

ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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Anal. Chim. Acta, Vol. 27, No. 1, p. 1-100, July 1962

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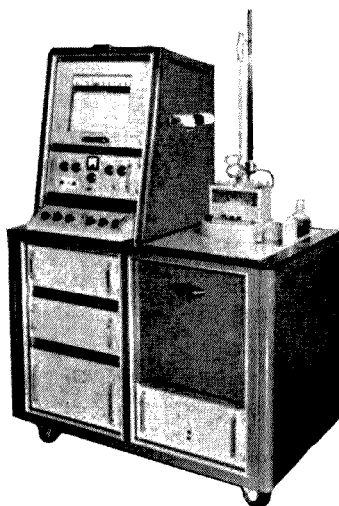
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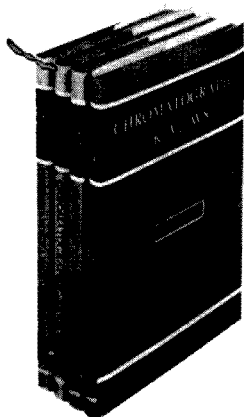
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VOLUME 4 *Covering the year 1961*

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6½ x 9½" viii + 184 pages 39 tables 41 illus. 1962

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- 1) *Chem. Eng. News*, 1960, 38 (16), 115.
- 2) Callear, A. B. and Cvetic, R. J., *Canad. J. Chem.*, 1955, 33, 1256-67.
- 3) Hishta, C., et al., *Anal. Chem.*, 1960, 32 (7), 680.

4-(2-PYRIDYL-AZO)-RESORCINOL DISODIUM SALT (PAR)

A colorimetric reagent for cobalt and other metals PAR has been claimed to be the most sensitive of all reagents for the colorimetric estimation of cobalt, the most sensitive water-soluble reagent for uranium, and perhaps the only water-soluble reagent for the colorimetric determination of lead¹. In addition, it is a versatile complexometric indicator in direct titrations of metal ions with EDTA², and of indium with nitrilo-triacetic acid³.

- 1) Pollard, F. H., Hanson, P. and Geary, W. J., *Anal. Chim. Acta*, 1959, 20, 26-31.
- 2) Wehber, P., *Z. anal. Chem.*, 1959, 166, 186-9.
- 3) Busev, A. I. and Kanaev, N. A., *C.A.*, 1959, 53, 18747c.

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During the last thirty years many thousands of copies of this B.D.H. booklet on pH values have been distributed in the United Kingdom and abroad. The seventh edition, entitled "pH Values and their Determination" is now available. It has been completely re-written in relation to current theory and practice, and includes a discussion of electrometric methods. Copies are free.

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For gravimetric determinations of copper

A solution of o-(toluene-p-sulphonamido)-aniline in 65% ethanol precipitates copper ions quantitatively and selectively, forming an insoluble green compound (C₁₁, H₁₃, N, O, S), Cu, readily dried to constant weight at 110°C. and non-hygroscopic. The reagent is useful for determining copper in brass and other alloys, as no other common metal ion forms an insoluble complex.

- 1) Billman, J. H., Janetos, N. S. and Chernin, R., *Anal. Chem.*, 1960, 32, 1342-4.

'PHOSPHATE ESTERS IN METABOLISM'

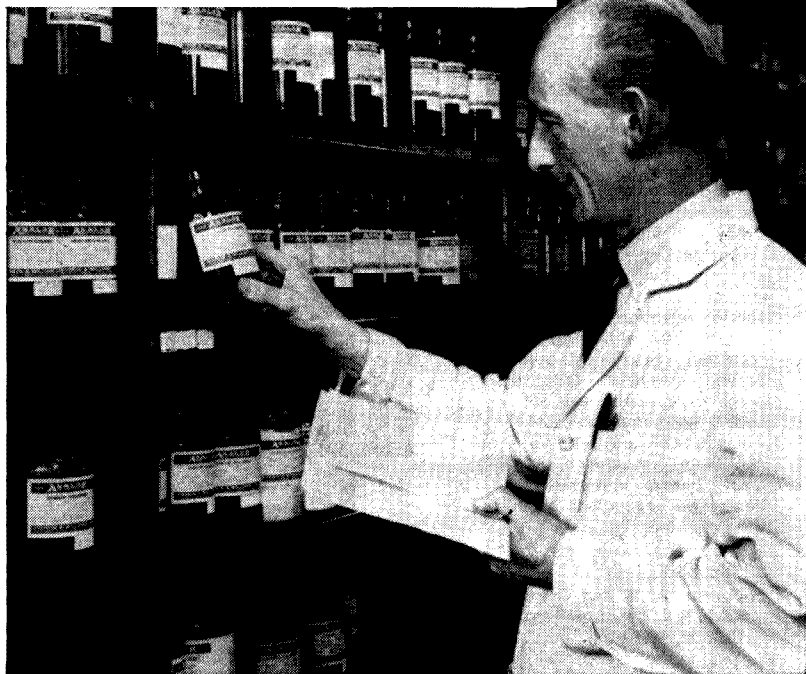
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 27, No. 1, July 1962

SPECTROPHOTOMETRIC DETERMINATION OF THALLIUM
AS THALLIUM TETRIODIDE

Iodide ions react with thallic ions at pH 2-8 to form a complex iodide, which is suitable for the spectrophotometric determination of thallium. The reaction has a sensitivity of 0.05 μg Tl per cm^2 for $\log I_0/I = 0.001$ and obeys Beer's law up to 40 p.p.m. Optimum conditions for the reaction have been established. The standard deviation is 0.6%. The effects of temperature and pH, the ratio of thallium to reagent, stability of the complex, its conformity to Beer's law, and the rate of color formation were studied. The effect of many diverse ions was examined.

D. BETTERIDGE AND J. H. YOE, *Anal. Chim. Acta*, 27 (1962) 1-8

DIRECT SPECTROPHOTOMETRY OF SILVER IN A NON-
AQUEOUS MEDIUM

Silver in the range 0.01-10 p.p.m. is extracted from aqueous solution containing anthranilic acid diacetic acid into methyl isobutyl ketone as silver di-*n*-butylammonium salicylate without interference from 10-fold amounts of Mg, Ca, Zn, Pb, Al, Cu(II), Mn(II), Ni, Co(II), Fe(III), Bi or any compatible common anion. Hg(II) is co-extracted slightly but can be retained in the aqueous phase with EDTA. Spectrophotometric determination of the extracted silver is done with pyrogallol red at 390 μ in 4-cm cuvettes. The colour system is stable and reproducible. No special purification of reagents is necessary even for the lowest concentrations of silver.

R. M. DAGNALL AND T. S. WEST, *Anal. Chim. Acta*, 27 (1962) 9-14

STUDIES ON ADSORPTION INDICATORS

PART II. *p*-ETHOXYCHRYSOIDINE AS ADSORPTION INDICATOR

p-Ethoxychrysoidine is studied as adsorption indicator in the direct titration of silver with iodide, bromide, thiocyanate and chloride at pH 4-5. The explanation given by SCHULEK AND PUNGOR for the colour changes has been modified in the light of compound formation on the surface of the precipitate. The silver compound of *p*-ethoxychrysoidine has been isolated; its behaviour provides a suitable explanation for the colour changes as well as the pH changes in the titrations.

K. N. TANDON AND R. C. MEHROTRA, *Anal. Chim. Acta*, 27 (1962) 15-19

SPECTROFLUOROMETRIC DETERMINATION OF HYDRAZINES,
AND ITS APPLICATION TO DETERMINATION OF
BENZYLHYDRAZINE IN BIOLOGICAL SAMPLES

(in German)

A spectrofluorometric determination of strong reducing substances such as hydrazine and alkyhydrazines is described. It is based on the reduction of 1,2-naphthoquinone-4-sulfonic acid to the fluorescent 1,2-dihydroxynaphthalene-4-sulfonic acid. The assay of microgram quantities of hydrazines in blood plasma and of benzylhydrazine in animal organs and urine is reported.

M. ROTH UND J. RIEDER, *Anal. Chim. Acta*, 27 (1962) 20-26

CHRONOPOTENTIOMETRY OF URANIUM(IV)

The chronopotentiometry of uranium at platinum electrodes has been investigated. A determination of uranium has been devised based on the conversion of the uranium to uranium(IV) and the oxidation of the uranium(IV). The effect of several possible interfering substances has been checked.

D. G. DAVIS, *Anal. Chim. Acta*, 27 (1962) 26-30

A MODIFIED SINGLE SOLUTION METHOD FOR THE DETERMINATION OF PHOSPHATE IN NATURAL WATERS

A single solution reagent is described for the determination of phosphorus in sea water. It consists of an acidified solution of ammonium molybdate containing ascorbic acid and a small amount of antimony. This reagent reacts rapidly with phosphate ion yielding a blue-purple compound which contains antimony and phosphorus in a 1 : 1 atomic ratio. The complex is very stable and obeys Beer's law up to a phosphate concentration of at least 2 $\mu\text{g}/\text{ml}$. The sensitivity of the procedure is comparable with that of the stannous chloride method. The salt error is less than 1%.

J. MURPHY AND J. P. RILEY, *Anal. Chim. Acta*, 27 (1962) 31-36

TITRATIONS WITH CERIUM(IV) SOLUTION IN NITRIC ACID MEDIA: APPLICATION TO DETERMINATIONS OF IRON, URANIUM AND PLUTONIUM

(in French)

A method is described for titrimetric determination of iron, uranium or plutonium in nitric acid media. The element is reduced with titanium(III) solution in presence of sulfamic acid, and titrated with cerium(IV) solution. Precautions normally taken for nitric acid media are unnecessary. The method is rapid and precise and is readily applicable to determinations of plutonium or irradiated uranium.

J. CORPEL AND F. REGNAUD, *Anal. Chim. Acta*, 27 (1962) 36-39

THE DETERMINATION OF BROMIDE AS BROMINE CYANIDE

(in German)

The previously developed selective iodometric method for determination of bromide has been verified and improved.

E. SCHULEK AND L. LADÁNYI, *Anal. Chim. Acta*, 27 (1962) 40-43

COULOMETRIC TITRATION OF COPPER(II) WITH ELECTROGENERATED CHROMIUM(II)

The current efficiency for the electrogeneration of chromium(II) for use as a coulometric titrant was studied for several supporting electrolytes. With a mercury cathode and a 0.1 M chromic sulfate-0.1 M potassium chloride medium, 0.8 to 2.8 mg of copper(II) in 110 ml of solution can be titrated using potentiometric end-point detection.

A. J. BARD AND A. G. PETROPOULOS, *Anal. Chim. Acta*, 27 (1962) 44-49

THERMOGRAVIMETRIC ANALYSIS: TEMPERATURE LIMITS AND RATE OF HEATING

In the case of the decomposition of carbonates and hydrates, the Polanyi-Wigner equation often applies. A mathematical expression relating the temperature at a given stage of the reaction to the rate of decomposition, fraction of reactant left, initial weight and area of the compound and finally the rate of heating has been derived from the above equation. For a given thermobalance the minimum detectable rate of decomposition and fraction of reactant left are fixed so that the observed final decomposition temperature is a function of the rate of heating for a constant weight and area of material. Using this equation, values for the final decomposition temperatures have been calculated and compared with data found in the literature for the decomposition of calcium carbonate and for the dehydration of potassium chrome alum and orthoboric acid. The equation also has been applied to the dehydration of 5-nitrobarbituric acid trihydrate as determined by us.

A. BERLIN AND R. J. ROBINSON, *Anal. Chim. Acta*, 27 (1962) 50-57

GRAVIMETRIC DETERMINATION OF URANIUM (VI) WITH N-BENZOYLPHENYLHYDROXYLAMINE

Uranium(VI) can be quantitatively precipitated by N-benzoylphenylhydroxylamine at pH 5.4. The precipitate is weighed after ignition to U_3O_8 , or directly as $UO_2(C_{13}H_{10}O_2N)_2$. Cerium(III), thorium, lead and bismuth can be masked with magnesium-EDTA complex. Iron(III), titanium(IV), zirconium and molybdenum(VI) and small amounts of aluminium can be precipitated with the reagent and filtered before uranium(VI) is determined in the filtrate by proper adjustment of acidity. Fluoride, carbonate and organic acids interfere.

J. DAS AND S. C. SHOME, *Anal. Chim. Acta*, 27 (1962) 58-62

SEPARATION OF HYDROXY ACIDS BY ION EXCHANGE CHROMATOGRAPHY

Factors affecting the chromatographic separation of hydroxy acids by means of anion exchange resins in the borate form have been studied. With the acids studied the separation factor increases for a decreased borate concentration in the eluant. With complicated mixtures it is recommended to employ stepwise elution with solutions of increasing concentration.

B. ALFREDSSON, L. GEDDA AND O. SAMUELSON, *Anal. Chim. Acta*, 27 (1962) 63-67

THE SORPTION OF POLYMETAPHOSPHATE ON ANION EXCHANGE RESINS

From a solution of sodium polymetaphosphate, strongly basic anion exchange resins can retain a greater amount of polymetaphosphate than that corresponding to the exchange capacity. Sodium ions are held by the polymetaphosphate form of the resin and these sodium ions can be exchanged for other ions.

R. GRUNDELIUS AND O. SAMUELSON, *Anal. Chim. Acta*, 27 (1962) 67-70

THE METAL COMPLEXES OF SOME AZO AND AZOMETHINE DYE STUFFS

PART II. DETERMINATION OF STABILITY CONSTANTS AND PREPARATION OF SOLID COMPLEXES

The stability constants of the complexes of 4-(2-pyridylazo)-resorcinol (I) with copper(II), cobalt(II), zinc(II), lead(II), and uranium(VI) were determined by potentiometric titration in aqueous media, and were shown to have very high values, the stability constant of the copper(II) complex approaching that of the copper(II)-EDTA complex. The nickel(II) complex has shown to behave anomalously. The stability constants were also determined by this method in 1:1 dioxan/water, and the values obtained compared with those for the complexes of salicylidene-2-aminopyridine (II), 2-(*o*-hydroxy-phenyl-imino-methyl)-pyridine (III), and benzeneazoresorcinol (IV). It is shown that chelation by (I) is terdentate, involving the pyridine nitrogen, the *o*-hydroxyl group, and the azo nitrogen farthest from the heterocycle.

The solid copper(II) complexes of these four ligands were prepared; in the solid complexes the azo nitrogen nearest the heterocycle plays a greater part than in the complexes in solution.

W. J. GEARY, G. NICKLESS AND F. H. POLLARD, *Anal. Chim. Acta*, 27 (1962) 71-79

4-CARBOXY-1,2-CYCLOHEXANEDIONEDIOXIME COMPLEXES OF NICKEL(II) IN ALKALINE MEDIA

The reactions of 4-carboxy-1,2-cyclohexanedionedioxime and nickel(II) were studied in alkaline media. Spectrophotometric studies indicate the presence of a 1:1 complex ion, NiD⁻. Magnetic susceptibility measurements on a series of solutions of varying ratios of *vic*-dioxime and nickel(II) showed that the 1:1 complex ion was diamagnetic and that two paramagnetic complexes, probably NiD₂⁴⁻ and NiD₃⁷⁻, are present in solution. The stability constants for the three complexes were calculated from spectrophotometric and magnetic susceptibility data. The log *K* values were found to be log *K*₁ = 28.74 ± 0.60, log *K*₂ = 0.76 ± 0.15, and log *K*₃ = 3.67 ± 0.73 respectively.

C. V. BANKS AND J. P. LAPLANTE, *Anal. Chim. Acta*, 27 (1962) 80-89

THE SOLVENT EXTRACTION OF SOME METAL CUPFERRATES WITH BUTANOL

(Short Communication)

K. N. MUNSHI AND A. K. DEY, *Anal. Chim. Acta*, 27 (1962) 89-90

A NEW ELECTROANALYTICAL METHOD: COULOSTATIC OR CHARGE-STEP METHOD

(Short Communication)

P. DELAHAY, *Anal. Chim. Acta*, 27 (1962) 90-93

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(Short Communication)

J. W. WINCHESTER AND W. H. PINSON, *Anal. Chim. Acta*, 27 (1962) 93-94

A NOTE ON THE BEER-LAMBERT LAW

(Short Communication)

J. R. BROCK, *Anal. Chim. Acta*, 27 (1962) 95-97

STUDIES ON ADSORPTION INDICATORS, PART III. BENZENE AZO-1-NAPHTHYLAMINE AS ADSORPTION INDICATOR

(Short Communication)

K. N. TANDON AND R. C. MEHROTRA, *Anal. Chim. Acta*, 27 (1962) 97-99

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Vol. 27 (1962)

ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
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Anal. Chim. Acta, Vol. 27 (1962)

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SPECTROPHOTOMETRIC DETERMINATION OF THALLIUM
AS THALLIUM TETRIODIDE

D. BETTERIDGE AND JOHN H. YOE

*Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia, Charlottesville,
Va. (U.S.A.)*

(Received November 3rd, 1961)

All methods for the determination of thallium have been well reviewed by ANDERSON¹ up to 1950. SANDELL² and also CLARKE AND CUTTITTA³ have reviewed spectrophotometric methods up to 1958. Since 1958 SHCHEMELEVA⁴ has proposed a method involving methyl violet and a thallium chloride complex; this has also been investigated by EFREMOV AND CHZHI-GU SYUI⁵, RADU⁶, and KOVAŘIK AND MOUČKA⁷. Investigations on the halide complexes and ion association systems involving them, have been made by BUSEV AND TIPTSOVA⁸⁻¹¹. The methods available fall into three classes: (1) Thallium(III) is reduced and a colored oxidation product is produced in the process, *e.g.*, iodine or oxidized azo dyes.

(2) Chelate compounds, *e.g.*, dithizone³.

(3) Complex halides, *e.g.*, $TlCl_6^{3-}$, TlI_4^{1-} .

Our investigation was on the thallium iodide complexes. The principle of the method is that thallium(III) in the presence of four or more fold excess of iodide forms a tetriodide anionic complex, which absorbs at 400 $m\mu$. Although discovered independently, this method is a modification of BUSEV AND TIPTSOVA's⁹⁻¹¹. The determination of optimum conditions is described in the following pages.

EXPERIMENTAL

Apparatus

Beckman spectrophotometers, models DU and DK2, with matched 1-cm quartz cells. Beckman model G pH meter.

Reagents

Iodide. Iodide ions were obtained by using either a methiodide or potassium iodide. The methiodides of the several tertiary ammonium compounds tried were all satisfactory. Their preparation is simple.

Pyridine methiodide was prepared by adding 2 ml of iodomethane to 2 ml of pyridine dissolved in anhydrous acetone. After 1 h the precipitate was filtered, dried by suction and kept in a desiccator in a cupboard for protection against light. For routine analysis no further purification is necessary. For mole ratio studies some of the product was recrystallized from anhydrous alcohol. The compound is very hygroscopic.

Nicotinohydroxamic acid methiodide was prepared by refluxing 1 g of nicotinohy-

droxamic acid dissolved in alcohol with 2 ml of iodomethane. Evaporation of the alcohol leaves the methiodide. It may be purified by dissolving in dimethylformamide and reprecipitating with ether. This compound is not very hygroscopic but like all methiodides it is sensitive to light.

For routine work a 0.025% or 0.05% solution in 95% ethanol was used. It is not very stable and a fresh solution should be prepared every few days.

Thallium. Dissolve 3 g of thallic oxide in concentrated nitric acid, add a little bromine water and boil the solution a few min to convert any thallic ions to thallic. Filter and standardize the solution with 8-quinol by the method of MOELLER AND COHEN¹².

*Buffer solutions*¹³. Either the citrate buffer of KOLTHOFF or the SØRENSEN buffer of pH 2 is suitable. Stock solutions were made 1 M instead of 0.1 M so that smaller volumes could be used.

Kolthoff buffer. Mix 91.1 ml of 1 M citric acid and 8.9 ml of 1 M monopotassium citrate to give a buffer of pH 2.2

Sørensen buffer. Mix 50 ml of 1 M HCl with 50 ml of a solution 1 M with respect to both glycine and sodium chloride. The buffer has a pH of 2.

Diverse ions. Solutions of diverse ions were prepared from analytical grade salts and were usually made up to contain either 10 mg or 1 mg per ml of solution.

Water. Triply-distilled.

95% Alcohol.

Determination of optimum conditions for the reaction

In moderately acid solution the complex has a maximum absorption at 400 m μ . At 400 m μ there is virtually no absorption by the reagent (Fig. 1).

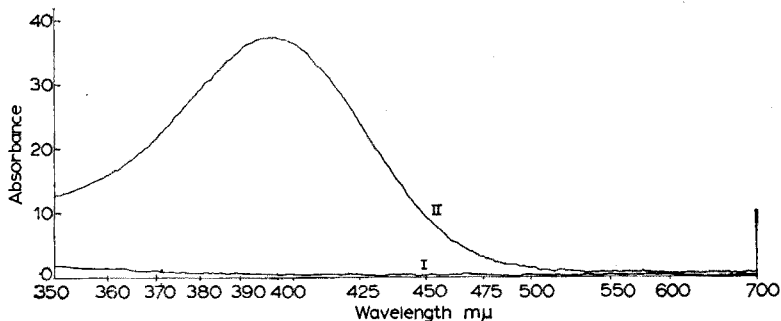


Fig. 1. Absorbance curves for reagent (Curve I) and complex (Curve II) against 70% ethanol in both instances. Concentration of thallium 6 p.p.m.

Effect of pH

The reaction is greatly affected by changes in pH. Over the pH range 1 to 3, however, it is constant and unaffected to any great extent by the medium (Fig. 2). At higher pH values the color abruptly vanishes; at lower pH values it was impossible to say unequivocally what was happening. In hydrochloric acid medium the color presumably faded because of complex chloride formation and in all cases one would expect iodine to be released.

Effect of ethanol

The intensity and stability of the color is greatly affected by the alcohol concentration (Fig. 3). BUSEV AND TIPTSOVA⁸ used a 3000-fold excess of potassium iodide to

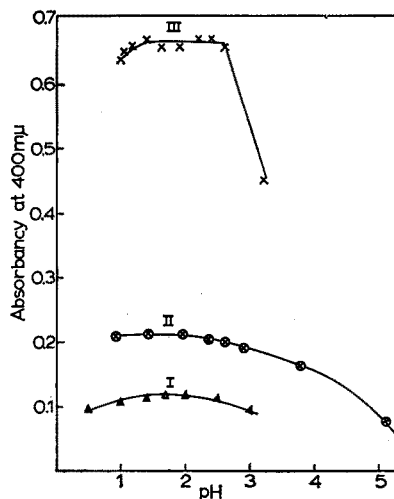


Fig. 2. Effect of pH on complex formation. Curve I, 2 p.p.m., Tl^{3+} , HNO_3 used for pH adjustment. Curve II, 4 p.p.m., Tl^{3+} , citrate buffer used for pH adjustment. Curve III, 1.2 p.p.m., Tl^{4+} , glycine-NaCl-HCl buffer used.

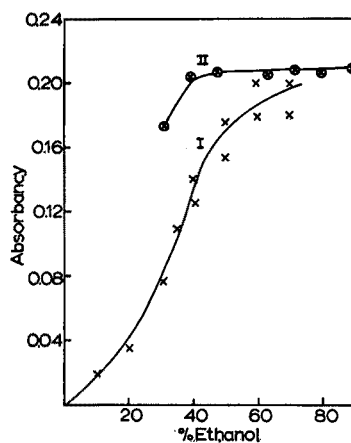


Fig. 3. Effect of ethanol on the absorbance of the complex. 4 p.p.m. Tl^{3+} . Curve I, using 10-ml flask, Curve II, using 25-ml flask.

stabilise the color in water, but if a 70% ethanolic solution is used only a slight excess is needed. Ethanol is slightly more effective than methanol and is much more effective than dimethylformamide.

Stability of complex

When made up in water the color faded at the rate of 30% in 1 h. In 70% ethanol

the absorption was constant for several hours. It decreased by 6% after 2 days and after 6 days by 40%. In some instances, however, it was noted that the color increased slightly on standing and therefore, if possible, all readings should be taken within 30 min of mixing the solutions.

Order of addition of reagents

There is an appreciable difference in the absorption if the reactants are varied in the order of mixing. The important factor is the alcohol concentration. Either the alcoholic solution of reagent must be present and thallium added to it, or the thallium

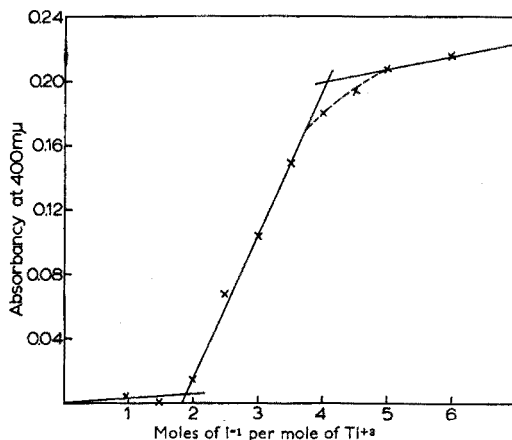


Fig. 4. Mole ratio method using pyridinemethiodide as source of iodide ions. Moles of I⁻ to 1 mole of Tl³⁺.

solution must be mixed with the bulk of the ethanol before the addition of reagent, or when small volumes (10 ml) are used the reagent solution must be added quickly with shaking. The order of addition of buffer solution is not critical.

Beer's law, range and sensitivity

The absorption is linear up to 40 p.p.m. of thallium. The optimum range is 10–20 p.p.m. The sensitivity is 0.02 μg Tl per cm² for log I₀/I = 0.001.

Temperature

When the reaction was carried out at 15° and at 35°, respectively, no significant difference in absorption from that at room temperature was observed.

Structure of the complex

The mole ratio method¹⁴, method of continuous variations^{15,16}, and slope-ratio method¹⁷ unequivocally point to a complex containing 4 moles of reagent to 1 of thallium. Since the reaction proceeds regardless of the source of iodide the fundamental color group is TlI₄¹⁻. When BUSEV *et al.*¹¹ use diantipyrynylbutane in addition to potassium iodide, they are almost certainly adding a bulky cation so that an ion

association system¹⁸ suitable for extraction into an organic layer is formed. Comparison with their readings and readings with different methiodide indicates that the added ion makes virtually no difference to the color of the solution.

Other complexes are formed but in these instances the evidence is less convincing because the slope-ratio method fails, the mole ratio is not sensitive enough and the

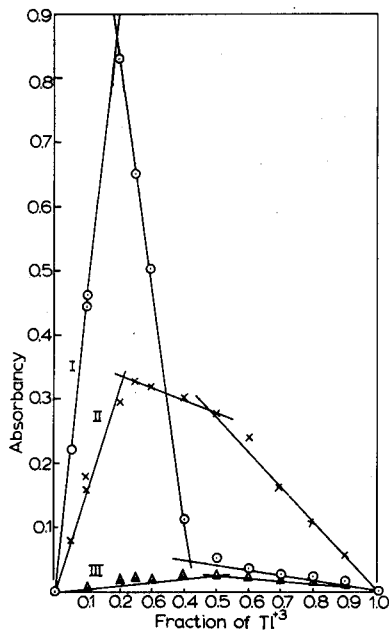
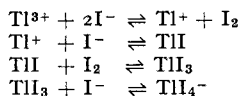


Fig. 5. Continuous variations using pyridinemethiodide as source of iodide ions $0-10^{-5}$ moles of Tl^{3+} and methiodide, Curve I, absorbance at $400\text{ m}\mu$; Curve II, at $330\text{ m}\mu$; Curve III, at $500\text{ m}\mu$.

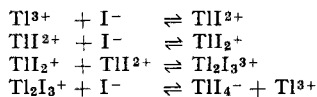
only positive evidence is obtained by the method of continuous variations. It seems fairly certain that a 2 : 1 complex of iodide to thallium is formed and there are indications of 1 : 1 and 3 : 2 complexes. No evidence of a 3 : 1 complex was found. When potassium iodide was used a 6 : 1 complex seemed to be formed. Since methiodides dissociate in water readily to give iodide ions there seems no obvious reason for the difference in behaviour of potassium iodide and the methiodides. However, it might be due to an ion pair formation between the TlI_4^- ion and the quaternary ammonium ion. The latter ion might then sterically hinder the formation of the TlI_6^{3-} ion. Ion pair formation is indicated by the extraction of the complex with quaternary amines and by the isolation and characterisation of diantipyrynylbutane thallium tetraiodide by BUSEV AND TIPTSOVA¹¹.

For the reaction in water BUSEV AND TIPTSOVA⁸ propose the following mechanisms,



In 80% ethanol using standard procedures we detected no iodine, thallos ion, precipitate of thallos iodide or thallic iodide. On the addition of water iodide was released

and the complex decomposed. A more natural mechanism would be the stepwise addition of iodide ions to thallic ion, which would retain the same valency throughout. However no TlI_3 was detected. A possible mechanism which would fit the observed facts is,



Further work in the field of thallium halide complexes is necessary before this or any other mechanism can be definitely established.

Effect of diverse ions

In a solution containing 2 p.p.m. of Tl^{3+} , the following ions caused a 10% positive error at the concentrations in p.p.m. given in parenthesis: BO_3^{3+} (15), Co^{2+} (75), Cu^{2+} (15), Fe^{3+} (2), Ga^{3+} (100), Ni^{2+} (150), Pb^{2+} (20), Sc^{4+} (100), Ti^{4+} (30), and V^{4+} (50). The following gave a 10% negative error: Ag^{1+} (<1), Al^{3+} (100), Bi^{3+} (100), Ca^{2+} (100), Ce^{4+} (100), Cl^{1-} (1000), CO_3^{2-} (100), Cr^{3+} (100), Hg^{1+} (7), Hg^{2+} (7), In^{3+} (100), Li^{1+} (>100), Mn^{2+} (50), PO_4^{3-} (50), Se^{+} (<100), Sn^{2+} (40), SO_3^{2-} (5), SO_4^{2-} (100), UO_2^{2+} (100), Y^{3+} (>100), Zn^{2+} (>2000). In the presence of EDTA the tolerances for the 4 ions tested were: Cu^{2+} (50), Fe^{3+} (10), Hg^{1+} (10), and Hg^{2+} (10); the 10% error for the copper and iron being positive, and that for mercury being negative. In mixtures of two or more ions the interferences were approximately additive in most cases. Interferences at a thallium concentration of 10 p.p.m. in place of the 2 p.p.m. solution were measured to see if the critical factor is the ratio of interfering ion to thallium or whether an absolute amount of foreign ion causes the same error. In general, the interference varied in proportion to the amount of thallium present, although this was not always true, e.g. tin(II).

Removal of interferences

BUSEV *et al.*¹¹ recommend adding EDTA, making ammoniacal, bringing back to pH 3 and then making an extraction. This is principally to overcome the interference of iron(III), copper and lead ions. We tried a similar procedure. The complex can be readily extracted into butanol or similar solvents, but it was found to be less stable than in ethanol. The color fades until it reaches some constant point. The time taken to reach this point varies with the solvent; when ethyl acetate was used 15 min was required. *n*-Butanol and iso-butylmethyl ketone took longer. To determine the efficiency in overcoming interferences *n*-butanol saturated with water was used to extract a solution containing thallium, the interfering ions and EDTA. The color of the extract was compared with that of one in which all ingredients, except the interfering ions were present. It was found that the method was partially effective in preventing interference. The greatest improvement was in the case of ferric ions where five times as much could be tolerated, but improvement was so slight in the cases of copper and lead that it was concluded that there was little advantage in using an extraction procedure. If EDTA was added to the ethanolic mixture the interference was reduced by the same extent as in the extraction method. Whereas excess EDTA could be readily tolerated in the extraction method, and indeed an excess led to a slight increase in absorption, in the ethanolic method a slight excess of EDTA gave

low results. EDTA may be used to overcome interference of iron(III) and copper(II) in the ethanolic method if an excess of zinc is added. Any excess EDTA is complexed by the zinc and an excess of zinc does not cause any interference. If EDTA is used, however, when the interferences are not limited to Fe^{3+} , Cu^{2+} , Pb^{2+} or Bi^{3+} , there is clear indication that interferences that do not normally cause any trouble become intolerable. Hence it was decided that the use of EDTA offers little or no advantage. The differences in the success of BUSEV *et al.*¹¹ may be accounted for by the use of a slightly lower pH.

An attempt was made to remove mercury by deposition on copper. The method has been used by BLYUM AND UL'YANOVA¹⁹, who used a copper wire, which was cleaned every few min until no deposit was seen. A modification of this was tried by us; fresh copper was used until no more deposit was seen. Some loss of thallium occurred and it took a long time, but mercury was removed. Next copper powder was tried. Best results were obtained when 10 mg of copper powder was added to a solution containing 40 μg of thallium and 100 μg of mercury(II) with a few drops of bromine water. The efficiency depended on the amount of copper used and, to a lesser extent, on the time of standing; 5 min was found to be best. After 5 min the copper was filtered off, the solution boiled, EDTA added to complex the dissolved copper, and the thallium determination was completed as usual. It was found that although the mercury was removed, only about 75 percent of the thallium was recovered.

PROCEDURE

Thallium must be in the trivalent state. If it is not, oxidize by boiling for not longer than 3 min with a little bromine water. Remove the excess bromine with a drop of phenol (25% in acetic acid). If a 10 ml flask is used, pipette out a 2-ml aliquot and add 0.2 ml of buffer. Rapidly add with swirling 7 ml of reagent and shake. Make up to mark with water and shake again. Read at 400 $m\mu$ against a reagent blank.

If a 25-ml flask is needed, or preferred, take up to 5-ml aliquot, add 0.2 ml buffer and 10 ml of ethanol and shake. Add 8 ml of reagent, shake, and make up to mark with water, and thoroughly mix.

If iron(III) and copper are the predominant interferences add 300 p.p.m. of zinc and 0.3 ml of 0.1 *M* EDTA before adding the buffer.

Precision

The precision was determined by determining the same amount of thallium (12 p.p.m.) eleven times. The absorbance was 0.725 and the standard deviation 0.004 (0.6%).

The standard deviation was also determined for thallium (12 p.p.m.) in the presence of 1 p.p.m. Fe^{3+} , 3 p.p.m. Hg^{2+} , 5 p.p.m. Pb^{2+} , 20 p.p.m. Sn^{2+} , 20 p.p.m. Bi^{3+} , 300 p.p.m. Zn^{2+} and 100 p.p.m. Ni^{2+} . The average absorbance for eleven determinations was 0.675 (an error of 7%) but the standard deviation was the same as that for thallium in the absence of interfering ions, namely, 0.004 (0.6%).

SUMMARY

Iodide ions react with thallic ions at pH 2-8 to form a complex iodide, which is suitable for the spectrophotometric determination of thallium. The reaction has a sensitivity of 0.05 μg Tl per cm^2 for $\log I_0/I = 0.001$ and obeys Beer's law up to 40 p.p.m. Optimum conditions for the reac-

tion have been established. The standard deviation is 0.6%. The effects of temperature and pH, the ratio of thallium to reagent, stability of the complex, its conformity to Beer's law, and the rate of color formation were studied. The effect of many diverse ions was examined.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique du thallium(III) sous forme de tétraiodure. L'influence de la température et du pH a été examinée, ainsi que celle de divers ions étrangers. On a déterminé également le rapport thallium/réactif, la stabilité du complexe et la vitesse de formation de la coloration.

ZUSAMMENFASSUNG

Thallium(III) bildet mit Iodid-Ionen einen Komplex, der sich zur spektrophotometrischen Bestimmung des Thalliums eignet. Die Reaktion ist stark abhängig vom pH. Die Absorption wird durch Temperaturänderungen (zwischen 15° und 35°) nicht beeinflusst. Es werden Angaben gemacht über Struktur und Stabilität des Komplexes sowie über die Störung der Reaktion durch Fremdionen und deren Ausschaltung.

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DIRECT SPECTROPHOTOMETRY OF SILVER IN A NON-AQUEOUS MEDIUM

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(Received November 20th, 1961)

A highly selective extraction system for the separation of silver down to 0.05 p.p.m. has recently been described by BETTERIDGE AND WEST¹. Silver was extracted into methyl isobutyl ketone (hexone) as silver di-*n*-butylammonium salicylate and determined by a dithizone procedure following back-extraction into an aqueous phase with dilute nitric acid. Difficulty was experienced with the instability of the dilute solution of silver dithizonate and the many factors which must be closely controlled to obtain reproducible results with dithizone at such low dilutions.

We have recently evolved a spectrophotometric method for the determination of μg amounts of silver in aqueous solution based on the use of the chromogenic reagent, pyrogallol red². The method is not as sensitive as the dithizone procedure, but does not require rigid control of experimental conditions and is considerably more reproducible with respect to a standard calibration curve. The pyrogallol red procedure is less selective than the dithizone one, but since it is used in nearly neutral solutions, controlled addition of EDTA can render it highly selective so that only copper and possibly other metals which form coloured EDTA chelates would still interfere. In view of the fact that such metals are not co-extracted with silver using the di-*n*-butylamine salicylate system in the presence of anthranilic acid diacetic acid, it was decided to apply the pyrogallol red method to silver following the extractive separation. In addition, colour formation was attempted directly in the hexone phase, thus eliminating the back-extraction and subsequent re-extraction of the previous method¹.

In preliminary experiments, the hexone extract obtained by the recommended procedure¹ was adjusted to a measured pH of 7 by means of acetic acid, an aqueous ethanolic solution of pyrogallol red was added, and the solution was diluted with ethanol and water in proportions sufficient to obtain a single phase. The colour was slow to develop but once formed was stable on dilution. At the apparent pH of the hexone extract (pH 10) maximum colour formation was produced after 1.5 h, but on dilution as above there was severe instability. Omission of water reduced the optimum time for colour formation to 15 min, but the colour of the diluted solution slowly decomposed though this was not serious for 60–90 min. More troublesome, however, was a white precipitate which was observed to form during development of colour and which intensified considerably on dilution with ethanol. In addition the peak of the absorption band of the silver complex was affected so that maximum colour intensity relative to the reagent blank was now obtained at 410 $m\mu$, instead of 390 $m\mu$ as before. Reproducibility was low because of the precipitation, though

better results were obtained by filtration immediately before absorption measurements.

Subsequently, systematic variation of the conditions revealed that the ethanol was responsible for precipitation. When it was eliminated from the procedure (apart from the small amount added with the pyrogallol red reagent) and the volume was made up with hexone, no difficulty was encountered owing to precipitation. Reproducible results were obtained when the colour was developed for 20 min and measurements were made within a few minutes of subsequent dilution. In the hexone medium the absorption should be measured against reagent at $390\text{ m}\mu$ as in aqueous solution, but the gradient of the calibration curve for $10\text{--}100\text{ }\mu\text{g}$ of silver is steeper thus providing higher precision (*cf.* Fig. 1). The colour system developed in the organic medium does

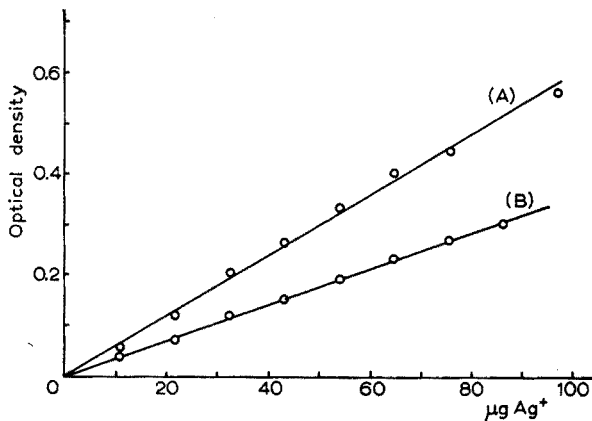


Fig. 1. Calibration curves for silver-pyrogallol red. (A) In Hexone ($390\text{ m}\mu$ 4-cm cell). (B) In Water ($390\text{ m}\mu$ 4-cm cell).

not possess the remarkable stability of silver-pyrogallol red developed in an aqueous phase², but it is quite satisfactory for routine measurements; the colour does not decrease appreciably for at least 90 min.

The hexone solvent is not very expensive, but it may be readily recovered free from di-*n*-butylamine (b.p. 160°) or ethanol (b.p. 72°) by simple distillation, collecting the fraction distilling in the range $115\text{--}120^\circ$.

INTERFERENCES

It has already been shown that none of the common anions which is compatible in solution with silver interferes with either the extraction method¹ or the pyrogallol red determination². Mercury(II) was found to be the only cation which accompanied the silver (*ca* 10%) through the di-*n*-butylamine/salicylate separation when extraction was carried out from aqueous solutions containing an excess of the weak complexan anthranilic acid diacetic acid (AADA)¹; only copper(II) and aluminium(III) caused interference with the recommended procedure using pyrogallol red².

The range of cations previously tested for their interference in the aqueous silver-pyrogallol red procedure was extended to include nickel, cobalt(II), iron(III), manganese(II), and bismuth present in a 10 molar ratio relative to silver. All of them interfered, but the effect of manganese was not very serious (Table I). The interferences were overcome by adding a controlled amount of EDTA to the test solution.

The necessary amount was found by direct complexometric titration of the foreign metals on a separate aliquot of solution. The silver ion present in the solution did not interfere with the titration. The interference of aluminium has now also been overcome. In a previous paper² the interference could not be overcome because a reliable method of finding the EDTA equivalence of aluminium had not been found. Large

TABLE I
DETERMINATION OF 50 μg Ag^+ IN PRESENCE OF 10 MOLAR RATIOS OF INTERFERING ION

Interfering ion	Titration system	Colour change	EDTA $\text{ml } 10^{-3}\text{M}$	Solution	Optical density ^a
Ni	Omega Chrome Red	Red - yellow	—	(A) Unmasked	0.193
	B Acetate Buffer pH ₄ ³	Fair end-point	1.15	(B) EDTA added	0.182
Co	Alizarin Complexan ⁴	Red - yellow	—	(A) as above	0.250
	Acetate Buffer pH 4.3	Good end-point	0.92	(B) as above	0.189
Mn	Solochrome Black T. ⁵	Mauve - blue	—	(A) as above	0.192
	Ammonia Buffer (Ascorbic & Tartaric Acid)	Good end-point	1.55	(B) as above	0.190
Bi	Xylenol Orange ⁶	Red - yellow	—	(A) as above	0.000
	HNO_3 pH 1.3	Good end-point	0.66	(B) as above	0.189
Fe(III)	Chromeazurol S. ⁷	Blue - red	—	(A) as above	0.057
	Chloroacetate buffer pH 2-3 (60°)	Fair end-point	0.60	(B) as above	0.180
Al	Xylenol Orange ⁶	Yellow - red	—	(A) as above	0.077
	Acetate Buffer pH 5.4 (Back titration with Pb^{2+})	Good end-point	0.60	(B) as above	0.180

^a Measured in 4-cm cells at 390 μm . Expected value: 0.188.

amounts of coloured ions would of course still interfere by virtue of the colour of their EDTA complexes. However, such interference may be overcome by prior extraction of the silver as its di-*n*-butylammonium salicylate. Since mercury(II) is the only ion known to be partially co-extracted with silver, a similar process was now applied to remove its interference. The mercury in an aliquot of the solution was titrated (Table II) and the necessary amount of EDTA was then added to the test solution before extraction. The silver was then determined in the extract by the pyrogallol red procedure. It will be seen that the interference of a 10 molar amount of mercury(II)

TABLE II
50 μg OF Ag^+ IN PRESENCE OF 10 MOLAR RATIO OF Hg(II). (PYROGALLOL RED COLOUR SYSTEM DEVELOPED IN EXTRACT AND MEASURED AT 390 μm IN 4-CM CUVETTES)

Solution	Masking agent	Optical density
Ag	—	0.323
Ag + Hg(II)	—	0.402
Ag + Hg(II)	0.95 ml 10^{-3}M EDTA	0.319

(relative to silver) can be eliminated. The mercury(II) was titrated directly with 10^{-3} M EDTA in the presence of the silver using a pH 7 pyridine acetate buffer and xylenol orange as indicator.

It was re-confirmed simultaneously that copper(II) and aluminium did not accompany silver into the organic phase when extraction was carried out by the di-*n*-butylamine salicylate system.

Thus by virtue of the extraction process and direct colour formation in the organic layer with pyrogallol red, a reliable and reproducible method has been evolved for the spectrophotometric determination of silver in the range 10–100 μ g (1–10 p.p.m.) in the presence of 10 molar ratios of any of the cations examined in this study, *i.e.* Mg, Ca, Zn, Pb, Al, Cu(II), Hg(II), Ni, Co(II), Mn(II), Fe(III), and Bi. Other cations were not examined, but since the great majority of them are chelated efficiently by EDTA, etc., the method could almost certainly be extended to deal with the determination of silver in the presence of almost all other cations. None of the common anions other than the halides caused interference, *i.e.* nitrate, perchlorate, sulphate, phosphate and acetate.

EXTRACTION FROM VERY DILUTE SOLUTION

The determination of concentrations of silver down to 0.01 p.p.m. is a problem of vital concern in effluent analysis and consequently experiments were undertaken to apply the pyrogallol red method to such a procedure. Since the smallest concentration of silver that can be reliably determined in the hexone extract is *ca.* 1 p.p.m., the feasibility of applying the di-*n*-butylamine/salicylate system as a means of concentration was examined. The efficiency of extraction was first of all tested radiochemically with ^{110}Ag as tracer in a solution of known total silver concentration. The activities of the separated hexone and aqueous phases were determined in a liquid-counting Geiger-tube which had been coated with silicone to minimise adsorption of silver. It was established that, discounting differences in absorption for the two media, a partition coefficient of 320.5 was readily obtained in a single (one-pass) extraction of 10 μ g of silver from 1 l of near neutral solution containing anthranilic acid diacetic acid, with 50 ml of the hexone reagent (Table III).

Thus virtually complete extraction of silver in the range down to 0.01 p.p.m. was readily obtained in a single operation. Despite the protective coating on the glassware adsorption of ^{110}Ag still occurred and it could only be removed by washing with inactive silver nitrate solution, dilute nitric acid, dilute potassium cyanide solution and finally distilled water. Thus it is apparent that great care must be taken in the determination of silver at such low concentrations.

TABLE III
SUMMARY OF RADIOCHEMICAL DATA [^{110}Ag]

System examined	Counts/min	Net count
Background	53	—
Aqueous phase following extraction	88	35
Hexone phase following extraction	11,271	11,218

$$\text{Partition coeff.} = \frac{[^{110}\text{Ag}]_{\text{org.}}}{[^{110}\text{Ag}]_{\text{aq.}}} = 320.5$$

When the efficiency of extraction of silver at 0.01 p.p.m. concentrations into 50 ml of hexone had been established, a pyrogallol red procedure was developed for direct spectrophotometric determination in the hexone extract. A reaction time of 1.75 h was required to ensure stable colour formation between pyrogallol red and silver ions in hexone at this lower dilution. The permissible time limit of measurements is 1.75 ± 0.5 h under these conditions.

DISCUSSION

The combination of the selective ion-association extraction system based on silver di-*n*-butylamine salicylate and direct development of the coloured compound with pyrogallol red [$\text{Ag}_2(\text{C}_{19}\text{H}_8\text{O}_8\text{S})$] in the hexone extract ensures a rapid and sensitive method for the determination of silver down to 0.01 p.p.m. No anion or cation which is compatible in solution with silver ion causes interference except mercury(II) and significant interference from this can be prevented by controlled addition of EDTA before extraction. The solution colours are stable after a reaction time of 75 min and for 1 h thereafter. In the extraction of 100 μg of silver from 1 l of solution a straight line calibration curve is obtained which passes through the origin; results obtained for less than 10 μg of silver tend to be somewhat low owing to adsorption of silver on glassware⁸.

EXPERIMENTAL

Determination of 10–100 μg of silver (1–10 p.p.m.)

Apparatus

Unicam SP. 600 Spectrophotometer and 4-cm cuvettes.

Reagents

Extraction Reagent A. 3.2 g of A.R. salicylic acid and 30 ml of di-*n*-butylamine dissolved in, and diluted to 1 l with methyl isobutyl ketone.

Masking Agent. 10^{-1} M solution of the sodium salt of anthranilic acid diacetic acid (AADA).

10^{-4} M Pyrogallol Red. 10.5 mg of pyrogallol red (BDH) dissolved in 250 ml of absolute ethanol.

Procedure

Transfer an aliquot of solution of pH *ca.* 7, containing less than 100 μg of silver/10 ml to a 50 ml separating funnel and add the necessary amount of EDTA if mercury(II) is present (see Note). Add 0.4 ml of AADA solution, 1 ml of 5 M sodium nitrate (A.R.) solution, and 5 ml of extraction solution A and enough water to give a constant volume (*i.e.* 16.4 ml). Shake the separating funnel by continuous inversion for 1 min, run off the aqueous layer and wash the hexone phase with *ca.* 10 ml of distilled water. Transfer the organic phase to a 50-ml graduated flask together with 5 ml of hexone washings, add 5 ml of 10^{-4} M pyrogallol red and allow the contents to stand for 20 min before further dilution. Finally dilute to 50 ml with hexone and immediately measure the optical density at 390 $m\mu$ in a 4-cm cell against a reagent blank containing no silver, but carried through the same procedure.

The calibration curve is determined by taking aliquots of standard silver solution through the above procedure.

Note. In the presence of mercury(II), take a separate aliquot of solution and determine the mercury(II) content (also other metals if present) by EDTA titration at pH 7 using a pyridine buffer and xylenol orange as indicator. The EDTA titre represents the amount of EDTA that must be added to the silver solution before extraction.

Determination of 10–100 µg of silver (0.01–0.1 p.p.m.)

Extraction Reagent B. 3.2 g salicylic acid A.R. and 70 ml of di-*n*-butylamine dissolved in, and diluted to 1 l with, methyl isobutyl ketone.

Procedure

Transfer 1 l of solution of pH *ca.* 7 containing 100 µg of silver, to a 2 l separating funnel treated with a protective silicone film ("Repelcote", Hopkin and Williams). Add 5 ml of 5 *M* sodium nitrate solution, 0.4 ml of AADA solution and 50 ml of extraction reagent B.

Shake by continuous inversion for 1 min and chill thoroughly in ice water to obtain a clear solution (*ca.* 10 min). Run off the aqueous layer. Transfer the organic phase (now less than 40 ml) to a 50 ml graduated flask. Wash the funnel with 5 ml of hexone and add to the graduated flask. Finally add 5 ml of 10⁻⁴ *M* pyrogallol red and quickly dilute to 50 ml with hexone. Mix the contents of the flask thoroughly and allow to stand for 1.5–1.75 h before measurement of the extinction of the solution at 390 mµ as above in a 4-cm cuvette against a reagent blank carried through the above procedure.

SUMMARY

Silver in the range 0.01–10 p.p.m. is extracted from aqueous solution containing anthranilic acid diacetic acid into methyl isobutyl ketone as silver di-*n*-butylammonium salicylate without interference from 10-fold amounts of Mg, Ca, Zn, Pb, Al, Cu(II), Ni Co(II), Mn(II), Fe(III), Bi or any compatible common anion. Hg(II) is co-extracted slightly but can be retained in the aqueous phase with EDTA. Spectrophotometric determination of the extracted silver is done with pyrogallol red at 390 mµ in 4-cm cuvettes. The colour system is stable and reproducible. No special purification of reagents is necessary even for the lowest concentrations of silver.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique de l'argent, en milieu non-aqueux. L'argent est extrait d'une solution aqueuse renfermant l'acide anthranilique-N,N-diacétique, au moyen d'isométhylbutylcétone. Le dosage spectrophotométrique de l'argent extrait est ensuite effectué à l'aide de rouge de pyrogallol à 390 mµ.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Bestimmung von Silber durch Extraktion aus Anthranil-N,N-diessigsäure-haltiger wässriger Lösung mit Methyl-isobutylketon und Ueberführung in den Pyrogallolrot-Komplex.

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STUDIES ON ADSORPTION INDICATORS

PART II. *p*-ETHOXYCHRYSOIDINE AS ADSORPTION INDICATOR

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(Received August 31st, 1961)

SCHULEK AND ROZSA¹ used *p*-ethoxychrysoidine as adsorption indicator in the titration of iodide and thiocyanate with silver ions. The same indicator was also used in the titration of silver with iodide ions². The indicator is said to be unsuitable for the direct titration of bromide and chloride with silver ions². The titrations were done in neutral medium, where the end-point is very sharp in the case of iodide but vague in the titration of bromide, thiocyanate, and chloride.

It has been shown in the present studies that titrations of silver with halide or thiocyanate ions can be carried out with very sharp end-points if the medium is made slightly acidic (pH 4-5). The colour change from orange yellow to rose red occurs on the coagulated precipitate exactly at the equivalence point. In the titration of halide or thiocyanate with silver ion, the dye is strongly adsorbed from the very beginning and though the end-point is marked by a sharp colour change from rose red to orange yellow on the coagulated precipitate, it is also accompanied by a slight displacement of the dye from the precipitate to the solution. On the other hand, if titrations are carried out in highly acidic medium (pH 2 or below), no colour change is observed. In presence of excess of halide ions the precipitate adsorbs the red cations of the dye; and when excess of silver ions is added, the dye is transferred from the precipitate to the solution almost completely without any change of colour. In slightly acidic medium (pH 4-5) titrations are possible up to a dilution of 0.002 *N* with iodide, 0.01 *N* with bromide, and 0.02 *N* with thiocyanate and chloride ions (Table I). The titrations with bromide and chloride ions should be carried out in subdued light. It is difficult to explain all the above observations on the existing theories of adsorption indicators.

In a recent communication³ from these laboratories, evidence regarding the chemical nature of adsorption in the case of congo red has been furnished. In a search for similar evidence an attempt was made in the present work to prepare the compound of *p*-ethoxychrysoidine with silver. The compound has been isolated and its properties have been studied in order to explain its behaviour as an indicator in argentometric titrations.

EXPERIMENTAL

Materials used

Potassium chloride, potassium bromide, potassium iodide, potassium thiocyanate and silver nitrate were analytical reagent grade (B.D.H.).

แผนกห้องสมุด กรมวิทยาศาสตร์
กระทรวงอุตสาหกรรม

TABLE I

Silver nitrate solutions ^a Volume (ml) N	Drops of indicator	Vol. and conc. of halide solution	Change at the end-point	Detailed conditions
10.0 of 0.1	4	9.98-10.0 ml of 0.1 N KI	Yellow ppt. → red ppt.	Colour change is very sharp and reversible occurring on the coagulated precipitate
10.0 of 0.01	2	9.98-10.0 ml of 0.01 N KI	Yellow suspension → red suspension	Colour change occurs in the suspension phase, sharp and reversible
10.0 of 0.002	2	9.98-10.02 ml of 0.002 N KI	Yellow suspension → red suspension	Colour change occurs in the suspension phase, sharp and reversible
10.0 of 0.1	2-3	9.98-10.02 ml of 0.1 N KBr	Orange yellow ppt. → red ppt.	Colour change occurs on the coagulated precipitate. Titration should be performed in subdued light
10.0 of 0.01	2	9.97-10.02 ml of 0.01 N KBr	Orange yellow suspension → red suspension	Colour change occurs in suspension phase
10.0 of 0.1	2-3	9.99-10.03 ml of 0.1 N KSCN	Orange precipitate → red precipitate	Colour change occurs on the coagulated precipitate, sharp and reversible.
10.0 of 0.02	2	9.98-10.05 ml of 0.02 N KSCN	Orange precipitate → red precipitate	Colour change occurs on the coagulated precipitate, sharp and reversible
10.0 of 0.1	2	9.97-10.04 ml of 0.1 N KCl	Orange precipitate → red precipitate	Before the end-point part of the dye remains unadsorbed, and at the end-point it is completely adsorbed
10.0 of 0.02	1-2	9.96-10.05 ml of 0.02 N KCl	Orange suspension → red precipitate	Coagulation occurs just at the end-point.

^a 3-5 ml of 0.001 N HNO₃ was added for each titration.

The B.D.H. adsorption indicator *p*-ethoxychrysoidine was used. Its base was isolated and a 0.2% solution in ethanol was used as indicator during the titrations.

Preparation of the dye base

10 g of the indicator was dissolved in 5 l of hot water to which 10 ml of 1 N nitric acid was added. The filtered solution was treated with excess of 4 N ammonium hydroxide solution, added drop by drop with constant stirring. The lemon yellow precipitate of the basic dye was allowed to settle, filtered, washed well with water and dried at 110°.

Preparation of silver compound of p-ethoxychrysoidine

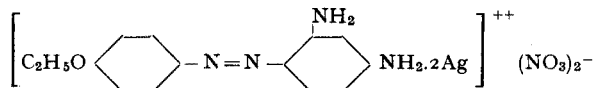
0.25 g of the basic yellow dye was dissolved in 5 ml of ethanol and 25–30 ml of ether. It was shaken with 0–2 ml of 1 N nitric acid and 5 ml of 20% silver nitrate solution. The orange coloured precipitate was formed in the ethereal layer, which was separated and the precipitate was filtered and dried in vacuo (Table II).

TABLE II

Sample No.	Amount of basic yellow dye (g)	Vol. of 1 N nitric acid (ml)	Yield (g)	% Silver
1	0.2565	0.0	0.5026	36.15
2	0.2560	0.5	0.3938	36.21
3	0.2558	1.0	0.2760	36.18
4	0.2562	1.5	0.1614	—
5	0.2568	2.0	0.0524	—

In bulk, the compound is stable only in ether or when it is dissolved in absolute alcohol. It is hydrolysed when dissolved in water and changes into a dark brown product, probably containing silver oxide. The hydrolysis is catalysed by light. When the orange solution in absolute alcohol is treated with iodide solution, a red precipitate is formed.

The probable formula of the compound is



It dissolves in dilute nitric acid, probably owing to the formation of a soluble nitrate of the dye base.

Explanation of colour changes during the titrations

p-Ethoxychrysoidine is a basic dye and changes colour from red to yellow in the pH range 4–5.5; its cations are red in colour. The explanation which is given by SCHULEK AND PUNGOR⁴ for the colour changes during the titration of silver with iodide ions, is difficult to understand, for they observe that the cations (red) are adsorbed on the positively charged precipitate, and on account of the positive charge on the surface of the precipitate protons are repelled, thereby changing the cations of the dye (red) into neutral molecules (yellow), a phenomenon apparently corroborated by

the change in the concentration of hydrogen ions in the supernatant solution. It is, however, difficult to understand how the cations would be primarily attracted by the positively charged silver halide precipitate. Also, the colour on the positively charged precipitate is not yellow, it is orange (with thiocyanate or chloride) or orange yellow (with bromide or iodide) whereas the neutral molecules of dye, after expulsion of protons as suggested by SCHULEK AND PUNGOR, would be lemon yellow in colour and not orange.

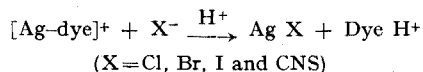
TABLE III

PH CHANGES IN TITRATION OF 50 ml OF 0.001 *M* AgNO₃ WITH HALIDE AND THIOCYANATE
Indicator: 10 drops of 0.2% *p*-ethoxychrysoidine. Initial pH adjusted with 0.001 *M* HNO₃

0.01 <i>M</i> <i>KX</i> ^a % equiv.	pH changes							
	<i>KI</i>		<i>KBr</i>		<i>KSCN</i>		<i>KCl</i>	
	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>
0	5.12	4.36	5.12	4.39	5.11	4.36	5.10	4.38
20	5.08	4.33	5.09	4.36	5.09	4.34	5.09	4.37
40	5.06	4.31	5.08	4.36	5.08	4.33	5.08	4.36
60	5.06	4.31	5.08	4.38	5.08	4.33	5.08	4.36
80	5.10	4.31	5.10	4.38	5.09	4.33	5.09	4.36
90	5.12	4.31	5.12	4.38	5.10	4.33	5.10	4.36
95	5.15	4.31	5.14	4.38	5.12	4.33	5.12	4.36
100	5.38	4.46	5.28	4.48	5.22	4.41	5.17	4.40
105	5.38	4.47	5.28	4.49	5.23	4.41	5.17	4.40
110	5.40	4.47	5.30	4.49	5.24	4.41	5.18	4.40
120	5.42	4.48	5.32	4.49	5.26	4.42	5.19	4.40
140	5.46	4.49	5.36	4.50	5.29	4.42	5.22	4.41
160	5.50	4.50	5.40	4.51	5.32	4.43	5.25	4.41

^a X = Cl, Br, I or SCN

On the other hand, the colour changes are readily explained if it is assumed that the primarily adsorbed silver ions on the positively charged precipitate form an orange compound with the dye molecules on the surface of the precipitate. The silver-dye compound is less stable than the silver halide or thiocyanate and, therefore, just before the end-point, the halide or thiocyanate ions react with the compound, setting free the dye molecules, red cations of which are adsorbed on the negatively charged precipitate. Thus at the end-point the colour change from orange to red occurs on the precipitate.



The above reaction also explains why pH changes occur during the titrations. The dye cations lose protons during the formation of the compound with silver on the positively charged surface of the silver halide precipitate; when the compound on the surface of the precipitate changes into dye cations hydrogen ions are adsorbed from the solution.

It has been assumed that the primarily adsorbed silver ions on the surface of the precipitate form the compound with dye molecules. The amount of silver-dye compound formed on the surface of the precipitate would, therefore, be directly pro-

portional to the primarily adsorbed silver ions. According to the adsorbability rule of PANETH, FAJANS, HAHN and coworkers⁵, the adsorbability of the silver ions would increase in the order AgCl, AgSCN, AgBr, AgI. Thus silver ions are adsorbed most on the iodide precipitate and least on the chloride precipitate, and the amount of silver-dye compound formed on the surface of the precipitate would be a maximum on silver iodide and a minimum on silver chloride precipitate under similar conditions. Similarly, the adsorption of the dye cations on the negatively charged precipitate would be a maximum on silver iodide and a minimum on silver chloride under similar conditions. A corresponding decrease in hydrogen ion concentration should occur in the solution at the end-point when the silver-dye compound is transformed into dye cations. On these considerations, it would be expected that at the end-point, a greater change in pH would be observed in the silver iodide titration than in the silver chloride titration and it would follow the order

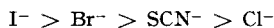


Table III is in full agreement with this expectation. This table shows the pH changes which occur during the titrations of 0.001 *M* silver nitrate solution with 0.01 *M* potassium iodide, bromide, thiocyanate and chloride solutions respectively.

The positively charged silver halide precipitate, on the surface of which silver-dye compound is formed, is highly sensitive to light and if it is exposed to direct sunlight for a second, it is immediately changed to a dark coloured precipitate. This is corroborated by the behaviour of the isolated compound as well, which is decomposed in a similar manner.

ACKNOWLEDGEMENT

One of the authors (K.N.T.) is grateful to the University Grants commission for a travel grant, and the authorities of the University of Gorakhpur and Bareilly College for providing facilities to carry out these investigations.

SUMMARY

p-Ethoxychrysoidine is studied as adsorption indicator in the direct titration of silver with iodide, bromide, thiocyanate and chloride at pH 4-5. The explanation given by SCHULEK AND PUNGOR for the colour changes has been modified in the light of compound formation on the surface of the precipitate. The silver compound of *p*-ethoxychrysoidine has been isolated; its behaviour provides a suitable explanation for the colour changes as well as the pH changes in the titrations.

RÉSUMÉ

L'éthoxychrysoïdine a été examinée en vue de son utilisation comme indicateur d'adsorption pour le titrage direct de l'argent, au moyen d'iodure, de bromure, de thiocyanate et de chlorure. Le composé argent-*p*-éthoxychrysoïdine a été isolé. Son comportement permet d'expliquer les changements de coloration et de pH observés au cours des titrages.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Eignung von Aethoxychrysoïdin als Adsorptionsindikator für die Titration von Silber mit Jodid, Bromid, Chlorid und Thiocyanat. Auf Grund der Eigenschaften des isolierten Silber-*p*-Aethoxychrysoïdins konnte die Farbänderung bei der Titration erklärt werden.

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Spektrofluorometrische Bestimmung von Hydrazinen und deren Anwendung zur quantitativen Bestimmung von Benzylhydrazin in biologischen Proben

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(Eingegangen den 29. November 1961)

In den letzten Jahren wurden eine Anzahl Monoaminoxidasehemmer des Alkylhydrazintyps in die Therapie eingeführt. Um das Schicksal solcher Präparate im Organismus studieren zu können, benötigten wir eine empfindliche Methode zur Bestimmung von Alkylhydrazinen. Im Laufe von Versuchen zur Auffindung eines dazu geeigneten Verfahrens fanden wir, dass Alkylhydrazine mit 1,2-Naphtochinon-4-sulfonsäure (NCS) unter Bildung einer stark fluoreszierenden Substanz reagieren. Wir haben diese Reaktion näher untersucht und beschreiben nachfolgend ihre Anwendungsmöglichkeiten für die Analytik stark reduzierender Substanzen, insbesondere von Hydrazinen.

DIE REAKTION

Prinzip

Die zu analysierende wässrige Hydrazin- oder Alkylhydrazinlösung wird auf einen geeigneten pH-Wert eingestellt und dann eine Lösung von Natrium-1,2-Naphtochinon-4-sulfonat in verdünnter Salzsäure als Reagens zugesetzt. Das entstehende Gemisch weist unter langwelligem UV-Licht eine blaue Fluoreszenz auf. Die Intensität dieser Fluoreszenz, die proportional zur Hydrazin-Konzentration ist, wird spektrofluorometrisch gemessen.

Mechanismus

Wie aus unseren Untersuchungen hervorgeht, ist die Fluoreszenz auf die Bildung von 1,2-Dihydroxy-naphtalin-4-sulfonsäure zurückzuführen. Eine solche Reduktion von NCS durch Hydrazine wurde bisher nicht beschrieben. Die Herstellung der 1,2-Dihydroxy-naphtalin-4-sulfonsäure durch Reduktion von NCS mit schwefliger Säure ist aber seit langem bekannt¹. Auf letztere Weise hergestellte 1,2-Dihydroxy-naphtalin-4-sulfonsäure zeigt in schwach saurer Lösung ein Fluoreszenz-maximum bei 470 m μ und ein Aktivierungsmaximum bei 340 m μ . Nach der Reaktion von NCS mit Hydrazinen beobachtet man dieselben Maxima und auch der von Süs² beschriebene Blaufärbungs-Test für die 1,2-Dihydroxy-naphtalin-4-sulfonsäure verläuft positiv.

Die Reduktion von NCS durch Hydrazine erfolgt unter optimalen Verhältnissen

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stoechiometrisch, da pro M Hydrazin oder Alkylhydrazin praktisch $1 M$ 1,2-Dihydroxy-naphtalin-sulfonsäure gebildet wird.

Einige wichtige Bedingungen

Das pH, bei dem die Operationen stattfinden, ist wichtig. Der günstigste pH-Wert für die Reduktion ist nicht immer identisch mit dem pH-Wert der maximalen Fluoreszenz. *) Abweichungen vom pH-Optimum können die Fluoreszenzintensität der zu messenden Lösung merklich herabsetzen (s. Fig. 1).

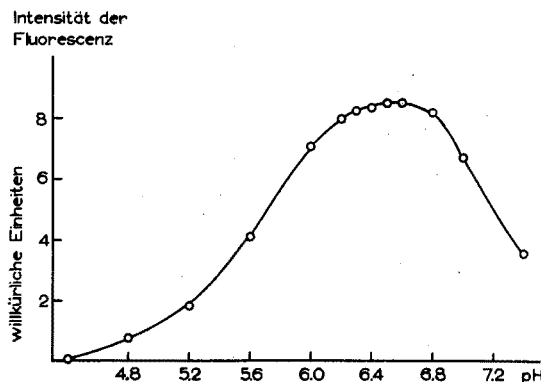


Fig. 1. Einfluss des pH. Zu je 2 ml $2 \cdot 10^{-5} M$ Hydrazinlösungen von abgestuften pH-Werten wurden 0.2 ml 0.01% NCS-Lösung in 0.1 N HCl zugesetzt. Die Fluoreszenz wurde nach 8 Min gemessen.

Die Zeit ist ebenfalls von Bedeutung. Die Fluoreszenzintensität nimmt bis zur 8 Min nach dem Ansetzen der Reaktion zu, um nachher bis zur 20 Min praktisch konstant zu bleiben. Die Ablesung erfolgt am besten 4 Sek nachdem die Küvette in den Strahlengang des Aktivierungslichtes eingesetzt wurde, weil eine längere Bestrahlung die Fluoreszenz verdünnter Lösungen verändern könnte.

Der Zusatz von BORSÄURE oder Natriumtetraborat zu Lösungen von 1,2-Dihydroxy-naphtalin-4-sulfonsäure verursacht eine Verschiebung des Aktivierungsmaximums auf $360 m\mu$, des Fluoreszenzmaximums auf $440 m\mu$ und des pH-Optimums auf 7.0–7.5. Dabei ist die Intensität der Fluoreszenz auf das 7-fache erhöht. Diese Änderungen beruhen wahrscheinlich auf der Bildung eines Borsäurekomplexes der 1,2-Dihydroxy-naphtalin-4-sulfonsäure, ähnlich wie dies für andere *o*-Dihydroxyderivate bekannt ist³. Sie müssen in Fällen berücksichtigt werden, bei denen sich die Anwesenheit von Borsäure nicht vermeiden lässt.

Spezifität

NCS wird durch Hydrazin, Monoalkylhydrazine, N_1N_2 - und N_1N_1 -Dialkylhydrazine

*) So wird zum Beispiel ncs durch Ascorbinsäure und Natriummetabisulfit bei pH 1 sehr gut reduziert; die Fluoreszenz des Reaktionsgemisches, die bei diesem pH gering ist, kann aber durch Einstellen des pH auf 4.5 (optimaler Wert für die Fluoreszenz der 1,2-Dihydroxy-naphtalin-4-sulfonsäure) mehr als 10-mal verstärkt werden. Die direkte Durchführung der Reduktion bei pH 4.5 würde eine viel schwächere Fluoreszenz ergeben. Für die Bestimmung von Hydrazinen lassen sich dagegen ohne Nachteil sowohl die Reduktion als auch die Messung der Fluoreszenz bei einem einzigen pH-Wert durchführen. In diesem Fall betragen die optimalen pH-Werte 6.0 für Benzylhydrazin und 6.6 für Hydrazin und Isopropylhydrazin.

reduziert. Dagegen sind Acyl- und Acylalkylhydrazide unwirksam. Cystein reagiert nur schwach. Ascorbinsäure und Natriummetabisulfit ($\text{Na}_2\text{S}_2\text{O}_5$) reagieren quantitativ, aber nur in stark saurem Milieu.

Fluorimeter

Jedes gute Spektrofluorimeter, bei dem schmale Banden von Aktivierungs- und Fluoreszenzlicht getrennt gewählt werden können, eignet sich für die Messungen. Wir verwenden ein Aminco-Bowman-Spektrofluorimeter. Als Lichtquelle wurde für die quantitativen Messungen wegen der guten Stabilität ihres UV-Lichtes eine Hochdruckquecksilberdampfampe (Philips SP 500 W) benützt. Hingegen verwenden wir für die Ermittlung der Fluoreszenzspektren, bei der vor allem ein kontinuierliches Spektrum des Aktivierungslichtes erwünscht ist, die übliche Xenonlampe.

Berechnungen und Eichkurve

Die Konzentration der untersuchten reduzierenden Substanz in einer Probe errechnet man unter Verwendung der Messwerte der Probe und des Standards. Beide Werte müssen auf dem geraden Teil der Eichkurve liegen. Die letztere wird durch Messungen von Lösungen mit abgestuftem Gehalt ermittelt. Zum Beispiel gibt man

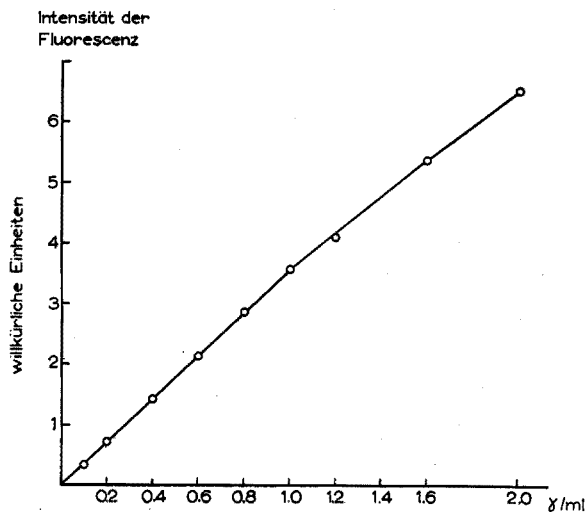


Fig. 2. Eichkurve von Benzylhydrazin-hydrochlorid

zu je 2 ml verschieden konzentrierter Benzylhydrazinhydrochlorid-Lösungen in pH 6-Puffer (s. unter Reagenzien) 0.2 ml 0.01% NCS-Lösung in 0.1 N HCl zu und misst die Fluoreszenzintensität nach genau 8 Min (Fig. 2).

BESTIMMUNG VON BENZYLHYDRAZIN IN BIOLOGISCHEN PROBEN

Die nachfolgend angegebene METHODE FÜR BLUTPLASMA ermöglicht die direkte Bestimmung von Hydrazin oder jedes Alkylhydrazins in enteweißten Proben. Für Organe wie Leber oder Gehirn lässt sie sich nicht anwenden, da deren Homogenate nach der Ente Weissung noch zu viele interferierende Substanzen enthalten. Hier

muss das Hydrazin zuerst in ein organisches Lösungsmittel extrahiert werden. Als Beispiel geben wir eine Extraktionsprozedur für die BESTIMMUNG VON BENZYLHYDRAZIN IN ORGANEN UND IM URIN an.

Reagenzien

Die Reagenzien für alle drei Methoden sind hier zusammengestellt. Es werden benötigt:

Für die Bestimmung von Hydrazinen im Plasma: Nr. 1-5

Für die Bestimmung von Hydrazinen in Organen: Nr. 1,2,6-13.

Für die Bestimmung von Hydrazinen im Urin: Nr. 1,2,7-13.

Bei allen Substanzen, für die nichts anderes angegeben ist, handelt es sich um Merck's Reagenzien pro analysi. Destilliertes Wasser wurde durchwegs verwendet.

(1) *Phosphatpufferlösung*. Ihr pH-Wert muss für das zu bestimmende Hydrazin optimal sein (d.h. für Benzylhydrazin 6.0, für Hydrazin und Isopropylhydrazin 6.6). Sie wird durch Mischung einer 0.2 M Lösung von Kaliumdihydrogenphosphat mit einer 0.2 M Lösung von Dinatriumhydrogenphosphat im geeigneten Verhältnis zubereitet.

(2) 0.01% NCS-Reagens. 10 mg Natrium-1,2-Naphtochinon-4-sulfonat werden in 100 ml 0.1 N HCl gelöst. Die Lösung ist im Dunkeln bei 3° 3 Tage lang haltbar.

(3) *Standard-Lösung (für Bestimmungen im Plasma)*. 0.2 ml einer Lösung zu 10 γ /ml des zu bestimmenden Hydrazins + 1.8 ml Phosphatpuffer (Nr. 1).

(4) 20% (G/V) *Metaphosphorsäure HPO₃*. Stangen von Metaphosphorsäure (enthaltend Natriumpyrophosphat als härtenden Zusatz) werden zerkleinert und in Wasser gelöst. Die Lösung ist bei Zimmertemperatur eine Woche lang und bei -18° unbegrenzt haltbar.

(5) 20% (G/V) *Trinatriumphosphat*. Zu 20 g Na₃PO₄ · 12H₂O puriss. (Merck) gibt man Wasser ad 100 ml zu. Bei Zimmertemperatur haltbar.

(6) *McIlvaine-Puffer pH 3*. 33.64 g Citronensäuremonohydrat + 14.64 g Dinatriumphosphatdihydrat + Wasser ad 1 L.

(7) 5 N NaOH (für Urin 1 N NaOH).

(8) *Chloroform*. Enthält ca. 1% Aethanol zur Stabilisierung. Vor Gebrauch wird es je einmal mit dem halben Volumen 0.1 N HCl und 0.1 N NaOH und zweimal mit Wasser gewaschen.

(9) *Natriumsulfat, wasserfrei*.

(10) 0.1 N HCl.

(11) 0.4 N NaOH.

(12) *Standard-Lösung (für die Benzylhydrazinbestimmung in Organen und Urin)*. 20 ml gewaschenes Chloroform (Nr. 8) werden 2 Min mit 5 ml 0.1 N HCl geschüttelt. In ein Reagensglas werden 0.8 ml HCl-Phase, 0.02 ml einer wässrigen Lösung zu 100 γ /ml Benzylhydrazinhydrochlorid, 0.2 ml 0.4 N NaOH und 0.98 ml Phosphatpuffer pH 6 (Nr. 1) einpipettiert und gemischt.

(13) *Leerprobe*. Gleich wie Nr. 12, aber mit 1 ml Phosphatpuffer jedoch ohne Benzylhydrazinlösung.

Bestimmung von Hydrazinen in Blutplasma

Es werden Doppelproben angesetzt. Ein Kontrollplasma, am besten vom gleichen Tier vor der Medikation, wird in jeder Bestimmungsreihe miteinbezogen. Als Anti-

koagulans wird den Blutproben 1.5 o/oo Kaliumoxalat zugesetzt. Erfolgt die Bestimmung nicht sofort, so darf das Plasma über Nacht bei -18° aufbewahrt werden.

0.1 ml Plasma werden in ein Zentrifugenglas einpipettiert und mit 1.8 ml destilliertem Wasser verdünnt. Man mischt, gibt 0.1 ml 20%ige Metaphosphorsäurelösung zu, schüttelt und zentrifugiert 5 Min. Aus der überstehenden Flüssigkeit entnimmt man 1.5 ml und überträgt sie in ein Reagensglas. Das pH wird durch Zusatz von 20%igem Trinatriumphosphat auf den für das zu bestimmende Hydrazin optimalen Wert eingestellt (z.B. bringt man es für Benzylhydrazin durch Zusatz von ungefähr 0.9 ml Trinatriumphosphatlösung auf 6.0). Die genaue Menge Trinatriumphosphatlösung, die man zusetzen muss, wird für die erste Probe einer Reihe mit einem empfindlichen Indikatorenpapier (z.B. Lyphan) oder einem pH-Meter ermittelt. Diese Menge wird dann ohne weitere pH-Kontrolle zu allen weiteren Proben zugesetzt.

Sofort nach Einschalten einer Stoppuhr wird pro 1 ml der Lösung 0.1 ml 0.01 %ige ncs-Lösung zugegeben. Man schüttelt, überträgt die Flüssigkeit in eine Quarzküvette von 1×1 cm Innenmass und misst die Fluoreszenz nach genau 8 Min bei 340/470 m μ Aktivierungs/Fluoreszenz-Wellenlängen. Die ncs-Lösung wird in gleicher Weise einer Standard-Probe (Nr. 3) und einer Puffer-Leerprobe (Nr. 1) zugesetzt.

Bestimmung von Benzylhydrazin in Organen und Geweben

Nach dem Tode des Tieres werden die Organe rasch entnommen. 1 Gewichtsteil Organ wird in einem Glashomogenisator nach Potter mit 2.5 Volumteilen McIlvaine-Puffer pH 3 homogenisiert. 1.75 ml Homogenat und 1.25 ml Wasser werden in ein 10–15 ml-Zentrifugenglas mit Schliffstopfen einpipettiert. Man setzt Doppelproben an. Die Proben können bei diesem Stadium eine Nacht bei -18° aufbewahrt werden. Nachdem sie gegebenenfalls wieder auf Zimmertemperatur gebracht wurden, werden sie 15 Min mechanisch geschüttelt und 10 Min bei 1000–1500 g zentrifugiert. 2 ml der obenstehenden Flüssigkeit werden in ein 15 ml-Zentrifugenglas mit Schliffstopfen einpipettiert. Man gibt 0.2 ml 5 N NaOH, 6 ml Chloroform und 0.75 g Na₂SO₄ zu, schüttelt 15 Min und zentrifugiert 10 Min. In ein weiteres 15 ml-Zentrifugenglas pipettiert man 4 ml Chloroformphase und 1 ml 0.1 N HCl ein, schüttelt 5 Min und zentrifugiert 1 Min. In ein Reagensglas gibt man 0.8 ml der salzsauren wässrigen Phase, 0.2 ml 0.4 N NaOH und 1 ml Phosphatpuffer pH 6. Man mischt, gibt 0.2 ml 0.01 %ige ncs-Lösung zu und misst die Fluoreszenzintensität nach genau 8 Min bei 340 m μ Aktivierungs- und 470 m μ Fluoreszenz-Wellenlänge. Die Reaktion wird in gleicher Weise mit einer Standard-(Nr. 12) und einer Leerprobe (Nr. 13) durchgeführt.

Proben aus Organen von unbehandelten Kontrolltieren ergeben praktisch gleiche Messwerte wie der Reagenzienblank. Es darf deshalb auf die Verarbeitung der Organe von Kontrolltieren verzichtet und jeweils einfach der Reagenzien-Leerwert von den Messwerten abgezogen werden.

Bestimmung von Benzylhydrazin im Urin

Das Vorgehen entspricht demjenigen bei der Bestimmung in Organen, nur erübrigt sich die Behandlung mit McIlvaine-Puffer pH 3. In ein 15 ml-Zentrifugenglas mit Schliffstopfen gibt man 0.5 ml Urin, 1 ml Wasser, 0.5 ml N NaOH, 6 ml Chloroform und 0.75 g Na₂SO₄ zu. Die Extraktion mit Chloroform, das Zurückextrahieren mit 0.1 N HCl und die Messung bei pH 6 erfolgen gleich wie bei den Organen. Die End-

lösung muss gegebenenfalls mit Phosphatpuffer pH 6 verdünnt werden, damit deren Gehalt an Benzylhydrazin in den linearen Bereich der Eichkurve zu liegen kommt.

Ausbeute und Reproduzierbarkeit

Die Ausbeute der Methode für Plasma wurde durch Zusatz bekannter Mengen Benzylhydrazin-hydrochlorid (1–20 γ /ml) zu Plasma normaler Ratten untersucht. Sie betrug im Durchschnitt 95%. 10 Proben mit 10 γ /ml ergaben eine Ausbeute von 94.8% mit einer Standardabweichung von $\pm 1.7\%$.

Versuche, in denen bekannte Mengen Benzylhydrazinhydrochlorid (20 γ /g) zu Leber, Gehirn, Niere und Rücken Fett von Meerschweinchen zugesetzt wurden, ergaben eine Ausbeute von 80 bis 90%. So fanden wir z.B. bei 10 Bestimmungen in der Leber eine durchschnittliche Ausbeute von 83.9% mit einer Standardabweichung von $\pm 2.8\%$. Im Herzmuskelgewebe war die Ausbeute viel kleiner (56%). Möglicherweise wird ein Teil des Benzylhydrazins durch einen normalen Bestandteil des Herzens gebunden und so der Extraktion entzogen.

Im Urin betrug die Ausbeute nach Zusatz von 40 γ /ml Benzylhydrazin-hydrochlorid 82%.

RESULTATE

Als Beispiele geben wir hier Resultate wieder, die unter Verwendung der Blutplasma-Methode erhalten wurden.

Weibliche Meerschweinchen wurden mit Nembutal (35 mg/kg i.p.) narkotisiert. Man befestigte in einer Arteria Carotis eine Polyäthylenkanüle, durch welche Blutproben zu beliebigen Zeitpunkten entnommen werden konnten und die gleichzeitig für die Injektion des Präparates diente. Nach Auffangen von 0.5 ml Blut (für die Bestimmung des Nullwertes) aus der Kanüle wurden 20 mg/kg Benzylhydrazinhydrochlorid injiziert. Zu den gewählten Zeitpunkten wurden jeweils 0.5 ml Blut entnommen.

Die gemessenen Konzentrationen, ausgedrückt als γ Benzylhydrazinhydrochlorid pro ml Plasma, sind in Tab. I angegeben.

TABELLE I

Tier Nr.	Gewicht	Benzylhydrazinkonzentration im plasma (γ /ml) nach						
		5 Min	30 Min	1 St	2 St	3 St	5 St	7 St
1	1040 g	33.8	11.4	9.6	5.2	3.3	1.8	0.9
2	855 g	29.0	15.1	12.1	6.8	3.4	1.8	1.1

Die Methode zur Bestimmung von Benzylhydrazin in Organen wurde in eingehenden Untersuchungen über den Stoffwechsel einiger speziellen Benzylhydrazinderivaten verwendet, über die später berichtet werden soll.

ZUSAMMENFASSUNG

Es wird eine fluorimetrische Methode zur Bestimmung stark reduzierender Substanzen wie Hydrazin und Alkylhydrazine beschrieben. Sie beruht auf der Reduktion der 1,2-Naphtochinon-4-sulfonsäure zur fluoreszierenden 1,2-Dihydroxy-naphtalin-4-sulfonsäure. Eine Methode zur

quantitativen Bestimmung von Mikrogram-Mengen von Hydrazinen in Blutplasma und von Benzylhydrazin in Organen und Urin von Tieren wird angegeben.

SUMMARY

A spectrofluorometric determination of strong reducing substances such as hydrazine and alkylhydrazines is described. It is based on the reduction of 1,2-naphthoquinone-4-sulfonic acid to the fluorescent 1,2-dihydroxynaphthalene-4-sulfonic acid. The assay of microgram quantities of hydrazines in blood plasma and of benzylhydrazine in animal organs and urine is reported.

RÉSUMÉ

Le dosage spectrofluorimétrique de substances fortement réductrices telles que l'hydrazine et les alkylhydrazines est décrit. Il est basé sur la réduction de l'acide 1,2-naphtoquinone-4-sulfonique en une substance fluorescente: l'acide 1,2-dihydroxynaphtalène-4-sulfonique. Une méthode a été mise au point pour le dosage des hydrazines dans le plasma sanguin et de la benzylhydrazine dans les organes et l'urine d'animaux en quantités de l'ordre du microgramme.

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Anal. Chim. Acta, 27 (1962) 20-26

CHRONOPOTENTIOMETRY OF URANIUM(IV)

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(Received December 29th, 1961)

Previously it has been shown that chronopotentiometry of high accuracy can be achieved either by the use of a shielded horizontal plane electrode^{1,2} or by adjustment of the electrolysis current such that the transition time is approximately a constant for all determinations³. This study was undertaken to extend precision chronopotentiometry to the analysis of uranium solutions.

The reduction of uranium(VI) at a platinum electrode was not found to be useful because the value of $E_{1/4}$ was too close to the potential at which hydrogen ion was reduced to allow a separation of waves. Since the sacrifice of the physical stability of solid electrodes was undesirable, the uranium(VI) was converted to uranium(IV) and chronopotentiograms with anodic current were recorded. Relatively rapid and accurate results were obtained for the analysis of uranium solutions containing from 2-12 mmoles of uranium per l.

EXPERIMENTAL

The apparatus used to supply a constant electrolysis current and to record chrono-

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potentiograms was the same as previously reported^{2,3}. The cell used in this study was similar to that described by BARD¹. The working electrode in this cell consists of a platinum disk sealed in soft glass tubing in such a manner that the glass tube provides a shield around the electrode surface. The electrode can be orientated either up or down to prevent disturbance of the diffusion layer by convection. In this case both orientations give substantially the same results, indicating that there was little change in density due to electrolysis. The projected area of the electrode was 0.90 cm². A glass tube fitted with a rubber bulb at the upper end was used to flush the electrolysis products out of the shield after each run. One to two min were then allowed for the solution to become quiet before recording a chronopotentiogram.

The platinum wire auxiliary electrode was enclosed in a compartment separated from the main cell by a sintered glass disk. This compartment was filled with a small part of the solution being analyzed. The saturated calomel reference electrode was placed in contact with solution by means of a salt bridge containing 1.0 *M* sulfuric acid. All measurements were made at 25.0 ± 0.1°.

All reagents were of the best obtainable commercial quality and were used as received, without purification. Uranium(VI) perchlorate stock solution was prepared by evaporating a solution of uranium(VI) acetate with excess perchloric acid several times. The final solution was 1.0 *M* in perchloric acid. The uranium(VI) solution was standardized by the method of KOLTHOFF AND LINGANE⁴.

PROCEDURE

A sample of the stock solution was passed through a zinc amalgam (95% Zn, 5% Hg) reductor column. The column was then washed with 1 *M* perchloric acid. This procedure results in almost complete reduction of the uranium(VI) to uranium(III)⁵. Uranium(III) was found to be easily oxidized at the platinum electrode (Fig. 1, curve I) but because of the ease with which uranium(III) is oxidized by air, useful analytical

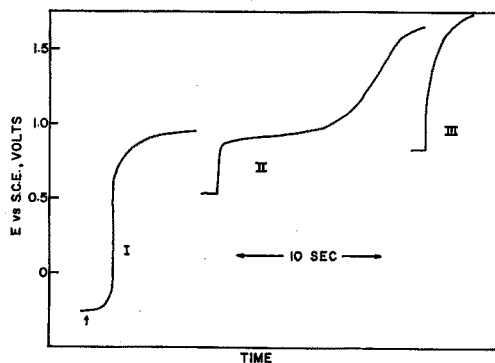


Fig. 1. Chronopotentiograms of uranium in 1 *M* perchloric acid. I. mixture U(III) and U(IV) - reduced electrode. II. U(IV) - freshly reduced electrode. III. U(IV) - oxidized electrode.

results could not be obtained. To ensure the uranium being completely in a single oxidizable valency state, air was bubbled through the effluent from the reductor column for 10 ± 1 min. The rate at which air was sucked through the solution was such that individual bubbles could just be distinguished and counted. After air had

been passed for about 5 min, the deep green color of uranium(III) faded to a light green, characteristic of uranium(IV). This solution was then diluted to exactly 250 ml with air-free 1 *M* perchloric acid. The use of air-free perchloric acid was found to be necessary to avoid negative errors due to the slow oxidation of uranium(IV) by air.

Concurrently with the adjustment of the uranium to the tetravalent state, the platinum working electrode was strongly oxidized by anodic polarization in 1 *M* perchloric acid. The electrode was then placed in the uranium(IV) solution. Before a chronopotentiogram was taken the electrode was reduced to approximately 0.0 V *vs.* S.C.E. to remove any oxide film on the electrode. The working electrode was then made the anode, a chronopotentiogram recorded and the transition time, τ , measured². The electrode was again reduced as before, in preparation for the next chronopotentiogram. The first result was usually discarded because the chronopotentiogram did not have a typical shape. Evidently complete reduction of the oxide film did not occur or a recent oxidation-reduction cycle was necessary for best results⁶.

RESULTS AND DISCUSSION

Media

Various supporting electrolytes, including sulfuric, acetic and perchloric acids were tried. It was found that useful chronopotentiograms were not obtained in sulfuric acid. The uranium(IV) is not oxidized at reducing enough potentials to eliminate interference from the oxidation of water. Evidently the potential of the U(VI)-U(IV) couple is shifted due to complex formation between uranium(IV) and sulfate ions. This probably accounts for the very slow rate of oxidation of uranium(IV) by air in sulfuric acid medium^{4,5}.

Both acetic and perchloric acids proved to be useful media from the point of view of well developed chronopotentiograms. However, uranium(IV) was more subject to air oxidation in acetic acid than in perchloric, although both were inferior to sulfuric in this respect. All subsequent work was done in 1 *M* perchloric acid.

Electrode pretreatment

It was found that the condition of the electrode had a great effect on the chronopotentiograms of uranium(IV). Fig. 1 shows chronopotentiograms taken with a freshly reduced electrode (curve II) and an oxidized electrode (curve III). When the electrode was strongly oxidized no oxidation of uranium was found (uranium reduced the oxide of platinum only slowly). If the electrode was completely reduced to 0.0 V *vs.* S.C.E., the subsequent chronopotentiogram was well developed (curve II). These two curves are the extreme cases. If the electrode became only partially oxidized, as would occur by the taking of one chronopotentiogram similar to curve II, the transition time was found to be reduced even though some oxidation occurred.

The procedure adopted included a strong oxidation before the electrode was used, to ensure a clean, "platinized" electrode after reduction⁶. Separate electrode reductions were carried out between each run to ensure the reduction of any oxide formed on the electrode during the previous run. This precaution was found necessary for accurate results.

Results and interferences

Table I shows the variation of $i\tau^{1/2}/C$ with concentration. The average value of

$i\tau^{1/2}/C$ indicates that the electrode reaction is the two electron oxidation of uranium(IV) to uranium(VI). This conclusion is based on the fact that the reduction of cerium(IV) to cerium(III) had an $i\tau^{1/2}/C$ value of about 200 when a slightly larger electrode was used². The standard deviation was found to be 1.4%.

TABLE I
CHRONOPOTENTIOMETRY OF URANIUM(IV) IN 1 M PERCHLORIC ACID

Uranium(IV) taken mM	$i\tau^{1/2}/C$ ($A \text{ sec}^{1/2} \text{ cm}^2/\text{mole}$)
2.13	390
2.99	379
4.26	376
	383
	376
	387
	383
6.40	386
8.54	376
10.65	380
11.50	373
12.80	384
Average	381
	Standard deviation 1.4%

TABLE II
POSSIBLE INTERFERENCES WITH THE CHRONOPOTENTIOMETRY OF URANIUM(IV). ALL SOLUTIONS
4.26 mM IN URANIUM AND 10.0 mM IN THE FOREIGN SUBSTANCE

Foreign substance	$i\tau^{1/2}/C$ ($A \text{ sec}^{1/2} \text{ cm}^2/\text{mole}$)
—	381 ^a
(VO ₂) ₂ SO ₄	383
CoCl ₂	376
K ₂ Cr ₂ O ₇	387
Ni(C ₂ H ₃ O ₂) ₂	394
HC ₂ H ₃ O ₂	481
Ni(NO ₃) ₂	415
NiCl ₂	382
(NH ₄) ₂ MoO ₄	383 ^b

See Table I

A precipitate was formed when the sample and the ammonium molybdate were mixed. Most of this precipitate remained in the reduction column.

There appear to be two main sources of error in this determination. Despite the precaution of diluting the uranium(IV) solution with air-free perchloric acid and passing nitrogen over the solution in the cell, some small amount of uranium(IV) becomes oxidized by air tending to cause low results, especially at low concentrations. Of about equal importance is the increase in the apparent transition caused by the partial

oxidation of the electrode. This effect is also only noticeable at low concentrations. These 2 sources of error tend to cancel each other so that reasonably accurate results can be obtained even at concentrations of a few mmoles. At concentrations below this level the wave for electrode oxidation becomes relatively large and distorts the uranium(IV) oxidation wave to the point where transition times can no longer be accurately measured.

Any substance which is present in, or can be reduced to, an oxidation state which is oxidized before or with the uranium(IV) will interfere with this procedure — *e.g.*, iron, iodide, or titanium. Table II lists several other possible interfering substances which were tested.

It is evident from examination of Table II that nitrate and acetate ions cause serious errors in this determination, but even chromium and vanadium do not interfere. Apparently any chromium or vanadium reduced in the reductor is oxidized again by the passage of air.

ACKNOWLEDGEMENT

Gratitude is expressed to DANIEL ORGERON who did part of the experimental work and to the National Science Foundation for its support.

SUMMARY

The chronopotentiometry of uranium at platinum electrodes has been investigated. A determination of uranium has been devised based on the conversion of the uranium to uranium(IV) and the oxidation of the uranium(IV). The effect of several possible interfering substances has been checked.

RÉSUMÉ

Un dosage de l'uranium par chronopotentiométrie a été examiné, en utilisant des électrodes de platine et en procédant à l'oxydation de l'uranium, puis de l'uranium(IV). L'influence de diverses substances gênantes possibles a été examinée.

ZUSAMMENFASSUNG

Beschreibung einer chronopotentiometrischen Methode zur Bestimmung von Uran unter Anwendung von Platinelektroden.

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A MODIFIED SINGLE SOLUTION METHOD FOR THE DETERMINATION OF PHOSPHATE IN NATURAL WATERS

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(Received January 8th, 1962)

In a recent communication¹ the authors described a molybdenum blue method for the determination of soluble phosphate in sea water, in which a single reagent solution is used. This procedure, in which the formation and reduction of phosphomolybdic acid is brought about by an acidic molybdate solution containing ascorbic acid, has a number of advantages over methods using stannous chloride². In particular, the molybdenum blue colour is stable for long periods and the salt error correction is much smaller.

STRICKLAND *et al.*³ consider that the reproducibility of the ascorbic acid method is superior to that of the stannous chloride process, but has found that some sea waters tend to give higher results with the former reagent. He has attributed this effect to the hydrolysis of organic phosphorus compounds to phosphate during the long period required for the development of the molybdenum blue colour. We have recently carried out phosphate determinations by the ascorbic acid method on sea water enriched with dissolved organic phosphorus compounds (*viz.* sodium glycerophosphate, inositol hexaphosphoric acid, diphenylamino phosphate and lecithin), and in no case were the results higher than those obtained by the stannous chloride procedure. Determinations made by both methods on sea water inoculated with either living or dead and partially decomposed cultures of *Phaeodactylum tricornutum*, gave identical results. It seems probable that generally no appreciable hydrolysis of organic phosphorus compounds occurs with the ascorbic acid reagent. It is possible, however, that very labile phosphorus compounds might lead to high results such as those found by STRICKLAND *et al.*³.

This paper describes a single solution reagent which has most of the advantages of the original procedure, but in which the colour develops rapidly. It is based on the finding that if antimony (as potassium antimonyl tartrate solution) is added to a phosphate solution containing the original single solution reagent, an intense bluish-purple colour forms rapidly.

JEAN⁴ has described a method for the determination of phosphate in steel, in which phosphomolybdic acid is reduced by ascorbic acid in the presence of bismuth. A blue-coloured complex is formed, which reaches its maximum intensity in about 30 min; this is extracted with amyl alcohol. We have found that the aqueous solution becomes turbid owing to the hydrolysis of bismuth to a basic salt, and that the method, if used without extraction, has a sensitivity only about half that attainable by the use of ascorbic acid alone.

Experiments made by adding various amounts of antimony to the single solution reagent showed that the optimum antimony concentration was 0.4 mg per 50 ml final volume. At this concentration the colour attained its maximum intensity in both distilled water and sea water in about 10 min and remained constant for at least 24 h. Greater concentrations of antimony did not lead to more rapid colour development. At concentrations of above *ca.* 4 mg of antimony per 50 ml of solution, a turbidity of basic antimony salt was formed.

The absorption maximum of the phosphomolybdenum blue formed in the presence of antimony is at 882 $m\mu$. The phosphomolybdenum blue yielded by either the stannous chloride or the ascorbic acid method has its absorption maxima at lower wavelengths (Fig. 1). This suggested that antimony might be a component of the

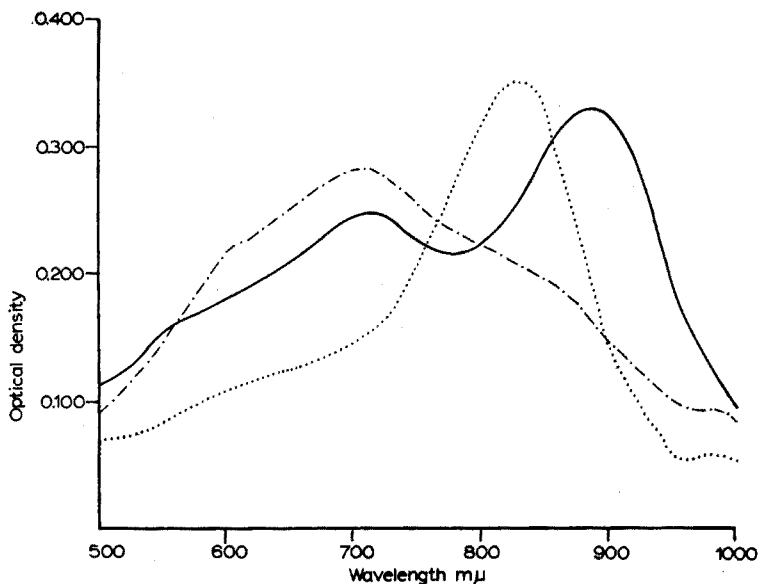


Fig. 1. Absorption curves for molybdenum blue formed with various reducing agents ($3.0 \mu\text{g}$ P as PO_4^{3-} in 50-ml flasks; 7.62-cm cells) — — — reduced with stannous chloride; reduced with ascorbic acid; ——— reduced with ascorbic acid + antimony.

molybdenum blue compound absorbing at 882 $m\mu$. In order to determine the atomic ratio of antimony to phosphorus in the complex, the complex formed from 10 μg of phosphate-phosphorus was quantitatively extracted with iso-butyl methyl ketone. The solvent was evaporated and the residue was treated with 9 *M* hydrochloric acid and zinc⁵. The stibine and hydrogen formed were passed into 0.2% *w/v* mercuric chloride solution. After the gas evolution had continued for 30 min, the antimony absorbed in the mercuric chloride solution was determined photometrically using methyl fluorone⁶. Duplicate experiments gave antimony: phosphorus atomic ratios of 1 : 0.97 and 1 : 0.94 for the complex.

EXPERIMENTAL

All measurements of optical density were made with a Unicam S.P. 500 spectrophoto-

meter, modified to use 7.62 and 15.24 cm cells (3 and 6 inch respectively). Distilled water was used in the compensating cell.

Reagents

(1) *Sulphuric acid (5 N)*. Dilute 70 ml of concentrated sulphuric acid to 500 ml.

(2) *Ammonium molybdate*. Dissolve 20 g of A.R. ammonium molybdate in water and dilute to 500 ml. Store the solution in a Pyrex glass bottle.

(3) *Ascorbic acid (0.1 M)* Dissolve 1.32 g of ascorbic acid in 75 ml of water. This solution should, if possible, be prepared on the day it is required as the ascorbic acid easily becomes oxidised. If it is necessary to keep the solution it can probably be stabilised by addition of 25 mg of ethylenediaminetetraacetic acid (disodium salt) and 0.5 ml of formic acid per 75 ml of solution.

(4) *Potassium antimonyl tartrate (1 mg Sb/ml)*. Dissolve 0.2743 g of potassium antimonyl tartrate in distilled water and dilute to 100 ml.

(5) *Mixed reagent*. Mix thoroughly 125 ml of 5 N sulphuric acid and 37.5 ml of ammonium molybdate. Add 75 ml of ascorbic acid solution and 12.5 ml of potassium antimonyl tartrate solution. This reagent should be prepared as required as it does not keep for more than 24 h.

Standard phosphate solutions

Stock phosphate solution. Prepare a solution containing 0.1757 g of potassium dihydrogen phosphate per l. This solution contains 40 mg P (as phosphate)/l. Prepare, as required, a solution containing 0.2 μg P (as phosphate)/ml by dilution of the stock phosphate solution.

Treatment of apparatus

Fill the calibrated flasks, which are to be used for the determination, with concentrated sulphuric acid, allow them to stand overnight, and then rinse thoroughly. It is preferable to keep a set of flasks to be used only for the determination of phosphate, and after use to wash them and to keep them filled with water until required again. If this is done the treatment with sulphuric acid is only required occasionally.

Procedure

Pipette 40 ml of the sea water sample into a 50-ml calibrated flask, add 8 ml of the mixed reagent from a tilt measure, dilute to volume with water, and mix well. After not less than 10 min measure the optical density of the solution at 882 $m\mu$ using cells of an appropriate length. Determine the reagent blank in the same manner using freshly distilled water. Calibrate the method using 1, 2 and 4 μg phosphorus as phosphate (these amounts are appropriate for a 15-cm cell), and make up to approximately 40 ml with distilled water before adding the reagent. The calibration curve only needs occasional checking as it remains constant and appears to be independent of changes in the batches of reagents. For normal purposes the salt error is negligible (less than 1%).

Beer's law and reproducibility

Replicate calibration runs were made using 1–10 μg of phosphorus (as phosphate) in 40 ml of distilled water. The optical densities of the resulting molybdenum blue

complexes were measured at 882 $m\mu$ in 7.62-cm cells. The results (Table I) show that Beer's law is obeyed over this concentration range, and that the method gives an excellent reproducibility.

As a further test of the reproducibility of the method with sea water, seven replicate analyses were made on a natural sea water, poor in phosphate. The average optical density (measured in a 15.24-cm cell), less reagent blank, was 0.164 ± 0.0007 , corresponding to a concentration of $18.6 \pm 0.1 \mu\text{g P(as phosphate)}/\text{l}$ in the sea water.

TABLE I
CALIBRATION OF METHOD

$\mu\text{g PO}_4^{3-}-\text{P}$	Optical density ^a			Mean ^a	Optical density increment/ $\mu\text{g PO}_4-\text{P}$
1	0.110	0.110	0.110	0.110	0.1100
2	0.220	0.220	0.221	0.220	0.1100
3	0.331	0.331	0.331	0.331	0.1103
4	0.442	0.442	0.441	0.442	0.1105
5	0.554	0.554	0.555	0.554	0.1108
8	0.884	0.884	0.885	0.884	0.1105
10	1.100 ^b	1.100 ^b	1.101 ^b	1.100 ^b	0.1100

^a Measured at 882 $m\mu$ in 7.62-cm cells (less reagent blank 0.021).

^b Measured in 4-cm cell calculated for 7.62-cm cell.

TABLE II
DETERMINATION OF SALT ERROR OF METHOD

Chlorinity (‰)	$\mu\text{g PO}_4-\text{P}$ added	Optical density ^a		Salt Error (%)
		Mean	Less blank ^b	
0.00	0.0	0.042	—	—
0.00	1.0	0.262	0.220	—
19.61	0.0	0.045	0.003	—
4.90	1.0	0.262	0.219	-0.5
9.80	1.0	0.263	0.220	+0.5
14.70	1.0	0.266	0.222	+0.9
19.61	1.0	0.267	0.222	+0.9
0.00	4.0	0.927	0.885	—
4.90	4.0	0.926	0.884	-0.1
9.80	4.0	0.922	0.879	-0.7
14.70	4.0	0.922	0.879	-0.7
19.61	4.0	0.929	0.884	-0.1

^a Measured in 15.24-cm cells at 882 $m\mu$.

^b Blank reckoned proportional to chlorinity.

Salt error

In most molybdenum blue methods for the determination of silicon and phosphorus, less intense colours are developed with the same amount of silicon or phosphorus, in the presence of sea water salts, than in distilled water. The effect is particularly pronounced when the stannous chloride method is used for the determination of phosphate in oceanic waters; in this case the salt error amounts to *ca.* 15%.

The salt error of the rapid single solution method was studied. Filtered sea water,

which had been stored in polyethylene bottles to remove phosphate⁷, was diluted with distilled water to give waters having chlorinities ranging between 4.90 and 19.6‰. Duplicate phosphate determinations were made on 40-ml portions of distilled water and of the original sea water, and on 40-ml aliquots of the diluted sea waters enriched with 1 μg and 4 μg of phosphorus as phosphate. The results (Table II) show that at both levels of phosphate concentration the salt error was below 1‰. The rate of colour development in sea water was similar to that in distilled water, and the colour once formed, was stable for at least 24 h.

Interferences

The interference of several ions, which are known to interfere in molybdenum blue methods for the determination of phosphate, was investigated. Determinations were made using 40-ml aliquots of distilled water containing these ions, both alone and in the presence of 10 μg of phosphate - P. The results are shown in Table III: they indicate that no interference is caused by copper, iron or silicate at concentrations many times greater than their greatest reported concentration in sea water. Arsenate produces a similar colour to phosphate, but since according to recent work⁸⁻¹⁰ its concentration in sea water is only *ca* 2.5 μg As (as arsenate)/l, it will not interfere seriously in the determination (a sea water containing this amount of arsenic will give an optical density in a 15-cm cell only 0.003 greater than the reagent blank).

TABLE III
EFFECT OF OTHER IONS ON DETERMINATION OF PHOSPHATE

Ion	Concentration of element ($\mu\text{g}/50$ ml)	Optical density at 822 $m\mu$ (4-cm cells)		
		No added $\text{PO}_4^{3-}-\text{P}$	+ 10 $\mu\text{gPO}_4^{3-}-\text{P}$	Difference
—	—	0.012	0.593	0.581
Copper(II)	500	0.018	0.585	0.567
Iron(III)	2500	0.017	0.598	0.581
Silicate	500	0.014	0.594	0.580
Arsenate	50	1.144*	1.752*	0.608
Arsenate	1	0.020	0.614	0.594

* Measured in 1-cm cell calculated for 4-cm cells.

SUMMARY

A single solution reagent is described for the determination of phosphorus in sea water. It consists of an acidified solution of ammonium molybdate containing ascorbic acid and a small amount of antimony. This reagent reacts rapidly with phosphate ion yielding a blue-purple compound which contains antimony and phosphorus in a 1:1 atomic ratio. The complex is very stable and obeys Beer's law up to a phosphate concentration of at least 2 $\mu\text{g}/\text{ml}$. The sensitivity of the procedure is comparable with that of the stannous chloride method. The salt error is less than 1%.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage du phosphate dans l'eau de mer, au moyen de molybdate d'ammonium, en présence d'acide ascorbique et d'antimoine. Il se forme rapidement un composé violet bleu, renfermant antimoine et phosphore dans un rapport atomique de 1 : 1.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Phosphat in Meerwasser mit Hilfe von Ammoniummolybdat in Gegenwart von Ascorbinsäure und Antimon. Der gebildete blau-violette Komplex wird spektrophotometrisch gemessen.

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CERIMETRIE EN MILIEU NITRIQUE. APPLICATION AU DOSAGE DU FER, DE L'URANIUM ET DU PLUTONIUM

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(Recu le 22 Octobre, 1961)

La volumétrie par le sulfate cérique, après réduction à la colonne de Jones, est une des méthodes les plus précises parmi les méthodes rapides de détermination du fer, de l'uranium et du plutonium. Mais en milieu nitrique, elle devient impraticable à moins d'effectuer préalablement un changement de milieu par évaporation en présence d'acide sulfurique concentré. Ceci complique les manipulations et en augmente la durée, surtout dans le cas du plutonium, où il est nécessaire d'effectuer ces opérations en boîte à gants, et, à plus forte raison, pour l'uranium irradié qui nécessite une protection $\alpha\beta\gamma$.

En pratique, les solutions d'uranium et de plutonium dont on désire contrôler la teneur se trouvent le plus souvent en milieu nitrique. L'acide nitrique est en effet l'acide le plus employé industriellement, que ce soit pour la tenue de l'appareillage à la corrosion, ou pour le procédé chimique proprement dit.

Dans le but d'effectuer un contrôle à la fois précis, rapide, et compatible avec les contraintes imposées par les protections contre les rayonnements α et $\beta\gamma$, une nouvelle méthode a été développée, permettant d'effectuer directement la cérimétrie en milieu nitrique. Cette méthode est applicable au dosage du fer, de l'uranium et du plutonium dans le même domaine que celui de la volumétrie classique.

PRINCIPE DE LA MÉTHODE

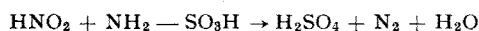
L'action gênante des ions nitrates dans une cérimétrie classique s'exerce de deux

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manières: d'abord, on ne peut réduire l'élément à doser par du zinc amalgamé, qui réduit aussi l'acide nitrique; ensuite, l'acide nitrique est toujours en équilibre avec de petites quantités d'ions nitreux qui réagissent avec la solution cérique en donnant des points équivalents instables et mal définis.

Pour remédier au premier inconvénient, l'amalgame de zinc est remplacé par une solution de titane(III) en excès; Fe(III), U(VI), Pu(VI) ou Pu(IV) sont réduits respectivement en Fe(II), U(IV) et Pu(III). L'excès de titane(III) est détruit ensuite spontanément par réaction avec les ions NO_3^- et accessoirement par l'air.

Pour éviter la présence des ions NO_2^- susceptibles soit de réoxyder partiellement la forme réduite de l'élément à doser, soit de réagir avec la solution titrante, on ajoute de l'acide sulfamique qui, avec les nitrites, donne une réaction du type:



La fin du dosage est ensuite effectuée de la façon habituelle au moyen d'une solution titrée de cérium(IV), en présence d'orthophénanthroline ferreuse comme indicateur d'oxydoréduction.

RÉACTIFS

- (a) Solution constituée d'un mélange d'acides nitrique et sulfurique, tel que la normalité de chaque acide soit égale à l'unité (HNO_3 N, H_2SO_4 N).
- (b) Solution de chlorure titanéux R. P. à 15% environ de TiCl_3 .
- (c) Solution titrée de cérium(IV) environ 10^{-2} N, en milieu sulfurique N.

MODE OPÉRATOIRE

Diluer la prise d'essai avec la solution HNO_3 N, H_2SO_4 N de façon à obtenir un volume voisin de 50 ml.

Ajouter en agitant 0.5 g environ d'acide sulfamique en poudre et 1 ml de la solution concentrée de titane(III). Attendre 5 min, en maintenant l'agitation, la destruction complète de l'excès de titane(III).

Ajouter 1 ml d'orthophénanthroline ferreuse $2.5 \cdot 10^{-3}$ M, quelques gouttes de chlorure ferrique dans le cas de l'uranium pour catalyser l'oxydation, et effectuer la volumétrie.

RÉSULTATS - DISCUSSION

Acidité du milieu

Des essais préliminaires ont été effectués en milieu nitrique pur pour examiner les conditions les plus favorables à la destruction de l'excès de titane(III) en un temps de 5 min. Les résultats sont rassemblés dans le tableau I; ils montrent que les conditions les plus favorables correspondent à une concentration d'ions NO_3^- comprise entre 0.2 et 1 N. En-dessous de 0.1 N, l'observation visuelle montre la présence d'un excès de titane(III) non détruit; au-dessus d'une acidité comprise entre 1 N et 2 N, la réduction du corps à doser est incomplète et les résultats sont trop faibles.

Mais, d'une part, il faut conserver un milieu suffisamment acide pour effectuer la volumétrie et il n'est donc pas possible d'opérer à des acidités aussi faibles que 0.1 N; d'autre part, à des concentrations comprises aux environs de 1 N, l'oxydation du titane(III) par les ions nitrates est presque instantanée et l'on peut craindre une réduction

incomplète de l'élément à doser. C'est la raison pour laquelle on a choisi d'opérer dans un mélange d'acides nitrique et sulfurique, l'acide sulfurique ralentissant la réoxydation du titane(III).

Une série d'essais a été effectuée avec du fer (Tableau II) en vue de fixer la concentration pour chacun des acides nitrique et sulfurique. Une acidité normale nitrique et

TABLEAU I
INFLUENCE DE L'ACIDITÉ NITRIQUE EN MILIEU NITRIQUE PUR SUR LE DOSAGE DU FER

Acidité	Volume de Ti(III) ajouté	Fe introduit	Fe trouvé
HNO ₃ 0.2 N	1 ml	38.4 mg	38.4 mg
HNO ₃ 0.5 N	1	38.4	38.3
HNO ₃ 0.5 N	5	192.0	192.0
HNO ₃ 0.8 N	5	96.0	95.5
HNO ₃ 1.2 N	5	96.0	95.5
HNO ₃ 2.4 N	5	96.0	93.0
HNO ₃ 4.0 N	5	96.0	87.4

TABLEAU II
DOSAGE DU FER DANS DES MÉLANGES D'ACIDES NITRIQUE ET SULFURIQUE À DIFFÉRENTES CONCENTRATIONS

Acidité du milieu	Volume de Ti(III) ajouté	Fe introduit	Fe trouvé
HNO ₃ 0.5 N	5 ml	192.0 mg	192.0 mg
HNO ₃ 0.2 N /H ₂ SO ₄ N	5	192.0	193.0
HNO ₃ 0.5 N /H ₂ SO ₄ 0.5 N	1	38.4	38.4
HNO ₃ 0.5 N /H ₂ SO ₄ 2 N	5	192.0	191.7
HNO ₃ 0.5 N /H ₂ SO ₄ 4 N	5	192.0	199.7
HNO ₃ 0.5 N /H ₂ SO ₄ 6 N	5	192.0	>>200
HNO ₃ N /H ₂ SO ₄ N	1	38.4	38.4
HNO ₃ N /H ₂ SO ₄ 5 N	1	38.4	38.5

normale sulfurique a donné les meilleurs résultats; en ce milieu, la vitesse d'oxydation du titane(III) par les ions NO₃⁻ est rapide sans être instantanée. L'acidité globale qui est de 2 N convient parfaitement au dosage par le cérium. On a choisi d'opérer dans un volume de 50 ml de façon à pouvoir, dans la plupart des cas, négliger l'acidité apportée par la prise d'essai.

Influence de l'excès de titane

La quantité de titane(III) dépend évidemment de la quantité de l'élément à doser. La quantité proposée dans le mode opératoire ci-dessus est applicable à un dosage

effectué sur environ 100 mg de plutonium, (ou l'équivalent en fer ou uranium, compte tenu de la masse moléculaire et du nombre d'électrons mis en jeu). Le rapport moléculaire Ti/Pu est alors de l'ordre de 2.

En vue de chiffrer l'excès maximum permis, des essais à blanc ont été effectués, en milieu HNO_3N , $\text{H}_2\text{SO}_4\text{N}$. Pour un volume total de 50 ml, un essai à blanc avec 5 ml de titane(III) a donné un virage à une goutte près, tandis qu'avec 10 ml de titane(III) l'essai à blanc donnait un résultat positif. L'excès maximum, pour les conditions définies dans le mode opératoire, peut donc être chiffré aux environs de 5 ml. Il faut noter qu'il est plus correct de chiffrer l'excès de titane(III) en valeur absolue, plutôt qu'en rapport Ti/élément à doser.

Applications

Après la mise au point effectuée sur le fer, la méthode a été essayée avec succès sur des solutions nitriques d'uranium et de plutonium, et elle est actuellement utilisée en contrôle de routine. Le temps nécessaire pour effectuer un dosage n'excède pas dix minutes, même en boîte à gants, et la simplicité des manipulations la rend applicable à des dosages d'uranium irradié en enceinte $\alpha\beta\gamma$. La sensibilité et la précision sont comparables à celles de la volumétrie classique.

RÉSUMÉ

La méthode décrite permet d'effectuer le dosage du fer, de l'uranium ou du plutonium en milieu nitrique par volumétrie. L'élément à doser est réduit par une solution de titane(III) en présence d'acide sulfamique, puis dosé par une solution de sulfate cérique. Ce procédé évite les manipulations qu'il faut effectuer d'ordinaire pour chasser l'acide nitrique. La méthode est rapide et précise, et sa simplicité la rend facilement applicable au dosage du plutonium ou de l'uranium irradié.

SUMMARY

A method is described for titrimetric determination of iron, uranium or plutonium in nitric acid media. The element is reduced with titanium(III) solution in presence of sulfamic acid, and titrated with cerium(IV) solution. Precautions normally taken for nitric acid media are unnecessary. The method is rapid and precise and is readily applicable to determinations of plutonium or irradiated uranium.

ZUSAMMENFASSUNG

Beschreibung einer titrimetrischen Methode zur Bestimmung von Eisen, Uran oder Plutonium in salpetersaurer Lösung. Nach Reduktion mit Titan-(III)-Lösung in Gegenwart von Sulfaminsäure wird das Metall mit Cerium-(IV)-Lösung titriert.

ZUR BESTIMMUNG VON BROMID ÜBER BROMCYAN

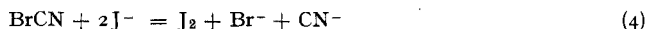
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(Eingegangen den 15. Oktober, 1961)

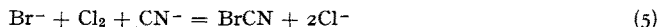
Einer von uns (E. S.) beschrieb vor einigen Jahren ein titrimetrisches Mikroverfahren zur Bestimmung von Bromidionen¹. Das Wesen dieser Methode ist folgendes:

Das Bromidion wird in neutralem oder schwach saurem Medium mit einer überschüssigen Menge von Chlorwasser zu Bromchlor oxydiert (1) und das Bromchlor mit Kaliumcyanid zur Bromcyan und Chloridion umgesetzt (2). Gleichzeitig reagiert das Kaliumcyanid mit dem Chlorüberschuss unter Bildung von Chlorcyan und Chloridionen (3). Das Bromcyan kann neben dem Chlorcyan und dem in überschüssiger Menge angewandten Kaliumcyanid jodometrisch titriert werden (4):



Das Verfahren erwies sich besonders zur Bestimmung von wenig Bromid neben viel Chlorid als geeignet, da auch grössere Chloridmengen nicht stören und das Doppelte der ursprünglichen Bromidmenge titriert wird. Bezüglich des Anwendungsgebietes der Methode verweisen wir auf unsere früheren Mitteilungen².

KOLTHOFF UND BELCHER^{3,4} beschreiben das Verfahren zwar eingehend, veranschaulichen den Reaktionsverlauf jedoch mit der summierten Gleichung:



Formell ist diese Gleichung zwar richtig, jedoch entspricht sie nicht dem Verlauf der Reaktion, da sie nicht die nacheinander sondern die nebeneinander ablaufenden Reaktionen (1), (2) summiert, womit die Bildung des vom Standpunkt des Verfahrens besonders wichtigen Bromchlors⁴ nicht zum Vorschein kommt und die dem Verfahren zugrunde liegende Reaktion (3) ausser Acht gelassen wird.

Die mit den Gleichungen (1)–(4) veranschaulichten Reaktionen dürfen nämlich nicht summiert werden. Einen Beweis hierfür lieferten Versuche, das Bromidion mit Chlorwasser in Gegenwart von Cyanidionen zu Bromcyan zu oxydieren. In diesem Falle reagiert das freie Chlor zum grössten Teil mit dem Cyanidion (Gleichung 3) und nur zu einem geringeren Prozentsatz mit dem Bromidion (Gleichung 1). Auf diese Weise ist die Oxydation des letzteren nicht quantitativ, das Verfahren für analytische Zwecke also nicht geeignet.

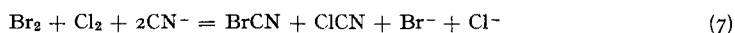
In vorliegender Arbeit soll nun auf einige — bisher überhaupt nicht oder nur wenig bekannte — Teilprozesse der Reaktion, bzw. auf ihre Anwendbarkeit im Makromassstabe aufmerksam gemacht werden.

Bereits in der ursprünglichen Arbeit wurde betont, dass das Chlorwasser bei der mit Gleichung (1) veranschaulichten Oxydation im Überschuss vorhanden sein muss, da die Ergebnisse widrigenfalls etwas niedriger ausfallen als der theoretische Wert.

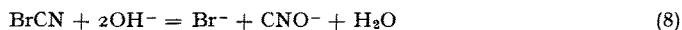
Unsere früheren Untersuchungen über die analytische Anwendbarkeit des Bromchlors bewiesen eindeutig, dass die niedrigeren Ergebnisse durch die sogenannte "homolytische" Dissoziation des Bromchlors verursacht werden⁵.



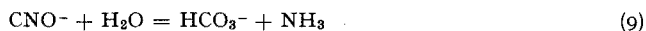
Während nämlich die über Bromcyan durchgeführte jodometrische Titration der mit äquivalenten Mengen von Brom- bzw. Chlorwasser hergestellten 0.01 N Bromchlorlösungen um 1.5–2% niedrigere Werte liefert, stimmen die Ergebnisse der mit Chlor- bzw. Bromüberschuss hergestellten Lösungen mit den theoretischen Werten genau überein. Die homolytische Dissoziation kann also mit einem Chlor- bzw. Bromüberschuss zurückgedrängt werden. Übrigens bildet sich Bromcyan nur aus der Hälfte der homolytisch dissozierenden Bromchlor-Moleküle; aus der anderen Hälfte entsteht Chlorcyan:



Auch machte unsere frühere Mitteilung darauf aufmerksam, dass das gebildete Bromcyan — besonders in alkalischem Medium — sehr leicht hydrolysieren kann, was gleichfalls die Möglichkeit eines Fehlers in sich birgt:



bzw.



Die Alkalität des Reaktionsgemisches muss daher mit Borsäure gepuffert werden. Nach unseren Erfahrungen muss mit der Hydrolyse im 0.01 N Massstabe jedoch auch schon während einer Wartezeit von wenigen Minuten gerechnet werden — besonders dann, wenn die Raumtemperatur mehr als 20° beträgt. Der Fehler kann in diesem Falle bis —1.5% erreichen.

Wenn man die Kaliumcyanidlösung jedoch vorher neutralisiert — zweckmässig

TABELLE I

Einwaage Br— mg	Verbrauch 0.01 N Na ₂ S ₂ O ₃ ml	Gefunden Br— mg	Fehler	
			mg	%
0.977	2.54 2.54	2.54	0.975	—0.002 —0.21
2.454	6.40 6.42	6.41	2.460	+0.006 +0.24
4.830	12.53 12.53	12.53	4.810	—0.02 —0.42
9.703	24.20 24.16	24.18	9.662	—0.04 —0.42

mit destillierter (20%iger) Salzsäure, in Gegenwart von Methylrot als Indikator* — so kann der sich aus der Hydrolyse ergebende Fehler ausgeschaltet werden (Tabelle I).

Unserer neueren Untersuchungen ergaben ferner, dass die jodometrische Inaktivität des bei der Reaktion gebildeten Chlorcyans auf die ausserordentlich grosse Stabilität seines Cyanidkomplexes $\text{Cl}(\text{CN})_2^-$ zurückzuführen ist⁶.

TABELLE II

Einwaage Br- mg	Verbrauch 0.1 N $\text{Na}_2\text{S}_2\text{O}_8$ ml		Gefunden Br- mg	Fehler	
				mg	%
9.703	2.41 2.43	2.42	9.669	-0.044	-0.45
20.25	5.06	5.06	20.22	-0.03	-0.15
40.22	10.02 10.04	10.03	40.08	-0.14	-0.35

Da wir früher nur im 0.001¹ bzw. in 0.01² N Massstabe gearbeitet hatten, untersuchten wir auch die Möglichkeiten der Anwendung des Verfahrens in 0.1 N Massstabe. Es zeigte sich, dass die Methode auch hier gut anwendbar ist, jedoch muss die ursprüngliche Vorschrift — infolge der relativ grossen Tension des Bromchlors — etwas abgeändert werden, da sonst ein konstanter Fehler 1–1.5% auftritt. Die Ergebnisse sind in Tabelle II zusammengefasst; die Genauigkeit der Methode beträgt $\pm 0.5\%$.

BESCHREIBUNG DES VERFAHRENS

Durchführung des Verfahrens im 0.1 N Massstabe

Die 10–40 mg Bromid enthaltende, auf Methylrot neutrale Lösung wird in einen SCHULEKschen Bromierungskolben³ pipettiert und mit Wasser auf 30–35 ml verdünnt. Man verschliesst den Kolben mit dem mit einem Hahntrichter versehenen Glasstopfen, setzt das Innere des Kolbens unter schwachen Unterdruck und verschliesst den Hahn. In den trichterförmig ausgebildeten Teil giesst man nun 25–30 ml Chlorwasser (gesättigt, frisch hergestellt, bromfrei) und öffnet hierauf den Hahn. Sobald das Chlorwasser in den Kolben eingelaufen ist, wird der Hahn sofort geschlossen und der Kolbeninhalt durchgeschüttelt**. Man giesst nun 15 ml 5%ige Kaliumcyanidlösung (mit destillierter Salzsäure auf Methylrot neutralisiert) in den Trichter, stellt den Kolben für einige Minuten in Eiswasser und lässt die Lösung aus dem Trichter gleichfalls in den Kolben einlaufen. Der Hahn wird sofort verschlossen und der Kolbeninhalt wiederholt energisch durchgeschüttelt. In den kelchförmig erweiterten Kolbenhals (nicht in den Trichter) werden nun 10 ml 5%ige Kaliumjodidlösung (frisch hergestellt) pipettiert und nach 2 (!) Min — berechnet vom Zeitpunkte der Zugabe der Kaliumcyanidlösung — lässt man durch Lockern des Schliffes auch diese Lösung zum Reaktionsgemisch fliessen und spült den Kolbenhals mit wenig Wasser nach. Es werden nun noch 5 ml 10%ige Salszaure (aus destillierter, bromidfreier Säure verdünnt) in

* Die so durchgeführte Neutralisation der 5%igen wässrigen Kaliumcyanidlösung kann unter einem guten Abzug gefahrlos bewerkstelligt werden.

** War das Mengenverhältnis des Bromidions und Chlorwassers richtig gewählt, so wird die anfangs braune Farbe des freigelegten Broms strohgelb bzw. verschwindet sie.

den Kolben gebracht, dann verschliesst man diesen erneut, stellt ihn für 20 Min an einem dunklen Ort beiseite und titriert das ausgeschiedene Jod schliesslich mit 0.1 N Natriumthiosulfat-Messlösung (mit 1% Isobutylalkohol stabilisiert; 1%ige Kartoffel-Stärke­lösung (mit 0.1% Salicylsäure abgebaut bzw. konserviert) als Indikator). 1 ml 0.1 N Natriumthiosulfat-Messlösung entspricht 3.996 mg Bromid.

Durchführung des Verfahrens in 0.01 N Massstabe

Abweichend von der ursprünglichen Vorschrift wird neutralisierte Kaliumcyanid­lösung verwendet wodurch der Zusatz von Borsäure überflüssig wird.

ZUSAMMENFASSUNG

Das vor Jahren ausgearbeitete selektive jodometrische Bromidbestimmungsverfahren wurde überprüft und verfeinert.

SUMMARY

The previously developed selective iodometric method for determination of bromide has been verified and improved.

RÉSUMÉ

Les auteurs ont examiné à nouveau et perfectionné leur méthode précédemment décrite, pour le dosage iodométrique des bromures.

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COULOMETRIC TITRATION OF COPPER(II) WITH ELECTRO-GENERATED CHROMIUM(II)

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(Received November 2nd, 1961)

Chromium(II) is one of the most powerful reductants used in titrimetric analysis¹. Because chromous ion reacts rapidly with oxygen, elaborate precautions are necessary in preparing and storing standard solutions for titrations. These circumstances suggest the application of coulometric electrogeneration of chromium(II) as a titrant.

Several early investigators in the field of coulometric titrations unsuccessfully attempted the electrogeneration of chromous ion². Generally either 100% current efficiency for the electroreduction of chromium(III) could not be attained, or the chromium(II) produced reduced hydrogen ion during the titration at a sufficiently rapid rate to cause sizeable errors. Recently two studies describing the coulometric titration of oxygen with chromous ion have been reported^{3,4}. The present study was undertaken to examine the current efficiency for the electrogeneration of chromium(II), and to apply this titrant to the determination of substances other than oxygen.

EXPERIMENTAL

Apparatus and reagents

The titration was performed in an H-cell with a 175-ml cathode (titration) chamber and a 50-ml anode chamber (Fig. 1). These two chambers were separated by a fine-porosity sintered glass disk and a saturated potassium chloride-agar plug. The anode was a cadmium rod enclosed in a glass tube with a sintered glass bottom. Nitrogen, passed through two tubes containing amalgamated zinc and 0.1 *M* chromous chloride in 1 *M* sulfuric acid, was bubbled through all chambers before and during the titration. These precautions were taken to prevent the diffusion of oxygen and products formed at the anode into the cathode chamber. A mercury pool cathode with an area of 19.6 cm² could be introduced and removed through a side-arm fitting on the titration cell. The anode chamber contained 5 *M* calcium chloride for chromic chloride supporting electrolytes, and 0.1 *M* potassium chloride for the chromic sulfate solutions. Stirring was accomplished with a magnetic stirrer; the stirrer bar resting on the mercury cathode.

A Sargent Coulometric Current Source, Model IV (E. H. Sargent, Chicago, Ill.) was employed. Potentiometric end-point detection, employing a mercury pool indicator electrode and a saturated calomel electrode with a fiber salt bridge, followed the usual practice. The functioning of the mercury pool indicator electrode was not affected by stirring rate, vibrations, etc.

Standard copper(II) and nickel(II) solutions were prepared by dissolving the pure metals in nitric acid and diluting to volume. The saturated calcium chloride solutions were filtered before use. All other reagents were used without further purification.

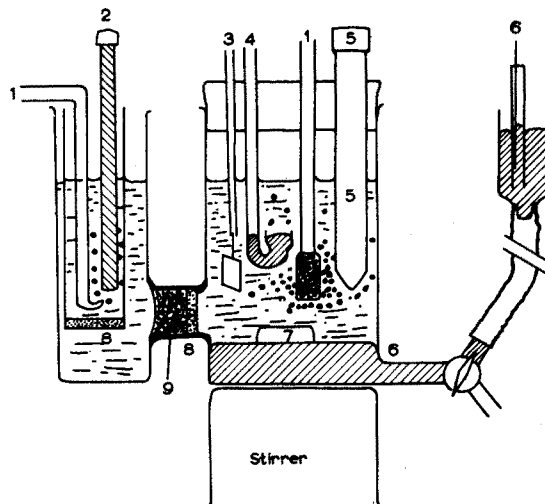


Fig. 1. Coulometric titration cell. 1, nitrogen inlets; 2, cadmium anode; 3, platinum indicator electrode (used only in preliminary experiments); 4, mercury pool indicator electrode; 5, saturated calomel electrode; 6, mercury pool cathode; 7, magnetic stirring bar; 8, fine porosity sintered glass disks; 9, agar-potassium chloride plug.

Procedure

Supporting electrolyte solution was freshly prepared and deaerated for about 15 min before use. The mercury pool was introduced and the solution was pre-titrated to the approximate end-point potential of the titration. The mercury pool was withdrawn and the sample solution was added and deaerated. Finally the mercury pool was reintroduced, and the sample titrated. This procedure effectively eliminated oxidation of mercury by any oxygen initially contained in the supporting electrolyte sample solutions, and allowed pre-reduction of impurities in the supporting electrolyte.

CURRENT EFFICIENCY FOR GENERATION OF CHROMIUM(II)

The current efficiency for the electroreduction of chromium(III) was determined from current-potential curves of solutions with and without chromic ion present⁵. Polarographic studies show that the reduction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is quite irreversible, but becomes more reversible with increasing concentrations of chloride ion. In saturated calcium chloride solutions the reduction of chromic chloride is polarographically reversible⁶.

Current-potential curves at a large mercury pool electrode for various concentrations of chromic chloride in saturated calcium chloride are shown in Fig. 2. These curves were obtained by recording the potential of the mercury pool electrode with time at a constant current density, and plotting the steady state potential (after about 30 sec) against current. The curves indicate that current efficiencies of greater than 99% should be obtainable for current densities of 5 to 9 mA/cm² (Table I). The

current efficiency determined by actual titration of the electrogenerated chromous ion with standard ceric sulfate or potassium dichromate solutions, however, appeared much lower. Attempts to use chromous ion, electrogenerated in a saturated calcium chloride solution, for the titration of copper(II) were also unsuccessful; the rate of the

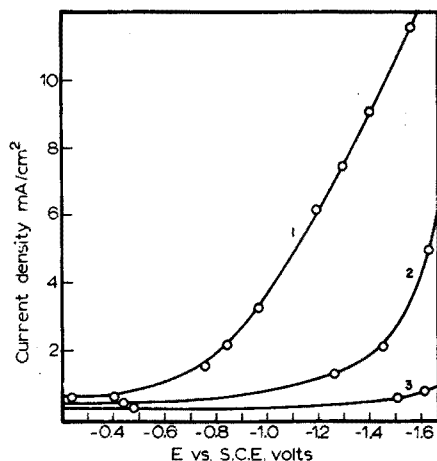


Fig. 2. Current-cathode potential curves for the reduction of chromium(III) chloride. The solution contained saturated calcium chloride and 1, 0.1 *M* chromic chloride; 2, 0.01 *M* chromic chloride; 3, supporting electrolyte alone.

TABLE I
PREDICTED CURRENT EFFICIENCIES FOR THE ELECTROREDUCTION OF CHROMIUM(III)

Current density <i>mA/cm</i> ²	Current efficiency %
<i>0.1 M chromic chloride</i> — <i>saturated calcium chloride</i>	
0.5	94
1.0	96
2.0	97
6.0	99.2
7.0	99.4
9.0	99.2
11.0	98.2
<i>0.1 M chromic sulfate</i> — <i>0.1 M potassium chloride</i>	
0.1	85
0.3	91
1.0	98
1.5	97
2.0	96
3.0	80

titration reaction appeared slow and large (15–20%) positive errors were obtained. The difference between the predicted and the apparent current efficiencies was attributed to some reduction of hydrogen ion by the chromous ion.

MEITES determined chromium by reduction to the chromous state (at about –1.1 V vs. S.C.E., apparently not at 100% current efficiency), and then controlled

potential coulometric reoxidation at -0.40 V. vs. S.C.E., in 6 M hydrochloric acid⁷. Under these conditions, chromous ion apparently did not react very rapidly with hydrogen ion. Although the reaction of chromium(II) with hydrogen ion is generally a slow reaction, in the present study this reaction may have been either catalyzed by impurities in the calcium chloride (all brands of "reagent-grade" calcium chloride were found to contain sizeable amounts of impurities) or induced by the titration reactions.

Current-potential curves obtained in a chromic sulfate -0.1 M potassium chloride solution, the medium used by JAMES AND STEPHENS⁴, are shown in Fig. 3. Because of

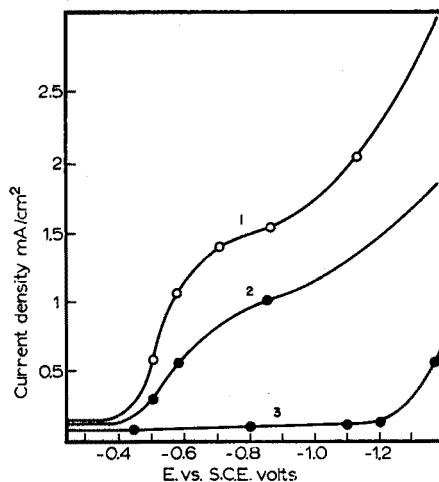


Fig. 3. Current-cathode potential curves for the reduction of chromium(III) sulfate. The mercury cathode had an area of 19.6 cm². The solution contained 0.1 M potassium chloride and 1, 0.1 M chromic sulfate; 2, 0.01 M chromic sulfate; 3, supporting electrolyte alone.

the slow rate of ligand exchange in chromium complexes, these curves are probably characteristic of chromium(III)-sulfate complexes. Under these conditions the current efficiency is largest (about 98%) at a current density of 1 mA/cm², and drops off sharply at both higher and lower current densities (Table I). The narrow range of effective current densities is caused by the low limiting current plateau for the reduction of the current-potential curves. Since JAMES AND STEPHENS obtained titration efficiencies of better than 99.5% for the determination of oxygen under these conditions, some direct electrode reduction of oxygen itself (rather than by reaction with chromous ion) must take place⁸. The overall reduction of oxygen may also occur by the oxidation of the mercury to mercurous chloride which is then cathodically reduced.

PERFORMANCE DATA

In chloride media, the titration of copper(II) proceeds in two steps, first to copper(I) and then to the metal⁹. A typical potentiometric titration curve for the titration of copper(II) with electrogenerated chromous ion, employing a mercury pool indicator electrode is shown in Fig. 4. The titration reaction was quite rapid initially, but establishment of steady indicator electrode potentials became slow toward the end-

point. At the chloride and reactant concentrations employed, the second titration step, copper(I) to the metal, was not readily obtained. The magnitude of the potential change at the equivalence point is quite small, and exact location of the end-point was often difficult. The size of the end-point potential change is larger when a platinum indicator electrode is employed⁹, but we preferred to keep platinum out of the titration cell for fear of catalyzing the reduction of hydrogen ion by chromous ion. Table II summarizes data for the titration of copper(II) with chromium(II) using

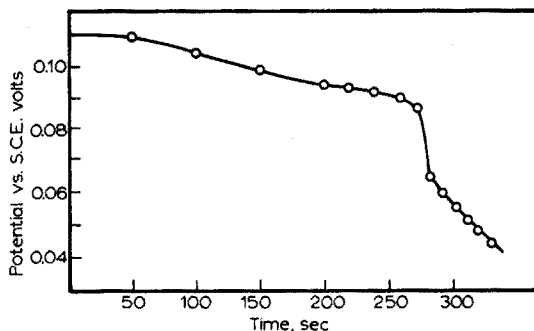


Fig. 4. Titration of 1.339 mg of copper(II) in 105 ml of 0.1 *M* chromic sulfate and 0.1 *M* potassium chloride at a 19.6 cm² mercury cathode at a current of 9.66 mA. The potential of a mercury pool indicator electrode was measured vs. a S.C.E. with a pH meter.

TABLE II

COULOMETRIC TITRATION OF COPPER(II)

Supporting electrolyte was 0.1 *M* chromic sulfate and 0.1 *M* potassium chloride, and the volume was about 110 ml. The area of the mercury generator cathode was 19.6 cm², and the current was 9.66 mA.

Copper taken (mg)	Copper found (mg)	Error (mg)
0.804	0.805	+0.001
0.804	0.795	-0.009
1.339	1.305	-0.034
1.339	1.313	-0.026
1.790	1.761	-0.029
1.790	1.750	-0.040
1.790	1.757	-0.033
2.280	2.226	-0.054
2.280	2.239	-0.041

potentiometric end-point detection. That the error is somewhat negative is suggestive of difficulty in locating, or in obtaining complete reduction of copper(II) at the end-point, rather than loss of high current efficiency or side reactions.

Several titrations of nickel(II) with electrogenerated chromium(II) were attempted. The reaction appeared slow and is probably not useful analytically. An interesting observation during the titration is that the only well-defined "break" in the potentiometric titration curve occurs at the completion of reduction of nickel(II) to nickel(I), rather than to the metal. Although nickel(I) has been reported in cyanide solutions, no evidence has been presented for its presence in a chloride medium.

Since the titrations were performed in the presence of nitrate ion (introduced in the standard solutions), one might wonder about its interference during titrations with chromous ion. Titrimetric methods for nitrate involving chromous solutions have been described¹⁰, but the reaction between nitrate and chromous ion is slow, and only proceeds faster at elevated temperatures and in the presence of a catalyst. Apparently the rate of this reaction, as compared to the rate of reduction of copper(II) with chromium(II), is sufficiently slow so as not to interfere in the titration, although the drifting of the indicator electrode potential sometimes noted after the equivalence point may be caused by the chromium(II)-nitrate reaction. The direct cathodic reduction of nitrate ion occurs at potentials more negative than that attained by the mercury cathode in these titrations¹¹. During other titrations with chromium(II), it might be advisable to eliminate nitrate ion from the titration medium.

CONCLUSION

Chromium(II) can be generated at close to 100% current efficiency by reduction of chromium(III). The present study indicates that reduction of chromic sulfate, rather than chromic chloride in concentrated chloride media, appears to be more useful, although other supporting electrolytes bear investigation. Since mercury itself is a good reducing agent in a chloride medium, oxidants with potentials above +0.25 V vs. N.H.E. may react with mercury. Direct titrations with chromium(II) are therefore limited to those oxidants with potentials between *ca.* +0.25 and -0.4 V vs. N.H.E. For many titrations in this range, electrogenerated titanium(III) or iron(II) ethylenediaminetetraacetate⁵ can also be used. The widest application of coulometric titrations with chromium(II) will probably be in the determination of oxygen.

SUMMARY

The current efficiency for the electrogeneration of chromium(II) for use as a coulometric titrant was studied for several supporting electrolytes. With a mercury cathode and a 0.1 M chromic sulfate-0.1 M potassium chloride medium, 0.8 to 2.8 mg of copper(II) in 110 ml of solution can be titrated using potentiometric end-point detection.

RÉSUMÉ

Description d'une méthode coulométrique pour le dosage du cuivre(II), au moyen de chrome(II), formé électrochimiquement. Divers électrolytes de base ont été examinés.

ZUSAMMENFASSUNG

Beschreibung einer coulometrischen Methode zur Bestimmung von Kupfer-(II) mit elektrolytisch erzeugten Chrom-(II)-Lösung.

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THERMOGRAVIMETRIC ANALYSIS: TEMPERATURE LIMITS AND RATE OF HEATING

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(Received November 1st, 1961)

There are several factors which must be controlled in order to obtain reliable and reproducible thermolysis curves with the thermobalance. Among these are the arrangement of the furnace, container and thermocouple, the quantity and physical condition of the sample, the nature and pressure of the atmosphere surrounding the sample and finally the rate of heating the sample.

Experimental studies of some of these factors have been previously reported. In investigations of solid state reactions for dehydration or decomposition with evolution of gas some investigators^{1,2}, interested primarily in determining the mechanism for the formation of nuclei, the initiation and propagation of the reaction, followed the reaction through microscopic observation of large crystals. Other investigators, interested only in the kinetics of a particular solid state reaction used either powdered material³⁻⁶ or large crystals⁷.

We have found in the literature only the article of RICHER AND VALLET⁸ dealing experimentally with the influence of mass, physical condition of the sample, atmosphere and the rate of heating upon the final decomposition temperature of calcium carbonate. Insufficient specifications of these conditions have resulted in controversies among a number of authors⁹⁻¹⁰ regarding the shape of the thermolysis curves obtained. Because of this situation we have made further studies of the effect of sample size, its physical condition and the rate of heating upon the final decomposition temperature.

In the following pages an equation has been derived relating the decomposition temperature to the weight and surface area of the sample. The validity of this equation has been tested by using the decomposition data of RICHER AND VALLET⁸ and also our own data for the dehydration of 5-nitrobarbituric acid.

In the derivation of the equation a fundamental assumption must be made on the effect of heat transfer on this problem. It has been assumed that the reaction is relatively slow at the rate of heating used and that once a steady state is established between the ambient temperature and the temperature of the sample, this steady state is not disturbed during the course of the reaction. Under these conditions the problem of heat transfer does not need to be considered.

In the decomposition of many hydrates and carbonates there is an extremely rapid nucleation followed by a rapid surface growth. In such cases the rate of decomposition

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is governed by the progression of the resulting interface toward the center of the crystal. The Polanyi-Wigner equation (1) thus applies to the decomposition

$$-\frac{d\mathcal{N}}{dt} = S_2 \mathcal{N} v e^{-E_2/RT} \quad (1)$$

\mathcal{N} = number of molecules at the interface; $-\frac{d\mathcal{N}}{dt}$ = number of molecules decomposing at the interface per unit of time; S_2 = entropy factor; v = vibration frequency.

In the case of the decomposition of hydrates and carbonates where the loss in weight is measured, JACOBS AND TOMPKINS¹¹ have given equation (2) for the rate of decomposition

$$\frac{d\alpha}{dt} = \frac{\Gamma M}{W_0 N} S_2 v \bar{\mathcal{N}} A e^{-E_2/RT} \quad (2)$$

α = fraction of the sample decomposed;

$$\Gamma = \left(1 - \frac{v_B M_B}{v_A M_A} \right)^{-1}$$

v_A, v_B = moles of A reacting and moles of B produced; M_A, M_B = molecular weights of reactant A and product B; M = molecular weight of the compound undergoing decomposition; W_0 = initial weight of material; N = Avogadro's number; $\bar{\mathcal{N}}$ = number of molecules per cm² at the interface; A = area in cm² at the interface.

The area of the interface between the reactants and products for the reaction



varies with time and is in general a power function of the undecomposed fraction:

$$A = A_0 (1 - \alpha)^z \quad (4)$$

where A_0 = initial area of the interface. With investigations of the rate of decomposition on the thermobalance one can vary the temperature as a linear function of time. Equation (5) expresses this relation after differentiation

$$dt = \left(\frac{dt}{dT} \right)_c dT \quad (5)$$

where $(dt/dT)_c$ is the reciprocal of the rate of heating. A combination of equations (2) and (4) with equation (5) gives the following expression:

$$\frac{d\alpha}{dT} = \frac{\Gamma M}{W_0 N} S_2 v \bar{\mathcal{N}} A_0 (1 - \alpha)^z \left(\frac{dt}{dT} \right)_c e^{-E_2/RT} \quad (6)$$

By taking the logarithm of this equation and rearranging one obtains an expression for the reciprocal of the absolute temperature:

$$\frac{1}{T} = -\frac{R}{E_2} \left[\ln \left(\frac{d\alpha}{dT} \right) - \ln (1 - \alpha)^z - \ln A_0 \left(\frac{\Gamma M}{W_0 N} S_2 v \bar{\mathcal{N}} \right) \right] + \frac{R}{E_2} \ln \left(\frac{dt}{dT} \right)_c \quad (7)$$

In order to apply this equation to the determination of the temperature (T_2) at which

the decomposition reaction is virtually completed certain assumptions about $d\alpha/dT$ and $(1 - \alpha)^z$ must be made. Both these quantities are dependent upon the thermo-balance used. However, for a given balance they remain constant and therefore their logarithms are constant when the quantity of sample, its physical condition or the rate of heating is varied. The smaller the fraction undecomposed that can be detected the smaller is the intercept and the larger T_2 . This means that with a more sensitive instrument the final detectable decomposition temperature is somewhat larger.

In order to make data from different sources comparable, it is preferable to take T_2 as the temperature at which, let us say, 98% of the reaction has taken place. At such a point it should be easier in most cases to determine T_2 with precision. However, the data from the literature available for the present study were not presented in a fashion allowing such a definition. T_2 was therefore defined as the temperature at which the decomposition reaction is virtually completed.

If $1/T_2$ from equation (7) is plotted *versus* $\ln (dt/dT)_c$ for a constant amount of material and surface area one should get a straight line with the slope R/E_2 and an intercept of

$$+ \frac{R}{E_2} \left[-\ln \left(\frac{d\alpha}{dT} \right) + \ln (1 - \alpha)^z + \ln A_0 \left(\frac{FM}{W_0 N} S_2 W \bar{V} \right) \right]$$

The initial weight of material and the initial area of the sample effect the position of the plot with respect to the $1/T_2$ axis. At constant rate of heating an increase in the initial area of the sample gives a lower final temperature while an increase in the initial weight of the material gives a higher final temperature. Since for similar geometric shapes of material the differential increase in volume is larger than the differential increase in weight, an increase in weight of the material produces an increase in the final decomposition temperature in spite of the fact that the area of the sample increases at the same time.

By varying A_0 and W_0 at a constant rate of heating one can determine under given experimental conditions the contribution of the factor

$$\frac{R}{E_2} \ln A_0 \left(\frac{FM}{W_0 N} S_2 W \bar{V} \right)$$

to the apparent final decomposition temperature since both $d\alpha/dT$ and $(1 - \alpha)^z$ remain constant.

Experimentally if one has one T_2 value and the activation energy for a certain reaction (or two values for T_2 at two different rates of heating) one can determine in the first case T_2 for any rate of heating and in the second case the activation energy of the reaction as well as T_2 .

The activation energies may also be calculated from the same data by the method proposed by FREEMAN AND CARROLL⁵. Using the Polanyi-Wigner equation these authors developed equation (8) which permits the calculation of the activation energy and the order of the reaction from one thermolysis curve obtained using a linear increase of temperature with time.

$$-\frac{E/R \Delta(1/T)}{\Delta \ln X} = \frac{\Delta \ln (-dX/dt)}{\Delta \ln X} - x \quad (8)$$

where X is the mole fraction of the reactant and x the order of the reaction. However, this method has not been utilized in the present work.

If one knows the exact relation between the change in the surface area and the change in weight one may determine at a constant rate of heating the same quantities as are determined under conditions of variable rate of heating.

EXPERIMENTAL AGREEMENT WITH THE THEORETICAL CURVE

The validity of equation (7) was tested on experimental data taken from the literature and also on the dehydration data of 5-nitrobarbituric acid trihydrate obtained in our laboratories. The investigation of the dehydration of 5-nitrobarbituric acid was of interest because of the thermogravimetric studies of the salts of this acid made by the authors¹²⁻¹⁵.

The acid was dehydrated in a Chevenard thermobalance in a stream of dry nitrogen flowing at the rate of 1 l per h. Such a rate of flow kept the atmosphere in the neighborhood of the sample reasonably free of water vapor produced during the dehydration and at the same time did not disturb either the mechanical or thermal equilibrium of the thermobalance. Samples of about 80 mg were used in No. 000 crucibles forming a layer 3-4 mm thick in the bottom.

TABLE I

FINAL DECOMPOSITION TEMPERATURE AS A FUNCTION OF THE RATE OF HEATING AT CONSTANT WEIGHT OF SAMPLE

T_f°	$\Delta t/\Delta T$ in sec/°	T_f°	$\Delta t/\Delta T$ in sec/°
<i>Decomposition of CaCO₃</i>			
	A, in N ₂		B, in CO ₂
	956	1187	189
	983	1195	72.0
	1025	1204	36.0
	1044	1213	22.8
	1083	1228	11.8
	<i>C, Dehydration of KCr(SO₄)₂ · 12H₂O</i>		<i>D, Dehydration of H₃BO₃</i>
	359	373	360.0
	369	395	72.0
	374	423	36.0
	387		
	402		
	428		
		<i>E, Dehydration of 5-nitrobarbituric acid trihydrate</i>	
		365	55.4
		383	24.0
		397	12.0

In Table I are listed the decomposition temperatures in relation to the rate of heating as calculated from the data of RICHER AND VALLET⁸ for the decomposition of calcium carbonate in dry nitrogen and in carbon dioxide atmospheres. The temperatures presented for the dehydration of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to $\text{KCr}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were calculated from the data of MAURET AND VICAIRE¹⁶, while those for the dehydration of orthoboric acid to metaboric acid, under 4 mm Hg of water vapor, were calculated from the data of HALADJIAN AND CARPÈNI¹⁷. Lastly, in Table I are the final dehydra-

tion temperatures related to the rate of heating for the dehydration of 5-nitrobarbituric acid trihydrate as determined in our laboratories.

The inverse of the final decomposition temperatures for the compounds listed in Table I has been plotted in Fig. 1 as a function of the logarithms of the inverse of the rates of heating. It was ascertained that the experimental data fit this theoretically derived curve very well.

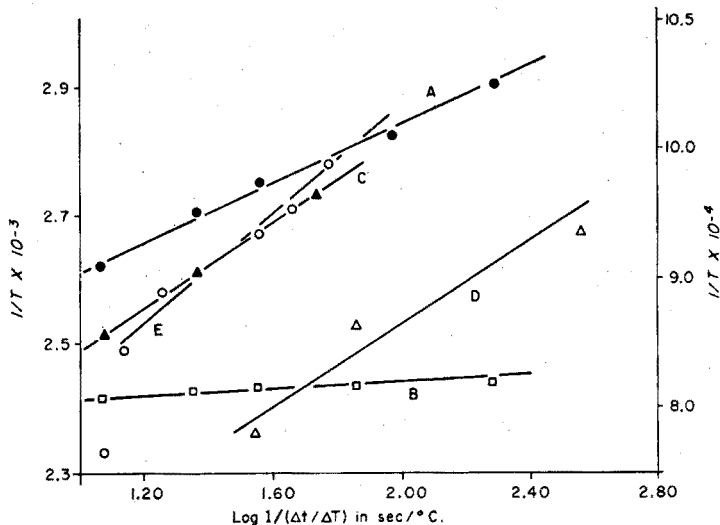


Fig. 1. Final decomposition temperature as a function of the rate of heating. $1/T \times 10^{-4}$ scale: A, CaCO_3 powder in dry N_2 ; B, CaCO_3 powder in CO_2 . $1/T \times 10^{-3}$ scale: C, dehydration of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; D, Dehydration of H_3BO_3 ; E, Dehydration of 5-nitrobarbituric acid trihydrate.

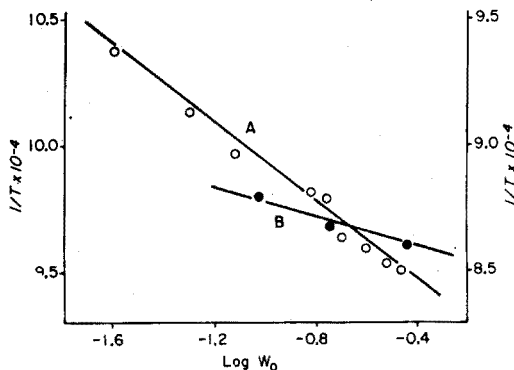


Fig. 2. Final decomposition temperature as a function of the mass of the sample for the decomposition of CaCO_3 . $1/T \times 10^{-4}$ scale: A, Powdered CaCO_3 . $1/T \times 10^{-4}$ scale: B, crystal of CaCO_3 .

The influence of the mass and physical state upon the final decomposition temperature of calcium carbonate has also been studied by RICHER AND VALLET⁸. In Fig. 2 the variation in the final decomposition temperature as a function of the weight of the sample, as calculated from the data of RICHER AND VALLET, is plotted for both powdered and a single crystal of calcium carbonate.

The data for the decomposition of calcium carbonate, both in dry nitrogen and in carbon dioxide show a very linear behavior as predicted by equation (7). From the slope of curve A we have calculated an apparent activation energy of 44 kcal for the decomposition of calcium carbonate in dry nitrogen. This value is in general agreement with the values found in the literature which vary from 31 to 44 kcal^{4,18,19}. An apparent activation energy of 210 kcal was calculated from the slope of curve B for the decomposition of calcium carbonate in a carbon dioxide atmosphere. This shows the effect of recombination of carbon dioxide in the decomposition of calcium carbonate.

The experimental points for the partial dehydration of chrome alum fit the straight line, curve C, very well except at high rates of heating. This deviation seemed to indicate that the temperature of the sample, at the point where the reaction seemed to be complete was still appreciably higher than the ambient temperature which was measured by the thermocouple. From the slope of curve C, an apparent activation energy of 11.5 kcal was calculated. MAURET AND VORSANGER²⁰ have calculated the activation energy for this reaction from the values of the initial dehydration rates and obtained a value of 18.5 kcal. The disagreement between the two values might be due to the difference in the water vapor pressure; the value of 11.5 kcal was obtained under a water vapor pressure varying between 14 and 17 mm of Hg, while the activation energy of 18.5 kcal was obtained for a water vapor pressure of 10 to 11 mm Hg.

It should be pointed out that the activation energies found by MAURET AND VORSANGER for potassium and ammonium alums (38 and 32 kcal respectively) and for potassium and ammonium chrome alums (18.5 and 17.5 kcal respectively) differ from the values of 31.2 and 22.6-30.0 kcal respectively found by GARNER AND COOPER²¹ and ANOUS *et al.*²² for potassium chrome alum, and from the values of 16.6 and 16.4 kcal respectively found by ACOCK *et al.*²³, for potassium and ammonium alums.

The experimental points for the dehydration of orthoboric acid as represented on curve D show reasonable linearity. A value of 14.3 kcal was obtained from the slope of curve D for the apparent activation energy of dehydration. The dehydration of orthoboric acid to metaboric acid has been shown to be a reversible reaction¹⁷. A value of 15.5 kcal has been calculated by us from the data given by URUSOV²⁴ for the heat of dehydration of this reaction. The reaction is endothermic and it appears that under the experimental conditions by which 14.3 kcal was obtained by us for the apparent activation energy, no energy in excess of the heat of dehydration is required for this reaction to occur. HALADJIAN AND CARPENI¹⁷ have shown that the reaction is catalyzed by traces of water vapor, and it is therefore probable that in a dry atmosphere the value for the apparent activation energy for the dehydration of orthoboric acid is appreciably higher.

The experimental data for the dehydration of 5-nitrobarbituric acid trihydrate show very good linearity. A value of 14 kcal is obtained for the apparent activation energy from the slope of curve E. This value compares with 11 kcal that we obtained from values of initial dehydration rates done in isothermal conditions.

Since equation (7) was derived from the Polanyi-Wigner equation we have checked to ascertain for what values of the dehydration activation energies this equation can be applied.

For the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (TOPLEY²⁵) the activation energy was 16 to

18 kcal, for $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (ACOCK *et al.*²³) the activation energies were respectively 16.4 and 16.6 kcal. In the case of the dehydration of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ (TOPLEY AND HUME²⁴) an activation energy of 38.40 kcal was found, and for the dehydration of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (GARNER AND COOPER²¹) an activation energy of 31.2 kcal. In both of these cases the Polanyi-Wigner equation was not applicable.

The value of 14 kcal that we found for 5-nitrobarbituric acid corresponds to the values where the Polanyi-Wigner equation appears to be applicable.

In the case when there are changes in the mass or physical state of the sample a study of the slope of curve A in Fig. 2 for the decomposition of powder calcium carbonate shows that in order to obtain an apparent activation energy similar to that calculated from curve A in Fig. 1 (*i.e.* 44 kcal) one has to introduce a variation in weight to the $2/3$ power only, ($W_0^{2/3}$). One obtains then an apparent activation energy of 40.6 kcal for the powdered calcium carbonate in dry nitrogen. If a similar calculation is made for the crystal of calcium carbonate one obtains an apparent activation energy of 88.5 kcal. BRUŽS⁷ has determined the activation energies for many metallic carbonates (Fe, Pb, Co, Zn, Hg) when present in large crystals and he has found "all these reactions to have a high temperature coefficient." The mean value for the "critical increment" of 80 kcal seems to be characteristic of the carbonate ion in the crystal. On the other hand MASKILL AND TURNER⁶ found that with large crystals of calcium carbonate the disintegration and decomposition throughout most of the heating period is likely to be much faster than should correspond to the original grain size because the setting in of the rapid disintegration yields much finer material. They also found that the critical increment of energy for small particle size of calcium carbonate is 95 kcal.

CONCLUSION

The various dehydration and decomposition reactions studied show that the final decomposition temperatures follow in general the equation derived by us from the Polanyi-Wigner equation. The values for the apparent activation energies of these reactions agree reasonably well with the apparent activation energies calculated by other methods for these reactions.

SUMMARY

In the case of the decomposition of carbonates and hydrates, the Polanyi-Wigner equation often applies. A mathematical expression relating the temperature at a given stage of the reaction to the rate of decomposition, fraction of reactant left, initial weight and area of the compound and finally the rate of heating has been derived from the above equation. For a given thermobalance the minimum detectable rate of decomposition and fraction of reactant left are fixed so that the observed final decomposition temperature is a function of the rate of heating for a constant weight and area of material. Using this equation, values for the final decomposition temperatures have been calculated and compared with data found in the literature for the decomposition of calcium carbonate and for the dehydration of potassium chrome alum and orthoboric acid. The equation also has been applied to the dehydration of 5-nitrobarbituric acid trihydrate as determined by us.

RÉSUMÉ

Les auteurs ont examiné les divers facteurs pouvant intervenir dans l'établissement de courbes de thermolyse, à l'aide d'une thermobalance. Appliquant l'équation de Polanyi-Wigner, ils ont calculé les températures de décomposition du carbonate de calcium, de l'alun de chrome et potassium, de l'acide orthoborique et de l'acide nitro-5-barbituriquettrihydrate.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Faktoren, die den Verlauf thermolytischer Kurven beeinflussen. Mit Hilfe der Gleichung von Polanyi-Wigner wurden die Zersetzungstemperaturen von Calciumcarbonat, Kalium-chromalaun, Orthoborsäure und 5-Nitro-barbitursäure-trihydrat errechnet.

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GRAVIMETRIC DETERMINATION OF URANIUM(VI) WITH
N-BENZOYLPHENYLHYDROXYLAMINE

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(Received August 31st, 1961)

To avoid the defects of cupferron, N-benzoylphenylhydroxylamine was introduced by SHOME¹ for the determination of metals. Cupferron has been used to precipitate uranium(IV)² from acidic solution and uranium(VI)³ from neutral solution. Both precipitates must be ignited to U₃O₈ before being weighed. In the present investigation it was observed that N-benzoylphenylhydroxylamine forms an orange-red complex with uranium(VI) in weakly acidic solution and the metal can be determined by weighing the precipitate directly. Uranium(VI) can also be separated from allied elements. Uranium(IV) forms a light yellow flocculent precipitate from more acidic solutions so that the determination and separation of uranium(IV) with the reagent may also be possible.

The formation of a complex between uranium(VI) and benzoylphenylhydroxylamine is indicated by the appearance of an orange colour at pH 3.0. The complex can be extracted from aqueous solutions with chloroform⁴ at pH 3.5; it is obtained as an orange-red precipitate at or above pH 4.4, which turns into a brick red granular form on digestion. In this form the complex remains insoluble even if the pH is lowered to 3.7; the composition of the precipitate is UO₂(C₁₃H₁₀O₂N)₂.

For separations, attempts were made to precipitate uranium in presence of foreign ions after complexing them with EDTA (disodium dihydrogen ethylenediaminetetraacetate) because no complex between uranium(VI) and EDTA is formed^{5,6}. However, the precipitation of uranium(VI) was incomplete in the presence of EDTA, though on addition of magnesium chloride solution it was completely precipitated. Hence magnesium-EDTA complex was used as the masking agent in the separation of uranium from other ions. However, the magnesium-EDTA complex did not prevent the precipitation of iron, aluminium, titanium, zirconium or molybdate completely. These elements were, therefore, first precipitated from more acidic solutions, filtered off and uranium(VI) was then determined in the filtrate by raising its pH. The range for complete precipitation of iron¹ is pH 3.0 to 3.5, while titanium¹, zirconium⁷ and molybdenum(VI)⁸ are completely precipitated respectively from 1.0 to 0.15 N, 2.4 N and 0.01 to 2.5 N hydrochloric acid solutions. Aluminium is completely precipitated¹ between pH 3.6 and 6.4. For complete precipitation of aluminium at pH 4.0 a large excess of the reagent is required, which causes the precipitation of some uranium; initially the aluminium precipitate is somewhat sticky and may absorb some uranium. For these reasons separation from aluminium was possible only when it was present in relatively small amounts.

EXPERIMENTAL

Reagents

Uranyl nitrate solution. Ammonium uranate was precipitated from uranyl nitrate solution containing EDTA with ammonium hydroxide, filtered, washed, dissolved in nitric acid and diluted. The strength of the solution was determined by precipitation with ammonia and then weighing as U_3O_8 .

Magnesium-EDTA complex. 1 M EDTA and 1 M magnesium chloride solutions were separately prepared. When required 5 ml of each solution were mixed and added to the metal solutions.

Foreign ions. When uranium was determined in presence of other ions, titanium was added as sulphate, zirconium as chloride and molybdenum as ammonium molybdate. All the other metals were added as the nitrates.

Benzoylphenylhydroxylamine solution. A solution of the reagent in 95% ethyl alcohol was used for the precipitation of uranium.

All the chemicals used were of A.R. grade.

Properties and composition of the complex

The complex when freshly precipitated as an orange flocculent mass was somewhat soluble in water above 60°, but the red granular form obtained after digestion for some time was less soluble. However, it was soluble in chloroform, ether, acetone and 50% alcohol, though the solubility in carbon tetrachloride was low and in 20% alcohol it was negligible. Hence during the precipitation of uranium(VI) the amount of alcohol added should never exceed 20% of the total volume of the solution. The complex decomposed when treated with moderately concentrated mineral acid or sodium hydroxide, or when heated to 204–206°. The pure complex was analysed for uranium, by igniting a known weight of it to the oxide (uranium found 34.20%; theor. 34.20%), and for nitrogen by Kjeldahl's method (nitrogen found 4.07%; theor. 4.02%). The results indicate that its composition is $UO_2(C_{13}H_{10}O_2N)_2$.

The magnetic susceptibility (χ_0) of the complex was experimentally determined and the value was found to be $-0.280 \cdot 10^{-6}$ ($H_{max} = 8.3 \cdot 10^3$ Oersteds) showing the compound to be diamagnetic, which is in accordance with the above formula assigned to the complex.

Determination of uranium

A known quantity of the uranium solution was diluted to 200 ml with distilled water and heated to 40–50°, and the solution of benzoylphenylhydroxylamine (about 0.3 g in 10 ml of ethanol) was added slowly with constant stirring. Ammonium hydroxide

TABLE I
DETERMINATION OF URANIUM AS OXIDE OR AS THE COMPLEX

U taken (mg)	Weighed as oxide		Weighed as the complex	
	U found (mg)	Error (mg)	U found (mg)	Error (mg)
44.6	44.5	—0.1	44.6	0.0
42.5	42.4	—0.1	42.4	—0.1
41.9	41.8	—0.1	41.8	—0.1
31.4	31.4	0.0	31.4	0.0

(2 *N*) solution was then added dropwise to raise the pH of the solution to 5.4. The mixture was then allowed to stand on a warm water bath (40–50°) with occasional stirring for about 1.5 h. A drop or two of ammonium hydroxide was added if necessary to maintain the pH. The precipitate was filtered, washed and ignited to the oxide. The oxide was dissolved in a few drops of concentrated nitric acid, evaporated, again converted to U₃O₈ and weighed. The results in Table I indicate that uranium(VI) was quantitatively precipitated by benzoylphenylhydroxylamine.

In another series of experiments uranium(VI) was precipitated as described above, filtered on a sintered glass crucible, washed with warm water (40–50°) and dried at 110° to constant weight. The metal content was calculated on the basis that the precipitate contained 34.29% uranium. The results are also given in Table I.

Effect of reagent concentration

The precipitation of uranium was carried out using different amounts of the reagent, the other conditions remaining the same. For complete precipitation of the metal the least amount of reagent required was about thrice the theoretical amount.

Effect of pH

Solutions containing uranium(VI) and N-benzoylphenylhydroxylamine (thrice the amount theoretically required) were adjusted to different pH values with dilute ammonium hydroxide (2 *N*), digested as usual, filtered and the pH of the filtrate was measured with the aid of a Cambridge pH meter (bench model). The precipitates were washed with warm water (40–50°) and weighed. The precipitation of uranium was complete between pH 5.2 and 5.6. Above pH 6.0 precipitation was incomplete; the precipitate was of a different nature and of indefinite composition.

Separation of uranium(VI) using magnesium-EDTA solution as masking agent

To a mixture containing a known amount of uranyl nitrate solution and the desired amount of foreign ion, 10 ml of magnesium-EDTA complex solution were added. The mixture was diluted to 300 ml, heated to 40–50° and precipitation of uranium was carried out as described above. The results of various separations of uranium(VI) are given in Table II.

TABLE II

DETERMINATION OF URANIUM IN PRESENCE OF FOREIGN METALS BY MASKING THEM WITH Mg-EDTA COMPLEX

<i>U taken</i> (mg)	<i>Foreign ion</i>		<i>U found</i> (mg)	<i>Error</i> (mg)
	<i>Present</i>	<i>Amount added</i> (mg)		
41.9	Ce ³⁺	25	41.8	—0.1
41.9	Ce ³⁺	50	41.6	—0.3
41.9	Th ⁴⁺	25	41.6	—0.3
41.9	Th ⁴⁺	50	41.8	—0.1
42.6	Pb ²⁺	25	42.4	—0.2
42.6	Pb ²⁺	50	42.5	—0.1
42.6	Bi ³⁺	25	42.7	+0.1
42.6	Bi ³⁺	50	42.5	—0.1

Separation of uranium(VI) by adjustment of acidity

When separation from iron(III), aluminium, titanium(IV), zirconium or molybdenum(VI) was studied, the foreign ion was added to a known quantity of the uranium solution and the mixture was diluted with water to about 300 ml. Concentrated hydrochloric acid or dilute ammonium hydroxide (2 N) was added to adjust the solution to the proper acidity. Titanium, zirconium and molybdenum were precipitated with N-benzoylphenylhydroxylamine from solutions which contained 0.15 N, 2.4 N and 1 N hydrochloric acid respectively. When iron and aluminium were precipitated, ammonium hydroxide was added to adjust the pH to 3.5 and 4.0 respectively.

Titanium was precipitated by N-benzoylphenylhydroxylamine in the cold. The mixture was allowed to stand for 1 h, filtered and washed. In other cases, the solutions were heated to 50–60°, sufficient reagent solution was added to give complete precipitation of the foreign metal, and the solution was digested on a hot water bath with occasional stirring. The time for digestion was about 1.5 h in the case of iron or aluminium and 30 min for zirconium or molybdenum(VI). The precipitates were filtered and washed. In all the above cases the wash liquid contained 1% (w/v) of the reagent and the acidity of the wash liquid was the same as that of the solution from which the precipitation was carried out.

TABLE III
DETERMINATION OF URANIUM AFTER SEPARATION FROM FOREIGN METALS

<i>U taken</i> (mg)	<i>Foreign ion</i>		<i>U found</i> (mg)	<i>Error</i> (mg)
	<i>Present</i>	<i>Amount added</i> (mg)		
44.6	Fe ³⁺	30	44.6	0
44.6	Fe ³⁺	35	44.8	+0.2
44.6	Fe ³⁺	35	44.8	+0.2
44.6	Al ³⁺	10	44.5	−0.1
44.6	Al ³⁺	15	44.7	+0.1
44.6	Ti ⁴⁺	10	44.6	0
44.6	Ti ⁴⁺	15	44.4	−0.2
44.6	Zr ⁴⁺	20	44.6	0
44.6	Zr ⁴⁺	25	44.8	+0.2
44.6	Mo ⁶⁺	30	44.5	−0.1
44.6	Mo ⁶⁺	35	44.4	−0.2

The filtrate together with the washings were concentrated to about 200 ml, and filtered if any organic matter appeared during the prolonged boiling. Uranium(VI) was then precipitated from the filtrate by the addition of a further amount of reagent and by raising the pH as previously described. Results are shown in Table III.

Interferences

Organic acids, and carbonate and fluoride ions prevent the precipitation of uranium(VI) partially or completely. Beryllium precipitates under similar conditions, therefore separation of uranium from beryllium cannot be done. Chromium(III), vanadium(V)

and tungsten(VI) are not masked by the magnesium-EDTA complex. Separation of the metal from chromium(VI) is not possible because the reagent is oxidized. Separation of the metal from large amounts of aluminium is not possible, as has already been stated.

SUMMARY

Uranium(VI) can be quantitatively precipitated by N-benzoylphenylhydroxylamine at pH 5.4. The precipitate is weighed after ignition to U_3O_8 , or directly as $UO_2(C_{13}H_{10}O_2N)_2$. Cerium(III), thorium, lead and bismuth can be masked with magnesium-EDTA complex. Iron(III), titanium(IV), zirconium and molybdenum(VI) and small amounts of aluminium can be precipitated with the reagent and filtered before uranium(VI) is determined in the filtrate by proper adjustment of acidity. Fluoride, carbonate and organic acids interfere.

RÉSUMÉ

Une méthode est proposée pour le dosage gravimétrique de l'uranium(VI), au moyen de la N-benzoylphénylhydroxylamine. Le précipité obtenu peut être calciné sous forme de U_3O_8 ou pesé directement comme $UO_2(C_{13}H_{10}O_2N)_2$. Par masquage ou précipitation préalables, il est possible de doser l'uranium accompagné de cérium(III), de thorium, de plomb, de bismuth, de fer, de titane, de zirconium et de molybdène. Les fluorures, carbonates et acides organiques gênent.

ZUSAMMENFASSUNG

Beschreibung einer gravimetrischen Methode zur Bestimmung von Uran-(VI) mit Hilfe von N-Benzoylphenylhydroxylamin. Der gebildete Niederschlag kann entweder direkt als $UO_2(C_{13}H_{10}O_2N)_2$ oder als U_3O_8 nach Glühen gewogen werden. Thorium, Cerium-(III), Blei und Wismut können mit EDTA maskiert werden; Eisen-(III), Titan-(IV), Zirkonium und Molybdän sowie kleinere Mengen Aluminium werden bei geeignetem pH vorher ausgefällt. Fluoride, Karbonate und organische Säuren stören.

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SEPARATION OF HYDROXY ACIDS BY ION EXCHANGE
CHROMATOGRAPHY

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(Received December 4th, 1961)

In earlier papers it has been shown that an anion exchange resin in the borate form is a valuable tool for the separation of various hydroxy acids which are formed during the degradation of monosaccharides and cellulose^{1,2}. The separation is carried out by chromatographic elution with a solution of sodium tetraborate. In the present work the influence of the eluant concentration has been studied in more detail and conditions have been found which permit the isolation of certain acids which could not be separated under the working conditions previously used.

EXPERIMENTAL

The hydroxy acids used were the same as those studied in the earlier paper². The ion exchange column, which was filled with Dowex 1-X8 (< 400 mesh), had an inner diameter of 33 mm and a height of 330 mm. The large column diameter was chosen in order to permit an isolation and identification of the acids obtained in the eluate. The chromatographic separations were carried out with the same equipment and working conditions as earlier except that the eluant concentration and the flow rate were varied. Some of the analyses were made using an Autoanalyzer from Technicon Instruments Corp., Chauncey, New York. In this machine the acids were oxidized with dichromate in sulfuric acid medium and the residual dichromate was determined colorimetrically.

RESULTS AND DISCUSSION

In the earlier paper² it was shown that several saccharinic acids could be separated from each other by elution with 0.07 M sodium tetraborate solution. However, the separation of lactic, glycolic, α,β -dihydroxyisobutyric and β,γ -dihydroxybutyric acids is incomplete even if a comparatively long column is used (Fig. 1). Experiments have, therefore, been carried out at lower concentrations under otherwise constant conditions. From the positions of the elution peaks the volume distribution coefficients, D_V , have been calculated for the two dihydroxybutyric acids. The calculation has been made according to the equation:

$$D_V = \bar{v}/X - \alpha$$

where \bar{v} is the peak elution volume, X the volume of the resin bed and α the void fraction of the resin bed ($\alpha = 0.4$).

From Fig. 2 it is seen that a plot of $\log D_V$ against $-\log c$, where c is the eluant concentration, gives straight lines of different slopes. The lines diverge for a lower borate concentration, which means that a lower concentration gives a higher ratio between the distribution coefficients. This ratio, which is called the separation factor,

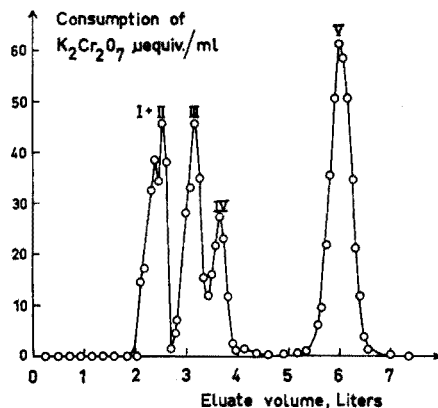


Fig. 1. Separation of lactic and glycolic acids (I + II), α, β -dihydroxyisobutyric acid (III), β, γ -dihydroxybutyric acid (IV) and α -D-isosaccharinic acid (V). Eluant: $0.07 M Na_2B_4O_7$. Flow rate: $0.3 \text{ ml cm}^{-2} \text{ min}^{-1}$.

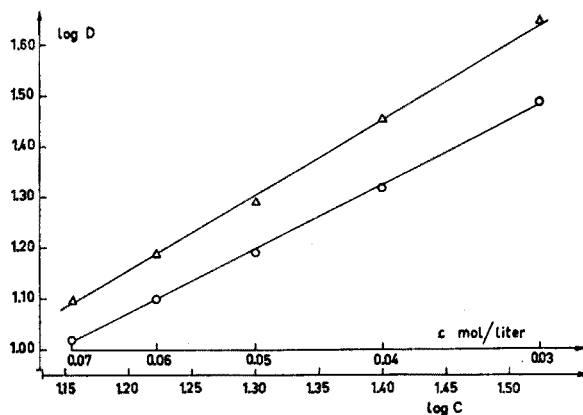


Fig. 2. The correlation between the distribution coefficient (D_V) and the eluant concentration (c). Δ β, γ -dihydroxybutyric acid; \circ α, β -dihydroxyisobutyric acid.

has a predominating influence upon the efficiency of a chromatographic separation. The elution curves illustrated in Fig. 3 show that a quantitative separation of the two dihydroxybutyric acids is obtained in $0.04 M$ solution and that this separation is complete even if the flow-rate is increased. The separation of lactic and glycolic acids is incomplete under these conditions.

At a lower concentration an excessive broadening of the elution bands corresponding to the dihydroxybutyric acids occurs, whereas the separation of lactic and

glycolic acids is improved. In 0.02 *M* borate solution this separation is still far from complete (Fig. 4). In 0.015 *M* solution the separation is not complete but good enough

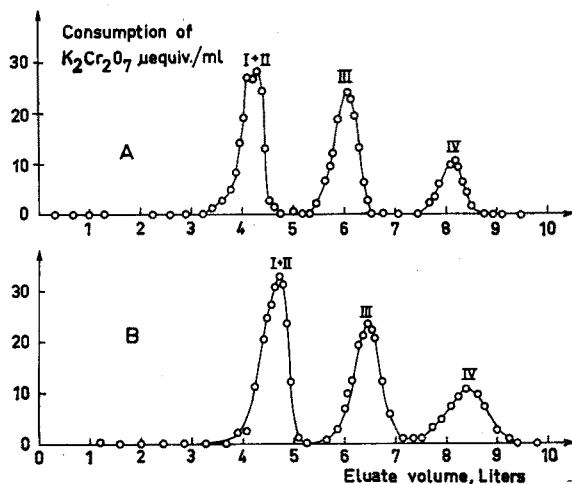


Fig. 3. Separation of lactic and glycolic acids (I + II), α,β -dihydroxyisobutyric acid (III) and β,γ -dihydroxybutyric acid (IV). Eluant: 0.04 *M* $\text{Na}_2\text{B}_4\text{O}_7$. Flow rates: (A) 0.3 $\text{ml cm}^{-2}\text{min}^{-1}$; (B) 1.2 $\text{ml cm}^{-2}\text{min}^{-1}$.

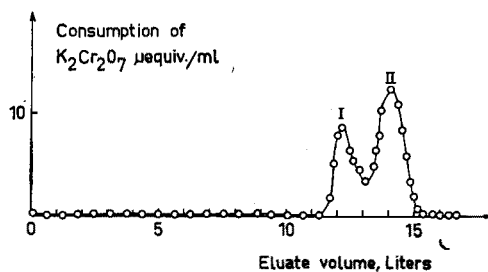


Fig. 4. Separation of lactic (I) and glycolic (II) acids. Eluant: 0.02 *M* $\text{Na}_2\text{B}_4\text{O}_7$. Flow rate: 0.3 $\text{ml cm}^{-2}\text{min}^{-1}$.

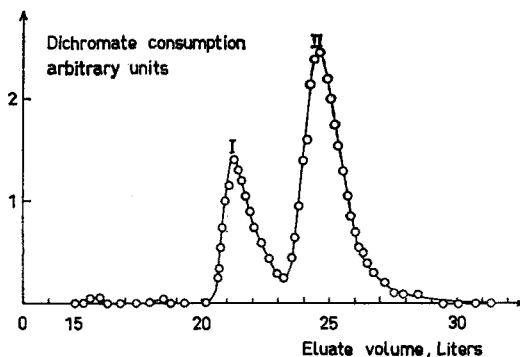


Fig. 5. Separation of lactic (I) and glycolic (II) acids. The dichromate consumption was recorded by the Autoanalyzer and is given in cm indicated on the paper strip. Eluant: 0.015 *M* $\text{Na}_2\text{B}_4\text{O}_7$. Flow rate: 0.3 $\text{ml cm}^{-2}\text{min}^{-1}$.

to permit a rough determination of the two acids. As may be seen from Fig. 5, the eluate volumes are so large that this method cannot be recommended for separations of lactic and glycolic acids for practical purposes.

It should be mentioned that the separation of α,β -dihydroxyisobutyric and β,γ -dihydroxybutyric acids has also been studied with eluants containing sodium tetraborate and boric acid. The results were less satisfactory than those obtained with pure sodium tetraborate solutions.

With complicated mixtures containing for instance lactic, glycolic, as well as the two dihydroxybutyric acids together with saccharinic acids with 5 and 6 carbon atoms it is recommended to make a stepwise elution with borate solution of increasing concentration. In the first step it is recommended to use a 0.04 *M* solution; and after the elution of β,γ -dihydroxybutyric acid, the concentration should be increased to 0.07 *M* in order to speed up the elution of the higher saccharinic acid. In such experiments it was observed that when a repacked column was used for the first time the separation was poorer than it was after a number of runs. Table I shows the number of theoretical plates in a column after a varying number of runs. The number of

TABLE I
NUMBER OF THEORETICAL PLATES IN VARIOUS RUNS AFTER REPACKING THE COLUMN
Elution with 0.07 *M* Na₂B₄O₇; flow rate: 0.3 ml cm⁻² min⁻¹

Run number	Number of theoretical plates
1	350
2	450
3	600
4	1000
8	1020
17	960

theoretical plates was calculated according to the plate theory³ from the width of the isosaccharinic acid band. It is seen that in the fourth run the number of theoretical plates was almost three times higher than in the first run. The conditions were then stabilized and the column exhibited an almost constant behavior during a great number of runs. To avoid difficulties when using freshly packed columns it is recommended to pass a large volume of eluant through the column at high speed so that the resin bed becomes closely packed before the column is employed for difficult chromatographic separations.

ACKNOWLEDGEMENT

The financial support of the Swedish Technical Research Council is gratefully acknowledged.

SUMMARY

Factors affecting the chromatographic separation of hydroxy acids by means of anion exchange resins in the borate form have been studied. With the acids studied the separation factor increases for a decreased borate concentration in the eluant. With complicated mixtures it is recommended to employ stepwise elution with solutions of increasing concentration.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Faktoren, welche die chromatographische Trennung von Oxy-säuren mit Anionenaustauschern in der Borat-Form beeinflussen. Geringere Boratkonzentration im Eluierungsmittel ergibt einen höheren Trennungsfaktor.

RÉSUMÉ

Une étude a été effectuée sur les divers facteurs pouvant influencer la séparation chromatographique des hydroxyacides au moyen d'échangeurs d'anions, étant des résines sous forme de borates.

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THE SORPTION OF POLYMETAPHOSPHATE ON ANION EXCHANGE RESINS

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(Received December 1st, 1961)

As demonstrated by SAMUELSON¹, anion exchange resins can be used for the separation of high polymer anions from common anions. This is explained by the fact that the network structure of the resin is too narrow to permit a penetration of the high polymer anions into the resin particles. Such separations are quite successful with many polyelectrolytes² provided that the conditions are chosen so that a decomposition of the macro-anion is avoided and that the adsorption at the surface of the resin particles is negligible³.

Although, under certain working conditions, polymetaphosphate is only slightly affected by anion exchange resins^{4,5} it is noteworthy that this polyelectrolyte can be retained quantitatively when other conditions are chosen. As demonstrated by PETERS AND RIEMAN⁶, polymetaphosphate can be taken up quantitatively by means of a strongly basic anion exchange resin in its chloride form and is held so strongly by the resin that it cannot be eluted completely unless the polymetaphosphate is decomposed. The aim of the present work is to elucidate further the behavior of strongly basic anion exchange resins in polymetaphosphate solutions and to draw attention to a source of error which can appear when anion exchange resins are used in certain separations where polymetaphosphate is involved.

EXPERIMENTAL

Sodium polymetaphosphate was prepared by melting sodium dihydrogen phosphate in a platinum dish for 2 h at 750° and chilling rapidly in ice water.

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Six ion exchange columns of standard type were filled with weighed amounts of Dowex 1-X8 (Cl^- ; 100–200 mesh). The height and diameter of the columns were 110 and 9 mm respectively.

The exchange capacity was determined by eluting the chloride ions from two columns with 300 ml of 1 *M* ammonium nitrate solution and subsequent titration with silver nitrate. The deviation between the two determinations was less than 1%. The capacity of the other four columns was calculated from the average.

The chloride determinations in solutions containing polymetaphosphate were made after hydrolysis with nitric acid.

In the phosphorus determination a sample (containing a maximum of 0.5 mg P) was hydrolyzed with 5 ml of concentrated nitric acid in a 100-ml volumetric flask at 100° for 30 min. After cooling, 25 ml of a mixed reagent (ammonium molybdate and ammonium vanadate)⁷ was added and the volume adjusted to 100 ml. In order to avoid excessive acidity in the final solution⁸, the mixed reagent contained only half the recommended quantity of nitric acid. The transmission was measured in a Beckman DU spectrophotometer. Standard solutions were prepared from sodium dihydrogen phosphate, and analyzed at the same acid concentration.

The determinations of sodium and potassium were carried out in a Beckman DU spectrophotometer with a flame attachment.

RESULTS AND DISCUSSION

While it has been demonstrated that polymetaphosphate can be taken up quantitatively by means of an excess of Dowex 1 in the chloride form no experiments have been published which demonstrate the total amount of polymetaphosphate which can be taken up by a given amount of resin. Preliminary experiments showed that the uptake of polymetaphosphate from sodium polymetaphosphate solution was greater than the exchange capacity. It could, therefore, be assumed that the polymetaphosphate taken up by the resin retained a certain amount of sodium ions which could not be removed by washing with water. This is confirmed by the results presented in Table I, which show that columns pretreated with excess sodium polymetaphosphate

TABLE I
UPTAKE OF SODIUM POLYMETAPHOSPHATE ON DOWEX 1-X8 (Cl^-)

	Column 1	Column 2
Exchange capacity, mequiv.	11.61	11.63
Pretreatment, ml 0.2 <i>N</i> (NaPO_3) _n	1000	1500
Elution, ml 1 <i>M</i> NH_4NO_3	300	200
NH_4NO_3 -eluate: Cl mmoles	0.0	0.0
P mmoles	11.13	11.04
Na mmoles	1.28	1.49
Hydrolyzate: Cl mmoles	0.0	0.0
P mmoles	1.67	1.91
Na mmoles	0.004	0.003
Total P mmoles	12.80	12.95

and carefully washed with water retained a large amount of sodium ions. The sodium ions were eluted quantitatively with 1 *M* ammonium nitrate solution which also

eluted most of the phosphate. Subsequently, the resin was removed from the column and treated with 80 ml of 3 *M* nitric acid at 82° for 50 h to hydrolyze the polymetaphosphate remaining in the resin. The hydrolyzate was separated from the resin by filtration.

The hydrolyzate contained negligible amounts of sodium and about 14% of the total amount of phosphate taken up. Both the eluate and the hydrolyzate were free from chloride ions. The total number of mmoles of phosphorus taken up by the resin was about 11% higher than the exchange capacity of the column. The difference between these quantities was, within the limits of experimental errors, equivalent to the amount of sodium ions retained in the column.

It might, of course, be expected that the sodium ions held by the polymetaphosphate form of the resin could be exchanged for other cations, *i.e.*, that the resin would behave as a cation exchanger. To study this question two columns filled with the chloride form of the resin were treated with polymetaphosphate and washed carefully with water. Subsequently, the columns were treated with 2.3 l of 0.1 *M* potassium chloride and washed carefully with water. A chloride solution was chosen instead of nitrate because the chloride ions exhibit a lower ion exchange affinity than nitrate ions. As may be seen in Table II, less than 10% of the phosphorus was obtained in this eluate. After hydrolysis with 80 ml of 3 *M* nitric acid as described above, the hydrolyzate was analyzed. An appreciable amount of potassium was found in the hydrolyzate, whereas the sodium content was negligible. The results confirm that an anion exchange resin pretreated with polymetaphosphate solution acts as a cation exchanger.

TABLE II
EXCHANGE OF SODIUM FOR POTASSIUM ON DOWEX I-X8
(pretreated with sodium polymetaphosphate)

	Column 3	Column 4
Exchange capacity, mequiv.	11.73	11.63
Pretreatment, ml 0.2 <i>N</i> (NaPO ₃) _n	1500	1000
Treatment, ml 0.1 <i>M</i> KCl	2300	2300
KCl-eluate: P mmoles	1.02	1.01
Hydrolyzate: P mmoles	11.61	11.70
Na mmoles	0.003	0.006
K mmoles	0.47	0.48

It is evident that this behavior of anion exchange resins with solutions containing polymetaphosphate can give rise to serious errors in separations where it is desired to apply anion exchange resins to remove ions which interfere in the determination of various cations, for instance, the alkali metals. With cation exchange resins no complications of this type occur⁹ and it is, therefore, recommended to use cation exchange resins instead of anion exchangers when it is desired to separate cations from anions in solutions containing polymetaphosphate.

ACKNOWLEDGEMENT

The financial support of the Swedish Technical Research Council is gratefully acknowledged.

SUMMARY

From a solution of sodium polymetaphosphate, strongly basic anion exchange resins can retain a greater amount of polymetaphosphate than that corresponding to the exchange capacity. Sodium ions are held by the polymetaphosphate form of the resin and these sodium ions can be exchanged for other ions.

RÉSUMÉ

Les auteurs ont effectué une recherche sur l'adsorption de polymétaphosphate sur des résines, échangeurs d'anions, fortement basiques. On constate que la quantité adsorbée dépasse la capacité de la résine.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Adsorption von Polymetaphosphat an stark basischen Anionenaustauschern. Es wird gezeigt dass der Austauscher eine grössere Menge Polymetaphosphat zurückhält als seiner Kapazität entspricht.

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THE METAL COMPLEXES OF SOME AZO AND AZOMETHINE DYESTUFFS

PART II¹. DETERMINATION OF STABILITY CONSTANTS, AND PREPARATION OF SOLID COMPLEXES

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(Received September 20th, 1961)

STABILITY CONSTANTS OF METAL COMPLEXES

The constants obtained in this work are practical stability constants obtained by potentiometric titration, following the methods outlined by IRVING AND ROSSOTTI². Except with benzeneazoresorcinol all constants were measured at a constant ionic strength of 0.1. With the latter compound $\mu \rightarrow 0$ as the ligand precipitated in solutions of higher ionic strength. All ligands except (I) are insoluble in water, and stability constants were therefore determined in 1:1 dioxan/water mixtures; for reagent (I) the constants were also determined in water. The titration technique is described in the experimental section.

Stability constants were obtained from the formation curves by the methods discussed by IRVING AND ROSSOTTI³. Where $K_1/K_2 < 10^{2.5}$ the "Correction Term" method was used; where $10^{2.5} < K_1/K_2 < 10^5$, or where the curve was unsymmetrical the method of interpolation at $\frac{1}{2} \bar{n}$ values was used. Finally, where $K_1/K_2 > 10^5$, the method of interpolation at a variety of \bar{n} values was used.

Because of the low solubility in water of the metal complexes, the overall concentration of 4-(2-pyridylazo)-resorcinol was $2.25 \cdot 10^{-4} M$, and the overall concentration of metal ions was half this value. At this dilution it was difficult to obtain

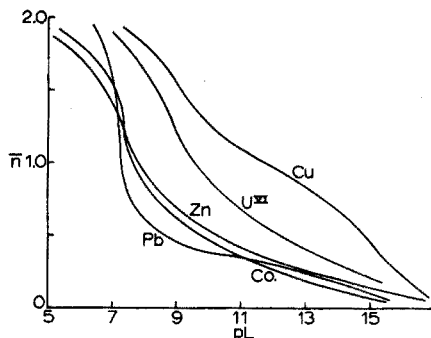


Fig. 1. Formation curves for 4-(2-pyridylazo)-resorcinol chelates in water.

reproducible titration curves; because of the low concentration of ligand, the pH drop caused by release of hydrogen ions on chelation was small, so that the smallest error in reading a pH value resulted in a much greater overall error than if the pH drop had been larger. With all metal ions studied, several titrations were necessary before satisfactory curves were obtained. However, except for nickel(II), formation curves for all the complexes were obtained, and though the values of the stability constants obtained are subject to a wider error than is desirable (± 0.3 unit), they served the purpose of this investigation. The formation curves for 4-(2-pyridylazo)-

TABLE I
STABILITY CONSTANTS OF 4-(2-PYRIDYLAZO)-RESORCINOL IN WATER

M^{++}	Cu	UO ₂	Zn	Co	Pb
log K_1	14.8	12.5	10.5	10.0	8.6
log K_2	9.1	8.4	6.6	7.1	7.1(?)

resorcinol and the metal ions studied are plotted in Fig. 1, and the stability constants are listed in Table I. The values of the proton-ligand stability constants used in calculation of pL were:

$$\log {}^cK_1^H = 12.31 \text{ (spectrophotometric value)}^1; \log {}^cK_2^H = 5.50; \log {}^cK_3^H = 2.69$$

The interpretation of these values of stability constants in terms of the chelating structures of the ligands studied will be considered later in the discussion.

The experimental data for copper(II) and cobalt(II) yielded normal formation curves, but with zinc(II) and uranium(VI), although a symmetrical pattern was followed, the experimental points were not all exactly on the curve. The curve for lead was not strictly symmetrical, the second molecule of ligand appearing to be attached much more rapidly than the first. The most unusual behaviour was exhibited by nickel(II). Chelation occurred normally up to pH 4.50, when the pH gap between the ligand titration curve and the curve in the presence of nickel(II) began to decrease rapidly. This continued until at pH 6.50, \bar{n} had dropped to 0.137. Thereafter the pH gap increased, and titration proceeded normally; this behaviour occurred reproducibly in every titration with nickel(II), and because of this no formation curve is drawn. It should be noted that the visible spectrum of the nickel(II) complex was also found to be unusual¹, there being no appreciable absorption below pH 6.0.

The high order of stability of the complexes agrees with our observations, and those of WEHBER⁴, that under normal conditions 4-(2-pyridylazo)-resorcinol can only be used as a metal indicator in the complexometric titration of lead. The value of log K_1 for the lead(II) complex does not agree with that found by KRISTIANSEN *et al.*,⁵ who, making the assumption that only a 1:1 complex is formed, calculate a value of $3.0 \cdot 10^6$ from spectrophotometric data. Even in 1:1 dioxan/water the maximum concentration of ligand (I) which could be used without precipitation was $6.0 \cdot 10^{-4} M$, though the data obtained yielded more accurate formation curves than the data obtained for titration in water. The values of the proton-ligand stability constants used in the calculation of pL were respectively: 13.00 (spectrophotometric value),¹

7.15, and 2.41 (potentiometric values). As is shown in Fig. 2, the formation curves for copper(II), cobalt(II), zinc(II) and uranium(VI) are of the required symmetrical form. At this concentration level the lead(II) complex was insoluble, and as with titrations in water, the values of \bar{n} for nickel(II) did not increase steadily with pH. No formation curve could be drawn. The values of $\log K$ for the first four ions are given in Table II.

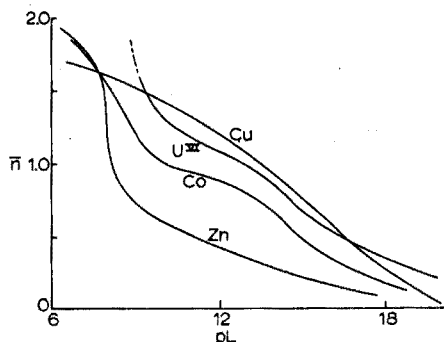


Fig. 2. Formation curves for 4-(2-pyridylazo)-resorcinol chelates in 1 : 1 v/v dioxan/water.

TABLE II

STABILITY CONSTANTS OF 4-(2-PYRIDYLAZO)-RESORCINOL IN 1 : 1 DIOXAN/WATER

M^{++}	Cu	UO_2	Co	Zn
$\log K_1$	16.4	16.2	14.8	11.2
$\log K_2$	8.9	9.6	8.2	7.8

The observed increase in $\log K$ on change from water to mixed solvent has been noted previously⁶ for a large number of organic ligands.

With benzeneazoresorcinol at the concentration level employed ($1.7 \cdot 10^{-3} M$) precipitation of the metal complexes greatly limited potentiometric studies. Lead(II) and uranium(VI) formed insoluble precipitates at this concentration, and precipitation occurred with copper(II) by $\bar{n} = 0.5$. With cobalt, as \bar{n} became > 1.0 , the readings of pH showed a tendency to drift back to more acid values. This behaviour has been noted previously by SNAVELY⁷ for, e.g., *o-o'*-dihydroxyazo dyestuffs, and attributed to formation of a cobalt(III) complex.

The values of $\log {}^cK_1^H$ used in calculation of pL were respectively: 13.60 (spectrophotometric value)¹, and 8.33 (potentiometric value). Formation curves were obtained for zinc(II) and nickel(II) in the usual way, and for copper(II) as far as $\bar{n} =$

TABLE III

STABILITY CONSTANTS OF BENZENEAZORESORCINOL IN 1 : 1 DIOXAN/WATER

M^{++}	Cu	Zn	Ni
$\log K_1$	13.9	10.8	8.2
$\log K_2$	—	11.9	9.1

0.6. A value of $\log K_1$ (Cu) was obtained at $\bar{n} = 0.5$, but a stability constant obtained from such a small portion of the formation curve is subject to an error probably as high as 0.5 unit. The values of $\log K$ are given in Table III.

As expected for a simple bidentate *o*-hydroxyazo dyestuff the 2:1 complexes are more stable than the 1:1 complexes. The zinc(II) complexes are appreciably more stable than the nickel(II) complexes — a reversal of the usual order. The coordination buffer region with zinc(II) was very marked, and the formation curve well defined.

In titration of salicylidene-2-aminopyridine (II) it was possible to maintain a higher overall concentration of ligand ($5 \cdot 10^{-3} M$); the experimental error in measurement of pH was therefore a lower fraction of the pH drop on chelation, with a consequent increase in the overall accuracy. On calculation of the proton-ligand stability constants (9.77, 6.37), it followed that only one proton was added to the ligand, as with 4-(2-pyridylazo)-resorcinol. The stability constants for copper(II), nickel(II), and cobalt(II) were accurately obtained; there was precipitation with uranium(VI) by $\bar{n} = 1.0$, and only $\log K_1$ could be obtained. Because of precipitation no values could be obtained for lead(II). The formation curve with zinc(II) was unsymmetrical; the buffer zone of co-ordination of the 1:1 complex was very marked, but the second molecule of ligand was added rather more slowly. The values of the stability constants obtained are given in Table IV.

TABLE IV
STABILITY CONSTANTS OF SALICYLIDENE-2-AMINOPYRIDINE IN 1:1 DIOXAN/WATER

M^{++}	Cu	Co	Ni	Zn	UO ₂
$\log K_1$	7.3	5.3	4.9	5.8	8.1
$\log K_2$	5.1	5.0	4.1	4.3	—

Even if zinc(II) is excluded on the grounds of the unsymmetrical formation curve, the IRVING-WILLIAMS order of stabilities⁸ is surprisingly not followed, for $\log K$ is greater for cobalt(II) than for nickel(II), and is greater for uranium(VI) than for copper(II). The first deviation is almost certainly explained by formation of a cobalt(III) complex, for many cobalt(III) complexes of salicylidene-imino compounds are known. The reason for $\log K_1(\text{UO}_2^{2+})$ being greater than $\log K_1(\text{Cu}^{2+})$ is less easy to decide, though this behaviour has been noted previously⁹ for the complexes of benzeneazo-*m*-cresol-4-sulphonate. In both of these compounds chelation is essentially between the *o*-hydroxyl group and the azo or imine nitrogen farthest from this hydroxyl group.

In the determination of the stability constants of 2-(*o*-hydroxy-phenyl-imino-

TABLE V
STABILITY CONSTANTS OF 2-(*o*-HYDROXY-PHENYL-IMINO-METHYL)-PYRIDINE IN 1:1 DIOXAN/WATER

M^{++}	Cu	Ni	UO ₂	Co	Zn	Pb
$\log K_1$	13.8	12.9	12.4	12.2	10.8	10.9
$\log K_2$	6.4	8.3	(9.1)	6.8	8.0	—

methyl)-pyridine (III) it was again possible to maintain a ligand concentration of $5 \cdot 10^{-3} M$, and the same remarks as to overall accuracy apply [see compound (II)]. In contrast with the isomer (II), *two* protons were added to the ligand in acid solution, the values of the ligand-proton stability constants being 11.80 (hydroxyl ionisation), 4.45, and 3.05. This effect will be fully considered in the discussion. The formation curves obtained are plotted in Fig. 3, and the stability constants are listed in Table V.

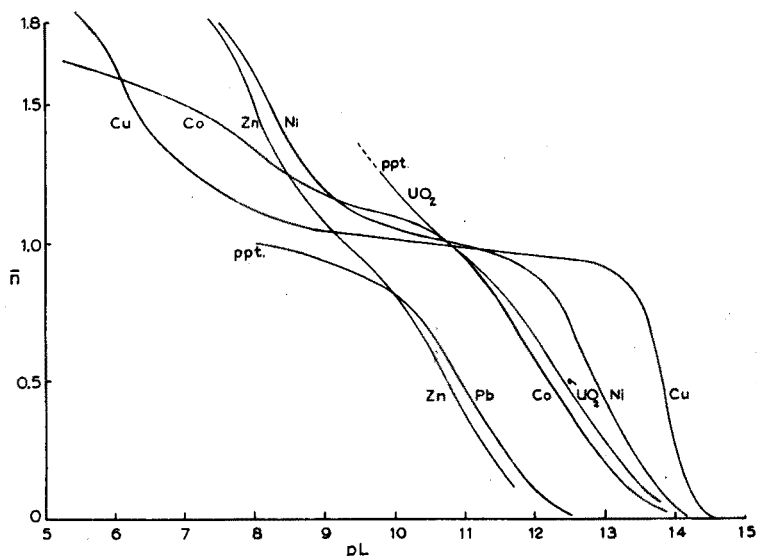
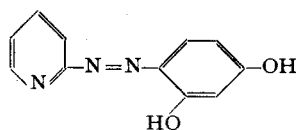


Fig. 3. Formation curves for 2-(*o*-hydroxy-phenyl-imino-methyl)-pyridine chelates in 1:1 *v/v* dioxan/water.

The IRVING-WILLIAMS order⁸ is seen to hold exactly for the 1:1 complexes, but the resistance of copper to forming a 2:1 complex with this terdentate ligand breaks up the order for both $\log K_2$ and $\log \beta_2$ (see Discussion).

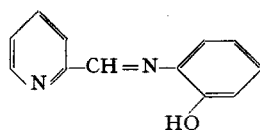
DISCUSSION

From the experimental results coordination by 4-(2-pyridylazo)-resorcinol (I) involves the pyridine nitrogen, the *o*-hydroxyl group, and the azo nitrogen farthest from the heterocyclic ring. Thus $\log K_1$ (Cu) for this ligand (16.43) is greater than that for 2-(*o*-hydroxyl-phenyl-imino-methyl)-pyridine (13.84), which in turn is very much greater than for salicylidene-2-aminopyridine (7.30):



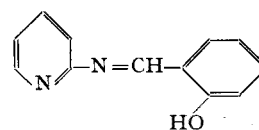
(I)

$$\log K_1(\text{Cu}) = 16.43$$



(III)

$$13.84$$



(II)

$$7.30$$

The value of $\log K_1$ for the imine (III) is almost double that of its isomer (II), and is clear evidence in favour of chelation involving two five-membered rings rather than

one six- and one four-membered ring. Further evidence of the terdentate nature of 4-(2-pyridylazo)-resorcinol, and the greater part in chelation of the azo nitrogen farthest from the heterocycle, may be adduced from the decrease in stability on change from a 1:1 to a 2:1 complex. Thus in the terdentate ligands (I) and (III) the value of $(\log K_1 - \log K_2)$ is large and almost equal (7.51 and 7.49 respectively). On the other hand, for the imine (II), in which the other imine nitrogen is involved and the bidentate arrangement is more favoured, the value of $(\log K_1 - \log K_2)$ is much smaller, *i.e.* 2.19. Further, whilst $(\log K_1 - \log K_2)$ is large for copper(II) with compounds (I) and (III), it is smaller for those ions more ready to be six-covalent. For example, with compound (III), the value of $(\log K_1 - \log K_2)$ is 7.49 for copper(II), 5.38 for cobalt(II) and 4.64 for nickel(II). Similarly, whilst the IRVING-WILLIAMS order holds for $\log K_1$ with both of these ligands, it is broken for $\log K_2$ and $\log \beta_2$.

The role of the *o*-hydroxyl group in 4-(2-pyridylazo)-resorcinol is readily apparent by comparison of the value of $\log K_1$ (Cu) for this ligand (16.43), with the value obtained by KLOTZ *et al.*¹⁰ for 2-*p*-dimethylaminophenyl-azo-pyridine. In the latter compound, chelation is bidentate between the pyridine nitrogen and the azo nitrogen farthest from the heterocycle, and $\log K_1$ (Cu) in aqueous media is 5.22. Even on allowing for the usual increase on change to mixed solvent, $\log K_1$ is still far below the value for compound (I).

The high value of $\log K_1$ (Cu) for benzeneazoresorcinol (13.9) calls for comment. Because of the strength of the bond from the pyridine nitrogen in chelation by compound (I), it might have been expected that the value of $\log K_1$ for the benzene analogue would be much lower. However, this is not so, since 4-(2-pyridylazo)-resorcinol is so strongly terdentate, and the benzene analogue strongly bidentate (moreover to the other azo nitrogen to that chiefly used in 4-(2-pyridylazo)-resorcinol), that any strict comparison would lead to errors in interpretation.

It was noted in the experimental work that the imine (II) adds only one proton, whilst the isomeric imine (III) adds two protons. ANGYAL *et al.*,¹¹ have suggested that 2-aminopyridine has a resonating structure as a result of which a proton preferentially attaches at the pyridine nitrogen. Hence this compound is a stronger base than pyridine. Exactly similar resonance may arise for salicylidene-2-aminopyridine (II), and, as verified experimentally, this compound is again a stronger base than pyridine. With 2-(*o*-hydroxyl-phenyl-imino-methyl)-pyridine (III) this resonance relationship between the two nitrogens cannot arise. By contrast with the isomer (II) therefore, the nitrogens would be expected to be more feebly basic and both potentially capable of adding a proton. The experimental results confirm this point.

Preparation of solid copper(II) complexes

4-(2-Pyridylazo)-resorcinol and 2-(*o*-hydroxyl-phenyl-imino-methyl)-pyridine have been previously shown^{12,13} to form stable 1:1 complexes with copper(II), the ligands being terdentate. This work has been confirmed. Similarly, copper(II) complexes of *o*-hydroxylazo dyestuffs have been prepared by many workers (see, for example, DREW *et al.*,¹⁴ or ELKINS AND HUNTER¹⁵) and shown to be 2:1 complexes, the ligand being bidentate. This has been shown to be true also for copper(II) and benzeneazoresorcinol.

From the stability constant measurements described above, it seemed likely that salicylidene-2-aminopyridine would form a 2:1 complex. However, only a 1:1

complex could be isolated, and it seems that the ligand is more strongly terdentate in the solid state than in solution.

The melting points of the complexes form an interesting series. The copper(II) complex with 4-(2-pyridylazo)-resorcinol did not melt below 270°, whereas that with the benzene analogue melted at 185° — a clear indication of the contribution of the pyridine nitrogen to coordination by the former compound. Further, the complexes of the imines (II) and (III) melted at almost identical temperatures. This confirms the view that in the solid state, the two imine nitrogens play an almost equal part in chelation. Thus by analogy it seems that in the solid state, both the azo nitrogens in 4-(2-pyridylazo)-resorcinol play an equal part in chelation, *i.e.* that co-ordination should be considered a function of the azo group as a whole rather than of one of the component nitrogen atoms. The fact that the copper(II) complex of compound (I) has a melting point at least 60° higher than the complexes of the imines (II) and (III) lends support to this idea.

EXPERIMENTAL

Potentiometric measurements

Measurements in water were made using an "E.I.L." 23A pH-meter fitted with an "E.I.L." glass and calomel electrode system enclosed in a polythene sheath. Measurements in dioxan/water were made using a "Cambridge" bench-type pH-meter fitted with a dip-type calomel electrode and a "yellow-cap" glass electrode. The two electrodes were sealed into ground glass joints which fitted into the necks of a glass titration cell. The latter was also fitted with a neck into which was placed a gas bubbler, so that the titration solutions could be stirred by, and maintained under, a stream of oxygen-free nitrogen. The nitrogen was presaturated by bubbling through solvent of the same composition as the titration solution, and the titration vessel was clamped in a thermostat at $25^\circ \pm 0.1^\circ$. The titration cell also had a pin-hole through which increments of standard alkali were added from an "Agla" micrometer syringe, horizontally mounted.

Titration solutions were prepared by mixing 25 ml of aqueous solution with 25 ml of dioxan containing the appropriate concentration of ligand. (In the titrations in water the overall volume was 75 ml). The aqueous part of the mixture consisted of pipetted volumes of perchloric acid, sodium perchlorate, and the metal sulphate dissolved in distilled water. Metal ions were omitted in titration of ligand alone, and both metal ions and ligand were omitted in the acid reference curve. After thorough mixing of the reaction components, the solution was purged with nitrogen till the pH-meter reading was constant. The mixture was then titrated with increments of standard alkali.

Calibration of pH-meter readings in 1:1 dioxan/water

This was effected by titrating 50 ml of 1:1 dioxan/water at $\mu = 0.1$ with increments of standard perchloric acid. The resulting plot of measured pH against true pH was linear, of unit slope, and with intercept on the measured pH axis = + 0.032.

Ligands and reagents used

The preparation of the parent ligands and purification of the reagents used has

been described.¹ Perchloric acid was AnalaR concentrated acid, diluted to the appropriate strength.

Preparation of copper(II) complexes

The copper(II) complex of 4-(2-pyridylazo)-resorcinol was prepared as described by LUI¹² from the ligand and cupric nitrate. It was a dark red crystalline solid, m.p. $> 270^\circ$. (Found: Cu, 15.2; N, 13.5. Calc. for $C_{11}H_8N_3O_2Cu \cdot H_2O \cdot NO_3$: Cu, 15.1; N, 13.4).

The copper(II) complex of 2-(*o*-hydroxy-phenyl-imino-methyl)-pyridine was prepared as described by MUTO,¹³ from the ligand and cupric chloride. It was a dark brown crystalline solid. Melting (m.p. 224°) was preceded by darkening at 140° and slight decomposition at 210° . (Found: Cu, 19.2; N, 8.3. Calc. for $C_{12}H_9N_2OCuCl \cdot 2H_2O$: Cu, 19.1; N, 8.4).

The copper complex of benzeneazoresorcinol was prepared following a general method of ELKINS AND HUNTER.¹⁵ Benzeneazoresorcinol (2.14 g) was dissolved in absolute alcohol to which a little dioxan had been added, and copper acetate (1 g) in 50% aqueous alcohol was added dropwise with good stirring. The mixture was allowed to stand overnight and was then poured into water. The dark brown solid was collected, washed with alcohol (some dissolution), and water, and dried at 120° , m.p. 185° . (Found: Cu, 12.9; N, 11.2. $C_{24}H_{18}N_4O_4Cu$ requires: Cu, 13.0; N, 11.3).

The copper complex of salicylidene-2-aminopyridine was prepared as follows. Salicylidene-2-aminopyridine (1.68 g) was dissolved in the minimum of absolute alcohol, and to it was added cupric chloride (0.72 g.) in absolute alcohol. There was an immediate precipitation, and the mixture was then refluxed for 30 min. The filtered product was washed well with water and dried at room temperature. It was a black crystalline solid, m.p. 219° . (Found: C, 48.8; H, 3.1; N, 10.1; Cu, 21.6, Cl, 11.5; $C_{12}H_9N_2OCuCl$ requires: C, 48.7; H, 3.0; N, 9.5; Cu, 21.5, Cl, 11.7).

ACKNOWLEDGEMENTS

We are indebted to DR. J. F. W. McOMIE for helpful discussions, and to PROFESSOR W. C. FERNELIUS of the University of Pennsylvania for valuable advice. One of us, (W. J. GEARY) acknowledges financial help from D.S.I.R. during tenure of a Research Studentship.

SUMMARY

The stability constants of the complexes of 4-(2-pyridylazo)-resorcinol (I) with copper(II), cobalt(II), zinc(II), lead(II), and uranium(VI) were determined by potentiometric titration in aqueous media, and were shown to have very high values, the stability constant of the copper(II) complex approaching that of the copper(II)-EDTA complex. The nickel(II) complex was shown to behave anomalously. The stability constants were also determined by this method in 1:1 dioxan/water, and the values obtained compared with those for the complexes of salicylidene-2-aminopyridine (II), 2-(*o*-hydroxy-phenyl-imino-methyl)-pyridine (III), and benzeneazoresorcinol (IV). It is shown that chelation by (I) is terdentate, involving the pyridine nitrogen, the *o*-hydroxyl group and the azo nitrogen farthest from the heterocycle.

The solid copper(II) complexes of these four ligands were prepared; in the solid complexes the azo nitrogen nearest the heterocycle plays a greater part than in the complexes in solution.

RÉSUMÉ

Les auteurs ont effectué une détermination des constantes de stabilité des complexes du 4-(2-pyridilazo)-résorcinol avec le cuivre, le cobalt, le zinc, le plomb et l'uranium, par titrage potentiométrique.

métrique en milieu aqueux. Les complexes du cuivre avec ce réactif, le salicylidène-2-aminopyridine, la 2-(*o*-hydroxy-phényl-imino-méthyl)-pyridine, et le benzèneazoresorcinol ont été préparés à l'état solide et examinés.

ZUSAMMENFASSUNG

Es wurden die Stabilitätskonstanten der Komplexe von Kupfer, Kobalt, Zink, Blei und Uran mit 4-(2-pyridylazo)-resorcin durch potentiometrische Titration in wässrigem Medium bestimmt. Die Werte werden verglichen mit denen der Komplexe mit Salicyliden-2-aminopyridin, 2-(*o*-hydroxyphenyl-imino-methyl)-pyridin und Benz-azo-resorcin. Die Kupferkomplexe dieser Verbindungen wurden isoliert und untersucht.

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4-CARBOXY-1,2-CYCLOHEXANEDIONEDIOXIME COMPLEXES OF NICKEL(II) IN ALKALINE MEDIA*

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(Received December 10th, 1961)

INTRODUCTION

The determination of the stability constants of the nickel(II) complexes of the *vic*-dioximes in aqueous media is very difficult because of the slight solubility of the *vic*-dioximes and of the bis(*vic*-dioximato-N,N')nickel(II) complexes. Several papers¹⁻⁵ have been published concerning the stability constants of nickel(II) complexes of *vic*-dioximes in 50% dioxane-50% water mixtures. WENGER *et al.*⁶ determined the stability constants for the three complexes of nickel(II) with 1,2-diaminoethanedione-dioxime in acid medium.

OKÁČ AND ŠIMEK⁷ and GERMAN⁸ reported that nickel(II) complexes of *vic*-dioximes were not oxidized in concentrated alkaline media. Under these conditions then, it should be possible to study the unoxidized complexes of nickel(II) with certain *vic*-dioximes.

The difficulties due to limited solubility have been overcome by the synthesis of 4-carboxy-1,2-cyclohexanedionedioxime (4-carboxynioxime or 4-CN)⁹. The pK values⁹ were determined for the three acidic hydrogens of 4-carboxynioxime and the results obtained were: $pK_1 = 4.85$, $pK_2 = 10.45$, $pK_3 = 12.37$.

THEORY

The step-wise stability constants for the complex ions, NiD^- , NiD_2^{4-} , and NiD_3^{7-} , were calculated from spectrophotometric and magnetic susceptibility data. The system may be described in the following manner,

$$[Ni^{2+}]_t = \sum_{i=0}^I [NiD_i^{2-3i}] + [NiOH^+] + [Ni(OH)_2(s)] + [HNiO_2^-] \quad (1)$$

$$[D^{3-}]_t = [D^{3-}] + \sum_{i=1}^I i [NiD_i^{2-3i}] \quad (2)$$

$$A = \epsilon_1 l [D^{3-}] + \epsilon_2 l [NiD^-] + \epsilon_3 l [NiD_2^{4-}] + \epsilon_4 l [NiD_3^{7-}] \quad (3)$$

* Contribution No. 866 from the Ames Laboratory of the U.S. Atomic Energy Commission: Paper No. XXVI in a series on "*Chemistry of the vic-Dioximes.*" The two previous papers in this series are No. XXIV, *Talanta*, 2 (1959) 235 and No. XXV, *Anal. Chim. Acta*, 21 (1959) 308. Abstracted from dissertation submitted by J. P. LAPLANTE to graduate faculty of Iowa State University, in partial fulfillment of requirements for the degree of Doctor of Philosophy, 1960.

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$$k_t = \frac{[\text{NiD}_t^{2-3t}]}{[\text{NiD}_{t-1}^{5-3t}][\text{D}^{3-}]_t} \quad (4)$$

$$K_4 = \frac{[\text{NiOH}^+]}{[\text{Ni}^{2+}][\text{OH}^-]} = 2.3 \times 10^3 \quad (5)$$

$$K_5 = \frac{[\text{Ni}(\text{OH})_2(\text{s})]}{[\text{Ni}^{2+}][\text{OH}^-]^2} = 1.54 \times 10^{17} \quad (6)$$

$$K_6 = \frac{[\text{H}\text{NiO}_2^-]}{[\text{Ni}(\text{OH})_2(\text{s})][\text{OH}^-]} = 6.0 \times 10^{-5} \quad (7)$$

where t refers to total concentration and the step-wise stability constant of the i th complex is given by k_i . It may be shown that D^{3-} is the only significant *vic*-dioxime species present in solutions approximately 9 M in potassium hydroxide. The values of K_4 , K_5 , and K_6 were determined by GAYER AND GARRETT¹⁰ and GAYER AND WOONTNER¹¹.

An expression for $[\text{Ni}^{2+}]$ may be obtained by substituting equations 5, 6, and 7 into equation 1,

$$[\text{Ni}^{2+}] = \frac{[\text{Ni}^{2+}]_t - [\text{NiD}^-]}{(1 + K_4[\text{OH}^-] + K_5[\text{OH}^-]^2 + K_5K_6[\text{OH}^-]^3)} \quad (8)$$

If it is assumed that the concentrations of NiD_2^{4-} and NiD_3^{7-} are negligible when the *vic*-dioxime to nickel ratio is one, then from equations 2 and 3 an expression for $[\text{NiD}^-]$ may be obtained,

$$[\text{NiD}^-] = \frac{A - \epsilon_1 l [\text{D}^{3-}]_t}{\epsilon_2 l - \epsilon_1 l} \quad (9)$$

Then substituting equations 2 and 8 into equation 4, one obtains the following expression for k_1

$$k_1 = \frac{[\text{NiD}^-](1 + K_4[\text{OH}^-] + K_5[\text{OH}^-]^2 + K_5K_6[\text{OH}^-]^3)}{([\text{Ni}^{2+}]_t - [\text{NiD}^-])([\text{D}^{3-}]_t - [\text{NiD}^-])} \quad (10)$$

The stability constant, k_1 , may now be calculated knowing $[\text{OH}^-]$, $[\text{Ni}^{2+}]_t$, $[\text{D}^{3-}]_t$, K_4 , K_5 , K_6 , and obtaining $[\text{NiD}^-]$ from equation 9. The following expression is obtained by subtracting equation 1 from equation 2,

$$[\text{D}^{3-}]_t - [\text{Ni}^{2+}]_t = \frac{[\text{D}^{3-}] + [\text{NiD}_2^{4-}] + 2[\text{NiD}_3^{7-}] - [\text{Ni}^{2+}]}{[\text{NiOH}^+] - [\text{Ni}(\text{OH})_2(\text{s})] - [\text{H}\text{NiO}_2^-]} \quad (11)$$

If it is assumed that $[\text{Ni}^{2+}] + [\text{NiOH}^+] + [\text{Ni}(\text{OH})_2(\text{s})] + [\text{H}\text{NiO}_2^-] \ll [\text{D}^{3-}]$ for high *vic*-dioxime to nickel ratios, and the expressions for $[\text{NiD}_2^{4-}]$ and $[\text{NiD}_3^{7-}]$ from equation 2 are substituted into equation 11, one can rearrange this equation to give the following expression for $[\text{D}^{3-}]$,

$$[\text{D}^{3-}] = \frac{-(1 + k_2[\text{NiD}^-]) + \{(1 + k_2[\text{NiD}^-])^2 + 8k_2k_3[\text{NiD}^-]([\text{D}^{3-}]_t - [\text{Ni}^{2+}]_t)\}^{\frac{1}{2}}}{4k_2k_3[\text{NiD}^-]} \quad (12)$$

The $[\text{D}^{3-}]$ was calculated by assuming reasonable values for k_2 and k_3 . The quantity, $[\text{NiD}^-]$, was obtained from magnetic susceptibility data. This value of $[\text{D}^{3-}]$ was used to calculate $[\text{NiD}_2^{4-}]$ and $[\text{NiD}_3^{7-}]$ in order to obtain $[\text{D}^{3-}]_t$ in equation 2. Then by an

iterative process, the best values for k_2 and k_3 were found, such that the computed $[D^{3-}]_t$ was within 1% of the experimental value. As a check, the values of k_1 , k_2 , and k_3 were used to calculate an absorption spectrum, which was compared with an experimentally obtained spectrum.

EXPERIMENTAL

Apparatus and materials

A Cary Recording Spectrophotometer, Model 14, was used to obtain all of the spectrophotometric data. Matched silica cells were used for the measurements in the ultraviolet, visible, and infrared regions. When required, silica slugs were used to give cell paths of 0.005, 0.02, 0.05, and 0.2 cm.

Magnetic susceptibility measurements were made on a Gouy type apparatus. This apparatus and its operation have been described by VANDER HAAR¹². The pH titrations were made using a Beckman Model G pH meter equipped with a Type E glass electrode.

Nickel(II) chloride stock solutions were prepared from special low-cobalt $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ obtained from the Baker Chemical Company. The solutions were prepared using deionized distilled water and were standardized by the heptoxime method¹³.

The 4-carboxy-1,2-cyclohexanedionedioxime was prepared in this Laboratory by the procedure of BANKS *et al.*⁹.

The potassium hydroxide was of certified reagent-grade quality and was obtained from Fisher Scientific Company. All other chemicals were of reagent-grade quality.

All computations were made on a Magnetic Drum Data-Processing Machine, Type 650, manufactured by International Business Machines Corporation.

The stock solutions were prepared by the following procedure. A weighed amount of 4-carboxynioxime was transferred to a 50-ml class A volumetric flask, an aliquot of standard nickel(II) chloride solution, 28 g of potassium hydroxide, and approximately 40 ml of distilled deionized water were added. The flask was placed in a cold water bath and shaken until the potassium hydroxide had dissolved. The solution was allowed to come to room temperature and then diluted to volume with distilled deionized water. It was transferred to a polyethylene bottle, with provisions for passing a gas continuously into it, and the bottle was then placed in a constant temperature bath. The temperatures used in this study were 25° and 50°. The solutions that were studied spectrophotometrically were prepared by removing 3-ml aliquots of the stock solution at various time intervals, diluting to a volume of 25 ml with 8.923 *M* potassium hydroxide and scanning immediately. The reference was air. All absorbancies were corrected for the absorbancy due to potassium hydroxide solutions.

Stoichiometry

In this investigation, an attempt has been made to show that there are three complex ions, NiD^- , NiD_2^{4-} and NiD_3^{7-} , present in concentrated alkaline media. To determine which absorption bands were due to the nickel(II) complexes of 4-carboxynioxime, two studies were made. In the first study, the stock solution was prepared in an atmosphere of helium. The concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were $1.446 \cdot 10^{-3}$, $1.446 \cdot 10^{-3}$ and 8.923 *M*, respectively, for Curve 1 of Figs. 1 and 2 and were $8.843 \cdot 10^{-3}$, $1.446 \cdot 10^{-3}$ and 8.923 *M*, respectively, for Curve 2 of Figs. 1 and 2. The solutions to be scanned were placed

in silica cells and sealed with Scotch Electrical Tape, No. 33. The solutions were scanned from 320–900 $m\mu$ at various intervals over a period of 96 h. The spectra did not change appreciably with time.

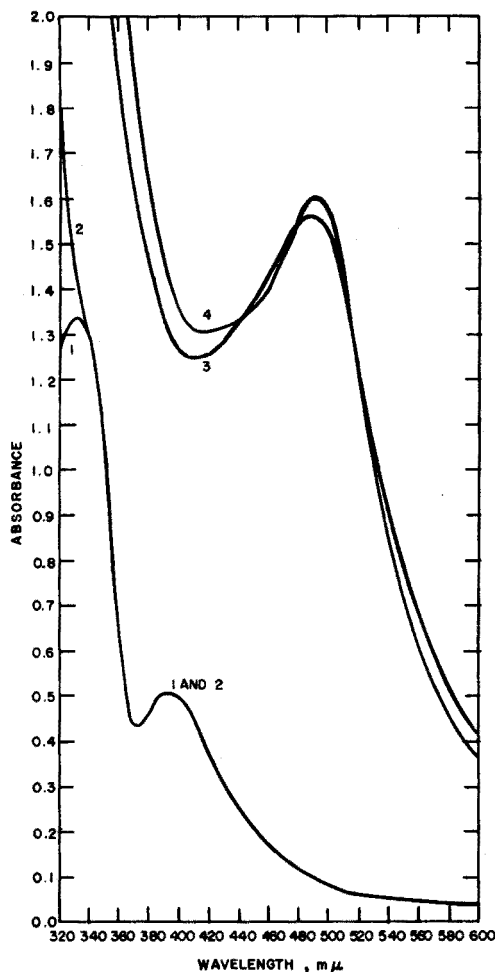


Fig. 1. Absorption spectra obtained from a rate study of a solution treated with oxygen. Cell length 0.2 cm. Curve 1, 0.0 h, $[4\text{-CN}] = [\text{Ni(II)}] = 1.446 \cdot 10^{-3} M$. Curves 2 (0.0 h), 3 (12.0 h), and 4 (29.0 h), $[4\text{-CN}] = 8.843 \cdot 10^{-3} M$, $[\text{Ni(II)}] = 1.446 \cdot 10^{-3} M$.

The second study was carried out at 50° in a similar manner, except that the cell was not sealed and oxygen was bubbled continuously through the stock solution. The concentrations of 4-carboxynioxime, nickel(II) chloride and potassium hydroxide were $8.843 \cdot 10^{-3}$, $1.446 \cdot 10^{-3}$, and $8.923 M$, respectively. The spectra obtained are shown in Curves 3 and 4 of Figs. 1 and 2.

Comparison of the absorption spectra obtained from the two studies indicates that the absorption bands at 335 and 393 $m\mu$ are due to nickel(II) complexes and the

absorption bands at 489 and 740 $m\mu$ are due to some oxidized complex of 4-carboxynioxime and nickel. The study also shows there is not a significant amount of the oxidized complex of 4-carboxynioxime and nickel(II) present immediately after preparation.

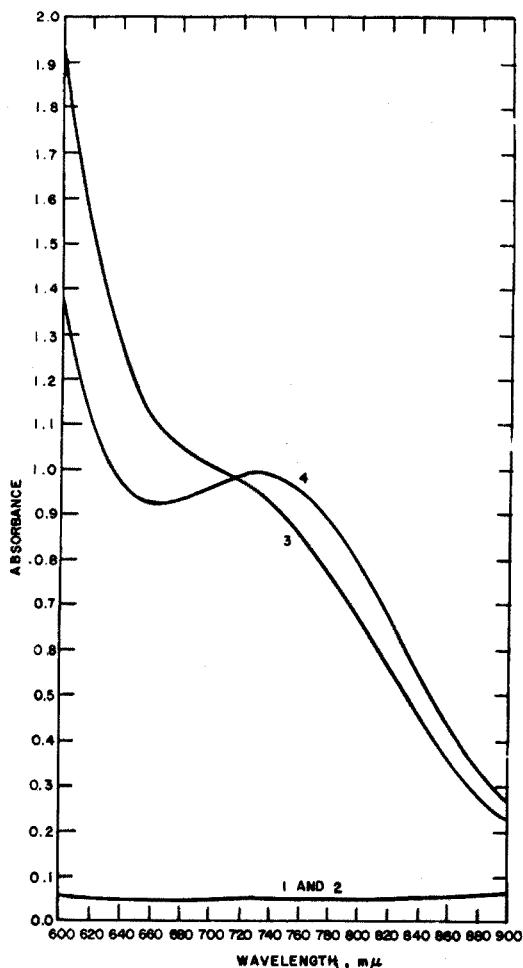


Fig. 2. Absorption spectra obtained from a rate study of a solution treated with oxygen. Cell length 1.0 cm. Curve 1, 0.0 h, $[4\text{-CN}] = [\text{Ni(II)}] = 1.446 \cdot 10^{-3} M$. Curves 2 (0.0 h), 3 (12.0 h), and 4 (29.0 h), $[4\text{-CN}] = 8.843 \cdot 10^{-3} M$, $[\text{Ni(II)}] = 1.446 \cdot 10^{-3} M$.

The *vic*-dioxime to nickel ratio in the nickel(II) complex was determined at 25° by the mole ratio method (Fig. 3). It was concluded that both the 335 and 393 $m\mu$ absorption bands were due to the NiD^- complex ion. There were no other changes in the slope of the lines in the mole ratio plots, thus complexes of higher 4-carboxynioxime to nickel ratios probably do not exist or they do not have any appreciable absorption in this region.

Magnetic susceptibility

Magnetic susceptibility measurements were made at 20° on a series of solutions immediately after they were prepared. The concentration of 4-carboxynioxime was varied from $4.727 \cdot 10^{-2}$ to $4.001 \cdot 10^{-1} M$, while the concentrations of nickel(II)

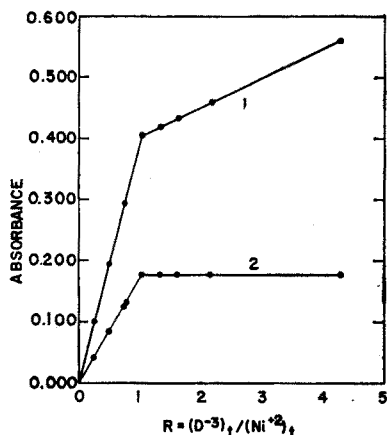


Fig. 3. Mole ratio plots for the determination of the 4-carboxynioxime to nickel(II) ratio. Curve 1, mole ratio plot obtained at 390 m μ . Curve 2, mole ratio plot obtained at 335 m μ .

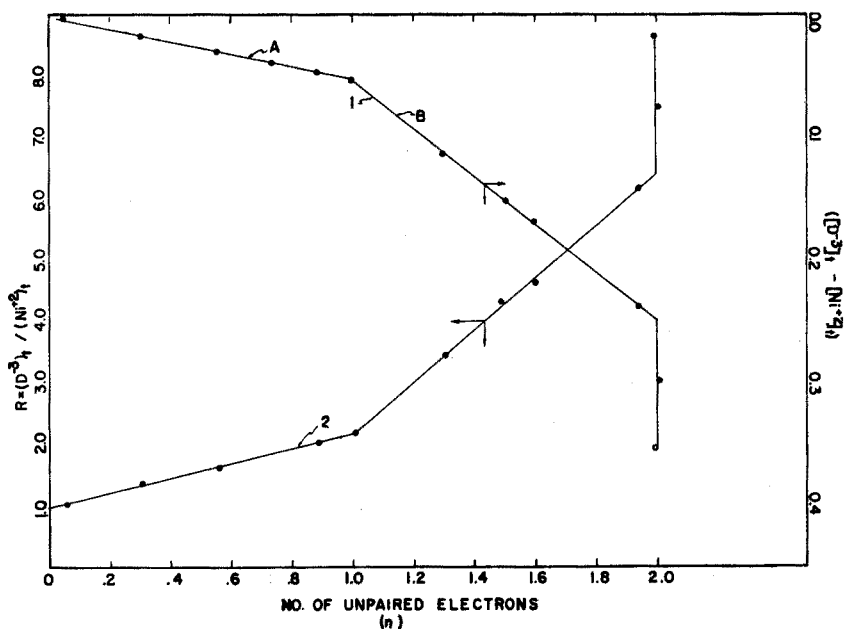


Fig. 4. Magnetic susceptibility measurements of 4-carboxynioxime-nickel(II) solutions.

chloride ($4.634 \cdot 10^{-2} M$) and potassium hydroxide ($8.923 M$) were held constant. The stock solutions were prepared by the procedure cited previously. The results are shown in Curve 2 of Fig. 4, from which it may be seen that the NiD^- complex ion is diamagnetic. The changes in the slope of the curve may be due to the formation of higher

complexes of 4-carboxynioxime and nickel. Three complexes could be formed having two unpaired electrons, a tetrahedral, NiD_2^{4-} , an octahedral, $\text{NiD}_2(\text{OH})_2^{6-}$ or an octahedral, NiD_3^{7-} . The change in slope at a ratio of *vic*-dioxime to nickel of approximately 2 : 1 may be the transition from the tetrahedral, NiD_2^{4-} , or octahedral, $\text{NiD}_2(\text{OH})_2^{6-}$, to the octahedral, NiD_3^{7-} . The magnetic susceptibility studies explain why CARLSON¹⁴ and GERMAN⁸ obtained unusual magnetic susceptibility data when the *vic*-dioxime to nickel ratios were between 1 : 1 and 4 : 1.

A study of the paramagnetic and diamagnetic nickel(II) complexes by MILLS AND MELLOR¹⁵ and SONE¹⁶ indicated that the diamagnetic complexes have an absorption band of appreciable intensity near 400 $m\mu$, while the paramagnetic complexes did not show any absorption in the region 250 to 600 $m\mu$. Similar results were observed in this study. The diamagnetic complex ion, NiD^- , had one absorption band at 393 $m\mu$, while the paramagnetic complexes did not exhibit any absorption bands in the region 250 to 600 $m\mu$.

Calculation of stability constants

The ϵ_1 of the *vic*-dioxime for each wave length was determined from a blank in which the 4-carboxynioxime and potassium hydroxide concentrations were $8.896 \cdot 10^{-3}$ and 8.923 *M*, respectively. The initial spectrum of a solution $1.446 \cdot 10^{-3}$, $1.446 \cdot 10^{-3}$, and 8.923 *M* in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively, was used to obtain A and ϵ_2 . It was assumed that the concentrations of NiD_2^{4-} and NiD_3^{7-} were not significant. With the $[\text{NiD}^-]$ obtained from equation 9 and K_4 , K_5 , and K_6 given previously, k_1 may be calculated from equation 10 for the corresponding wave lengths. The data are presented in Table I.

TABLE I
DETERMINATION OF k_1^a

$\lambda, m\mu$	A	ϵ_1 for D^{3-}	ϵ_2 for NiD^-	ϵ_3 for NiD_2^{4-} c	ϵ_4 for NiD_3^{7-} b	$\log k_1$
320	0.701	592.4	2461	4638	5902	28.73
330	0.710	205.7	2493	5106	4975	28.73
340	0.689	101.2	2419	5157	4532	28.73
350	0.584	62.39	2050	4098	3537	28.73
360	0.383	38.78	1345	2096	1956	28.73
370	0.292	21.36	1025	1433	1443	28.73
375	0.295	15.74	1036	1514	1478	28.73
380	0.308	10.12	1081	1797	1605	28.74
385	0.323	6.755	1134	1904	1687	28.74
390	0.332	3.934	1166	2055	1769	28.74
395	0.332	2.248	1166	2089	1773	28.74
400	0.330	1.686	1159	2067	1737	28.74
405	0.321	1.124	1127	1967	1668	28.74
410	0.304	1.124	1067	1791	1534	28.74
420	0.264	1.124	927.0	1405	1211	28.74
430	0.226	1.124	793.5	1055	948.2	28.74
440	0.197	1.124	691.7	799.9	763.2	28.74
450	0.180	2.482	632.0	681.1	615.5	28.74
460	0.161	2.248	566.3	415.8	478.7	28.74
470	0.148	2.248	519.7	263.0	372.8	28.74

TABLE I (continued)

$\lambda, m\mu$	A	ϵ_1 for D^{3-}	ϵ_2 for NiD^-	ϵ_3 for NiD_2^{4-} ^c	ϵ_4 for NiD_3^{7-} ^b	$\log k_1$
480	0.138	2.248	484.5	103.3	272.2	28.74
485	0.133	2.248	467.0	70.66	236.0	28.74
490	0.128	2.248	449.4	62.98	181.0	28.74
495	0.123	2.248	431.9	49.68	159.0	28.74
500	0.116	2.248	407.3	89.13	130.2	28.74
510	0.103	2.248	361.7	133.1	90.27	28.74
520	0.089	2.248	312.5	117.7	75.29	28.74
530	0.077	2.288	270.4	103.5	71.94	28.74
540	0.067	2.248	235.3	74.48	61.21	28.73
550	0.061	2.248	214.2	71.24	54.79	28.73
560	0.054	2.810	189.6	72.14	45.27	28.73
570	0.045	2.810	158.0	71.22	42.74	28.73
580	0.038	2.810	133.4	71.37	18.68	28.73
590	0.036	2.810	126.4	70.29	21.27	28.73
600	0.036	2.810	126.4	70.29	21.27	28.73

Av. $\log k_1 = 28.74 \pm 0.60$

Std. Dev. = 0.004

^a The absorption spectrum was obtained from a solution $1.446 \cdot 10^{-3} M$, $1.446 \cdot 10^{-3} M$, and $8.923 M$ in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, resp.

^b ϵ_4 was calculated from an absorption spectrum of a solution in which the *vic*-dioxime to nickel ratio was 6 : 1. The $[NiD_2^{4-}]$ was assumed to be negligible.

^c ϵ_3 was calculated from an absorption spectrum of a solution in which the *vic*-dioxime to nickel ratio was 2 : 1, using the values obtained previously for ϵ_1 , ϵ_2 , and ϵ_4 .

The values for k_2 and k_3 were obtained by the procedure cited previously. The $[D^{3-}]$ was calculated from equation 12. The concentration of NiD^- may be obtained from the difference between $[Ni^{2+}]_t$ and the sum of $[NiD_2^{4-}]$ and $[NiD_3^{7-}]$. The magnetic susceptibility is a direct measure of this sum, if it is assumed that the concentrations of Ni^{2+} , $NiOH^+$, $Ni(OH)_2(s)$ and $HNiO_2^-$ are not significant. The quantity $([D^{3-}]_t - [Ni^{2+}]_t)$, was calculated from either equation 13 or 14. The equation for the straight lines, A, and B of Curve 1 in Fig. 4 are,

$$n = 18.27 ([D^{3-}]_t - [Ni^{2+}]_t) + 0.0423 \text{ and} \quad (13)$$

$$n = 4.996 ([D^{3-}]_t - [Ni^{2+}]_t) + 0.754, \text{ respectively.} \quad (14)$$

With the value for $([D^{3-}]_t - [Ni^{2+}]_t)$ calculated from equation 13 and the corresponding values for the number of unpaired electrons (n), $[NiD^-]$, and the trial values for k_2 and k_3 , the best value for k_2 was found by holding the value of k_3 constant and varying the value of k_2 in equation 12. This value of $[D^{3-}]$ was used to calculate $[NiD_2^{4-}]$ and $[NiD_3^{7-}]$ in order to obtain $[D^{3-}]_t$ in equation 2. The value of k_2 was then adjusted so that the computed $[D^{3-}]_t$ in equation 2 was within 1% of the experimental value. Then with the same procedure and equation 14, the new value of k_2 was held constant and the value of k_3 adjusted. The iterations were continued until there were no changes in the values of k_2 and k_3 . The values for $\log k_2$ and $\log k_3$ are 0.76 ± 0.15 and 3.67 ± 0.73 , respectively.

It was found that the spectrum computed using the above values for k_1 , k_2 , and k_3

was almost identical with the experimental spectrum (Fig. 5). Therefore, the assumptions made concerning the NiD_2^{4-} and NiD_3^{7-} complex ions in the calculation of k_1 were justified.

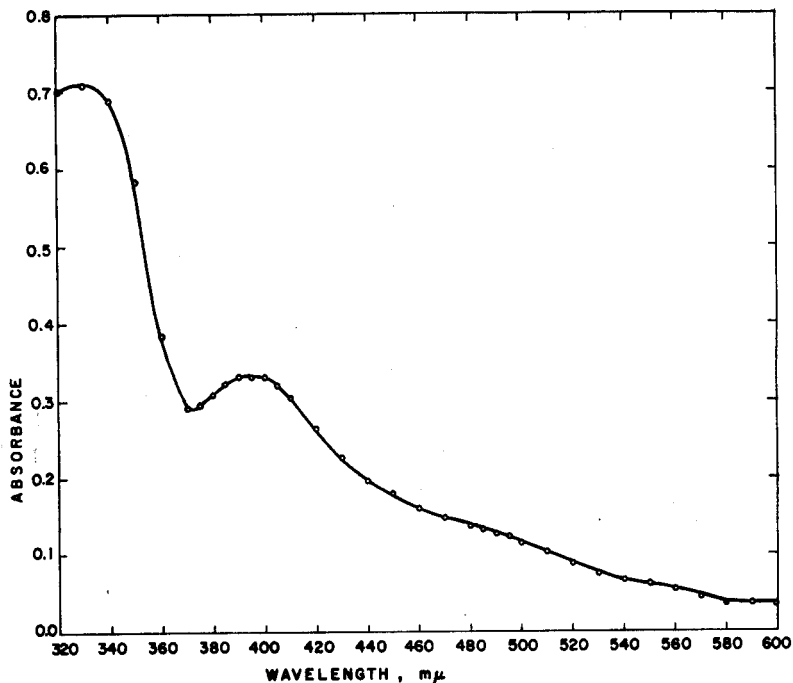


Fig. 5. Comparison of calculated and experimental absorption spectra; o-o-o- are the calculated values plotted on the experimentally recorded curve.

SUMMARY

The reactions of 4-carboxy-1,2-cyclohexanedionedioxime and nickel(II) were studied in alkaline media. Spectrophotometric studies indicate the presence of a 1:1 complex ion, NiD^- . Magnetic susceptibility measurements on a series of solutions of varying ratios of *vic*-dioxime and nickel(II) showed that the 1:1 complex ion was diamagnetic and that two paramagnetic complexes, probably NiD_2^{4-} and NiD_3^{7-} , are present in solution. The stability constants for the three complexes were calculated from spectrophotometric and magnetic susceptibility data. The $\log K$ values were found to be $\log K_1 = 28.74 \pm 0.60$, $\log K_2 = 0.76 \pm 0.15$, and $\log K_3 = 3.67 \pm 0.73$, respectively.

RÉSUMÉ

Les auteurs ont effectué une étude sur les réactions de la 4-carboxy-1,2-cyclohexanedionedioxime avec le nickel(II) en milieu alcalin. Les constantes de stabilité des trois complexes obtenus ont été déterminées par spectrophotométrie et mesures de susceptibilité magnétique.

ZUSAMMENFASSUNG

Die Reaktionen des Nickel-(2) mit 4-Carboxy-1,2-cyclohexan-dioxim in alkalischer Lösung wurden untersucht. Es wurden 3 Komplexe festgestellt, deren Stabilitätskonstanten auf Grund von spektrophotometrischen Daten und durch Messung der magnetischen Suszeptibilität berechnet wurden.

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Anal. Chim. Acta, 27 (1962) 80-89

Short Communications

The solvent extraction of some metal cupferrates with butanol

This communication records successful attempts to effect the quantitative separation of (1) titanium from zirconium or thorium, and (2) iron from aluminium, using cupferron as a complexing agent and butanol for solvent extraction. Further work is in progress.

GENERAL PROCEDURE

A saturated (0.4 to 0.5%) solution of cupferron in butanol was added to mixtures of the metal chlorides contained in separating funnels. After shaking, the metal contents of the aqueous and organic layers were separately determined. Brief details are given below.

Separation of titanium(IV) from zirconium(IV) or thorium(IV)

Mixtures containing known amounts of (1) titanic chloride and zirconyl chloride and (2) titanic chloride and thorium chloride, in approximately 0.1 *N* hydrochloric acid were separately examined. The pH of the mixtures was between 1.0 and 1.4. Titanium was determined gravimetrically in the alcohol layers by evaporation to dryness in a silica crucible followed by ignition to TiO₂.

Zirconium and thorium were determined in the respective aqueous layers, zirconium by precipitation as the double ammonium phosphate followed by ignition and weighing as ZrP₂O₇, and thorium by precipitation as oxalate, ignition at 1100° and weighing as ThO₂. Typical results obtained are given in Table I.

Iron(II and III), uranium(IV), manganese(II) and cadmium interfered in both separations; as little as 1 mg of titanium could be quantitatively extracted.

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Separation of iron(III) from aluminium(III)

The mixture contained known amounts of ferric chloride and aluminium chloride at pH 2-3. Iron was determined gravimetrically in the alcohol layer by evaporation to

TABLE I
SEPARATION OF VARIOUS METALS

Titanium from zirconium				Titanium from thorium				Iron from aluminium			
Titanium (mg)		Zirconium (mg)		Titanium (mg)		Thorium (mg)		Iron (mg)		Aluminium (mg)	
Added	Found	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
47.8	47.6	91.2	90.8	96.4	95.6	16.60	16.55	139.6	138.9	269.6	268.8
23.9	24.0	45.6	45.4	48.2	47.9	8.30	8.34	69.6	69.3	134.8	135.3
11.95	11.90	22.8	22.7	24.1	24.0	4.65	4.64	34.8	34.7	67.4	67.0
5.97	5.9	11.4	11.2	12.0	12.2	2.32	2.34	17.4	17.5	33.7	33.4

dryness and ignition to Fe_2O_3 . Aluminium was determined gravimetrically in the aqueous layer by precipitation with oxine. Typical results obtained are given in Table I.

Titanium(IV), uranium(IV), manganese(II) and cadmium interfered in this separation. As little as 1 mg of iron could be quantitatively recovered.

The authors are grateful to the Council of Scientific and Industrial Research for support and for the grant of a Fellowship to one of them (K.N.M.).

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Received February 6, 1962

Anal. Chim. Acta, 27 (1962) 89-90

A new electroanalytical method: coulostatic or charge-step method

The principle of an electroanalytical method, which is new to the writer's knowledge, is reported here for determinations in the 10^{-5} - 10^{-7} mol.l⁻¹ range. The method was originally developed for studies of adsorption and electrode processes, but it may prove useful in trace analysis because of its simplicity.

THEORY

Potential-time variations

Theory will be limited here to the most significant analytical application, namely to processes with mass transfer controlled by semi-infinite linear diffusion. The

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current density-potential curve for any given time after the beginning of electrolysis exhibits a plateau along which the current density I_a is generally proportional to the bulk concentration of reducible or oxidizable substance. One has for diffusion control

$$I_a = \pm nFC^0 \left(\frac{D}{\pi t} \right)^{1/2} \quad (1)$$

where the \pm sign holds for a cathodic and anodic process, respectively; n is the number of electrons in the electrode process; F the faraday; C^0 the bulk concentration of reducible or oxidizable species (in mol.cm⁻³); D the diffusion coefficient of this species; and t the time elapsed since the beginning of electrolysis. The potential of the electrode is initially set with a potentiometer at the value E_t at the foot of the I - E curve where the faradaic current (*i.e.*, current for reduction or oxidation) is practically equal to zero. The charge on the electrode is changed in a short time (a few tenths of a microsecond to a few milliseconds) with an instrument which allows flow of the charging current but prevents flow of the reverse current. (This requires only simple equipment.) The charge being supplied is such that E is brought to E_c in the plateau of the I - E curve. The cell is essentially at open circuit after charging, and consequently the faradaic current is only supplied by discharge of the double layer capacity. The charge on the electrode at potential E is $c_i(E - E_z)$, where c_i is the *integral* capacity per unit area of the double layer and E_z is the point of zero charge. The capacity c_i is a function of E . If the time required for charging from E_t to E_c is negligible in comparison with the values of t considered here, one has for the variation of potential from E_c to a value E in the plateau of the I - E curve, *i.e.*, for discharge of the double layer at constant current

$$(c_i)_E(E - E_z) - (c_i)_{E_c}(E_c - E_z) = \int_0^t I_a dt \quad (2)$$

Where $(c_i)_E$ and $(c_i)_{E_c}$ are the integral capacities of the double layer at E and E_c , respectively. We consider here only the case in which c_i is independent of potential over the interval $\Delta E = E - E_c$, and we obtain in that case from equations 1 and 2

$$\Delta E = \pm \frac{2nFC^0 D^{1/2}}{\pi^{1/2} c_i} t^{1/2} \quad (3)$$

The potential varies linearly with $t^{1/2}$, and the concentration C^0 can be determined from the slope of the ΔE vs. $t^{1/2}$ plot. The quantities D and c_i can be determined separately or, more conveniently, equation 3 can be written, $\Delta E = \pm PC^0 t^{1/2}$, where P is determined once for known C^0 's.

Since $c_i \approx 15$ -40 microfarads.cm⁻², depending on E , it follows from equation 3 that the method is of practical value for $C^0 = 10^{-5}$ to 10^{-7} mol.l⁻¹. Higher C^0 's can be determined but more conventional methods are available, e.g., polarography. For $c_i = 20$ microfarads.cm⁻², $D = 10^{-5}$ cm².sec.⁻¹ and $n = 2$, one has $\Delta E = 0.344 t^{1/2}$, $0.0344 t^{1/2}$ and $0.00344 t^{1/2}$ for $C^0 = 10^{-5}$, 10^{-6} and 10^{-7} mol.l⁻¹, respectively. Since t should not exceed 30-60 sec at room temperature to avoid excessive interference by convection, $C^0 = 10^{-7}$ mol.l⁻¹ appears to be the lower limit that can be determined. Interference by the residual current may raise this limit in some instances.

Correction for residual current

Reduction and/or oxidation of impurities and the solvent alter the above $E-t$ characteristic. Two limiting cases can be distinguished for the time-dependence of the residual current density I_r : (i) pure diffusion control with I_r varying with $t^{-1/2}$, and (ii) pure control by a chemical or an electrochemical reaction with I_r independent of t . In general, electrolysis of impurities is diffusion-controlled and electrolysis of the solvent is controlled by charge transfer. Convection may complicate matters. Correction of the potential-time curve, at a given t , should be feasible by subtraction of $|\Delta E|$ for the blank from $|\Delta E|$ for the analyzed substance provided it can be assumed that c_i remains the same when the analyzed substance is added to the blank.

General theory

Most of the following cases were analyzed quantitatively:

I. Single charge-step with double layer integral capacity independent of potential.

A. Steady-state faradaic current.

1. Faradaic current independent of potential.
2. Faradaic current varying with potential.

B. Faradaic current with transitory component.

1. Faradaic current independent of potential.
 - a. Diffusion control (plane, sphere, cylinder, etc.)
 - b. Diffusion with coupled chemical reaction.
2. Faradaic current varying with potential.
 - a. Reversible processes.
 - b. Irreversible processes.
 - c. Processes with coupled chemical reaction.

II. Multiple charge-step with double layer integral capacity independent of potential.

III. Processes with double layer integral capacity varying with potential.

Cases I correspond to electrode processes with convection or diffusion control. Case II might be of interest in the analysis of multi-component systems by the following procedure: the ΔE vs. t curve is determined first for the most easily reduced or oxidized substance, and a second step-charge is applied to the working electrode without interruption of electrolysis to bring E in the diffusion current range for the second substance; the latter is then determined from the new ΔE vs. t curve after correction for the first substance. Case II also corresponds to electrolysis with subsequent reversal of current. Case III is of interest when c_i varies so markedly with E as to preclude cases I and II.

COMPARISON WITH SOME OTHER ELECTROANALYTICAL
METHODS FOR TRACE ANALYSIS

The above method may prove useful as an analytical tool for trace analysis because it is simple and of rather general applicability for electrochemically reducible or oxidizable substances. The method is much simpler than square wave polarography, pulse polarography and faradaic rectification in which the difficulty resulting from the double layer capacity is circumvented in very ingenious ways but at the cost

of equipment complexity. This difficulty is entirely avoided here. The method is quite general since it suffices that a limiting or diffusion current be observed (this condition is not even essential) and applicability should be wider than for anodic and cathodic stripping. (Stripping methods, however, are applicable in some cases to concentrations well below the 10^{-7} mol.l⁻¹ level.) Combination of the present method with stripping methods might also be considered.

The expressions "coulostatic method" or "charge-step method" are suggested to designate this method. Likewise, the instrument for supplying a known charge might be called a coulostat by analogy with "potentiostat".

Details on theory and experiment will be published.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation.

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Received April 2nd, 1962

Anal. Chim. Acta, 27 (1962) 90-93

Preparation of carrier-free 65-day strontium-85 radiotracer*

Radioactive γ -emitting 65-day ⁸⁵Sr tracer has been successfully applied to the monitoring of ion exchange column separations of microgram quantities of strontium in the absolute age determination of minerals and rocks by the rubidium-strontium method^{1,2}. By means of the 0.51 meV γ -radioactivity, the ion exchange column may be monitored during elution by an external G-M counter, an advantage over the β -emitting ⁸⁹Sr and ⁹⁰Sr tracers, and the total chemical yield of the separation may also be determined. Sharper separations from calcium in calcium-rich samples, and from barium which follows the strontium from the column, are confidently and regularly attained. The health hazard in the laboratory is much less with 65-day ⁸⁵Sr than with 28-year ⁹⁰Sr tracer owing to its shorter half-life and γ radiation which is easily detected by a radiation monitor.

Strontium-85 is produced in good yield by bombardment of 0.5 g of rubidium chloride with 15 meV deuterons in the external beam of a classical cyclotron. Under these conditions radioactive strontium isotopes are produced from ⁸⁵Rb (72% abundant) and ⁸⁷Rb (28% abundant) by the following reactions: ⁸⁵Rb (d,2n)⁸⁵Sr (Q = -4.1 meV), ⁸⁵Rb(d,2n)^{85m}Sr → ⁸⁵Sr, ⁸⁷Rb(d,2n)^{87m}Sr → ⁸⁷Sr (stable). (The decay of 70-min ^{85m}Sr and 2.8-h ^{87m}Sr is complete in a few hours.) The stable isotopes ⁸⁶Sr,

* This work was supported in part by the United States Atomic Energy Commission and is publication No. 34 of the M.I.T. Age Studies Series.

^{87}Sr , and ^{88}Sr are also produced by (d,n) and (d,2n) reactions with ^{85}Rb and ^{87}Rb . Important additional radioactive isotopes produced by deuteron reactions with rubidium chloride are 18-min. ^{88}Rb , 18.6-day ^{86}Rb , and 37.3-min ^{38}Cl . Potassium present as an impurity in the target material gives rise to 12.5-h ^{42}K .

Bombardment conditions used at the MIT Cyclotron for production of ^{85}Sr radio-tracer are as follows. Crystals of rubidium chloride are packaged in a kitchen-grade aluminum foil envelope (ca. 5 mg/cm²) such that the thickness of rubidium chloride is about 0.2 g/cm², the maximum thickness penetrated by the deuterons to cause the desired nuclear reaction. Bombardment is carried out in the external beam at 20 μA for 1 h to produce about 1 millicurie of ^{85}Sr , depending somewhat on target placement in the cyclotron beam.

After cooling for 1–2 days to permit decay of short-lived nuclides, strontium is separated carrier-free from target rubidium chloride by cation exchange and elution with 2 *N* hydrochloric acid. The column operating conditions are identical to those used for separation of traces of strontium from dissolved mineral samples in the rubidium-strontium age determination procedure^{1,2}. A clear aqueous solution of the rubidium chloride target in a small volume is adsorbed on the top of a Dowex 50-X12 (300 mesh) column (2.5 cm diam \times 25 cm long) and eluted with Vycor-distilled 2 *N* hydrochloric acid. Two sharp bands of radioactivity, 18.6-day ^{86}Rb followed by 65-day ^{85}Sr , are detected by external monitoring during elution. The ^{85}Sr band is collected, evaporated to a small volume, passed through the column a second time for additional purification, diluted to 500 ml, and stored in polyethylene. Aliquots of 2 ml are used as spikes for mineral analysis and give about 1000 counts per minute in the column using an external G-M radiation monitor.

Reagent blanks which include tracer spike show no interferences in the isotopic analysis. Two experiments were carried out to test the purity from natural isotopes in the strontium tracer as follows. Approximately 10 times the volume of ^{85}Sr tracer normally used in an analysis was added to two aliquots of stable ^{86}Sr spike used in the mass spectrometric isotopic analysis. This ^{86}Sr spike is a solution of known strontium concentration which has been greatly enriched in ^{86}Sr . Mass spectrometric analyses of these two aliquots of ^{86}Sr spikes showed no measurable change in their isotopic compositions, to a limit of 0.3%, by addition of the extra large quantity of ^{85}Sr tracer.

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Received January 19th, 1962

A note on the Beer-Lambert law

The Beer-Lambert law is usually given in the form:

$$I_{\nu z}(z) = I_{\nu z}(0) e^{-K_{\nu} c_2 z} \quad (1)$$

where ν is the frequency of the radiation, K_{ν} is the absorption coefficient at that frequency and is independent of absorbent concentration, c_2 is the concentration of absorbent (2) in solvent (1), $I_{\nu z}$ is the z -component of the radiation flux and z the direction of radiation transmission. Various books and articles give a rather unsatisfactory deduction of eqn. (1); these various deductions fail to present the assumptions and the nature of the phenomenon described by the Beer-Lambert law. The purpose of this note is to present a deduction of eqn. (1) from a starting point which brings out the assumptions and the nature of the phenomenon described.

In order to point out the various restrictions and the nature of the phenomenon, we begin with the general *steady-state* energy equation¹ for radiation of frequency ν :

$$\vec{\nabla} \cdot \vec{I}_{\nu} = -A_{\nu} + \xi_{\nu} \quad (2)$$

where I_{ν} is the frequency ν radiation flux vector and A_{ν} and ξ_{ν} are the local volumetric rates of radiation absorption and emission respectively in the material medium.

Radiation in transfer through a continuous material medium may be absorbed, scattered and emitted. The Beer-Lambert law deduction requires that the scattering and emission of radiation in the material medium be negligible. In material systems to which the Beer-Lambert law is applied, scattering is usually negligible². With these restrictions eqn. (2) becomes:

$$\vec{\nabla} \cdot \vec{I}_{\nu} = -A_{\nu abs.} \quad (3)$$

Next it is assumed that there is but one component of \vec{I}_{ν} different from zero in magnitude, the z -component for example:

$$\frac{dI_{\nu z}}{dz} = -A_{\nu abs.} \quad (3)$$

It may be demonstrated theoretically and experimentally that to the linear approximation (small radiation fluxes) the local volumetric rate of radiation absorption is proportional to the radiation flux at that point. Therefore eqn. (3) becomes:

$$\frac{dI_{\nu z}}{dz} = -m_{\nu} I_{\nu z} \quad (4)$$

In eqn. (4) m_{ν} is the proportionality constant termed the absorption coefficient for radiation of frequency ν . Inasmuch as eqn. (4) is taken to be a valid statement, m_{ν} is a

function only of the state of the material medium for radiation of frequency ν . Therefore for an isotropic fluid:

$$m_\nu = m_\nu(p, T, c_1, c_2, \dots, c_{n-1}) \quad (5)$$

where p is the pressure, T the absolute temperature, and c_i the molar density of the i -th chemical species of the material medium.

It is now assumed that the material medium is a binary system consisting of a transparent (non-absorbent) solvent (1) and absorbent (2). Therefore:

$$m_\nu = m_\nu(p, T, c_2) \quad (6)$$

By a Taylor series expansion of eqn. (6):

$$\begin{aligned} m_\nu = m_{\nu(0,0,0)} + \left(\frac{\partial m_\nu}{\partial p}\right)_0 p + \left(\frac{\partial m_\nu}{\partial T}\right)_0 T + \left(\frac{\partial m_\nu}{\partial c_2}\right)_0 c_2 + \frac{1}{2} \left(\frac{\partial^2 m_\nu}{\partial T^2}\right)_0 T^2 + \frac{1}{2} \left(\frac{\partial^2 m_\nu}{\partial p^2}\right)_0 p^2 + \\ + \frac{1}{2} \left(\frac{\partial^2 m_\nu}{\partial c_2^2}\right)_0 c_2^2 + \left(\frac{\partial^2 m_\nu}{\partial T \partial c_2}\right)_0 T c_2 + \left(\frac{\partial^2 m_\nu}{\partial p \partial c_2}\right)_0 p c_2 + \left(\frac{\partial^2 m_\nu}{\partial p \partial T}\right)_0 p T + R_n \end{aligned} \quad (7)$$

In order to obtain eqn. (1) it is necessary that:

$$m_{\nu(0,0,0)} = 0 \quad (8)$$

$$\left(\frac{\partial m_\nu}{\partial p}\right)_0 = \left(\frac{\partial m_\nu}{\partial T}\right)_0 = 0 \quad (9)$$

$$\left(\frac{\partial^2 m_\nu}{\partial T^2}\right)_0 = \left(\frac{\partial^2 m_\nu}{\partial p^2}\right)_0 = \left(\frac{\partial^2 m_\nu}{\partial p \partial T}\right)_0 = \left(\frac{\partial^2 m_\nu}{\partial c_2^2}\right)_0 = 0 \quad (10)$$

$$R_n = 0 \quad (11)$$

where eqn. (8) follows from the requirement of a transparent solvent and eqns. (9), (10) and (11) from the requirement that K_ν in eqn. (1) be independent of c_2 . One has then for m_ν :

$$m_\nu = \left(\frac{\partial m_\nu}{\partial c_2}\right)_0 c_2 + \left(\frac{\partial^2 m_\nu}{\partial T \partial c_2}\right)_0 T c_2 + \left(\frac{\partial^2 m_\nu}{\partial p \partial c_2}\right)_0 p c_2 \quad (12)$$

Substituting eqn. (12) in eqn. (4) the integrated form is obtained:

$$I_{\nu z}(z) = I_{\nu z}(0) e^{-\int_0^z m_\nu d\xi} \quad (13)$$

If it is assumed that c_2 , T and p are not functions of z , one obtains eqn. (1):

$$I_{\nu z}(z) = I_{\nu z}(0) e^{-\left[\left(\frac{\partial m_\nu}{\partial c_2}\right)_0 + \left(\frac{\partial^2 m_\nu}{\partial T \partial c_2}\right)_0 T + \left(\frac{\partial^2 m_\nu}{\partial p \partial c_2}\right)_0 p\right] c_2 z} \quad (14)$$

where:

$$K_\nu = K_\nu(p, T) = \left[\left(\frac{\partial m_\nu}{\partial c_2}\right)_0 + \left(\frac{\partial^2 m_\nu}{\partial T \partial c_2}\right)_0 T + \left(\frac{\partial^2 m_\nu}{\partial p \partial c_2}\right)_0 p\right] \quad (15)$$

Recent experimental work³ in the visible light region for several systems known to obey the Beer-Lambert law has shown that:

$$[K_\nu = x_\nu - T]_{\text{optical}} \quad (16)$$

where x_p was termed a constant and T is the absolute temperature. According to the present deduction it may be concluded that:

$$\left[\left(\frac{\partial^2 m_p}{\partial T \partial c_2} \right)_0 = -1 \right]_{optical} \quad (17)$$

The constant

$$\left(\frac{\partial^2 m_p}{\partial p \partial c_2} \right)_0$$

remains to be determined.

As c_2 is increased, eqn. (II) is no longer a valid statement and K_p becomes a function of c_2 , T and p .

For a general multicomponent system of $n-1$ dilute chemical species in a transparent solvent (I), we obtain the extension of (I4):

$$I_{\nu_2}(z) = I_{\nu_2}(0) \exp \left[- \left\{ \sum_{i=2}^n K_{\nu_2 i} c_i \right\} z \right] \quad (18)$$

where:

$$K_{\nu_2 i} = \left[\left(\frac{\partial m_p}{\partial c_i} \right)_0 + \left(\frac{\partial^2 m_p}{\partial T \partial c_i} \right)_p T + \left(\frac{\partial^2 m_p}{\partial p \partial c_i} \right)_0 p \right]$$

The validity of the Beer-Lambert law in dilute multicomponent systems is well-known in spectroscopy⁴. It is found that as the absorbent concentrations are increased, interaction effects become important and eqn. (18) is not valid.

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² J. O. HIRSCHFELDER, C. F. CURTISS AND R. B. BIRD, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.

³ S. A. SHCHUKAREV, G. I. NOVIKOV AND A. V. SUVOROV, *Zhur. Neorg. Khim.*, 1 (1956) 2433.

⁴ See e.g., R. B. BARNES, R. C. GORE, U. LIDDEL AND VAN Z. WILLIAMS, *Infrared Spectroscopy*, Reinhold, New York, 1944.

Received January 8th, 1962

Anal. Chim. Acta, 27 (1962) 95-97

Studies on adsorption indicators

Part III. Benzene azo-1-naphthylamine as adsorption indicator

In the present communication, a new basic adsorption indicator, benzene azo-1-naphthylamine, is suggested for argentometric titrations; its behaviour is similar to that of *p*-ethoxychrysoidine¹. The indicator is of particular interest from the theoretical point of view.

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Benzene azo-1-naphthylamine changes colour from red-violet to orange-yellow in the pH range 3.7–5.0. The indicator is not satisfactory in neutral solutions. In slightly acidic medium (pH 4–5), silver can be titrated with iodide, bromide, thiocyanate, or chloride ions to sharp end-points. The colour changes from orange to violet on the coagulated precipitate exactly at the equivalence point, and is sharp and reversible. It is sharpest in the iodide titration, and becomes gradually less sharp in titrations with bromide, thiocyanate and chloride; titration is possible to a dilution of 0.002 *N* with iodide, 0.01 *N* with bromide and 0.02 *N* with thiocyanate and chloride. Moreover, titration with chloride or thiocyanate is possible only in a limited pH range (4–5), whereas the titration with iodide is possible up to pH 2.5. When silver is titrated with halide or thiocyanate using this indicator, the initial red-violet colour of the titration liquid changes to orange during the titration and just at the end-point it becomes intense violet. This change of colour is accompanied by a corresponding change in the hydrogen ion concentration of the supernatant solution (Table I). The phenomenon is exactly similar to that observed with *p*-ethoxychrysoidine, and is readily explained by the theory¹ of surface compound formation. In order to provide evidence for the explanation, the silver compound of benzene azo-1-naphthylamine was isolated and its properties studied.

TABLE I

pH CHANGES IN THE TITRATION OF 50 ml OF 0.001 *M* AgNO₃ WITH HALIDE AND THIOCYANATE. INITIAL pH ADJUSTED WITH 0.001 *N* HNO₃.

0.01 <i>M</i> <i>KX</i> ^a % equiv.	pH changes			
	<i>KI</i>	<i>KBr</i>	<i>KSCN</i>	<i>KCl</i>
0	4.26	4.27	4.26	4.28
20	4.23	4.25	4.24	4.26
40	4.28	4.29	4.26	4.28
80	4.36	4.34	4.31	4.31
95	4.42	4.36	4.34	4.33
100	4.61	4.47	4.43	4.38
105	4.63	4.47	4.43	4.39
120	4.66	4.48	4.44	4.40
160	4.69	4.49	4.46	4.40

^a X = Cl, Br, I or SCN

Reagents: All the reagents used were of analytical reagent grade (B.D.H.)

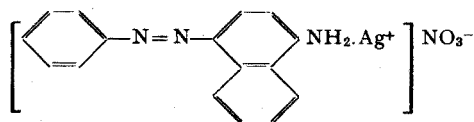
Benzene azo-1-naphthylamine (B.D.H.) was recrystallised from ethanol and a 0.2% solution in ethanol was used as indicator.

Procedure: For every 10 ml of silver nitrate solution to be titrated, 4 drops of indicator solution and 3–5 ml of 0.001 *N* nitric acid are added. When 0.1 *N* silver solution is titrated with halide or thiocyanate, the colour change from orange to violet occurs on the coagulated precipitate just at the equivalence point. In the titration of 0.01 *N* or more dilute solutions, the colour change from orange to violet appears in the suspension.

The silver compound of benzene azo-1-naphthylamine was prepared as follows. Benzene azo-1-naphthylamine base was extracted with ether. The solid obtained by evaporating the ether extract was recrystallised from ethanol. 0.25 g of this purified base was dissolved in 20 ml of ethanol and treated with 10 ml of 10% silver nitrate solution. It was immediately extracted with 100 ml of ether. The ethereal solution was

evaporated and dried under reduced pressure. The compound was found to contain 24.4–25.6% silver.

The compound is stable only in ether or ethanol solution. When the ethanolic solution of the compound is poured into water, the orange precipitate formed readily darkens owing to hydrolysis. When the orange precipitate is suspended in water and treated with potassium iodide solution, a violet precipitate is formed. Although the compound is only slightly soluble in dilute nitric acid, it tends to change into the nitrate of the dye base which is also slightly soluble. The probable formula of the compound is



One of us (K.N.T.) is grateful to the Scientific Research Committee (U.P.) for a grant and to Bareilly College for the provision of facilities.

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¹ K. N. TANDON AND R. C. MEHROTRA, *Anal. Chim. Acta*, 27 (1962) 15.

Received February 27th, 1962

Anal. Chim. Acta, 27 (1962) 97–99

Book Reviews

Heterocyclic Compounds, Vol. 7. Edited by R. C. ELDERFIELD, John Wiley and Sons, Inc., New York, London, 1961, vi + 878 pp., £15.

The latest addition to this well-known series deals with the chemistry of polycyclic compounds containing two hetero-atoms in different rings, five- and six-membered heterocycles containing three hetero-atoms, and their benzo-derivatives. Quite intentionally the coverage of topics varies considerably. Thus where no comprehensive review exists, the treatment is thorough. This particularly applies to the chapter on oxygen heterocycles (by W. B. Whalley), which will be particularly welcomed. Where reviews already exist, as for example of the *s*-triazines, the coverage is less detailed. The material for some of the chapters was submitted as much as ten years ago, but has been partially brought up-to-date by the editor. Such a chapter is that on carbolines.

Altogether, this is a useful volume though less generally so that some of its predecessors. The standard of production is excellent, in conformity with the rest of the series. The price seems unduly high and will ensure that the book is bought mainly by libraries.

E. J. FORBES (Birmingham)

Anal. Chim. Acta, 27 (1962) 99

Organic Syntheses, Vol. 40, Edited by M. S. NEWMAN, John Wiley and Sons Inc. New York—London, 1961, vi + 114 pp., 32s.

The appearance of a new volume in this series is always a matter of interest. Readers will not be disappointed. Some thirty-nine preparations covering a wide range of interests are described and annotated in the usual thorough and useful manner. Roughly twice as many aromatic as aliphatic compounds are dealt with. Some of the later volumes in this series have contained a fair proportion of preparations of only limited appeal. This criticism cannot be levelled at the present volume, where there has been a return to the smaller molecules. Thus well over half of the compounds mentioned have less than ten carbon atoms. Two, methane sulphonyl chloride and hydroxyurea, have only one. At the other end of the scale comes quinquephenyl.

Most of the preparations are modifications of experiments already described in the literature, but the fuller publication of details and attendant snags is most welcome. The convenient preparation of neopentyl alcohol from di-isobutylene has not been previously described. The present volume is a most useful addition to the series.

E. J. FORBES (Birmingham)

Anal. Chim. Acta, 27 (1962) 100

Announcement

CONFERENCES ON NUCLEAR REACTOR CHEMISTRY AND TECHNOLOGY

The Third Conference on Nuclear Reactor Chemistry and the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology will be held at Gatlinburg, Tennessee, next October 9, 10, and 11, under the sponsorship of Oak Ridge National Laboratory.

Third Conference on Nuclear Reactor Chemistry. Chemical behavior of reactor materials will be emphasized at this meeting. Subjects include: preparation of fuel, moderator, coolant, and nuclear poison materials and their properties in the presence and absence of nuclear radiation; particle behavior in nuclear reactors; and the chemistry of corrosion processes in nuclear reactors.

Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology. Subjects to be considered include: use of isotopes in analytical chemistry; instrumentation; analysis of organic moderators; spectroscopy; analytical developments in radiochemistry and nucleonics.

Enquiries should be directed to Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tennessee, Attention: W. R. GRIMES for Nuclear Reactor Chemistry, and C. D. SUSANO for Analytical Chemistry.

Logging reservations should be directed to: Reservation Services, Chamber of Commerce, Gatlinburg, Tennessee.

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ELSEVIER PUBLISHING COMPANY, AMSTERDAM

Printed in The Netherlands by

NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

COMPREHENSIVE ANALYTICAL CHEMISTRY

edited by **CECIL L. WILSON**

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