Die Titration wird potentiometrisch oder visuell mit Ferroin als Indikator durchgeführt. Die Methode wurde in der Praxis zur Analyse der Abwässer eines chemisch-pharmazeutischen Betriebes angewandt. Diese Abwässer von ungefähr 50 parallel erzeugten Präparaten enthielten ein Gemisch organischer und anorganischer Stoffe. Der chemische Sauerstoffbedarf lag im Bereich von 200 bis 2.000 mg O_2/l, der anorganische Rückstand bei 300 bis 1500 mg/l.

Reagentien und Geräte

Zur Herstellung der Lösungen wurden analysenreine Chemikalien verwendet: 0.05 N Hydrochinonlösung[2], Ferroinlösung, 40% Mangansulfatlösung, 6.5 N Schwefelsäure. Die potentiometrischen Titrationen wurden unter Benützung einer Platinelektrode als Indikationselektrode und einer gesättigten Kalomelelektrode als Referenzelektrode durchgeführt. Zur Messung wurde ein elektronisches Potentiometer

„Acidimetr EK" der Firma Dělba, Praha, benützt. Die Durchmischung der Probe erfolgte mit einem magnetischen Rührer.

Ergebnisse

Die Reaktionen zwischen den höheren Oxydationsformen des Mangans und Hydrochinon benutzten schon KREJZOVÁ, SIMON UND ZÝKA[3] zur indirekten Bestimmung von Manganoxyden. Wir haben festgestellt, dass es nicht nötig ist, das gebildete Mangan-III-Hydroxyd indirekt zu titrieren. Es ist möglich, die Titration des Mangans-III in einer saueren Lösung mit Hydrochinonlösung direkt durchzuführen. Im Gegensatz zu der Analyse einiger Präparate des Mangan-III-Oxyds oder Mangan-IV-Oxyds wird in unserem Falle die direkte Titration vermutlich durch die grössere Reaktivität der frisch ausgefällten höheren Oxydationsformen des Manganhydroxyds ermöglicht. In einem Medium von 1 bis 4 *N* Schwefelsäure verläuft die beschriebene Reaktion genügend schnell und quantitativ. Da die Fixation in einer alkalischen Lösung durchgeführt wird, ist es am günstigsten die Titration in 1 *N* Schwefelsäurelösung durchzuführen.

Bei der Sauerstoffbestimmung wurde wie folgt gearbeitet: Eine Probe wird in eine kalibrierte Flasche gebracht (von einem Gehalt von 250–300 ml) und nach Zugabe von 1 ml 40%iger $MnSO_4$-Lösung und 2 ml 70%igen KOH-Lösung wird die Flasche gut verschlossen und durchgeschüttelt. Nach dem Absetzen des flockigen Niederschlags wird die klare Lösung oberhalb des Niederschlags so weit abgezogen, dass der Rückstand in der Flasche einschliesslich des Niederschlags ungefähr 100 ml beträgt. Dann werden sofort 20 ml 6.5 *N* Schwefelsäure zugegeben und der Inhalt der Flasche gut durchgemischt.

Bei der potentiometrischen Titration wurde der Inhalt der Sauerstoffflasche in ein 250 ml Becherglass übergeführt und dann unter Rühren mit 0.05 *N* Hydrochinonlösung titriert. Am Anfang der Titration stabilisierte sich das Potential der Platin-Indikationselektrode sehr rasch, aber im Bereich des Äquivalenzpunktes ist es nötig, die Titrationslösung tropfenweise zuzugeben und auf die Stabilisierung des Potentials ungefähr eine Minute zu warten.

Eine Zugabe von 0.05 ml Masslösung verursacht im Äquivalenzbereich eine Veränderung von 250 mV. Das Potential des Inflexes liegt im Bereich von 700 mV gegenüber dem Potential der gesättigten Kalomelelektrode.

Die Visualtitration wurde direkt in der Sauerstoffflasche durchgeführt. Unter stetigem Rühren wurde die Masslösung zu der Suspension des dunkelbraunen Niederschlags gegeben. Vor dem Erreichen des Äquivalenzpunktes wurde zu der hell-gelben Lösung 3 bis 5 Tropfen des Ferroinindikators zugegeben und tropfenweise weitertitriert bis zur Bildung einer roten Färbung, die mindestens 1 Minute unverändert blieb.

Bei der Berechnung des Sauerstoffgehaltes wurde mit einer Korrektion für die zugegebenen Reagenzien gerechnet. Von dem Sauerstoffflascheninhalt wurden 3 ml abgezählt. 1 ml 0.05 *N* Hydrochinonlösung entspricht 0.4 mg Sauerstoffes.

Zur Feststellung der Genauigkeit und Richtigkeit der beiden beschriebenen Vorgänge wurde mit Luft gesättigtes destilliertes Wasser verwendet. Die Ergebnisse der potentiometrischen und visuellen Hydrochinonmethode wurden mit parallel durchgeführten Sauerstoffbestimmungen nach der WINKLER-Methode, bei welcher 0.05 *N* Thiosulfatlösung verwendet wurde, verglichen.

TABELLE I

GENAUIGKEIT DER ERGEBNISSE DER POTENTIOMETRISCHEN UND VISUELLEN AUSFÜHRUNG DER HYDROCHINONMETHODE UND DER WINKLER-METHODE IN DESTILLIERTEM WASSER

	Hydrochinonmethode		*Winkler-Methode*
	potentiometr. Indikation	*visuelle Indikation*	
Arithm. Durchschnitt von 10 Analysen (mg O_2/l)	8.50	8.48	8.51
Mittlere Abweichung (mg O_2/l)[a]	±0.015	±0.090	±0.036

[a] Gerechnet aus 10 Analysen nach der Formel $\sigma = \pm \sqrt{\frac{\Sigma \Delta^2}{n-1}}$.

TABELLE II

SAUERSTOFFBESTIMMUNG IN PHARMAZEUTISCHEN ABWÄSSERN

Probe Nummer	*mg O_2/l*			
	Hydrochinonmethode		*Winkler-Methode*	*Unterschied zwischen W-Meth. und H-Meth. (pot.)*
	potentiometr. Indikation	*visuelle Indikation*		
1	7.33	7.40	6.73	−0.60
2	8.15	8.20	5.64	−2.51
3	6.12	6.08	3.70	−2.42
4	4.30	4.35	0.10	−4.20
5	4.90	4.75	3.65	−1.25
6	8.53	8.80	3.03	−5.50

Die in der Tabelle I zusammengefassten Werte zeigen, dass die Ergebnisse aller drei Methoden praktisch übereinstimmen. Die genauesten Resultate wurden durch die potentiometrische Titration mit der Hydrochinonlösung erreicht. Die Sauerstoffbestimmung nach der Winkler-Methode ergab genauere Resultate als die visuelle Titration mit Hydrochinonlösung und Ferroinindikator. Trotzdem sind die Ergebnisse der letzteren Methode so genau, dass die visuelle Hydrochinonmethode ganz gut als Kontrollmethode für Wasserwirtschaftzwecke verwendbar ist.

Die beiden vorgeschlagenen Modifikationen wurden bei der Bewertung der Reinigungsverfahren für Abwässer aus pharmazeutischen Betrieben benützt. Einige Resultate der Sauerstoffbestimmung in diesen Abwässern sind in der Tabelle II angegeben. Die Ergebnisse, die mit den beiden Hydrochinonmethoden erreicht wurden, sind in allen Fällen höher als die Ergebnisse der parallel durchgeführten Winkler-Methode.

Die Richtigkeit der mit der Hydrochinonmethode erzielten Ergebnisse wurde im folgenden Versuch bewiesen. Aus den Proben der Abwässer, deren Analysenergebnisse in der Tabelle II angegeben sind, wurde der Sauerstoff durch Durchblasen von Stickstoff beseitigt. Die so behandelten Proben wurden im Verhältnis 1 : 1 mit destilliertem Wasser mit einem bestimmten Sauerstoffgehalt verdünnt. Dann wurde

TABELLE III

SAUERSTOFFBESTIMMUNG IN 1 : 1 VERDÜNNTEN ABWÄSSERN

Probe Nummer	*mg O_2/l*			
	Theorie	*H-Meth. (pot.)*	*W-Meth.*	*Unterschied zwischen Theorie und W-Meth.*
1	4.52	4.48	4.30	−0.22
2	4.52	4.40	3.21	−1.31
3	4.52	4.66	3.23	−1.29
4	4.52	4.53	2.20	−2.32
5	4.52	4.53	3.91	−0.61
6	4.52	4.71	1.80	−2.72

die Sauerstoffkonzentration in allen Mischungen nach den beiden Hydrochinonmethoden und auch nach der WINKLER-Methode bestimmt.

Die Werte in der Tabelle III zeigen, dass die Analysenergebnisse, die mit der Hydrochinonmethode erreicht wurden, mit dem wirklichen Sauerstoffgehalt übereinstimmen. Die WINKLER-Methode ergab auch in diesem Falle niedrigere Resultate. Der negative Abweichungswert war nach der Umrechnung auf die unverdünnte Probe ungefähr derselbe, wie der Abweichungswert, der zwischen den Sauerstoffbestimmungen mittels der Hydrochinonmethode und der WINKLER-Methode bei der gleichen ursprünglichen Probe festgestellt wurde. (Vergleiche Tabelle II und III; die Nummern der einzelnen Proben korrespondieren.)

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The effect of foreign ions on the spectrophotometric determination of boron with methylene blue

DUCRET[1] introduced methylene blue as a reagent for the spectrophotometric determination of boron. Borate reacts with fluoride to form borofluoride which probably reacts further with methylene blue to give a complex which can be extracted by 1,2-dichloroethane. Slightly soluble compounds are formed between methylene blue and many inorganic acids and neutral salts[2]. Most of these compounds are more soluble in 1,2-dichloroethane than in water and are therefore to some extent extracted together with the methylene blue–boron fluoride complex. DUCRET[1] pointed out that perchlorate, thiocyanate and trichloroacetate were extracted quantitatively, and that permanganate and nitrate were partly extracted by 1,2-dichloroethane.

HOLWECH AND SKAAR[3] used a modified DUCRET method to determine boron in small samples of high-purity silicon. In this modified procedure the fluoride buffer was replaced by a hydrogen fluoride solution, in which the borofluoride ions were formed more quickly. In order to increase the sensitivity the volumes were reduced to about one third. This modified method was used in the present investigation.

Apparatus

All extinction measurements were made with a Zeiss spectrophotometer PMQ II and 1.000-cm glass cells.

The sample solutions were prepared in 10- and 20-ml polyethylene bottles with stoppers equipped with a tapered plastic tube.

Reagents

All chemicals were of reagent grade quality. Ordinary distilled water from an all-metal still was used. 1,2-Dichloroethane ("purum" from Fluka AG) was redistilled and the fraction between 82.8° and 83.2° was used.

Standard solutions

Methylene blue solution, 0.0025 M: 0.935 g of methylene blue (G. T. Gurr Ltd.) was dissolved in water and diluted to 1 l. The solution was filtered through a Büchner filter funnel (porosity G 2) and kept in a dark place.

Standard boron solution, $25 \cdot 10^{-6}$ M boric acid: 0.6184 g of H_3BO_3 was dissolved in water and diluted to 1 l (10^{-2} *M*); 50 ml were diluted to 1 l ($0.5 \cdot 10^{-3}$ *M*) and then 50 ml of this solution were diluted again to 1 l ($25 \cdot 10^{-6}$ *M*).

Hydrofluoric acid, 10 M: 44 ml of a 40% HF solution were diluted with water to 100 ml and kept in a polyethylene bottle.

Procedure

The standard sample solutions were prepared by pipetting 1 ml of water, 1 ml of standard boron solution, 0.5 ml of 10 *M* hydrofluoric acid and 0.5 ml of 30% hydrogen peroxide into a 10-ml polyethylene bottle. A calibrated polyethylene pipette was used for the hydrofluoric acid solution. The solutions were mixed and the bottle was left for 2 h at room temperature. 2 ml of 0.0025 *M* methylene blue and 5 ml of 1,2-dichloroethane was added, and the mixture was shaken for 3 min by hand and then centrifuged.

The bottle fitted with a stopper with a tapered plastic tube, was inverted and the organic phase was squeezed into a 20-ml polyethylene bottle. Before inverting the bottle, some air was forced out, and when the bottle was inverted the pressure was released so that air and dichloroethane solution removed any residual drops of water from the tube. After this, nearly all the dichloroethane could be separated from the aqueous phase; 5 ml of water were added and the bottle was shaken for 3 min and then centrifuged. The dichloroethane phase was squeezed into a 1.000-cm glass cell as described above and the extinction was measured at 660 mμ (E_b).

In the blank solution only 2 ml of water were added before the hydrofluoric acid. When the interference of a foreign ion on the extinctions of the blank and standard sample solution was measured, either 1 ml of water and 1 ml of a solution of the ion, or 1 ml of standard boron solution and 1 ml of a solution of the ion were added.

Results and discussion

In an earlier investigation by LANGMYHR AND SKAAR[4] two constants RI_a and BI_a were introduced for indicating the interference produced by an ion a; concentrations were given as weight concentrations.

The constants used in the present paper are modified by using molar concentrations. The interference of a foreign ion i on the blank is denoted IB_i and the interference of the same ion on the recovery of boron is denoted IR_i. By definition $\mathrm{p}IB = -\log |IB|$ and $\mathrm{p}IR = -\log |IR|$ ($|x|$ = numerical value of x). Thus for $\mathrm{p}IB_i = 0$, any concentration of the foreign ion i increases the extinction to the same extent as the same concentration of boron; for $\mathrm{p}IB_i = 2$, the increase in extinction is only 1% of that of the same concentration of boron.

Interfering ions

All experimental data are given in Table I. Only the blank value (E_o) and the extinction of the standard boron test (E_b) are omitted; the average value of 37 tests was $E_o = 0.324$ and $E_b = 0.512$, the average deviation in both cases being 0.008. The average deviations between tests in the same series were 0.004 and 0.006 respectively.

From Table I it can be seen that some ions interfere to a considerable extent. For all solutions, except those containing hydrochloric acid, pIB values are less than pIR. For the following ions pIB was less than 3.0: MoO_4^{2-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, Hg^{2+}, SCN^-, NO_3^-, As^{3+}, Sb^{3+}, $S_2O_8^{2-}$, ClO_4^-, I^-, IO_4^-.

Values of pIB greater than 4 should be regarded with reservation. Boron is a common impurity in many reagents even of reagent grade quality. A contamination of 10 p.p.m. of boron in a reagent may yield a pIB value of about 4.

The less satisfactory reproducibility of some of the measurements (*e.g.* for $K_2Cr_2O_7$ and KIO_4) may have different reasons. The added salt may come to some equilibrium with the hydrogen peroxide and the hydrogen fluoride solution and reactions, *e.g.* precipitation, reduction, oxidation (and volatilization of hydrogen fluoride if strong mineral acid was added), may occur. In these cases pIB_i and pIR_i are given in brackets.

The percentage recoveries of boron added, which are given in brackets for $Ce(SO_4)_2$, $KFe(SO_4)_2$, As_2O_3, SbOCl and BiOCl, mean the percentage recoveries relative to the

TABLE I

THE INTERFERING EFFECTS OF FOREIGN IONS ON THE BLANK VALUE AND ON THE RECOVERY OF ADDED BORON

Foreign ion (i)	*Added as*[a]	*Molarity*[b]	$(E_i - E_0) \cdot 1000$ *at 660 mμ*	pIB_i	*% Recovery*[c] *of* $25 \cdot 10^{-9}$ *mol* H_3BO_3	pIR_i[d]
H^+	HCl	0.02	1	>4.6	101	>4.6
		0.1	-16	>5.3	87	5.2
		0.2	20	>5.6	70	5.1
		0.4	48	5.9		
		1	169	5.8		
Li^+	Li_2SO_4	0.02	-10	>4.6	100	>4.6
Na^+	NaCl	0.4	144	5.5		
		0.4	115	5.6	66	5.4
Mg^{2+}	$MgCl_2$	0.02	44	4.7	88	4.5
Ba^{2+}	$BaCl_2$	0.02	33	>4.6	90	4.6
		0.02	28	>4.6	87	4.5
UO_2^{2+}	$UO_2(Ac)_2$	0.004	-101	3.6	89	3.8
		0.01	-189	3.7		
Ce^{4+}	$Ce(SO_4)_2$[e]	0.0008	37	3.3		
		0.0008	-8	>3.2	86(100)	3.8
(Ti^{4+})	$K_2TiO(C_2O_4)_2$	0.02	24	>4.6	93	4.8
Zr^{4+}	$ZrOCl_2$	0.02	-17	>4.6	97	>4.6
VO_3^-	NH_4VO_3	0.004	61	3.8	98	>3.9
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	0.0002	26	>2.6		
		0.001	17	>3.3		
		0.002	-1	(>3.6)	105	(3.6)
		0.004	31	(>3.9)		
		0.004	(0.2%T)			
		0.01	(0.4%T)			
MoO_4^{2-}	Na_2MoO_4	0.00002	145	1.1	94	>1.6
		0.00004	239	1.2		
		0.0001	425			
		0.0001	418			
		0.02	674			
MnO_4^-	$KMnO_4$	0.004	114	3.6		
		0.004	82	3.7	104	>3.9
WO_4^{2-}	Na_2WO_4	0.002	18	>3.6		
		0.002	-2	>3.6	108	(3.7)
Fe^{3+}	$KFe(SO_4)_2$[e]	0.02	103	4.3	90(103)	4.6
$Fe(CN)_6^{3-}$	$K_3Fe(CN)_6$	0.0002	-105	2.3		
		0.0002	-111	2.3	101	>2.6
$Fe(CN)_6^{4-}$	$K_4Fe(CN)_6$	0.00004	3	>1.9		
		0.0002	-106	2.3		
Ni^{2+}	$NiSO_4$	0.02	-11	>4.6	103	>4.6
Zn^2	$ZnSO_4$	0.01	6	>4.3		
		0.02	74	4.4		
Cd^{2+}	$CdSO_4$	0.01	16	>4.3		
		0.02	60	4.5		
Hg^{2+}	$HgCl_2$	0.00002	155	1.1	82	2.3
		0.02	(0.05%T)			
Al^{3+}	$KAl(SO_4)_2$	0.02	29	>4.6	95	>4.6
CH_3CH_2OH	CH_3CH_2OH	3.4	103	6.5		
Ac^- see	NH_4^+, Pb^{2+}					
Citrate	Citric acid	0.02	24	>4.6		
$C_2O_4^{2-}$	$K_2C_2O_4$	0.02	76	4.4	85	4.4
CN^-	KCN	0.019	42	4.7		

TABLE I (Continued)

Foreign ion (i)	*Added as*[a]	*Molarity*[b]	*$(E_i—E_0) \cdot 1000$ at 660 mμ*	*pIB_i*	*% Recovery*[c] *of $25 \cdot 10^{-9}$ mol H_3BO_3*	*pIR_i*[d]
SCN^-	KSCN	0.0002	52	2.6	103	>2.6
		0.002	625		92	3.7
		0.02	(0.2%T)			
Pb^{2+}	$Pb(Ac)_2$	0.01	33	4.5	103	4.3
		0.02	51	4.6		
NH_4^+	NH_4Ac	0.04	23	>4.9	93	5.0
		0.04	38	5.0	88	4.8
NO_3^-	KNO_3	0.0001	91	2.1	90	2.3
		0.0004	295	2.1	77	2.5
		0.002	811			
		0.02	(0.2%T)			
PO_4^{3-}	KH_2PO_4	0.02	—1	>4.6	104	>4.6
As^{3+}	As_2O_3	0.0004	300	2.1	63(90)	2.3
		0.002	1043	2.3		
Sb^{3+}	SbOCl[f]	0.00001	78	1.1	64(91)	0.7
		0.00004	320	1.1		
		0.0008	>2000			
Bi^{3+}	BiOCl[f]	0.0004	—35	3.1	73(104)	2.5
		0.004	—143	3.5	15(21)	
		0.008	—250	3.5		
SO_4^{2-}, see	Li^+, Al^{3+}					
$S_2O_3^{2-}$	$Na_2S_2O_3$	0.02	186	4.0	66	4.1
$S_2O_7^{2-}$	$Na_2S_2O_7$	0.02	—14	>4.6	99	>4.6
$S_2O_8^{2-}$	$(NH_4)_2S_2O_8$	0.00004	13	>1.9		
		0.0002	—47	2.6		
SeO_3^{2-}	Na_2SeO_3	0.02	159	4.1	98	>4.6
Cl^-, see	Na^+, Ba^{++}					
ClO_4^-	$KClO_4$	0.000004	96	0.6		
		0.000008	178	(0.7)		
		0.000008	932		97	(>1.2)
		0.00002	(0.3%T)			
		0.00008	(0.15%T)			
Br^-	KBr	0.0004	41	3.0		
		0.0008	83	3.0		
		0.004	186	3.3		
		0.004	220	3.3	68	3.4
BrO_3^-	$KBrO_3$	0.002	312	2.8	71	3.2
		0.002	222	3.0		
		0.01	769			
I^-	KI	0.00002	331	0.8		
		0.00002	384		96	>1.6
		0.0002	(0.2%T)			
IO_4^-	KIO_4	0.000004	49	0.9	100	>0.9
		0.000008	121	0.8		
		0.00004	663			
		0.00004	126	(1.5)	104	(>1.9)
		0.00008	546			
		0.0004	238	(2.2)	108	(3.0)
		0.0004	1108			

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[a] The formulae are written without water of crystallization

[b] Molar concentration in the water phase before extraction

[c] The boric acid concentration (b) in the water phase before extraction was $5 \cdot 10^{-6}$ molar

[d] p(b) = 5.3

[e] In 0.1 *M* HCl

[f] In 0.2 *M* HCl

recovery in a solution containing the same hydrogen chloride concentration as indicated in the footnotes.

In the present investigation pIB_t values were only calculated when $0.035 < |E_t - E_o| < 0.350$, and p$IR_t$ values only when $0.035 < |(E_{t,b} - E_t) - (E_b - E_o)| < 0.350$. E_t and $E_{t,b}$ are, respectively, the extinctions (at 660 mμ) due to the foreign ion alone, and to the foreign ion plus boron. When the numerical values of the differences mentioned were less than 0.035, it was assumed that the real value was less than 0.050; in these cases pIB_t and pIR_t are given as greater than a value calculated on the basis of a difference of 0.050.

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Book Review

Méthodes Sélectionnées de Microanalyse Organique Quantitative, Volume I, par R. LÉVY et B. COUSIN, Dunod, Paris, 1961, 132 pp., relié toile souple, 15 N.Fr.

Ce livre, le premier d'une série de trois volumes de petit format, donne une description complète de l'organisation et du travail d'un laboratoire de microanalyse. Les auteurs ont choisi le format de poche afin que l'analyste puisse consulter facilement ce livre, même au laboratoire, au cours des différentes opérations d'une analyse. Ce premier volume contient les chapitres suivants: (1) Le laboratoire de microanalyse, (2) Balances et pesées microanalytiques, (3) Prélèvements microanalytiques.

Les auteurs, ayant l'expérience de nombreuses années de direction de laboratoires de microanalyse, donnent des descriptions détaillées des méthodes utilisées et de précieux renseignements.

Toutes les explications données sont claires et instructives, souvent illustrées de calculs montrant la grandeur des erreurs possibles. Cet ouvrage ne peut être que recommandé par chaque chef de laboratoire d'analyse. D'autre part, sa traduction en plusieurs langues, en particulier en anglais, est à souhaiter.

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1. Belcher, R. and Ingram, G., *Analyt. Chim. Acta,* 1950, **4,** 118, 401
2. Clark, S. J., "*Quantitative Methods of Organic Analysis*", pp42-76, Butterworth's Scientific Publications, 1956

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1. Whitehead, T. H., *J. Chem. Educ.*, 1959, **36,** 297
2. Williams, T. R. and Harley, J. D., *Chemist-Analyst,* 1961, **50,** 114
3. Davies, M. T., *Analyst*, 1959, **84,** 248

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Contaminations en chromatographie gaz-liquide d'esters d'acides gras radioactifs sur phase stationnaire polyester (M. Pascaud, Paris et Villejuif)

A gas chromatographic trap designed to collect compounds which tend to form aerosols (R. K. Stevens and J. D. Mold, Durham, N.C.)

Relative response of fatty acid methyl esters on the flame ionization detector (L. S. Ettre and F. J. Kabot, Norwalk, Conn.)

A vapour dilution system for detector calibrations (R. P. W. Scott, Cambridge)

The effect of the column tubing composition on the recovery of chlorinated hydrocarbons by gas chromatography (H. Beckman and A. Bevenue, Davis, Calif.)

Rotating unit for preparative scale gas chromatography. Part II - Theoretical aspects (S. Polezzo and M. Taramasso, Milan)

Influence of support modificants on substrate selectivity in gas chromatography (K. J. Bombaugh, Merriam, Kans.)

Herstellung von Eichgemischen im Bereich der inerten Gase und leichten Kohlenwasserstoffe, insbesondere für die Gaschromatographie (F. Kanne, Wesseling Bez. Köln)

Possibility for using a simple expression for peak symmetry characterization in gas chromatography (L. S. Ettre, Norwalk, Conn.)

Gas chromatography with stationary phases containing silver nitrate. IV. The methylcyclobutenes, methylenecyclobutane, C_6 dienes and related compounds (J. Shabtai, J. Herling and E. Gil-Av, Rehovoth)

The application of gas chromatography to the determination of retention data of some trimethyl-silyl ethers and trimethyl-silyl thioethers (F. H. Pollard, G. Nickless and P. C. Uden, Bristol)

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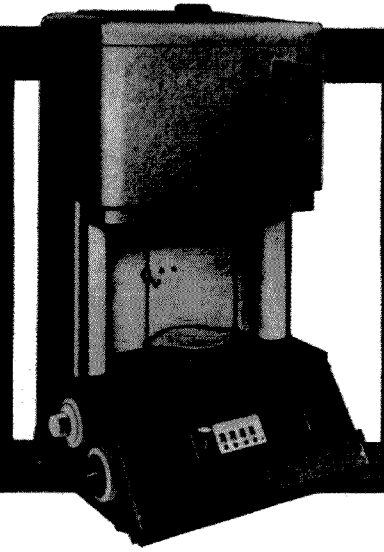

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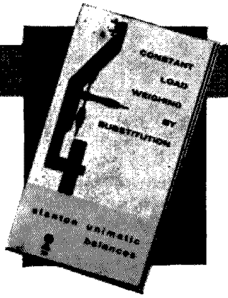

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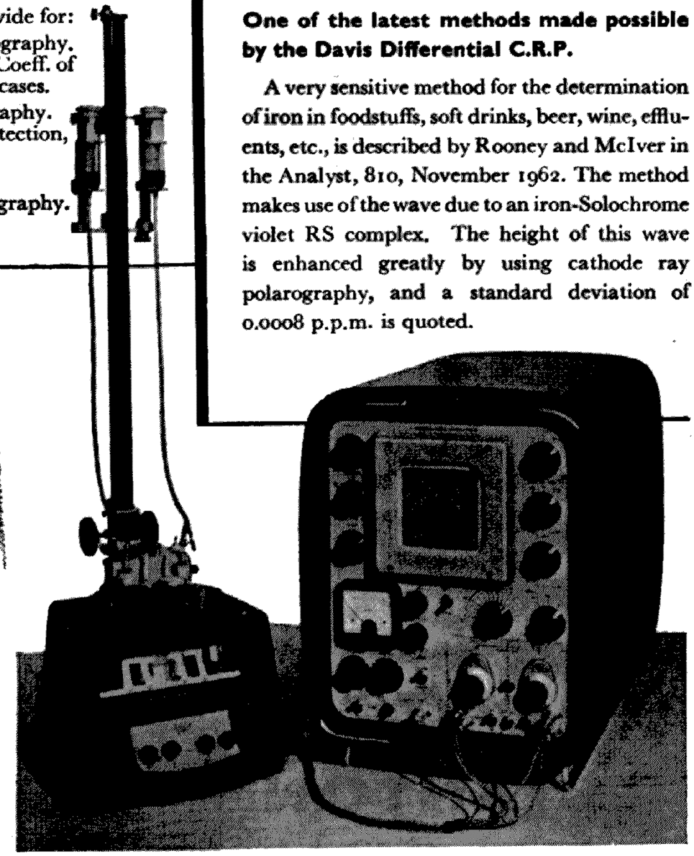

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