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Vol. 30, No. 1, January 1964

DETERMINATION OF AMIDES

A method has been developed for the quantitative determination of amides. The compound is saponified with a large excess of alkali and the resulting solution passed through a heated cation-exchange resin in the hydrogen form. The resin neutralizes the excess sodium hydroxide and converts the carboxylic salt to the free acid which is then titrated directly in the effluent with standard alkaline solution. The time required for a determination is less than one hour.

TH. M. BEDNARSKI AND D. N. HUME,

Anal. Chim. Acta, 30 (1964) 1–5.

DETERMINATION OF ORGANIC SUBSTANCES BY STANDARD CHROMOUS CHLORIDE SOLUTION

The reducibility of a number of organic compounds by a standard chromous chloride solution, prepared determinately from potassium dichromate, has been studied. Orange II, tartrazine, and azoxybenzene (after rearrangement in sulfuric acid medium to the corresponding azo compound) were quantitatively cleaved to the corresponding amines, while azobenzene was reduced only to hydrazobenzene (extent of reduction uncertain). Also quantitatively reduced were: propiolic acid to propenoic acid, diacetyl to acetoin, and benzil to benzoin. Hydrazobenzene, diphenylacetylene, 2-methyl-3-butyn-2-ol, 1-ethynyl-cyclohexanol-1, 2,5-dimethyl-3-hexyne-2,5-diol, 2,5-diphenyl-3-hexyne-2,5-diol, and acetylacetone were not reduced even at elevated temperatures.

R. S. BOTTEI,

Anal. Chim. Acta, 30 (1964) 6–10.

THE REACTION OF CHROMIUM WITH DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE

(in German)

Qualitative tests have shown that Cr(III) does not react with diphenylcarbazide (DCD) but with diphenylcarbazone (DCN) in organic solvents, aqueous solution and solid form. The formed dyestuff has the same absorption maximum as the product of the Cr(VI)–DCD reaction. Extraction tests with ^{51}Cr show that the latter reaction yields a violet chromium complex but side-reactions also occur. Thus the stoichiometry of the reaction cannot be definitely established, but it is extremely probable that a redox reaction is combined with complexation of Cr(III) by DCN. A reaction mechanism is proposed which leads to a resonance-stabilized, cationic complex.

H. MARCHART,

Anal. Chim. Acta, 30 (1964) 11–17.

THEORY OF TITRATION CURVES

II. LOCATIONS OF POINTS OF MAXIMUM SLOPE ON POTENTIOMETRIC HETEROVALENT ("ASYMMETRICAL") PRECIPITATION TITRATION CURVES

By a wholly rigorous general treatment of the potentiometric titration curve representing the titration of B^{m+} with A^{n-} to give the precipitate B_nA_m, where $n \neq m$, it is shown on taking into account the effect of dilution that:

(1) If $n/m > 1$, the inflection point must precede the equivalence point, but there is no inflection point if the initial concentration of the ion titrated is smaller than a certain value, which is determined by the values of m, n, and the solubility product of the precipitate.

(2) If $n/m < 1$, the inflection point may follow the equivalence point — though not by more than a certain definite amount — or may precede it or coincide with it. In every such case there is a concentration of A^{n-} that will cause the equivalence point to coincide with an inflection point; this concentration depends on the values of m, n, and the solubility product of the precipitate.

(3) Unless the difference between the equivalence and inflection points is negligibly small, the traditional treatment in which dilution is neglected gives seriously erroneous estimates of the location of the inflection point.

L. MEITES AND J. A. GOLDMAN,
Anal. Chim. Acta, 30 (1964) 18–27.

THEORY OF TITRATION CURVES

III. LOCATIONS OF POINTS AT WHICH pH = pK_a ON POTENTIOMETRIC ACID–BASE TITRATION CURVES; END-POINT ERRORS IN TITRATIONS TO PREDETERMINED pH VALUES

For the titration of a pure solution of a weak monobasic acid with a strong base, it is shown that the fraction of the equivalent volume of base added at the point where pcH = pK_a is exactly equal to 1/2 if and only if $pK_a = pK_w/2$, in which case it is independent of dilution. It is less than 1/2 if $pK_a < pK_w/2$ and is greater than 1/2 if $pK_a > pK_w/2$, and in either of these cases it depends on the concentrations of both acid and base. Explicit descriptions are given of the conditions under which pcH = pK_a either at the start of the titration or at the equivalence point. For the titration of either a weak or a strong acid with a strong base, exact equations are given for the titration error resulting from the termination of the titration at any preselected pcH value.

J. A. GOLDMAN AND L. MEITES,
Anal. Chim. Acta, 30 (1964) 28–33.

A SPECTROPHOTOMETRIC STUDY OF THE COLOUR REACTION BETWEEN CHLORANIL AND AROMATIC AMINES

The colour reaction between aromatic amines and chloranil was studied spectrophotometrically. A 1 : 1 adduct formed in solution, with some dissociation. The effects of solvents, acid and alkali were examined. The adducts exhibited intense, and characteristic, broad absorption bands, which could be used for the detection and estimation of an aromatic amine, in the absence of substances of similar light absorption characteristics. A correlation between the basicities of an amine and the light absorption of the adduct was established.

P. H. GORE AND B. B. WHEALS,
Anal. Chim. Acta, 30 (1964) 34–39.

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH *p*-(MORPHOLINO)-N-(4'-HYDROXY-3'-METHOXY) BENZYLIDINEANILINE

A sensitive spectrophotometric determination of osmium is based on the blue color (absorption maximum at 615 mμ) formed by reaction of osmium with *p*-(morpholino)-N-(4'-hydroxy-3'-methoxy)benzylidineaniline ("anil") in acetate–buffered solution containing ethanol to prevent formation of a precipitate. Full color development is attained in 1 h at room temperature, and the color is stable for several hours. The absorbance is reproducible. The optimum concentration range for 1-cm optical path is about 1 to 4 p.p.m. of osmium. Several transition elements interfere; osmium can be separated as its tetroxide by the usual distillation method. The blue product is a cationic complex formed by reaction of anil with osmium in a 2 : 1 mole ratio. When osmium is in excess a red cationic complex (absorption maximum at 466 mμ) is formed by a 1 : 1 reaction between osmium and the reagent. The 1 : 1 complex is slowly converted to the 2 : 1 complex by excess reagent.

G. H. AYRES AND C. W. MCDONALD,

Anal. Chim. Acta, 30 (1964) 40–48.

MICRODETERMINATION OF DISSOLVED OXYGEN IN WATER BY A RAPID SPECTROPHOTOMETRIC METHOD

A spectrophotometric method utilizing the dye indigo carmine has been applied to the analysis of dissolved oxygen in water samples. Oxygen concentration has been determined by the decrease in absorbance at 410 mμ of reduced indigo carmine solutions oxidized by dissolved oxygen. A simple modification of the sample compartment of a Bausch and Lomb Spectronic 20 or 340 spectrophotometer allows rapid and accurate measurements to be made within 3 min. Dissolved oxygen in the ranges of 0 to 10% and 0 to 100% saturation can be analyzed without many of the interferences inherent in the standard WINKLER method.

P. A. ST. JOHN, J. D. WINEFORDNER AND W. S. SILVER,

Anal. Chim. Acta, 30 (1964) 49–55.

A SIMPLE COLORIMETRIC METHOD FOR THE DETERMINATION OF AMMONIA IN SEAWATER

A method is proposed for the determination of trace amounts of ammonia in seawater. After calcium and magnesium have been chelated with CDTA, the blue colour obtained with hypochlorite and thymol–acetone is measured at 630 nm. The sensitivity is 1.3 ng NH_4^+-N/cm^2.

R. TH. ROSKAM AND D. DE LANGEN,

Anal. Chim. Acta, 30 (1964) 56–59.

POLAROGRAPHIC DETERMINATION OF LEAD AND TIN IN STEELS

A polarographic method is described for determining down to 0.01% lead and tin in iron and steel, using citric acid as supporting electrolyte. The sample is dissolved under purified nitrogen. Two curves are recorded for each sample solution: the first shows the sum of lead(II) and tin(II), and the second, after oxidation of tin(II) with a solution of iodine, gives a wave for lead only.

S. H. OMANG AND C. U. WETLESEN,

Anal. Chim. Acta, 30 (1964) 60–63.

THE DETERMINATION OF NICKEL IN IRON AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A procedure is described for the determination of 0.005 to 2% of nickel in low and high alloy irons and steels by atomic absorption spectrophotometry. The sample is dissolved in phosphoric–sulphuric acid and atomised in an atomic absorption spectrophotometer. The method is rapid and free from interferences; preliminary separations are not required and results obtained on standard samples are in good agreement with certificate values.

K. KINSON AND C. B. BELCHER,

Anal. Chim. Acta, 30 (1964) 64–67.

A THEORETICAL APPROACH TO THE SOLVENT EXTRACTION OF METAL CHELATES

A simplified theory for the solvent extraction of metal chelates is presented. Factors which are taken into account include the metal ion, the chelating reagent, aqueous complexing agents, adduct-forming substances, the organic solvent, temperature, rates of extraction, and other effects. Equations are developed for estimating the stoichiometries and the association constants of the involved species.

G. K. SCHWEITZER,

Anal. Chim. Acta, 30 (1964) 68–78.

THE SOLVENT EXTRACTION OF COBALT(III) FROM A TRISOXALATOCOBALTATE(III) SOLUTION INTO CHLOROFORM CONTAINING ACETYLACETONE

The rate of the extraction of cobalt(III) from aqueous solutions containing trisoxalatocobaltate(III) into chloroform containing acetylacetone has been investigated. The effects of pH, acetylacetone concentration, oxalate concentration, complex concentration, temperature, and possible change in oxidation state are reported.

G. K. SCHWEITZER AND E. W. BENSON,

Anal. Chim. Acta, 30 (1964) 79–83.

THE THERMAL PROPERTIES OF SOME SALICYLALDEHYDE, SALICYLALDIIMINE AND SALICYLALDEHYDE-ETHYLENEDIIMINE METAL CHELATES

The thermal properties of Cu(II), Ni(II), Co(II), Mg and Cd salicylaldehyde; Cu(II) and Ni(II) salicylaldiimine; and Cu(II) and Ni(II) salicylaldehyde-ethylenediimine complexes were studied by TGA, DTA, and pyrolysis techniques using the mass spectrometer. The $M(SAL)_2 \cdot 2H_2O$ type complexes dissociate by evolution of hydrate-bound water and then total disruption of the organic ligands. Only H_2O, CO, and CO_2 were detected in the pyrolysis gases of $Cu(SAL)_2 \cdot 2H_2O$ by the mass spectrometer.

W. W. WENDLANDT, S. IFTIKHAR ALI AND C. H. STEMBRIDGE,

Anal. Chim. Acta, 30 (1964) 84–90.

THIN-LAYER IONOPHORESIS OF INORGANIC SUBSTANCES (RADIONUCLIDES) AT LOW AND HIGH VOLTAGES

(in German)

Thin-layer ionophoresis was used for separating inorganic substances. Separations were carried out at 13 V/cm or 45 V/cm using radionuclides. The equipment used is described. High-voltage ionophoresis was conducted either under cooling or in an atmosphere of water vapour. Migration times under these conditions were 2 or 5 min, respectively.

A. MOGHISSI,

Anal. Chim. Acta, 30 (1964) 91–95.

DETECTION OF SOME ALIPHATIC SATURATED LONG-CHAIN HYDROCARBON DERIVATIVES BY THIN-LAYER CHROMATOGRAPHY

The aliphatic saturated long-chain alcohols, aldehydes, and diols were identified to a sensitivity of 50 μg from the parent hydrocarbons (C_{10}, C_{12}, C_{14} and C_{16}) by thin-layer chromatography using "Silica Gel G"-coated pyrex chromatoplates for the fixed phase and ethyl acetate–*n*-hexane mixtures as the mobile phase. Identification of the developed spots was made by a modified charring technique employing ground glass pyrex plates coated with pyrosulfuric acid. Identification of the 1,*n*-dicarboxylic acid from the *n*-mono- or the 1,*n*-hydroxycarboxylic acid derived from the same parent hydrocarbon was effected in a mobile phase of 7 : 3 : 3, v/v ethanol–ammonia (conc.)–tetrahydrofuran. The indicator spray employed was an ethanolic solution of bromothymol blue. The spray was followed by exposure to ammonia vapor for intensification of the yellow acid spots.

R_F value trends for the *n*-mono- and 1,*n*-bifunctional derivatives of the C_{10}, C_{12}, C_{14} and C_{16} aliphatic saturated hydrocarbons based on the —OH, —COOH and —CHO groups as the possible substituents are outlined.

M. G. SURYARAMAN AND W. T. CAVE,

Anal. Chim. Acta, 30 (1964) 96–100.

SALTING-OUT CHROMATOGRAPHY OF SERUM PROTEINS

The usefulness of salting-out chromatography is demonstrated by the separation of blood serum proteins on Sephadex. Conventional and highly porous ion exchangers generally can not be used because of irreversible sorption of protein.

R. N. SARGENT AND D. L. GRAHAM,

Anal. Chim. Acta, 30 (1964) 101–104.

QUANTITATIVE SEPARATION OF IRON, NICKEL AND CHROMIUM FROM MAGNESIUM USING AMMONIUM PYRROLIDINEDITHIOCARBAMATE IN PARTIALLY METHANOLIC MEDIUM

(Short Communication)

L. ROCKS AND H. MALISSA,

Anal. Chim. Acta, 30 (1964) 105–106.

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DETERMINATION OF AMIDES

THEODORE M. BEDNARSKI AND DAVID N. HUME

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(Received June 27th, 1963)

The classical approach to the determination of amides by chemical means is saponification in a procedure analogous to that used in the determination of carboxylic acid esters. The sample is heated with an excess of alkali hydroxide and the excess determined by titration. The chief disadvantage to this procedure is the slowness of the reaction which is particularly noticeable with higher molecular weight, secondary, and tertiary amides. Increasing the concentration of the alkali hydroxide in order to promote the nucleophilic attack and speed up the reaction has the compensating disadvantage of necessitating the determination of a rather small change in the large amount of alkali used. The present determination seeks to overcome this difficulty by hydrolyzing with a large excess of unstandardized alkali hydroxide and removing the excess by neutralization with a cation-exchange resin in the hydrogen form. The carboxylic acid salt is simultaneously converted to the free acid which then may be titrated directly with standard base. A similar approach has previously been applied to the determination of the salts of carboxylic acids[1,2] and to the determination of esters and alkali halides[3–5].

EXPERIMENTAL

Apparatus

A conventional chromatography column 40 cm in length and 2 cm internal diameter was equipped with a hot water jacket so that the temperature of the column could be maintained at approximately 80°. A 300-ml reservoir attached to the top of the column permitted the addition of considerable amounts of eluant without inconvenience (Fig. 1). Dowex 50 W-X8, 50 to 100 mesh, cation-exchange resin in the hydrogen form was used. Resin occupying a volume of about 50 ml was washed with water by decantation to remove any fine particles and transferred to the column as a slurry. The column usually contained approximately 120 meq. of resin. The resin was regenerated immediately following each determination by washing with 100 ml of 1 *N* hydrochloric acid and then with 300 ml of distilled water, after which time the washings from the column were free from acid. A Beckman Zeromatic pH meter, Model 9600, equipped with a glass electrode and calomel reference electrode was used in all titrations.

Materials

The amides used in this investigation were Eastman Kodak Company White Label chemicals, some of which were recrystallized or purified by distillation if it appeared to be necessary. The standard sodium hydroxide solution used in the titrations was stored in polyethylene containers and carefully protected from atmospheric carbon dioxide. Standardization was done against reagent-grade potassium acid phthalate using phenolphthalein as an indicator.

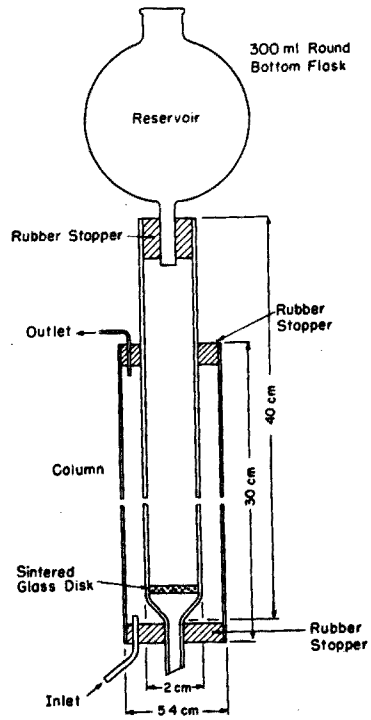

Fig. 1. Heated ion-exchange column.

Procedure

An accurately weighed sample containing approximately 3 to 8 meq. of amide is transferred to a 250-ml round bottom flask with a standard tapered ground glass neck. Fifty ml of approximately 2 *N* hydroxide is added together with one or two boiling stones. The flask may be fitted with a Vigreaux column if lengthy heating is necessary, and the solution is boiled under reflux for a period of not less than 15 min, nor more than 30 min. The heating time is found to vary with the amide used, increasing with the number of carbon atoms in the aliphatic chain. The completion of the reaction is observed by testing with indicator paper the evolving vapors for the presence of ammonia or volatile amine. On completion of the digestion period, about 80 ml of hot distilled water is added and the mixture transferred to the reservoir of the heated ion-exchange column, the flask rinsed with another 20 ml of water and the rinse added to the reservoir. The solution is allowed to percolate through the

column at a rate of 20 to 25 ml per min. A distinct reddening of the column may be noticed as the exchange of sodium for hydrogen occurs. When the sample has run through, the column is washed with an additional 150 ml of hot distilled water and the total 300-ml effluent is collected in a 400-ml beaker.

The carboxylic acid present is titrated potentiometrically with standard 0.35 *N* sodium hydroxide solution, and the end-point determined by inspection of the curve or by calculating the maximum change in pH for small increments of added base. A blank determination is run using 50 ml of the 2.0 *N* sodium hydroxide and the blank titration subtracted from the volume used in the determination.

RESULTS

The results obtained in the determination of eight amides are given in Table I. The average recovery, based on the assumption of pure material, is well over 99% with a standard deviation of about 0.5%. A single determination including saponification, titration, and regeneration of the resin takes approximately one hour.

TABLE I

DETERMINATION OF APPARENT PURITY OF AMIDES BY FINAL PROCEDURE

Sample size 3–7 mmoles

Compound	*Apparent purity (%)*	*Number of determinations*	*Standard deviation (%)*
Formamide	99.8	4	0.69
Acetamide	99.7	7	0.37
Propionamide	98.7	5	0.59
Butyramide	99.1	5	0.41
Benzamide	99.6	5	0.57
N-Methylformamide	99.7	4	0.37
N,N-Dimethylformamide	99.6	4	0.36
N,N-Dimethylacetamide[a]	97.5	4	0.45

[a] Purity in question.

DISCUSSION

Preliminary work in this investigation indicated the significant variables to be the time of heating with excess base, the nature of the eluant, the temperature of the ion-exchange column, and the mesh size and degree of cross-linking of the exchanger. Attempts to use cold water as an eluant indicated that some acids tend to pass very slowly through the column, evidently being retarded by diffusion into the gel phase. Ethanol, 50% to 95%, appeared to be a better eluant from the standpoint of speed, but its use introduced difficulties from another direction. Benzoic acid, for example, was eluted promptly but always gave results several per cent low. With acetic acid and 95% alcohol, the recovery was as low as 75% due to the formation of ethyl acetate, evidently catalyzed by the hydrogen-form resin. The use of acetone caused irreversible changes in the resin and the development of a red color. Hot water, the temperature being maintained by the heating jacket, appeared to be the most satisfactory means of eluting acids promptly and quantitatively. The 250-ml volume used was satisfactory for all acids examined other than benzoic acid, which was found to require a second 250-ml wash for complete recovery.

Formamide was found to hydrolyze the most rapidly of the amides studied. Acetamide was completely converted in 7 min for samples of one meq. size, and 15 min for eight meq. samples. None of the compounds studied required more than 30 min of heating. Butyramide, benzamide, and N,N-dimethylacetamide all required 20 min. Even a 75-min reflux of salicylamide, however, yielded only a 60% conversion, and this compound could not be determined. The saponification time would be expected to lengthen for higher molecular weight compounds, particularly those which are secondary and tertiary amides. Using acetamide, the sample size was found to be immaterial over a range of 1 to 8 meq. with no bias evident due to sample size, although the precision, as would be expected, was lower with small amounts.

The effects of degree of cross-linking and particle size of the resin were also observed. It was found that a resin containing 12% of divinylbenzene gave larger blanks than the 8% with no compensating improvement in other ways. Three different particle sizes were investigated: 20 to 50 mesh, 50 to 100 mesh, and 100 to 200 mesh. With the 20 to 50 mesh resin, equilibration was not rapid and if a flow rate better than 10 ml per min were used, the hydroxide solution was not completely exchanged. With the 50 to 100 mesh resin, a much faster flow rate was possible (20 to 30 ml per min) and the hydroxide was completely exchanged. With the 100 to 200 mesh resin, on the other hand, it was necessary to use suction to obtain a flow rate faster than a slow drip. This would introduce both a mechanical inconvenience and an unnecessary increase in the time per determination; therefore, 50 to 100 mesh resin was selected as standard.

Typical blank titrations were the order of 0.30 $\pm$ 0.02 ml of 0.35 *N* sodium hydroxide using 50 ml of 2 *N* sodium hydroxide. Increasing the amount of sodium hydroxide increased the blank, but not linearly. This persistent blank obtained on neutralizing alkali hydroxide with the resin would appear to be due to slight thermal degradation of the resin caused by local temperature rise as the sodium hydroxide comes in contact with the resin. Water samples passed through the

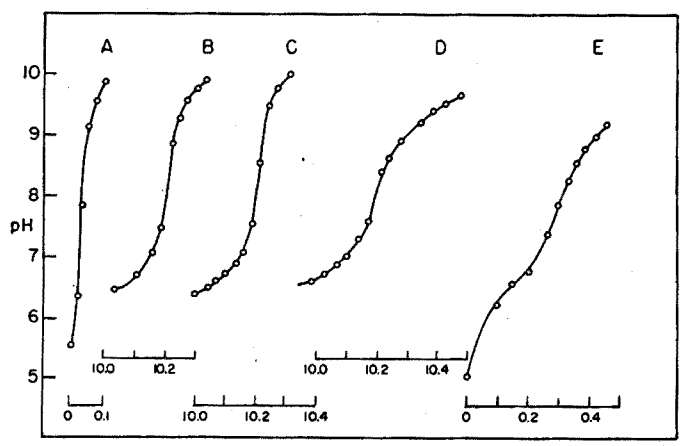

Fig. 2. Titration end-point curves of samples and blanks showing buffering effect. (A) Water. (B) Acetic acid in water. (C) Acetic acid in water, passed through column. (D) Sample: acetic acid in NaOH, passed through column. (E) Blank: NaOH passed through column.

resin give an entirely negligible blank but the appreciable sodium hydroxide blank continues even after long use of the resin and is clearly not due to ionic impurities in the sodium hydroxide. Titration curves of both samples and blanks show a buffer effect attributable to the unidentified degradation products of the resin (Fig. 2). Although not of consequence if the end-point is to be determined with a pH meter, the buffering effect makes the use of indicator end-points impractical in exact work. The explanation of the effect as due to local heating was tested by reacting a typical sodium hydroxide sample with the same amount of moist resin as in the column, but with vigorous agitation in a flask at ice temperature. Under these circumstances the blank was less than half the usual value. Blanks using 12% cross-linked resin were found to be about 30% higher than those with 8% cross-linked, a fact in harmony with the hypothesis that the rigid resin is unable to dissipate heat of reaction quickly enough to prevent degradation. It was observed that the use of potassium hydroxide in place of sodium hydroxide of the same concentration led to blanks about 50% higher.

This work was supported in part by funds from the U.S. Atomic Energy Commission under Contract AT(30-1)-905. We are indebted to Dr. Y. MARCUS of the Israel Atomic Energy Commission for the suggestion which led to the explanation of the high blank values.

SUMMARY

A method has been developed for the quantitative determination of amides. The compound is saponified with a large excess of alkali and the resulting solution passed through a heated cation-exchange resin in the hydrogen form. The resin neutralizes the excess sodium hydroxide and converts the carboxylic salt to the free acid which is then titrated directly in the effluent with standard alkaline solution. The time required for a determination is less than one hour.

RÉSUMÉ

Une méthode est proposée pour le dosage des amides. L'échantillon à analyser, après saponification, est passé à travers une résine échangeur de cations (sous forme hydrogène). La résine neutralise l'hydroxyde de sodium en excès et transforme le sel carboxylique à l'état d'acide libre. Ce dernier est titré directement dans l'effluent, au moyen d'une solution alcaline étalon. Cette analyse peut s'effectuer en moins d'une heure.

ZUSAMMENFASSUNG

Es wurde eine Methode zur quantitativen Bestimmung von Amiden entwickelt. Die Verbindung wird mit einem grossen Überschuss an Alkali verseift und die resultierende Lösung auf ein erhitztes Kationenaustauscherharz (H-Form) gegeben. Die überschüssige Lauge wird durch das Harz neutralisiert und die Säure in Freiheit gesetzt, welche dann direkt mit einer alkalischen Lösung titriert wird. Die Zeit, die zu einer Bestimmung notwendig ist, beträgt weniger als eine Stunde.

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DETERMINATION OF ORGANIC SUBSTANCES BY STANDARD CHROMOUS CHLORIDE SOLUTION

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(Received May 26th, 1963)

In a previous publication[1], it was shown that *p*-nitrobenzene-azoresorcinol and the monopotassium salt of acetylene dicarboxylic acid could be successfully analyzed using standard chromous chloride solution. The azo compound was quantitatively cleaved to the corresponding amines, while the acetylenic compound was reduced to the corresponding ethylenic compound.

The reducibility of a number of other azo and acetylenic compounds, as well as hydrazobenzene, azoxybenzene and some dicarbonyl compounds has been studied. This paper presents the results of this investigation.

EXPERIMENTAL

Apparatus

The apparatus for storing and dispensing standard chromous chloride solution, the titration cell, and the means of determining the end-point were fully described in an earlier publication[1].

Reagents

Standard solutions of chromous chloride and ferric alum were prepared by the procedures previously reported[1].

Samples

Solutions of tartrazine and orange II were prepared by dissolving weighed samples of National Aniline reagents in 475 ml of distilled water and 25 ml of glacial acetic acid.

Standard solutions of azobenzene and azoxybenzene were prepared by dissolving known amounts of recrystallized Brother's Chemical Company reagents in 95% ethanol or glacial acetic acid.

Samples of hydrazobenzene were prepared by weighing out various amounts of either Brother's Chemical Co., Matheson, Coleman and Bell Co., Eastman Kodak Co., or Amend Drug and Chemical Co. hydrazobenzene into tall-form electrolytic beakers. The samples were dissolved in a mixture of 10 ml of concentrated hydrochloric acid and 40 ml of either 95% ethanol or glacial acetic acid.

* Present address

Standard solutions of propiolic acid were prepared by dissolving known amounts of freshly distilled K and K Laboratories propiolic acid in oxygen-free distilled water. The acid was weighed in sealed ampoules which were prepared by the method of SIGGIA[2]. The ampoules were broken under oxygen-free distilled water and the solution was then quantitatively transferred to a volumetric flask and diluted to the mark. During the transfer, the solution was filtered free of glass by passing it through glass wool.

Samples of diphenylacetylene were prepared by weighing out various amounts of Matheson, Coleman and Bell Co. diphenylacetylene into tall electrolytic beakers. Samples were dissolved in either 95% ethanol or glacial acetic acid.

Solutions of 2-methyl-3-butyn-2-ol, 1-ethynyl-cyclohexanol-1, 2,5-dimethyl-3-hexyne-2,5-diol, and 2,5-diphenyl-3-hexyne-2,5-diol were prepared by dissolving small unknown amounts of Air Reduction Chemical Co. compounds in 40 ml of either 95% ethanol or glacial acetic acid.

Standard solutions of diacetyl were prepared by dissolving freshly distilled Eastman Kodak diacetyl in oxygen-free distilled water. The solution was standardized by the procedure of WILSON[3].

Samples of benzil were prepared by weighing out various amounts of Matheson, Coleman and Bell Co. benzil into tall electrolytic beakers and dissolving the solid in a mixture of 10 ml of concentrated hydrochloric acid and 40 ml of 1 : 1 glacial acetic acid and 95% ethanol.

Solutions of acetylacetone were prepared by dissolving small unknown amounts of Eastman Kodak acetylacetone in 40 ml of either 95% ethanol or glacial acetic acid.

Procedure

The procedure most frequently used was the indirect method of analysis[1]. This involved treating an oxygen-free solution of the compound in distilled water, 95% ethanol, or glacial acetic acid, which contained some hydrochloric acid, with an excess of 0.1000 *N* chromous chloride, allowing the reaction mixture to stand for a short time, and then back-titrating with standard ferric alum solution.

In the determination of orange II, the sample could not be added to a hydrochloric acid solution since a precipitate formed. Instead the sample was added to 3% sulfuric acid solution, a 1 : 1 mixture of 2% sulfuric acid and glacial acetic acid, or a solution of sodium bitartrate containing 15 g of salt per 50 ml of solution. The results using any of the media were the same. When a 2% sulfuric acid solution was used, some of the orange II precipitated when chromous chloride was first added, but the precipitate dissolved with further addition of the reductant.

Azoxybenzene could not be determined by the usual indirect procedure. The results were erratic. Samples were added to 1 : 1 sulfuric acid and allowed to stand for about 15 min so that the azoxy compound could first be rearranged to the corresponding azo compound. Before back-titrating the excess of chromous chloride, the reaction mixture had to stand for at least 3 min.

In the case of propiolic acid, as with the monopotassium salt of acetylenedicarboxylic acid[1], no hydrochloric acid was present in the reaction mixture. In hydrochloric acid medium, the results were low and erratic. Since propiolic acid is quite volatile, even in aqueous solution, aliquots were added to oxygen-free water and oxygen-free carbon dioxide was passed over the surface of the solution for a minute

before chromous chloride was added. It was also necessary to wait for at least 2 min before back-titrating the excess chromous chloride. A longer reaction time did not increase the amount of reduction.

Since diacetyl is very volatile, even in solution, aliquots were added to oxygen-free solutions containing 10 ml of concentrated hydrochloric acid, 40 ml of distilled water and excess chromous chloride. By this procedure, volatility losses should almost be nil since the diacetyl is instantaneously reduced by the chromous chloride already present in the solution.

Heating samples of hydrazobenzene to about 85°–90° and cooling to about 50° before back-titrating did not increase the amount of reduction. At times, small differences (2 to 3%) were observed for samples run at room temperature and those run at elevated temperatures. This, however, may be readily explained in that the value of the blank determination at elevated temperatures was not the same for all determinations since the temperature of the reaction mixture could not be rigorously controlled with the type of apparatus used.

Orange II and benzil may also be determined by direct titration which is carried out at about 60°, but even so the reaction becomes very slow near the end-point. In both cases the potential break at the end-point is about 200 mV.

TABLE I

ANALYSIS OF ORGANIC COMPOUNDS USING CHROMOUS CHLORIDE

	Meq. taken	*Excess chromous chloride (%)*	*Meq. found*	*Number of eq. of Cr(II) used per mole*	*Number of determinations*
Orange II	1.048	300	1.045±0.006[a]	4	3
	1.048		1.050±0.005		3
Tartrazine	1.168	250	1.165±0.003	4	3
Azoxybenzene	0.800	200–400	0.795±0.008	4	5
	0.884		0.881±0.004		7
Propiolic acid	1.214	200–400	1.212±0.005	2	4
Diacetyl	0.895	100–400	0.891±0.004	2	6

[a] Direct titration.

TABLE II

DETERMINATION OF BENZIL

Benzil taken (mg)	*Benzil found (mg)*	*Error (%)*
Direct titration		
276.5	276.3	−0.07
165.4	165.9	+0.30
117.7	117.3	−0.34
89.6	89.6	0.0
54.5	54.6	+0.18
35.7	35.7	0.0
Indirect determination (100–400% excess Cr^{2+})		
244.0	243.8	−0.49
162.5	162.5	0.0
139.1	138.5	−0.43
96.5	96.8	+0.31
73.2	73.1	−0.14
36.7	36.6	−0.27

Blanks using the same solvent conditions and procedures as were used for the samples were run on chromous chloride for each of the determinations. The blanks ranged from 0.05 to 0.20 ml.

RESULTS

The results obtained for orange II, tartrazine, azoxybenzene, propiolic acid and diacetyl are presented in Table I. In Table II are presented the data for benzil. Results are not reported for azobenzene since the sample was not very pure even after several recrystallizations from alcohol–water mixtures. The results were low but quite concordant (assuming 2 equivalents per mole, 1.000 meq. taken, found 0.863 ± 0.012). Heating the solutions did not increase the amount of reduction. Hydrazobenzene, diphenylacetylene, 2-methyl-3-butyn-2-ol, 1-ethynyl-cyclohexanol-1, 2,5-dimethyl-3-hexyne-2,5-diol, 2,5-diphenyl-3-hexyne-2,5-diol, and acetylacetone were not reduced even at elevated temperatures.

DISCUSSION

Unlike other azo compounds which have been studied, azobenzene is not cleaved by chromous chloride. Only 2 equivalents per mole of azobenzene are consumed while other azo compounds require 4 equivalents per mole. The reduction product of azobenzene is probably hydrazobenzene which was found not to be reduced with chromous chloride even at elevated temperatures. Why azobenzene should behave so differently is not understood and will be further investigated.

The difference in reducibility of the various acetylene compounds may be correlated with the polarographic behavior of acetylene compounds[4,5]. Compounds containing isolated acetylenic linkages are not reducible; however, compounds in which the triple bond is conjugated are reducible. Thus, the non-reducibility of 2-methyl-3-butyn-2-ol, 1-ethynyl-cyclohexanol-1, 2,5-dimethyl-3-hexyne-2,5-diol, and 2,5-diphenyl-3-hexyne-2,5-diol by chromous chloride may be attributed to the lack of conjugation in these compounds. Although the triple bond in diphenylacetylene is conjugated, as it is in acetylene dicarboxylic acid and propiolic acid, the difference in reducibility of these compounds by chromous chloride may be explained from the difference in ease with which these compounds are reduced at the dropping mercury electrode. Acetylene dicarboxylic acid is very easily reduced (—0.22 V *vs.* N.C.E. in 1 *N* hydrochloric acid) and propiolic acid should behave similarly. Diphenylacetylene is very difficult to reduce (—2.20 V *vs.* N.C.E.). The difference in ease of polarographic reduction is due to the different types of conjugation in the two types of compounds. The presence of the benzene nuclei in diphenylacetylene must contribute greatly to the resonance stabilization of this compound. The type of conjugation is similar to that of benzene which is not reduced at the D.M.E.

SUMMARY

The reducibility of a number of organic compounds by a standard chromous chloride solution, prepared determinately from potassium dichromate, has been studied. Orange II, tartrazine, and azoxybenzene (after rearrangement in sulfuric acid medium to the corresponding azo compound) were quantitatively cleaved to the corresponding amines, while azobenzene was reduced only to hydrazobenzene (extent of reduction uncertain). Also quantitatively reduced were: propiolic acid to propenoic acid, diacetyl to acetoin, and benzil to benzoin. Hydrazobenzene, diphenylacetylene, 2-methyl-3-butyn-2-ol, 1-ethynyl-cyclohexanol-1, 2,5-dimethyl-3-hexyne-2,5-diol, 2,5-diphenyl-3-hexyne-2,5-diol, and acetylacetone were not reduced even at elevated temperatures.

RÉSUMÉ

Une étude a été effectuée sur la réductibilité d'un certain nombre de composés organiques par une solution étalon de chlorure chromeux, préparée à partir de dichromate de potassium. Certaines substances peuvent être ainsi réduites quantitativement (acide propiolique, diacétyle, et benzile).

ZUSAMMENFASSUNG

Die Reduzierbarkeit einer Anzahl organischer Verbindungen mit einer aus Kaliumdichromat hergestellten Chromchlorid-Lösung wurde untersucht. Ein Teil der Verbindungen wurde quantitativ gespalten, ein anderer quantitativ reduziert, während einige selbst bei erhöhten Temperaturen nicht reduziert wurden.

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ÜBER DIE REAKTION VON CHROM MIT DIPHENYLCARBAZID UND DIPHENYLCARBAZON

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Die Farbreaktion von Chromat mit Diphenylcarbazid (im folgenden abgekürzt: DCD) wird wegen ihrer Selektivität und hohen Empfindlichkeit seit mehr als 60 Jahren mit gutem Erfolg für die quantitative Bestimmung von Chrom verwendet, ohne dass jedoch Reaktionsmechanismus und Natur des entstehenden Farbstoffes geklärt sind. Obwohl teils recht ausführliche Studien ausgeführt wurden, finden sich in der Literatur viele einander widersprechende Ergebnisse. Während einige Autoren[1] der Ansicht sind, es handle sich bei dem Farbstoff nur um Oxidationsprodukte des DCD, wird in der übrigen Literatur[3-7] meist die Auffassung vertreten, es liege ein farbiger Chromkomplex vor.

BOSE[5], der die Reaktion eingehend mit physikochemischen Methoden untersuchte, postuliert eine kombinierte Redox- und Komplexbildungsreaktion und einen Komplex des Cr(II) mit Diphenylcarbazon (im folgenden abgekürzt: DCN)

$$2\ Cr^{6+} + 3\ DCD \rightleftharpoons 2\ [Cr^{2+}\ DCN^{2-}] + \text{Diphenylcarbadiazon} + 4\ H^{+}$$

Bei dieser Annahme ging BOSE von folgenden Beobachtungen aus:

(*1*) Cr(VI) reagiert sowohl mit DCD als auch mit DCN;

(*2*) Cr(II) reagiert mit DCN, aber nicht mit DCD;

(*3*) Cr(III) reagiert mit keinem der beiden Reagenzien.

Ad (*1*) wäre zu sagen, dass nach KRUMHOLZ UND KRUMHOLZ[8] reines DCN *nicht* mit Cr(VI) reagiert.

Ad (*2*): PFLAUM UND HOWICK[6] wiesen darauf hin, dass BOSES[5] Versuche über die Reaktion des DCN in Wahrheit mit der 1:1 Verbindung DCD–DCN ausgeführt worden waren, sodass BOSES[5] Interpretation seiner Versuche teilweise unrichtig ist.

Ad (*3*): PFLAUM UND HOWICK[6] kommen auf Grund ihrer Versuche — abweichend von BOSE[5] — zu dem Schluss, dass auch Cr(III) sowohl mit DCD als auch DCN reagiert. Sie postulieren als Reaktionsprodukt einen Komplex des Cr(III) mit DCN.

BABKO UND PALII[1] behaupten auf Grund von Extraktionsversuchen, bei denen der Farbstoff in Amylalkohol ausgezogen und kein Cr im Extrakt gefunden wurde, dass keine Komplexbildung, sondern eine reine, selektive Redoxreaktion vorliege.

LICHTENSTEIN UND ALLEN[7] führten ebenfalls Extraktionsversuche aus, fanden aber — nach BABKO UND PALIIS[1] Vorschrift arbeitend — Cr in der organischen Phase wieder. Infolge dieser Widersprüche schien es angezeigt, einige Versuche auszuführen,

die vielleicht zur Klärung dieser Reaktion beitragen können. Hierbei sollte vor allem der Frage nachgegangen werden, ob DCN und DCD mit Cr(III) reagieren und ob Chrom als Komplex extrahierbar ist.

EXPERIMENTELLE RESULTATE

Reagentien

DCD p.a. (Riedel–de Haën), DCN p.a. (Merck), $[CrCl_2(H_2O)_4]Cl \cdot 2\ H_2O$ p.a., $CrCl_3$ wasserfrei, Lösungsmittel alle puriss., ^{51}Cr aus Bestrahlung von $(NH_4)_2CrO_4$ p.a. im Reaktor (Triga Mark II)*, durch Gammaspektrometrie auf radiochemische Reinheit geprüft.

(1) Reaktion Cr(III) mit DCN

(a) In organischen Lösungsmitteln. Es wurde Cr(III) mit DCN in einer Reihe organischer Lösungsmittel reagieren gelassen, wobei je 5 mg $[CrCl_2(H_2O)_4]\ Cl \cdot 2\ H_2O$ in je 5 ml Lösungsmittel gelöst und die Entwicklung der Färbung beobachtet wurde. Als Lösungsmittel wurden verwendet: Dimethylformamid (DMF), Aceton, Methylisobutylketon (MIBK), *t*-Butanol, Pyridin und Tributylphosphat (TBP). Bei einigen Lösungsmitteln wurde auch Wasser dem Reaktionsgemisch zugesetzt. Die charakteristische violette Farbreaktion trat in allen organischen Lösungsmitteln auf. Die Reaktionsgeschwindigkeit war allerdings sehr unterschiedlich: rasch in Aceton, mässig rasch in *t*-Butanol, langsam in MIBK und TBP, sehr langsam in DMF. In Pyridin trat erst nach 16 Stunden Reaktion ein. Zusatz von Wasser zu den organischen Lösungsmitteln verhinderte die Reaktion oder verlangsamte sie sehr stark: Während in Aceton innerhalb von 2 Minuten deutliche Färbung auftrat, wurde eine vergleichbare Intensität erst nach 24 Stunden erreicht, wenn 10% (Vol.) Wasser anwesend waren. Zusatz von NaOH wirkte kräftig katalysierend.

(b) In fester Form. 5 mg $[CrCl_2(H_2O)_4]Cl \cdot 2\ H_2O$ wurden mit 5 mg DCN in der Reibschale innigst verrieben. Es trat Reaktion ein und der Farbstoff konnte mit 1 *N* H_2SO_4 ausgezogen werden. Auch wasserfreies $CrCl_3$ reagierte beim Verreiben mit DCN.

(c) In wässeriger Lösung. 5 mg $[CrCl_2(H_2O)_4]Cl \cdot 2\ H_2O$ wurden in 5 ml Wasser gelöst und 5 mg DCN, das in 1 ml Aceton gelöst war, zugesetzt. Beim tropfenweisen Zusatz von wässerigem Ammoniak trat bald nach dem Ausfall von $Cr(OH)_3$ die blutrote Färbung der Enolform des DCN auf. Wenn nun vorsichtig mit 2 *N* H_2SO_4 angesäuert wurde, sodass das Hydroxid langsam in Lösung ging, trat die charakteristische violette Färbung auf.

(2) Reaktion Cr(III) mit DCD

5 mg DCD und 5 mg $[CrCl_2(H_2O)_4]Cl \cdot 2\ H_2O$ wurden in 5 ml Aceton gelöst und aus einer Kapillare sauerstofffreier Stickstoff (Waschflasche mit alkal. Pyrogallollösung) eingeleitet. Sobald alle Luft aus dem Reaktionsgemisch gespült war, wurde zur Katalyse einer etwaigen Reaktion etwas NaOH in fester Form zugesetzt. Eine Farbreaktion erfolgte jedoch nicht. Ein Kontrollversuch, bei dem DCN anstelle von DCD verwendet wurde, ergab sofortige Reaktion.

DCD reagierte auch in wässeriger Lösung und beim Verreiben *nicht* mit Cr(III).

* Für die Bestrahlung sei hier Herrn Dr. F. GRASS, Atominstitut der Österreichischen Hochschulen, herzlich gedankt.

(3) Enolisierung des DCN

Suspendiert man DCN in Wasser und setzt etwas NaOH zu, dann geht die Substanz mit blutroter Farbe in Lösung. Es tritt offenbar die Enolform des DCN auf (siehe auch BAMBERGER[9]).

In organischen Lösungsmitteln trat Enolisierung schon beim Lösen ein, wurde aber durch Basen katalysiert. Bei Versuchen in DMF konnte festgestellt werden, dass die Farbe des Enolates offenbar durch den Wassergehalt des Lösungsmittels stark beeinflusst wird. In vollkommen wasserfreiem DMF war das Enolat von violetter Farbe, die der typischen Farbe der Reaktion Cr(VI)–DCD glich. Die violette Farbe des Enolates schlug beim Zusatz von etwas Wasser nach Rot um und war gegen Säure nicht beständig.

(4) Absorptionsspektren

Die Absorptionsmaxima der bei obigen Versuchen erhaltenen farbigen Reaktionsprodukte wurden mit einem Beckman-(B)-Spektrophotometer für den sichtbaren Bereich bestimmt. Die Reaktionslösungen wurden hierzu jeweils soweit verdünnt, dass vernünftige Extinktion erhalten wurde. Fig. 1 zeigt die Absorptionsmaxima für die Reaktion DCN mit Cr(III), in Aceton (*a*), in wässeriger Lösung (*b*) und in fester Form im Auszug des Farbstoffes mit 1 *N* H_2SO_4 (*c*). Vergleich mit dem Absorptionsmaximum, das aus der Reaktion von DCD mit Cr(VI) (*d*) erhalten wird, legt nahe, dass bei beiden Reaktionen das gleiche Produkt erhalten wird.

Fig. 2 stellt die Maxima dar, die durch die Enolisierung des DCN erhalten wurden,

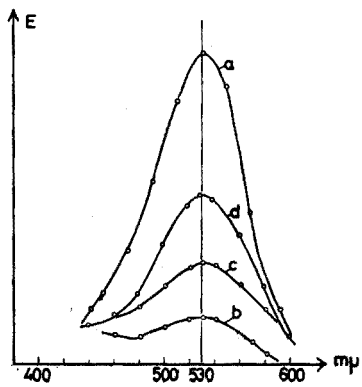


Fig. 1.

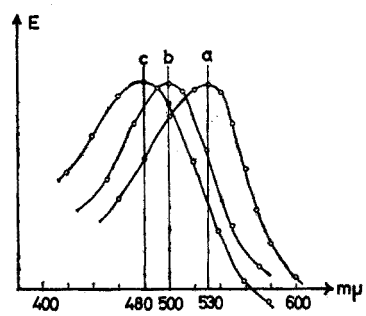


Fig. 2.

und zwar in wasserfreiem DMF (*a*), in einer Mischung DMF–H_2O (1 : 1) (*b*) und in H_2O (*c*). Die Lage des Enolat-Absorptionsmaximums weicht in wässeriger Lösung nur um *ca.* 50 mμ von der des Maximums der DCD–Cr(VI) Reaktion ab und stimmt im wasserfreien DMF mit ihm überein.

(5) Extraktionsversuche

Es wurde die Extrahierbarkeit des violetten Farbstoffes der DCD–Cr(VI) Reaktion und die Extrahierbarkeit des Chroms geprüft. Das Reaktionsgemisch enthielt je-

weils *ca.* 100 μg Cr und 12.5 mg Reagens in einem Volumen von 10 ml. Das Chrom war durch ^{51}Cr radioaktiv markiert, die Säurekonzentration wurde auf 0.9, 0.2 *N* Schwefelsauer sowie auf pH 4 eingestellt. Durch Sättigen der Lösung mit NH_4Cl gelang es, den Farbstoff quantitativ in Amylalkohol zu extrahieren. Die Gammaaktivität der wässerigen und der organischen Phase wurde hierauf mittels eines Szintillationsmesskopfes bestimmt. Wie aus Tabelle I hervorgeht, blieb stets ein beträchtlicher Anteil des Cr in der wässerigen Phase, der Grossteil der Cr-Aktivität wurde extrahiert.

Wenn die organische Phase erneut mit wässerigen Lösungen ins Gleichgewicht gesetzt wurde, blieb der Verteilungskoeffizient der Chromaktivität gleich dem des

TABELLE I

EXTRAKTION VON Cr(VI) MIT DCD UND DCN IN AMYLALKOHOL

Acidität	*Chrommenge (als Chromat) (μg)*	*Reagens*	*% Cr in der wäss. Phase*
0.9 *N*	100	DCD	33.5
0.2 *N*	93	DCD	15.4
pH 4	93	DCD	30.0
0.2 *N*	93	DCD + DCN(1 : 1)	35.3
pH 4	93	DCD + DCN(1 : 1)	40.1

Farbstoffes. Daraus geht hervor, dass es sich bei dem Farbstoff tatsächlich um eine Chromverbindung handelt. Für diese Komplexbildung war die Acidität von 0.2 *N* optimal; die Reaktion verlief aber in keinem Fall quantitativ, auch nicht, wenn neben dem DCD eine gleiche Menge DCN zugesetzt worden war.

DISKUSSION

Die Feststellung BOSES[5], DCN reagiere nicht mit Cr(III), trifft nicht zu. Vielmehr reagiert Cr(III) mit DCN sowohl in organischen Lösungsmitteln — was schon von PFLAUM UND HOWICK[6] berichtet wurde — als auch in fester Form, sowie (wenn auch schlechter) in wässeriger Lösung. In den organischen Lösungsmitteln wird die Reaktion durch Basen katalysiert. Wasser wirkt störend, was dadurch erklärt wird, dass Cr(III) je stabile Aquokomplexe bildet. Bei Abwesenheit von Wasser verläuft die Reaktion glatt, in wässeriger Lösung nur mit Cr(III) in statu nascendi (*z.B.* beim Lösen von $Cr(OH)_3$ in Säure).

Die Aussage PFLAUM UND HOWICKS[6] bezüglich der Reaktion von Cr(III) mit DCD ist dahingehend zu präzisieren, dass DCD in Abwesenheit von Oxidationsmitteln (Luftsauerstoff) *nicht* reagiert. Wenn diese Autoren eine Farbreaktion beobachteten, so war dies ausschliesslich eine Reaktion des DCN, das unter dem Einfluss des Luftsauerstoffes aus DCD entstanden war.

Bezüglich der Frage, ob die Reaktion Cr(VI)–DCD nur ein violettes Oxidationsprodukt oder einen Chromkomplex liefert, konnte in Übereinstimmung mit LICHTENSTEIN UND ALLENS[7] Extraktionsversuchen gezeigt werden, dass eine violette Chromverbindung auftritt. Der unhaltbaren Ansicht der Autoren BABKO UND PALIIS[1], dass es sich um eine reine, selektive Redox-Reaktion handle, dürfte die Beobachtung zugrunde liegen, dass violette Farbstoffe aus DCD und DCN auch durch Redox-Reaktion und Enolisierung entstehen können.

In Bezug auf die Wertigkeit des Chroms im entstehenden Komplex sind BOSE[5]

und PFLAUM UND HOWICK[6] verschiedener Ansicht; der erste postuliert einen Komplex des Cr(II), die zweitgenannten nehmen einen Komplex des Cr(III) an. BOSES[5] Schluss lag teilweise die Beobachtung zugrunde, Cr(III) reagiere weder mit DCD noch mit DCN. Da dies — wie oben beschrieben — nur für Cr(III) in hydratisierter Form zutrifft, kommt der Ansicht PFLAUM UND HOWICKS[6] die grössere Wahrscheinlichkeit zu.

Nach den gesamten bisher vorliegenden Versuchsergebnissen müssen für die Farbreaktion DCD–Cr(VI) folgende Schritte angenommen werden:

$$(1)\ 2\,Cr^{6+} + 3\,DCD \rightleftharpoons 2\,Cr^{3+} + 3\,DCN + 6\,H^{+}$$

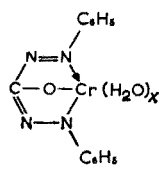
$$(2)\ Cr^{3+} + DCN \rightleftharpoons [CrDCN]^{+} + 2\,H^{+}$$

Diese Redoxreaktion mit nachfolgender Komplexierung läuft aber nicht ausschliesslich ab, sondern es treten Nebenreaktionen auf. Diese Nebenreaktionen sind *z.B.* Oxidation des DCN zu Diphenylcarbadiazon und Hydratisierung des Cr(III). Dass die Farbreaktion unter den angewendeten Versuchsbedingungen nicht quantitativ verläuft, geht aus den beschriebenen Extraktionsversuchen mit DCD hervor: stets lag ein Teil der Chromaktivität als extrahierbarer Komplex vor, ein Teil in nicht extrahierbarer Form (wahrscheinlich hydratisiert).

Da die Gleichgewichtslage aber nicht durch überschüssigen Komplexbildner (DCN) zugunsten des Komplexes verschoben werden konnte, muss auf Nebenreaktionen geschlossen werden. Daraus folgt, dass Versuche nach der Methode von JOB[10], wie sie *z.B.* von PFLAUM UND HOWICK[6] angestellt wurden, nur dann schlüssige Hinweise auf die Stöchiometrie der Reaktion liefern können, wenn die Gleichgewichtslagen der Nebenreaktionen berücksichtigt werden.

Da diese aber unbekannt sind, kann derzeit über die Stöchiometrie des in Frage stehenden Chromkomplexes nichts Endgültiges ausgesagt werden.

Bezüglich der Formulierung der Komplexbildung wäre jedoch noch folgendes zu bemerken: Eine Konstitution des DCN-Komplexes, wie sie BOSE[5] postuliert:

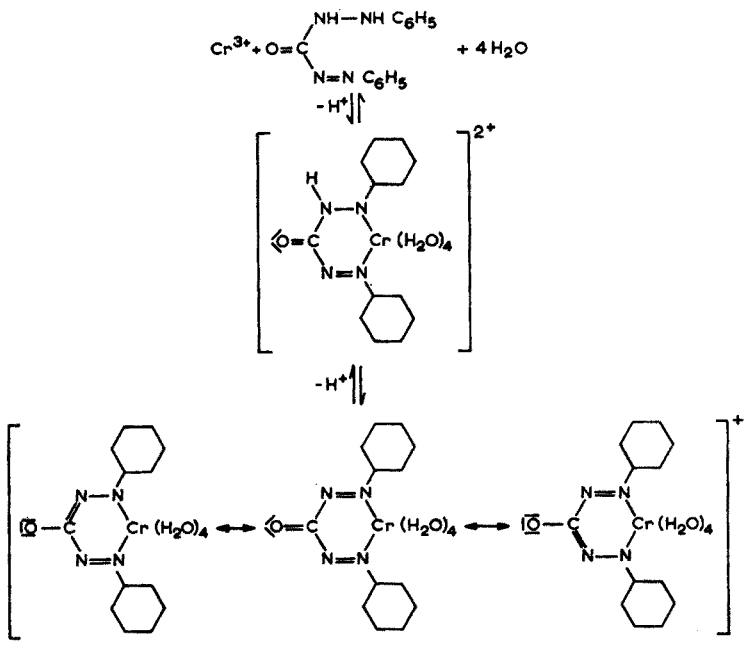


ist schon aus sterischen Gründen nicht anzunehmen.

PFLAUM UND HOWICK[6] wendeten gegen BOSES[5] Formulierung ein, dass in saurer Lösung eine Reaktion über die Enolform des DCN sehr unwahrscheinlich sei.

Dagegen muss geltend gemacht werden, dass ja Enolisierung auch nach der Komplexbildung eintreten kann. Es ist nämlich die Tatsache auffällig, dass der Chromkomplex und die Enolform des DCN bezüglich der Lage ihrer Absorptionsmaxima im Sichtbaren einander sehr nahe liegen, *bzw.* im nichtwässerigen System identisch sind (Fig. 1 und 2). Deshalb scheint es nicht unwahrscheinlich, für die intensive Farbe des Chromkomplexes in erster Linie Resonanz des Komplexbildners ähnlich wie im Enolation anzunehmen.

Folgende hypothetische Formulierung der Komplexbildung mit anschliessender Ausbildung eines resonanzfähigen Systems würde dieser Anschauung gerecht werden:



Danach entstünde primär ein Komplexion der Ketoform. Durch die Komplexbildung geht die freie Drehbarkeit um die C–N-Bindungen am Carbonylkohlenstoff verloren, sodass nach Abdissoziation des zweiten Protons eine ebene, symmetrische und damit hochresonanzfähige Konfiguration entsteht*.

Durch den Resonanzenergiegewinn wäre die Stabilität eines derartigen kationischen Komplexes auch bei pH 1 erklärt.

ZUSAMMENFASSUNG

Auf Grund qualitativer Versuche wurde gezeigt, dass Cr(III) nicht mit Diphenylcarbazid (DCD) reagiert, wohl aber mit Diphenylcarbazon (DCN), und zwar in organischen Lösungsmitteln, in wässeriger Lösung und in fester Form. Der entstehende Farbstoff hat das gleiche Absorptionsmaximum wie das Produkt der Reaktion Cr(VI) –DCD. Diese liefert auf Grund von Extraktionsversuchen mit ^{51}Cr einen violetten Chromkomplex, doch wurde gefunden, dass Nebenreaktionen auftreten. Deshalb kann über die Stöchiometrie der Reaktion nichts Endgültiges ausgesagt werden, doch handelt es sich mit grosser Wahrscheinlichkeit um eine Redoxreaktion gefolgt von Komplexierung des Cr(III) durch DCN. Es wird ein Reaktionsmechanismus vorgeschlagen, der zu einem resonanzstabilisierten, kationischen Komplex führt.

SUMMARY

Qualitative tests have shown that Cr(III) does not react with diphenylcarbazide (DCD) but with diphenylcarbazone (DCN) in organic solvents, aqueous solution and solid form. The formed dyestuff has the same absorption maximum as the product of the Cr(VI)–DCD reaction. Extraction tests with ^{51}Cr show that the latter reaction yields a violet chromium complex but side-reactions also occur. Thus the stoichiometry of the reaction cannot be definitely established, but it is extremely probable that a redox reaction is combined with complexation of Cr(III) by DCN. A reaction mechanism is proposed which leads to a resonance-stabilized, cationic complex.

* Es ist denkbar, dass auch das Elektronensystem des Metallatoms teilweise in das Resonanzsystem einbezogen wird.

RÉSUMÉ

Des essais qualitatifs ont montré que le chrome(III) réagit avec la diphénylcarbazone (DCN) en solvants organiques, en solution aqueuse et sous forme solide, et non avec la diphénylcarbazide (DCD). La coloration obtenue présente le même maximum d'absorption que le produit de réaction chrome(VI)–DCD. Des essais d'extraction avec ^{51}Cr ont montré que cette dernière réaction, donnant un complexe de chrome violet, est accompagnée d'autres réactions. Bien que la stoéchiométrie de la réaction ne peut pas être établie de façon définie, il est fort probable qu'il se produit à la fois une réaction redox et une complexation de Cr(III) par DCN. Un mécanisme de réaction est proposé.

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THEORY OF TITRATION CURVES

PART II. LOCATIONS OF POINTS OF MAXIMUM SLOPE ON POTENTIOMETRIC HETEROVALENT ("ASYMMETRICAL") PRECIPITATION TITRATION CURVES

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Descriptions of the potentiometric titration curves obtained for precipitation titrations in which the ions of the precipitate have numerically different valences* have been given by a number of authors[1-4], all of whom neglected the effect of dilution. It is generally accepted that the inflection point where the slope of such a curve is a maximum always differs from the equivalence point, occurring on that side of the equivalence point where the ion having the smaller numerical valence is present in excess, and that the difference between the inflection point and the equivalence point is always increased by decreasing the concentrations of the reacting solutions or by increasing the solubility product of the precipitate.

For the related case in which the ions of the precipitate have numerically equal valences**, entirely similar derivations lead to the conclusion that the inflection point at which the slope is a maximum always coincides with the equivalence point. In a preceding paper in this series[5], however, it was shown, by taking into account the effect of dilution, that in fact this inflection point can never coincide with, but on the contrary must always precede, the equivalence point, and that the error incurred by equating them may approach 100%; in fact, if the solution is assumed to be saturated with the precipitate at the very start of the titration, the inflection point may vanish entirely.

As the inclusion of the dilution effect leads to conclusions that contravene the common belief in the simple isovalent case, it seemed likely that it would do so in the heterovalent case as well. This expectation has been confirmed by a rigorous general examination of the problem, as described below. The extent to which the common beliefs regarding the heterovalent titration are in error is indicated by the fact that there are conditions under which the inflection point can coincide with the equivalence point in a titration of this type even though it can never do so in the "symmetrical" (isovalent) case.

DERIVATION OF A GENERAL EQUATION FOR THE INFLECTION POINT

We shall consider the general precipitation reaction

$$nB^{m+} + mA^{n-} = B_nA_m \qquad (1)$$

* Such titrations have been called "asymmetrical"; as will be proved below, this term is misleading, and we shall therefore call them "heterovalent" instead.

** Such titrations are hereafter called "isovalent".

whose equilibrium is governed by the solubility product

$$K = [B^{m+}]^n[A^{n-}]^m \tag{2}$$

Because equations applicable to the isovalent case (in which $m = n$) are in general merely special cases of those given below, it may be noted that the solubility product defined by eqn. (2) takes an unusual form when $m = n \neq 1$; for example, for a bivalent precipitate like barium sulfate it defines a solubility product that is the square of the usual one. Variations of activity coefficients and liquid–junction potentials during the titration are assumed to be negligible; this will be justifiable if a uniform and relatively large concentration of an indifferent electrolyte is present throughout. It is convenient to assume that the solution of B^{m+} being titrated is initially in equilibrium with solid B_nA_m; this avoids the discontinuity that would otherwise characterize the appearance of the first precipitate, and permits the entire titration curve to be described by a single equation. Though this assumption has not been explicitly stated, it has been implicitly made by all of the earlier authors on this subject. Differential adsorption on the precipitate is neglected.

The electroneutrality equation describing the titration of V_B^0 ml of $C_B^0 F$ BX_m with $C_T F$ Y_nA is

$$[Y^+] + m[B^{m+}] = [X^-] + n[A^{n-}] \tag{3}$$

It is convenient to define a parameter f by the equation

$$f = nV_TC_T/mV_B^0C_B^0 \tag{4}$$

so that $f = 1$ at the equivalence point. At any point during the titration, where V_T ml of the reagent Y_nA has been added,

$$[Y^+] = nV_TC_T/(V_B^0 + V_T) \tag{5a}$$

$$[X^-] = mV_B^0C_B^0/(V_B^0 + V_T) \tag{5b}$$

$$[A^{n-}] = K^{1/m}/[B^{m+}]^{n/m} \tag{5c}$$

Substituting eqns. (5) into eqn. (3) yields the following equation for the titration curve:

$$[B^{m+}] = \frac{nC_B^0C_T(1 - f)}{nC_T + mC_B^0f} + \frac{nK^{1/m}}{m[B^{m+}]^{n/m}} \tag{6}$$

Manipulation of eqn. (6) is facilitated by the introduction of two additional parameters: the charge ratio z and the dilution parameter r, defined by the equations

$$z = n/m \tag{7a}$$

$$r = C_B^0/C_T \tag{7b}$$

Substituting these definitions into eqn. (6) gives

$$[B^{m+}] = \frac{zC_B^0(1 - f)}{z + rf} + \frac{zK^{1/m}}{[B^{m+}]^z} \tag{8}$$

which is of the form

$$[B^{m+}]^{z+1} - \alpha[B^{m+}]^z - zK^{1/m} = 0 \tag{9}$$

where

$$\alpha = \frac{zC_B^0(1 - f)}{z + rf} \tag{10}$$

Now, if the indicator electrode is reversible toward B^{m+}, so that

$$E = E^{0\prime} + k \ln[B^{m+}]^* \tag{11}$$

one has

$$\frac{dE}{df} = \frac{1}{[B^{m+}]} \frac{d[B^{m+}]}{df} k$$

and

$$\frac{d^2E}{df^2} = \frac{[B^{m+}](d^2[B^{m+}]/df^2) - (d[B^{m+}]/df)^2}{[B^{m+}]^2} k \tag{12}$$

At the inflection point $d^2E/df^2 = 0$ while $[B^{m+}]$ of course remains finite; hence the inflection point is defined by the equation

$$[B^{m+}] \frac{d^2[B^{m+}]}{df^2} = \left(\frac{d[B^{m+}]}{df}\right)^2 \tag{13}$$

Differentiating eqn. (9) twice, imposing the inflection-point condition stated by eqn. (13), and simplifying, one obtains

$$[(z + 1)[B^{m+}] - \alpha z]^2 \frac{d^2\alpha}{df^2} = [(1 - z^2)[B^{m+}] + \alpha z^2] \left(\frac{d\alpha}{df}\right)^2 \tag{14}$$

where the values of $[B^{m+}]$, α, and the derivatives of α must all be taken at the inflection point. The derivatives are

$$\frac{d\alpha}{df} = -\frac{zC_B^0(z + r)}{(z + rf)^2} \tag{15a}$$

and

$$\frac{d^2\alpha}{df^2} = \frac{2zrC_B^0(z + r)}{(z + rf)^3} \tag{15b}$$

Substituting these into eqn. (14) and simplifying yields the final rigorous general description of the inflection point:

$$2[(z + 1)[B^{m+}] - \alpha z]^2 \frac{r(z + rf)}{zC_B^0(z + r)} = (1 - z^2)[B^{m+}] + \alpha z^2 \tag{16}$$

* The alternative case, in which the indicator electrode is reversible to A^{n-}, is trivial; combining an equation of the form

$$E = E^{0\prime} - j \ln[A^{n-}]$$

with eqn. (2) yields immediately an equation identical with eqn. (11). This in turn means that the reverse titration, of A^{n-} with B^{m+}, is only trivially different from the one discussed here. It may be dismissed by saying that it is fully described by replacing $[B^{m+}]$ with $[A^{n-}]$ and C_B^0 with C_A^0 and interchanging m and n wherever these quantities appear in the equations that follow.

THE CONSEQUENCES OF NEGLECTING DILUTION

When dilution is neglected by setting r equal to zero, the left-hand side of eqn. (16) vanishes, and one has simply

$$[B^{m+}] = \frac{z^2}{z^2 - 1}\alpha \tag{17}$$

at the inflection point. Substituting this into eqn. (9), and using the value of α given by eqn. (10) for $r = 0$, yields the following expression for the titration error:

$$f - 1 = \frac{1 - z^2}{C_B{}^0}\left(\frac{K^{1/m}}{z^{(2z-1)}}\right)^{1/(z+1)} \tag{18}$$

From these simple equations it follows that:

(*1*) If $z = 1$ (the isovalent case), there is an inflection at the equivalence point, because the right-hand side of eqn. (18) is then zero.

(*2*) If z has any other value, there cannot be an inflection at the equivalence point, because eqn. (17) then cannot be satisfied there: $[B^{m+}]$ is finite at the equivalence point, while $\alpha = 0$ there.

(*3*) If $z > 1$, the inflection point must precede the equivalence point, because the right-hand side of eqn. (18) is positive; but if $z < 1$ the inflection point must follow the equivalence point, because the right-hand side of eqn. (17) must be positive, and if $z^2/(z^2 - 1) < 0$ (as must be the case if $z < 1$) this can only be true if $\alpha < 0$, which eqn. (10) shows to be possible only if $f > 1$. That is, the inflection point always occurs in a solution containing an excess of the lower-valent ion.

(*4*) The titration error (*i.e.*, the value of $f - 1$ at the inflection point) is inversely proportional to the initial concentration of the ion titrated. If $z > 1$, a decrease of $C_B{}^0$ decreases the value of f at the inflection point, and the inflection point will vanish if $C_B{}^0$ is sufficiently small. If, however, $z < 1$, f may increase without limit as $C_B{}^0$ decreases.

For a real titration, in which r cannot equal zero, the first of these conclusions has already been shown to be false[5]. In the following discussion it will be shown that the others are also false.

CONDITIONS FOR THE EXISTENCE OF AN INFLECTION POINT

When r has a finite value, there are two conditions that must be satisfied if an inflection point is to occur at any physically meaningful — that is, both positive and real — value of f.

One condition is that the right-hand side of eqn. (16) must be positive. Clearly, the left-hand side of this equation cannot be negative. Nor can it be equal to zero, for then one would have to have both

$$(z + 1)[B^{m+}] - \alpha z = 0$$

and

$$(1 - z^2)[B^{m+}] + \alpha z^2 = 0$$

to preserve the equality. For both of these to be satisfied, it would be necessary to have $z = z - 1$, which is impossible. We shall accordingly write

$$(1 - z^2)[B^{m+}] + \alpha z^2 > 0 \tag{19}$$

Two cases may be discerned:

(1) If $z > 1$, there can be an inflection point only if

$$\frac{z^2}{z^2 - 1}\alpha > [B^{m+}] \tag{20}$$

at the inflection point. Since both $[B^{m+}]$ and the term in z must be positive, α must also be positive at the inflection point, and this cannot be so unless $f < 1$. Accordingly the inflection point must always precede the equivalence point.

(2) If $z < 1$, there can be an inflection point only if

$$\frac{z^2}{z^2 - 1}\alpha < [B^{m+}] \tag{21}$$

where the term in z is now negative while $[B^{m+}]$ must, of course, remain positive. This inequality may be satisfied by both positive and negative values of α as well as by $\alpha = 0$: the inflection point may precede the equivalence point, follow it, or coincide with it. If $\alpha < 0$ ($f > 1$), there is an upper limit to its numerical value in any particular titration, so that the inflection point cannot occur at indefinitely large values of f. The nature of this limit is discussed below [*cf.* Table II and the discussion of eqn. (29)], as are the conditions under which the inflection point will coincide with the equivalence point.

Equations (20) and (21) may be rearranged to yield the following criterion for the existence of an inflection point at a non-negative value of f:

$$\frac{\alpha}{[B^{m+}]^0} > 1 - \frac{1}{z^2} \tag{22}$$

where the initial concentration of B^{m+} is specified because the inequality cannot be satisfied anywhere if it is not satisfied in the original solution; from eqn. (8) it is evident that $[B^{m+}]$ decreases less rapidly than α. In the original solution, eqn. (10) shows that $\alpha = C_B{}^0$, and therefore eqn. (22) is equivalent to

$$\frac{C_B{}^0}{[B^{m+}]^0} > 1 - \frac{1}{z^2} \tag{23}$$

In the ordinary performance of a titration one has $[B^{m+}]^0 = C_B{}^0$, and then the condition expressed by eqn. (23) is trivial, but this is not so if solid B_nA_m is assumed to be present throughout. Then, at $f = 0$, it follows by rearranging eqn. (8) that

$$\frac{C_B{}^0}{[B^{m+}]^0} = 1 - \frac{zK^{1/m}}{([B^{m+}]^0)^{z+1}} \tag{24}$$

which may be combined with eqn. (23) to yield the requirement in the convenient form

$$([B^{m+}]^0)^{z+1} > z^3K^{1/m} \tag{25}$$

which permits calculation of the minimum value of $[B^{m+}]^0$ at which a meaningful inflection point can exist for any values of z, K, and m. From this in turn the corresponding minimum value of $C_B{}^0$ can be evaluated with the aid of eqn. (24). This leads to the typical results shown in Table I.

TABLE I

MINIMUM VALUES OF C_B^0 AT WHICH AN INFLECTION POINT CAN EXIST IN THE POTENTIOMETRIC PRECIPITATION TITRATION OF B^{m+} WITH A^{n-}

If $z\ (= n/m) < 1$, an inflection point can always exist. For a number of cases in which $z > 1$, this Table gives the minimum value of C_B^0 at which an inflection point can exist when n and m have the values given. The solution is assumed to be saturated with B_nA_m throughout.

n	m	*Minimum value of* C_B^0
2	1	$1.5\ K^{1/3}$
3	1	$2.062\ K^{1/4}$
4	1	$2.183\ K^{1/5}$
3	2	$0.9037\ K^{1/5}$
4	3	$0.6332\ K^{1/7}$

For $z < 1$, on the other hand, eqn. (22) constitutes a trivial requirement, for its right-hand side is negative while its left-hand side can only be positive at $f = 0$. In this case an inflection point at some value of f between 0 and 1 is always possible (although, as in the isovalent titration, it may not appear if the reagent is insufficiently concentrated, especially if the value of C_B^0 is not far above the minimum given in Table I).

A second criterion for the existence of a physically meaningful inflection point is that eqn. (16) must possess a real root. It may be written in the form

$$p\,[B^{m+}]^2 - q\,[B^{m+}] + s = 0 \tag{26}$$

where

$$p = 2(z + 1)^2 \tag{27a}$$

$$q = 4\alpha z(z + 1) + \frac{zC_T\,(z + r)\,(1 - z^2)}{z + rf} \tag{27b}$$

$$s = 2\alpha^2 z^2 - \frac{\alpha z^3 C_T\,(z + r)}{z + rf} \tag{27c}$$

and the requirement may be stated in the form

$$q^2 \geq 4ps \tag{28}$$

Introducing the values of p, q, and s from eqns. (27), this becomes

$$f - 1 \leq \frac{(z + r)\,(1 - z)^2}{8\,zr} \tag{29}$$

This has no practical significance if $z > 1$, for then, as was stated in the discussion of eqn. (20), the inflection point must precede the equivalence point; it is clear that eqn. (29) can always be satisfied if $f < 1$. But if $z < 1$, eqns. (29) and (21) state two independent necessary conditions, each of which takes the form of an upper limit to the value of f at which an inflection point can exist, and both of which must be satisfied at the inflection point of any titration. The information given by eqn. (29) regarding this limit is summarized in Table II for various values of z and r.

The values in Table II give the ultimate upper limit to the value of f at the inflection point, but eqn. (21) must also be satisfied, and this may prove to be a more

TABLE II

MAXIMUM VALUES OF f AT WHICH AN INFLECTION POINT CAN EXIST IN THE POTENTIOMETRIC PRECIPITATION TITRATION OF B^{m+} WITH A^{n-}

If $z\ (= n/m) > 1$, the inflection point must always precede the equivalence point. For a number of cases in which $z < 1$, this Table gives the maximum value of f, calculated from eqn. (29), at which an inflection point can exist when n, m, and r have the values shown.

n	m	*Maximum value of f if r =*		
		0.1	*1*	*10*
1	2	1.375	1.09375	1.06562
1	3	1.72222	1.22222	1.17222
1	4	1.98438	1.35156	1.28828
2	3	1.15972	1.03472	1.02222
3	4	1.08854	1.01822	1.01120

restrictive limit. For example, with $z = 1/2$ (*i.e.*, $m = 2$, $n = 1$) and $r = 1$ (where Table II indicates that f cannot at any rate exceed 1.09375 at the inflection point), eqn. (21) becomes

$$\frac{f - 1}{1 + 2f} < \frac{3[B^{m+}]}{C_B{}^0} \tag{30}$$

which, if $C_B{}^0 = 0.1$ and $K = 4 \cdot 10^{-18}$, is just satisfied when $f = 1.0000357$. In this case it is eqn. (21) that defines the maximum permissible value of f at the inflection point. As K increases, however, so does the value of f permitted at the inflection point by eqn. (21): if $K = 2 \cdot 10^{-3}$ and the other parameters have the same values as above, one has at $f = 2$ by eqn. (21)

$$0.0067 = -\alpha/3 < 0.067 = [B^{m+}]$$

which is certainly in accord with the demands of eqn. (21), so that in this example it would be eqn. (29) that would be the more restrictive. Clearly each individual case must be judged on its own merits.

CRITERION FOR COINCIDENCE OF THE INFLECTION POINT AND THE EQUIVALENCE POINT

As was mentioned above in connection with eqn. (21), for a real titration (in which $r > 0$), the inflection point may coincide with the equivalence point in an "asymmetrical" (heterovalent) titration though it may not do so in a "symmetrical" (isovalent) one. The traditional designations give misleading impressions regarding the symmetries of the titration curves, and we reiterate our earlier recommendation[5] that they be abandoned.

The conditions under which the inflection point can coincide with the equivalence point are easily defined with the aid of eqn. (16). It is necessary that that equation be satisfied when $f = 1$ and $\alpha = 0$; at that point it becomes

$$\frac{2r}{zC_B{}^0}\{(z + 1)[B^{m+}]\}^2 = (1 - z^2)[B^{m+}] \tag{31}$$

which may be rearranged and combined with eqn. (7b) to give

$$[B^{m+}] = \frac{(1 - z)\, zC_T}{2\,(1 + z)} \tag{32}$$

As has already been stated in connection with eqn. (21), this is possible only if $z < 1$.

The value of $[B^{m+}]$ pertinent to eqn. (32) is readily deduced from eqns. (6) and (8):

$$[B^{m+}] = \left[\left(\frac{n}{m}\right)^m K\right]^{1/(m+n)} = (zK^{1/m})^{1/(z+1)} \tag{33}$$

Equations (32) and (33) permit the calculation of values of C_T at which the inflection point will coincide with the equivalence point. For any particular value of z, this value of C_T depends only on the solubility product of the precipitate. Some typical values are given in Table III.

TABLE III

VALUES OF C_T AT WHICH THE INFLECTION POINT COINCIDES WITH THE EQUIVALENCE POINT IN THE POTENTIOMETRIC PRECIPITATION TITRATION OF B^{m+} WITH A^{n-}

If $z\ (= n/m) > 1$, the inflection point must always precede the equivalence point. For a number of cases in which $z < 1$, this Table gives the relation, calculated from eqns. (32) and (33), between C_T (the molar concentration of A^{n-} in the reagent solution) and K (the solubility product of the precipitate) that will cause the inflection point to coincide with the equivalence point when n and m have the values shown.

n	m	*Required value of* C_T
1	2	$7.559\ K^{1/3}$
1	3	$5.264\ K^{1/4}$
1	4	$4.399\ K^{1/5}$
2	3	$11.91\ K^{1/5}$
3	4	$13.54\ K^{1/7}$

As an example, it follows from this Table that the inflection point will coincide with the equivalence point in the titration of lead ion with iodate, where $z = 1/2$ and $K = 3.2 \cdot 10^{-13}$ (ref. 6), if and only if the titration is performed with $5.17 \cdot 10^{-4}\ M$ iodate. This is true regardless of the concentration of lead ion titrated. In view of the footnote accompanying eqn. (11), it may be pointed out that the inflection point can be made to coincide with the equivalence point in any heterovalent precipitation process: it is only necessary to titrate the ion of higher valence with a solution containing the appropriate concentration of the ion of lower valence.

CALCULATION OF THE LOCATION OF THE INFLECTION POINT

The equations derived above are not very conveniently adapted to the direct evaluation of f at the inflection point from values of the fundamental parameters C_B^0, K, m, r, and z. On the other hand, they can easily be used to find the value of K at which the inflection point occurs at any preselected value of f when the other parameters have any selected values.

Equation (16) can be transformed in straightforward fashion into the quadratic

$$\frac{z+1}{z}[B^{m+}]^2 + [(z-1)\beta - 2\alpha][B^{m+}] - \frac{\alpha z}{z+1}(z\beta - \alpha) = 0 \tag{34}$$

where $[B^{m+}]$ is the concentration, at the inflection point, of the ion titrated. The values of α and β are given by

$$\alpha = \frac{zC_B^0\,(1-f)}{z+rf} \tag{10}$$

and

$$\beta = \frac{C_B{}^0 (z + r)}{2r (z + rf)} \tag{35}$$

Assuming values for $C_B{}^0$, f, r, and z permits the evaluation of $[B^{m+}]$ at the inflection point*. From this one can calculate K by means of the equation

$$K = \left(\frac{[B^{m+}]^z([B^{m+}] - \alpha)}{z}\right)^m \tag{36}$$

which is easily obtained by combining eqns. (8) and (10).

A single example will suffice to illustrate the use of these equations and the magnitude of the error that may be incurred by neglecting dilution. Assume that an 0.1 M solution of a univalent ion is titrated with an 0.1 M solution of a divalent one, and that the "titration error" (which is the value of $(f - 1)$ at the inflection point) is -1.0%; then $m = 1$, $n = 2$, $C_B{}^0 = 0.1$, and $z = 1$, while $f = 0.990$. Calculating α and β from eqns. (10) and (35), substituting their values into eqn. (34), and solving the quadratic yields $[B^+] = 8.86 \cdot 10^{-4}$ at the inflection point, whereupon eqn. (36) yields $K = 8.50 \cdot 10^{-11}$. From eqn. (18), in which dilution is neglected, or from the equivalent expressions derived by earlier authors[3,4] who also neglected dilution, one calculates a titration error of -0.660% for these values of $C_B{}^0$, K, and z. That is, the neglect of dilution leads to a result that is in error by 34% under these not at all extreme conditions.

SUMMARY

By a wholly rigorous general treatment of the potentiometric titration curve representing the titration of B^{m+} with A^{n-} to give the precipitate B_nA_m, where $n \neq m$, it is shown on taking into account the effect of dilution that:

(1) If $n/m > 1$, the inflection point must precede the equivalence point, but there is no inflection point if the initial concentration of the ion titrated is smaller than a certain value, which is determined by the values of m, n, and the solubility product of the precipitate.

(2) If $n/m < 1$, the inflection point may follow the equivalence point — though not by more than a certain definite amount — or may precede it or coincide with it. In every such case there is a concentration of A^{n-} that will cause the equivalence point to coincide with an inflection point; this concentration depends on the values of m, n, and the solubility product of the precipitate.

(3) Unless the difference between the equivalence and inflection points is negligibly small, the traditional treatment in which dilution is neglected gives seriously erroneous estimates of the location of the inflection point.

RÉSUMÉ

Les auteurs ont effectué une étude théorique des courbes de titrage potentiométrique, par précipitation hétérovalente (B^{m+}/A^{n-}) avec localisation des points de pente maximum: (1) Si $n/m > 1$, le point d'inflexion doit précéder le point d'équivalence, mais il n'y a aucun point d'inflexion si la concentration initiale de l'ion titré est inférieure à une certaine valeur déterminée par m, n et le produit de solubilité du précipité. (2) Si $n/m < 1$, le point d'équivalence coïncide avec le point d'inflexion pour une concentration de A^{n-} dépendant des valeurs de m, n et du produit de solubilité du précipité. (3) Il faut tenir compte de la dilution lorsque la différence entre les points d'équivalence et d'inflexion n'est plus négligeable.

ZUSAMMENFASSUNG

Der theoretische Verlauf von Titrationskurven wird berechnet, für die Titration von B^{m+} mit A^{n-} unter Bildung des Niederschlages B_nA_m, wenn $n \neq m$ und wenn der Verdünnungseffekt berücksichtigt wird. Es wird folgendes abgeleitet:

* There are two inflection points; the one of interest is obtained by taking the negative sign in the general equation for the solution of the quadratic. The other inflection point is a point of minimum slope[7].

(1) $n/m > 1$: Der Wendepunkt liegt vor dem Äquivalenzpunkt. Es gibt keinen Wendepunkt, wenn die Anfangskonzentration des titrierten Ions unter einem bestimmten Wert liegt. Dieser Wert hängt von n, m und dem Löslichkeitsprodukt des Niederschlages ab.

(2) $n/m < 1$: Entweder der Wendepunkt liegt hinter dem Äquivalenzpunkt (und zwar maximal um einen genau definierten Betrag) oder vor dem Äquivalenzpunkt oder er koinzidiert mit ihm. Für jeden Fall gibt es eine Konzentration für A^{n-}, bei der die Koinzidenz auftritt. Diese Konzentration hängt von n, m und dem Löslichkeitsprodukt des Niederschlages ab.

(3) Die übliche Arbeitsweise, bei der die Verdünnung vernachlässigt wird, ergibt fehlerhafte Abschätzungen für die Lage des Wendepunktes, ausser, wenn der Unterschied zwischen Äquivalenz- und Wendepunkt vernachlässigbar klein ist.

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THEORY OF TITRATION CURVES

PART III. LOCATIONS OF POINTS AT WHICH pH=pK_a ON POTENTIOMETRIC ACID-BASE TITRATION CURVES; END-POINT ERRORS IN TITRATIONS TO PREDETERMINED pH VALUES

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In a preceding paper in this series[1] it was demonstrated that, in the potentiometric titration of a weak monobasic acid with a strong base, "the value of f [fraction titrated] at the point of minimum slope is exactly equal to 1/2 only if $K_a = K_w^{1/2}$, and is then unaffected by dilution. Otherwise it differs from 1/2, and the magnitude of the difference increases as the concentrations of the reagents decrease"; it also increases as K_a and $K_w^{1/2}$ become more disparate.

In evaluating pK_a from a potentiometric titration curve, it is customarily equated to the pH* at $f = 1/2$. The present paper shows that this is incorrect, and presents an explicit equation for the value of f (denoted by the symbol f_{pK_a}) at which the pcH is exactly equal to pK_a. The effect of dilution is easily taken into account, and it is shown that the variation of f_{pK_a} is similar to, but not identical with, that of the value of f at which the slope of the titration curve is a minimum.

DERIVATION OF AN EXPLICIT EQUATION FOR f_{pK_a}

For the titration of V_a^0 ml of a $C_a^0 F$ solution of a weak monobasic acid with $C_b F$ completely dissociated monoacidic base, we may write[1]

$$[H^+] = \frac{(1-f)\varrho C_a^0 - [H^+] + [OH^-]}{f\varrho C_a^0 + [H^+] - [OH^-]} K_a \qquad (1)$$

where the titration parameter f is defined by

$$f = \frac{V_b C_b}{V_a^0 C_a^0} \qquad (2)$$

and where

$$\varrho = \frac{V_a^0}{V_a^0 + V_b} = \frac{C_b}{C_b + fC_a^0} \qquad (3)$$

As LINGANE[2] pointed out, eqn. (1) is linear in f although it is of the third degree in $[H^+]$. Even when dilution is taken into account, it is always true that the rigorous equation describing the concentration of any particular species in an equilibrium

* We assume pH = pcH = $-\log_{10}[H^+]$, so that K_a is a formal dissociation constant or concentration constant.

system during a titration is linear in f although it is polynomial in that concentration. Consequently, as was stated by KOLTHOFF, MEEHAN AND SAMBUCETTI[3], considering the concentration as the independent variable (and f as the dependent one) always permits the convenient exact calculation of any titration curve regardless of the degree of its polynomial. This is most useful in systems where the equations are of cubic or even higher degree, as in heterovalent precipitation titrations[4-6].

To obtain the value of f at which pcH = pK_a, one need merely set [H$^+$] equal to K_a in eqn. (1). After rearrangement, one has

$$f_{pK_a}\varrho' C_a^0 + K_a - (K_w/K_a) = (1 - f_{pK_a})\varrho' C_a^0 - K_a + (K_w/K_a) \tag{4}$$

where ϱ' is the value of ϱ at f_{pK_a}.

Defining the dilution parameter r by the previously given equation[1]

$$r = C_a^0/C_b \tag{5}$$

we may write ϱ, in general, as

$$\varrho = 1/1 + rf \tag{6}$$

so that eqn. (4) may now be solved explicitly for f_{pK_a}. The result may be written

$$f_{pK_a} = \frac{1/2 - [K_a - (K_w/K_a)]/C_a^0}{1 + r[K_a - (K_w/K_a)]/C_a^0} \tag{7}$$

or[7]

$$f_{pK_a} = \frac{1/2 - 2(K_w^{1/2}/C_a^0)\sinh[2.30(pK_w/2 - pK_a)]}{1 + 2r(K_w^{1/2}/C_a^0)\sinh[2.30(pK_w/2 - pK_a)]} \tag{8}$$

DISCUSSION

From either of the preceding equations it is evident that f_{pK_a} is equal to 1/2, and is independent of r (*i.e.*, of dilution during the titration) and of C_a^0 (*i.e.*, of dilution prior to the titration), only if pK_a = pK_w/2. Otherwise, f_{pK_a} is *less* than 1/2 if K_a exceeds $K_w^{1/2}$, and is *greater* than 1/2 if K_a is smaller than $K_w^{1/2}$. The deviation of f_{pK_a} from 1/2, as a function of the difference between pK_a and pK_w/2, is symmetrical only if dilution is neglected — that is, if r = 0.

For f_{pK_a} to be physically meaningful (*i.e.*, to occur at $f \geqslant 0$), it is necessary that

$$C_a^0 \geq 2[K_a - (K_w/K_a)] \tag{9}$$

whenever $K_a > K_w^{1/2}$. There is no corresponding minimum value of C_a^0 if $K_a \leqslant K_w^{1/2}$, because then f_{pK_a} will always equal or exceed 1/2.

Values of f_{pK_a} have been calculated for various values of K_a and for $C_a^0 = C_b$ = 0.1 F (*i.e.*, r = 1), and are presented in Table I, which also gives, for purposes of comparison, the corresponding values of f at the first inflection point (where the slope is a minimum).

It is readily seen that, at any value of K_a, the value of f at the inflection point deviates more from 1/2 than does f_{pK_a}. If $K_a > K_w^{1/2}$, the inflection point precedes the point at which pcH = pK_a, and the latter in turn precedes the "half-way point" (where f = 1/2). On the other hand, if $K_a < K_w^{1/2}$, the inflection point follows the point at which pcH = pK_a, and the latter in turn follows the half-way point.

TABLE I

LOCATIONS OF f_{pK_a} IN WEAK ACID–STRONG BASE TITRATIONS

The values of f_{pK_a} given in the second column were computed for $C_a^0 = 0.1$ F, $r = 1$, and $K_w = 1.00 \cdot 10^{-14}$. The third column gives the corresponding values of f at the points where the slopes of the titration curves are smallest[1].

K_a	f_{pK_a}	f_t
$5 \cdot 10^{-2}$	0.000	—
$1 \cdot 10^{-2}$	0.364	0.111
$3 \cdot 10^{-3}$	0.456	0.360
$1 \cdot 10^{-3}$	0.485	0.463
$1 \cdot 10^{-4}$	0.498	0.496
$1 \cdot 10^{-5}$	0.4998	0.499
$1 \cdot 10^{-7}$	0.5000	0.5000
$1 \cdot 10^{-9}$	0.5002	0.5005
$1 \cdot 10^{-10}$	0.502	0.506
$1 \cdot 10^{-11}$	0.515	0.573
$5 \cdot 10^{-12}$	0.531	No inflection
$4 \cdot 10^{-13}$	1.000	No inflection

Figure 1 shows the manner in which the dependence of f_{pK_a} on K_a is affected by variations of pC_a^0 ($= -\log_{10} C_a^0$), and demonstrates that substantial errors may be incurred by taking pK_a to be equal to the pcH at $f = 1/2$ if K_a is widely different from $K_w^{1/2}$ and especially if the concentrations of the reagents are small. It should perhaps be emphasized that, when it is necessary to evaluate K_a from a titration curve, it

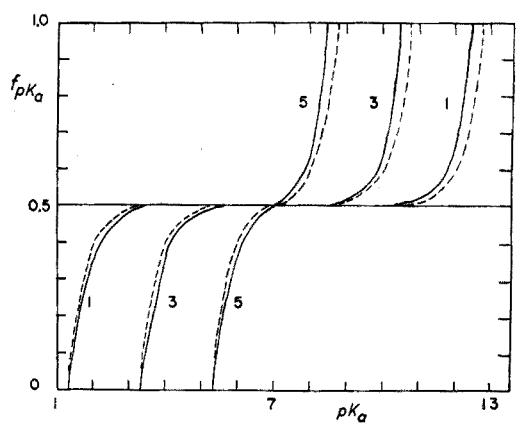

Fig. 1. The dependence of f_{pK_a} on pK_a. The number beside each pair of curves gives the corresponding value of pC_a^0. The dashed curves correspond to $r = 0$ and the solid ones to $r = 1$.

can easily be calculated exactly from the values of $[H^+]$ and f at any point on the curve. Of course it would be imprudent to carry out the calculation at only a single point, and it would be necessary to pay due attention to the errors associated with the experimental measurements of f and the pH.

Because $f = 0$ corresponds to the point on a titration curve where no titrant has

yet been added, we may deduce from eqns. (7) and (8) that a solution of a weak monobasic acid will possess a hydrogen-ion concentration numerically equal to K_a if

$$C_a^0 = 2[K_a - (K_w/K_a)] \tag{10}$$

which is equivalent to

$$K_a = \frac{C_a^0(1 + \sqrt{1 + 16K_w/(C_a^0)^2})}{4} \tag{11}$$

For values of C_a^0 greater than that given by eqn. (9), the hydrogen-ion concentration will exceed K_a; if the ratio C_a^0/K_a is sufficiently large, the hydrogen-ion concentration may be expressed by the customary approximation

$$[H^+] = \sqrt{C_a^0 K_a} \tag{12}$$

whose error under various conditions is easily evaluated[8,9]. For values of C_a^0 less than that given by eqn. (9), the hydrogen-ion concentration will be smaller than K_a. Therefore the lower limit of the parameter n defined by the equation

$$n = C_a^0/K_a \tag{13}$$

that is pertinent to an evaluation of the error involved in eqn. (12) (which may be written $[H^+] = n^{1/2}K_a$) should logically be 2 instead of 1 (ref. 8, 9). This is because, for $1 < n < 2$, the value of $[H^+]$ obtained from eqn. (12) is not only quantitatively incorrect but is larger than K_a while the true value is smaller.

Equation (10) is physically significant only if $pK_a < pK_w/2$. If $pK_a > pK_w/2$, the initial pcH will always be smaller than pK_a.

The foregoing discussion has indicated the conditions under which $[H^+]$ will be equal to K_a when $f = 0$. It is perhaps less obvious that $[H^+]$ may be equal to K_a at the equivalence point, where $f = 1$. But it is easily deduced from eqn. (7) that this will be the case if

$$C_a^0 = 2(1 + r)[(K_w/K_a) - K_a] \tag{14}$$

which is equivalent to

$$K_a = \frac{C_a^0(-1 + \sqrt{1 + 16K_w(1 + r)^2/(C_a^0)^2})}{4(1 + r)} \tag{15}$$

or, if $C_a^0 \gg 4K_w^{1/2}(1 + r)$

$$K_a \approx 2K_w(1 + r)/C_a^0 \tag{16}$$

It is clear that the approximate expression

$$[H^+] = \sqrt{\frac{K_w K_a(1 + r)}{C_a^0}} \tag{17}$$

customarily employed at the equivalence point will give results that are grossly in error unless C_a^0 greatly exceeds the value given by eqn. (14).

END-POINT ERRORS

In a preceding paper[1] we evaluated the error involved in titrating a strong or weak monobasic acid with a strong base to the inflection point of maximum slope. If the titration is instead terminated at a particular pcH value differing from that at the

equivalence point, it is a simple matter to calculate the resulting titration error[10,11]. For this purpose the pcH at the equivalence point need not be known, except in the trivial sense that one usually wishes to titrate to a pcH near that at the equivalence point in order to minimize the error. The use of nomograms[12] for the estimation of the error may be extremely valuable, but their preparation of course depends on prior calculations of pcH for various values of f, and these have often been performed with the aid of equations that are only approximate.

In the titration of a strong acid, the titration error may be rigorously expressed by

$$f - 1 = \frac{-(1 + r)\{[H^+] - (K_w/[H^+])\}}{C_a^0 + r\{[H^+] - (K_w/[H^+])\}} \tag{18}$$

or, alternatively[7],

$$f - 1 = \frac{-2(1 + r)K_w^{1/2} \sinh[2.30(pK_w/2 - pcH)]}{C_a^0 + 2r\,K_w^{1/2} \sinh[2.30(pK_w/2 - pcH)]} \tag{19}$$

In the titration of a weak monobasic acid with a strong base, the titration error is

$$f - 1 = \frac{-\{[H^+]/([H^+] + K_a)\} - (1 + r)\{[H^+] - (K_w/[H^+])\}/C_a^0}{1 + r\{[H^+] - (K_w/[H^+])\}/C_a^0} \tag{20}$$

or[7]

$$f - 1 = \frac{-1/2 + (1/2)\tanh[(2.30/2)(pcH - pK_a)] - 2(1 + r)\{\sinh[2.30(pK_w/2 - pcH)]\}(K_w^{1/2}/C_a^0)}{1 + 2r\{\sinh[2.30(pK_w/2 - pcH]\}(K_w^{1/2}/C_a^0)} \tag{21}$$

Equations (18)–(21) are easily derived by rearranging the fundamental electroneutrality equation applicable to the titration under consideration. The quantity $\{[H^+] - (K_w/[H^+])\}/C_a^0$, which appears in the numerator and denominator of eqn. (20), is the "correction" for "hydrolysis" according to KOLTHOFF AND STENGER[10]. From eqn. (20) it is obvious that the titration error is exactly equal to[10] $-\{[H^+]/([H^+] + K_a)\}$, and is independent of dilution, only if $pcH = pK_w/2$ at the end-point. It may be noted that the titration error depends on C_a^0 even if $r = 0$. Nevertheless, the "hydrolysis" term may be safely neglected in many situations[10]. To our knowledge, no previous discussion of the titration error in the titration of a weak acid with a strong base has ever presented an equation that takes both "hydrolysis" and the dilution effect into account.

SUMMARY

For the titration of a pure solution of a weak monobasic acid with a strong base, it is shown that the fraction of the equivalent volume of base added at the point where $pcH = pK_a$ is exactly equal to 1/2 if and only if $pK_a = pK_w/2$, in which case it is independent of dilution. It is less than 1/2 if $pK_a < pK_w/2$ and is greater than 1/2 if $pK_a > pK_w/2$, and in either of these cases it depends on the concentrations of both acid and base. Explicit descriptions are given of the conditions under which $pcH = pK_a$ either at the start of the titration or at the equivalence point. For the titration of either a weak or a strong acid with a strong base, exact equations are given for the titration error resulting from the termination of the titration at any preselected pcH value.

RÉSUMÉ

Lors du titrage d'un acide monobasique faible avec une base forte, on observe que la fraction du volume équivalent de base ajoutée, au point où $pcH = pK_a$, est exactement égale à 1/2 si, et seulement si, $pK_a = pK_w/2$, indépendamment de la dilution; $< 1/2$ si $pK_a < pK_w/2$ et $>$ que 1/2 si $pK_a > pK_w/2$. Dans ces deux derniers cas, il faut tenir compte des concentrations de l'acide et de la base. Des équations sont données pour l'erreur résultant de la fin du titrage à n'importe quelle valeur pcH choisie au préalable.

ZUSAMMENFASSUNG

Für die Titration von reinen Lösungen schwacher einbasischer Säuren mit starken Basen wird gezeigt, dass der Anteil des Äquivalentvolumens der zugefügten Base an dem Punkt, an dem pcH = pK_a genau 1/2 ist, aber nur dann, wenn $pK_a = pK_w/2$ ist. In diesem Falle ist das Volumen unabhängig von der Verdünnung. Es ist $< 1/2$, wenn $pK_a < pK_w/2$ und $> 1/2$, wenn $pK_a > pK_w/2$. In beiden diesen Fällen hängt es von der Konzentration der Säure und der Base ab. Ausführlich werden die Bedingungen beschrieben, bei denen entweder zu Beginn oder am Äquivalenzpunkt der Titration pcH = pK_a ist. Für die Titration von schwachen oder starken Säuren mit einer starken Base werden Gleichungen aufgestellt für den Titrationsfehler, der sich aus dem Titrationsende bei vorgewähltem pH-Wert ergibt.

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A SPECTROPHOTOMETRIC STUDY OF THE COLOUR REACTION BETWEEN CHLORANIL AND AROMATIC AMINES

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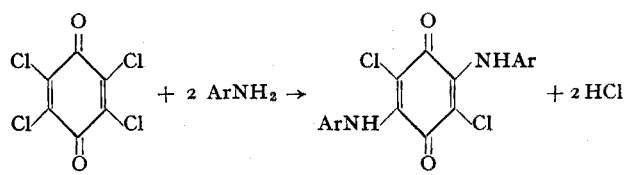
The colour-forming reaction between chloranil (I) and amines, carried out in dioxan solution, has been used qualitatively as a spot test for many years[1,2]. The coloured products usually remain in solution, but in some cases highly coloured, stable compounds have been isolated[3], sometimes[4] under conditions drastic enough to have involved a nuclear substitution reaction (*e.g.* (1)).



(I) (1)

Further, chloranil has been shown to effect dehydrogenation of tertiary aliphatic amines[5], with formation of coloured compounds, but these severe conditions find no parallel in the colour formation with aromatic amines in dilute solution at room temperature. Moreover, from these solutions crystalline derivatives have been obtained[6], which

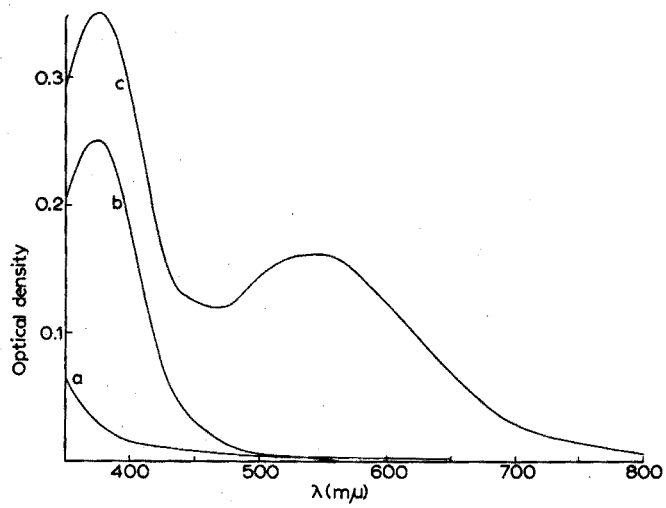


Fig. 1. Light absorption in chloroform. (a) Aniline (9.4 mg/ml); (b) chloranil (0.25 mg/ml); (c) adduct.

were described as 1 : 1 molecular adducts (occasionally 2 : 1) of aromatic amine and chloranil. The original compounds can be recovered quantitatively[3] from these adducts (*e.g.*, by treatment with dilute acid).

In the present spectrophotometric study of the reaction, the colour of the aniline–chloranil reaction was observed to be due to a broad band in the visible region, with a maximum at 542 mμ (Fig. 1). The intensity of this band did not obey the Beer–Lambert law, departures from which pointed to a degree of dissociation of the adduct. Unfortunately, the measurements were not sufficiently accurate to give precise values of ε_{max} (and hence of the association constant K of the reaction (2)). Where A and C are the initial concentrations of the amine and chloranil, respectively, and X is the concentration of the adduct at equilibrium, then

$$\text{Amine} + \text{Chloranil} \rightleftharpoons \text{Adduct}$$

$$K = \frac{X}{(A - X)(C - X)} \tag{2}$$

The observed data fitted the BENESI–HILDEBRAND relationship[7] (*i.e.*, eqn. (3)), where D = optical density at the absorption maximum (1-cm cell), thus indicating a 1 : 1 correspondence in the adduct.

$$\frac{AC}{D} = \frac{A}{\varepsilon} + \frac{1}{K\varepsilon} \qquad (\text{if } A \gg C) \tag{3}$$

The colour of the adduct is probably due to an electronic transition because of a charge transfer[8] from the amine (donor) to chloranil (acceptor) analogously to spectra recently investigated[9–12], between aromatic hydrocarbons and a number of quinones. In considering the high stability of these adducts in solution, it should be recalled that *p*-benzoquinone is an acceptor comparable with 1,3,5-trinitrobenzene[12,13], and chloranil will be stronger still.

The light absorption data of 29 amines are given in Table I. The colours of the solutions range through lilac, violet, blue, green, brown to black, corresponding to broad absorption bands, whose centres occur in the region 487–765 mμ. Approximate calculations show that most λ_{max} values are in the range of 1500–5000, with the exception of the somewhat more intense colours of the dialkylanilines ($\lambda_{max} \sim$ 6000–8000). The isomeric phenylenediamines gave well-developed colours, but measurements were unsuccessful as the solutions rapidly went opaque; 1- and 2-aminotriphenylenes gave black solutions, involving general light absorption throughout the visible region, but with no distinct absorption maxima. Although it has been stated[2] that no colour reaction is given by an aromatic amino acid, a well defined colour (λ_{max} at 515 mμ) was observed with anthranilic acid. However, 2,4,6-trichloroaniline, 2,4,6-tribromoaniline, *o*-, *m*- and *p*-nitroanilines, 1-, 2- and 4-aminophenanthrenes, 2-amino-2'-methylazobenzene, 4-amino-4'-methylazobenzene, and 4-dimethylaminoazobenzene all gave no colour reaction with chloranil, under the experimental conditions outlined.

Association constants (K) for the complexes could be estimated to be in the range 0.2–2.0; these values enable one to give identification limits, for quantitative work, of $0.2\text{–}2.5 \cdot 10^{-7}$ g of the amines.

Chloroform was found to be the most convenient solvent for routine work, although dioxan had been recommended originally[1,2]. Thirteen other solvents, however, gave satisfactory absorption curves with four amines which cover a wide section of the

spectrum, *viz.* *m*-chloroaniline (λ_{max} 497 mμ), aniline (λ_{max} 542 mμ), N-ethylaniline (λ_{max} 605 mμ) and N-diethylaniline (λ_{max} 765 mμ). The solvents comprise methanol, ethanol, propanol, isopropanol, benzene, toluene, cyclohexane, ethyl acetate, butyl acetate, amyl acetate, ether, dioxan, and carbon tetrachloride. The position of the absorption maxima remained unchanged throughout, and their intensity varied only slightly (approximately $\pm$ 10%).

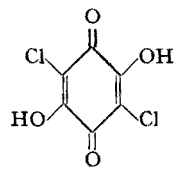
TABLE I

LIGHT ABSORPTION DATA OF ADDUCTS BETWEEN AROMATIC AMINES AND CHLORANIL, IN CHLOROFORM AT 20°

Amine	*Colour*	λ_{max} (mμ)
Aniline	Violet	542
α-Naphthylamine	Blue	645
β-Naphthylamine	Blue	635
3-Phenanthrylamine	Green	652
9-Phenanthrylamine	Brown	487
1-Aminotriphenylene	Black	No maximum
2-Aminotriphenylene	Black	No maximum
N-Methylaniline	Blue	602
N-Ethylaniline	Blue	605
N-Dimethylaniline	Blue	660
N-Diethylaniline	Green	765
Diphenylamine	Blue	647
Triphenylamine	Blue	660
o-Chloroaniline	Red-brown	512
m-Chloroaniline	Red-brown	497
p-Chloroaniline	Violet	520
o-Bromoaniline	Red-brown	515
m-Bromoaniline	Red-brown	502
p-Bromoaniline	Violet	535
o-Toluidine	Lilac	562
m-Toluidine	Lilac	550
p-Toluidine	Blue	580
o-Anisidine	Blue	586
m-Anisidine	Blue	575
p-Anisidine	Green	600
o-Phenylene diamine	Green	—[a]
m-Phenylene diamine	Brown	—[a]
p-Phenylene diamine	Green	—[a]
Anthranilic acid[b]	Red-brown	515

[a] Solution goes rapidly opaque.
[b] Solvent: acetone.

The addition of small amounts of acid (*N* HCl) or alkali (*N* NaOH) to the adduct in dioxan solution of each of these four amines in turn, resulted in a marked reduction of colour intensity, which was not merely a dilution effect. This can be explained, in the case of added acid, as a shift of the equilibrium away from the adduct by formation of the amine salt. The addition of alkali results in a gradual appearance of a brown colouration, which occurs even in the absence of amine. This involves the probable removal of chloranil by slow nucleophilic substitution with hydroxyl, with formation of derivatives such as chloranilic acid[14] (II).



(II)

From Table Ii t is seen that substitution at the nitrogen or in the nucleus by electron-releasing groups (methyl, phenyl, methoxy), or increasing conjugation (naphthyl instead of phenyl), shifts the maxima of the coloured absorption band towards longer wavelengths, in a regular pattern; conversely, electron-attracting substituents (chloro, bromo, carboxy) cause shifts to shorter wavelengths. It is also to be noted that the wavelengths increase in the sequence *m*- < *o*- < *p*-, no matter if the substituent is electron-releasing or electron-attracting.

According to the general theory of charge transfer spectra[15-17], one can relate the energy (E) of such a transition to the ionisation potential (I_D) of the donor molecule (amine), the electron affinity (E_A) of the acceptor molecule (chloranil) and the stabilisation (S) of the ion-pair produced, according to eqn. 4.

$$E = I_D - E_A - S \qquad (4)$$

If it may be assumed that the adducts are all of a similar type, then the term ($E_A + S$) will be reasonably constant. It should therefore be possible to correlate the energy of a particular transition with the ionisation potential of the amine used. Appropriate data on ionisation potentials of aromatic amines do not appear to be available, but with some justification a comparison can be made directly with the basicities of the amines, since both I_D and pK_a values are guides to the electron availability at the aromatic nucleus. As expected, an amine with a low pK_a value (corresponding to a low electron availability at the nitrogen, and a high electron availability at the aryl nucleus) would give an adduct whose energy of transition (E) is high, *i.e.* which absorbs at a short wavelength. Figure 2 represents a plot of literature

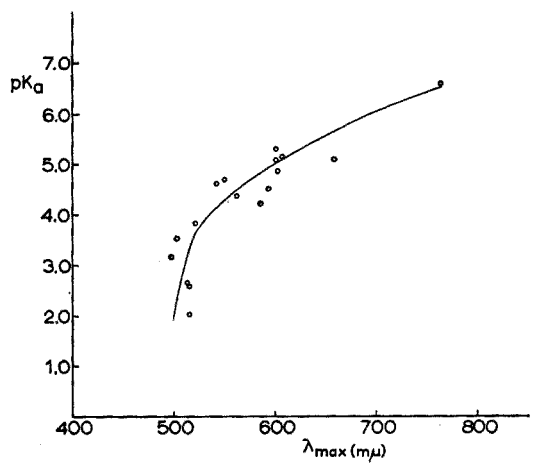


Fig. 2. Plot of pK_a of amines (H_2O) *vs.* λ_{max} of chloranil adducts.

pK_a values[18] of the aromatic amines *vs.* λ_{max} for the chloranil complexes. With the exception of some amines in which resonance effects are predominant (diphenylamine, α-naphthylamine, etc.), and which are not included in Fig. 2, the plot shows an approximate distribution according to the computed polynomial eqn. (5).

$$\lambda_{max} \text{ (in m}\mu) = 629.4 - 91.94\ pK + 17.23\ (pK)^2 \qquad (5)$$

From this curve the light absorption maximum of a chloranil complex may be approximately arrived at, if the pK_a value of the amine is known.

EXPERIMENTAL

Materials

The amines and chloranil were recrystallised (or redistilled), and the solvents redistilled before use. The stock solutions contained about 2.5 mg/ml of chloranil (*i.e.*, nearly saturated, in chloroform), or 100–150 mg/ml of amine.

Measurements

Aliquots of stock solutions were mixed, and made up to 10 ml in a volumetric flask.

TABLE II

OPTICAL DENSITY AT 542 mμ OF THE ADDUCT BETWEEN CHLORANIL AND ANILINE, IN CHLOROFORM, AT 20°

Chloranil concentration (moles/l)	*Aniline concentration (moles/l)*						
	0.054	*0.107*	*0.161*	*0.215*	*0.269*	*0.322*	*0.430*
0.000815		0.128		0.222		0.318	0.390
0.00122		0.179	0.260	0.332	0.408		
0.00163	0.134	0.242	0.348	0.450			

TABLE III

OPTICAL DENSITY AT 520 mμ OF THE ADDUCT BETWEEN CHLORANIL AND *p*-CHLOROANILINE, IN CHLOROFORM, AT 20°

Chloranil concentration (moles/l)	p-*Chloroaniline concentration (moles/l)*					
	0.039	*0.078*	*0.117*	*0.156*	*0.195*	*0.234*
0.000815	0.144	0.217	0.318	0.420	0.492	0.597
0.00122	0.175	0.325	0.494	0.646		
0.00163	0.238	0.461	0.666			

TABLE IV

OPTICAL DENSITY AT 647.5 mμ OF THE ADDUCT BETWEEN CHLORANIL AND DIPHENYLAMINE, IN CHLOROFORM, AT 20°

Chloranil concentration (moles/l)	*Diphenylamine concentration (moles/l)*				
	0.059	*0.118*	*0.236*	*0.355*	*0.473*
0.000815	0.045	0.081	0.149	0.205	0.246
0.00122	0.088	0.159	0.292	0.415	
0.00163	0.124	0.236	0.441	0.638	

The absorption curves were taken immediately, over the range 350–850 mμ, in a 1-cm cell, using a Unicam S. P. 500 Spectrophotometer, with the usual solvent blank. The optical densities at the maximum were then determined for a series of 3 concentrations of chloranil (0.000815, 0.00122 and 0.00163 moles/l) and up to 7 concentrations of the amine. Three typical sets of data are given in Tables II, III and IV.

Grateful acknowledgements are made to Professor M. J. S. DEWAR for gifts of the phenanthrylamines and aminotriphenylenes, to Dr. G. L. REED for carrying out the computation of the polynomial, and to Dr. D. N. WATERS for helpful discussions.

SUMMARY

The colour reaction between aromatic amines and chloranil was studied spectrophotometrically. A 1 : 1 adduct formed in solution, with some dissociation. The effects of solvents, acid and alkali were examined. The adducts exhibited intense, and characteristic, broad absorption bands, which could be used for the detection and estimation of an aromatic amine, in the absence of substances of similar light absorption characteristics. A correlation between the basicities of an amine and the ight absorption of the adduct was established.

RÉSUMÉ

La réaction colorée entre amines aromatiques et chloranile a été examinée spectrophotométriquement. Les bandes obtenues, intenses, larges et caractéristiques peuvent être utilisées pour l'identification et l'estimation d'amines aromatiques, en l'absence de substances présentant des caractéristiques d'absorption similaires.

ZUSAMMENFASSUNG

Die Farbreaktion zwischen aromatischen Aminen und Chloranil wurde spektralphotometrisch untersucht. Die Verbindungen besitzen intensive und charakteristische, breite Banden, die zum Nachweis und zur Bestimmung von aromatischen Aminen bei Abwesenheit von Substanzen mit störender Absorption dienen können. Es wurde eine Beziehung zwischen der Basizität des Amins und der Lichtabsorption aufgestellt.

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH *p*-(MORPHOLINO)-N-(4'-HYDROXY-3'-METHOXY)BENZYLIDINEANILINE*

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DUGAN AND HAENDLER[1] suggested the possible use of 4-(*p*-aminophenyl)morpholine as a reagent for aromatic aldehydes through the formation of crystalline condensation products, and tested the compound with several aromatic aldehydes, including vanillin which formed *p*-(morpholino)-N-(4'-hydroxy-3'-methoxy)benzylidineaniline (hereafter referred to as "anil" for brevity). A report[2] that this compound could be used as a sensitive test for iron suggested the possibility of color reactions with other transition elements, such as members of the platinum group. Preliminary tests of solutions of the platinum group elements treated with anil gave the following color indications: rhodium, no change; palladium, yellow; platinum, pink; iridium and ruthenium, purple; osmium, blue. Due to the intensity and the apparent stability of the color, the osmium system was studied in detail.

EXPERIMENTAL

Apparatus

Measurements in which absorbance at various wavelengths was of interest (preliminary tests, rate of color formation, effect of pH, etc.) were made with a Beckman Model DK-1 recording spectrophotometer. Precision measurements at fixed wavelength were made with a Beckman Model DU spectrophotometer, operated at constant sensitivity. Stoppered silica cells of 1.00-cm optical path were used. Measurements of pH were made with a Beckman Zeromatic pH meter, using glass and calomel electrodes. Calibrated weights and volumetric ware were used. Special glassware was constructed in the glass shop of The University of Texas.

Reagents

Standard osmium solution. Pure osmium tetroxide, sealed in glass ampoules, was obtained from A. D. Mackay, Inc., New York. The stock solution was prepared and standardized as described by AYRES AND WELLS[3], and found to contain 648 p.p.m. of osmium. Working solutions were prepared as needed by dilution of the stock solution.

* Condensed from a dissertation submitted by CURTIS W. McDONALD to the graduate school of The University of Texas in partial fulfilment of the requirements for the Ph.D. degree, January 1962.

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Anil color reagent. The anil reagent, not available commercially, was synthesized from materials readily available (Distillation Products Industries, Rochester, N. Y., or Matheson, Coleman and Bell, Norwood, Ohio), by methods described by KREMER, MELTSNER AND GREENSTEIN[4] and by DUGAN AND HAENDLER[1]. A mixture of 50 g of 1-chloro-4-nitrobenzene, 50 ml of morpholine, and 250 ml of ethanol, in a 500-ml round-bottom flask, was refluxed overnight, then evaporated over a steam bath to about one-half its original volume. After cooling, the yellow crystals of 4-(*p*-nitrophenyl)morpholine were filtered off, and recrystallized from alcohol. M.p. 152–153°. Ten grams of this product, dissolved in 100 ml of alcohol and with 0.5 g of 10% palladium on charcoal catalyst added, were reduced with hydrogen under pressure of 30 p.s.i. for 5 h. The reduced mixture containing the 4-(*p*-aminophenyl)morpholine was filtered twice to remove charcoal, and was then transferred to a 500-ml round-bottom flask, to which was added 10 g of vanillin, 150 ml of ethanol, and 10 ml of pyridine (catalyst). The mixture was refluxed for 9 h. The flaky yellow crystals formed on cooling were filtered off, washed with alcohol, then recrystallized from alcohol. M.p. 207–208°. The product, *p*-(morpholino)-N-(4'-hydroxy-3'-methoxy)-benzylidineaniline, was insoluble or only slightly soluble in water, methanol, ethanol, isopropanol and *n*-propanol, but was very soluble in N,N-dimethylformamide (DMF). Reagent solutions ($2.00 \cdot 10^{-3}$ *M* for use in the standardized procedure) were prepared by dissolving the desired quantity of anil in a small amount of DMF, then diluting to volume with ethanol; 5% (volume) of DMF was sufficient.

Buffer. Buffer of pH 3.5 was prepared by mixing 9 parts of 1.0 *M* acetic acid with 1 part of 1.0 *M* sodium acetate.

Other reagents. Substances used in interference tests were reagent-grade chemicals. The common cations were used in the form of nitrates or chlorides, and the anions were used in the form of sodium or potassium salts. Solutions of the platinum elements were prepared by dilution of stock standard solutions from previous investigations in this laboratory.

Recommended procedure

Into a 25-ml volumetric flask place 5 ml of pH 3.5 buffer and 10 ml of 95% ethanol. Add the osmium solution, not exceeding 6 ml, and 4 ml of $2.00 \cdot 10^{-3}$ *M* anil solution, and dilute to volume with distilled water. Measure the (apparent) pH, which should be within the range 4.3 to 4.7; if not within these limits, the osmium solution should be neutralized with HCl or NaOH. After one hour measure the absorbance at 615 mμ against a blank, prepared simultaneously with the sample, containing all reagents except the osmium.

The spectral curve of the blue osmium–anil complex is shown in Fig. 1, curve A. The system conforms to Beer's law up to about 4 p.p.m. of osmium, and shows only slight negative deviation from the law above that concentration. The slight deviation from the law offers no practical difficulty in analysis, because standards and unknowns would be prepared and measured under comparable conditions. The optimum concentration range for measurement at 1.00 cm optical path is about 1 to 4 p.p.m.

Reproducibility and sensitivity. Four samples of each of 8 different concentrations were prepared by the recommended procedure and measured at 615 mμ; the results are shown in Table I. The absorbance given is the mean of 4 samples at the concentration listed; the (absolute) precision is represented by an average deviation of

0.003 and a standard deviation of 0.004 absorbance unit. Based upon the first 5 concentrations, the specific absorptivity is 0.184 p.p.m^{-1} cm^{-1}, and the molar absorptivity is 3.49 · 10^4 l^{-1} mole^{-1} cm^{-1}.

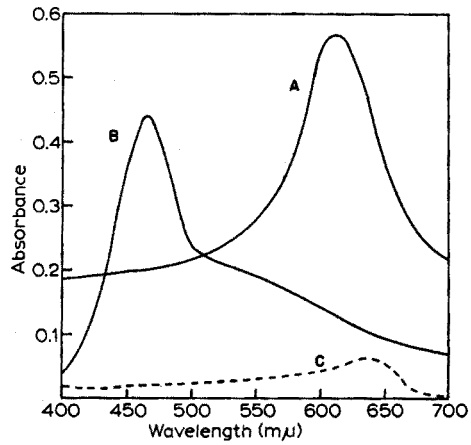


Fig. 1. Spectral curves. (A) 3.04 p.p.m. osmium + excess reagent (blue solution, 1:2 complex). (B) Excess osmium + reagent, in ratio > 5:1 (red solution, 1:1 complex). (C) Reagent blank *vs.* solvent.

TABLE I

CALIBRATION DATA, REPRODUCIBILITY AND SENSITIVITY

Osmium concn. (p.p.m.)	*Absorbance at 615 mμ*	*Absorptivity (p.p.m.$^{-1}$ cm^{-1})*
0.76	0.142	0.187
1.52	0.280	0.182
2.28	0.424	0.186
3.04	0.559	0.184
3.80	0.687	0.181
4.56	0.798	0.176
5.32	0.923	0.173
6.08	1.007	0.166

STUDY OF VARIABLES

All tests for the study of variables were made on solutions containing a final osmium concentration of 2.28 p.p.m. (1.2 · 10^{-5} *M*); this concentration is near the middle of the optimum concentration range. Other conditions were as given in the recommended procedure, except for the variable being studied.

Effect of amount of reagent

The volume of 2.00 · 10^{-3} *M* anil solution was varied from 1 to 7 ml. Full color development required a minimum of 4 ml of reagent per 25 ml final volume, corresponding to 3.2 · 10^{-4} *M*, and a mole ratio of reagent:osmium of 27:1. No change in absorbance was produced by larger amounts of reagent.

Rate of color development

The absorbance increased rapidly during the first 15 min and attained its maximum

value in 40 to 50 min; to provide a safety margin, a development time of 1 h was adopted for the standardized procedure. The color was stable for at least 6 h.

Effect of ethanol concentration

In preliminary tests in essentially aqueous medium, a blue precipitate formed slowly; the colored product could be kept in solution by the addition of organic solvents such as the lower alcohols or acetone. The color formed faster and was more stable in the ethanol system. The minimum amount of ethanol to give full color development was 10 ml per 25 ml final volume; including the ethanol of the anil reagent solution, this corresponds to 56% by volume.

Effect of pH and amount of buffer

Preliminary tests with the osmium–anil system showed it to be quite sensitive to pH, but by use of an appropriate buffer it was possible to get good reproducibility. Buffers of high capacity were required to bring the system into the quite narrow range of pH for maximum absorbance. A series of high capacity buffers covering the pH range 0.8 to 10.4 was prepared, using appropriate combinations of hydrochloric acid–sodium acetate, acetic acid–sodium acetate, and sodium dihydrogen phosphate–sodium hydroxide. Solutions for test were prepared by the standardized procedure, using 5 ml of a given buffer. After standing for 1 h the apparent pH of the semiaqueous mixture was measured, and then the absorbance at 615 mμ. The results are shown in

TABLE II

EFFECT OF PH ON ABSORBANCE

pH of buffer added	*Apparent pH of solution*	*Absorbance at 615 mμ*
0.8	1.8	0.048
1.2	2.2	0.079
1.8	2.8	0.120
2.5	3.3	0.378
3.2	4.3	0.419
3.6	4.6	0.424
3.8	4.8	0.402
4.1	5.1	0.392
4.4	5.3	0.360
4.6	5.5	0.339
4.9	6.1	0.332
5.6	6.6	0.248
6.6	7.3	0.214
7.3	8.0	0.144
10.4	10.8	0.027

Table II, in which the first column is the pH of the buffer added, and the second column is the apparent pH (pH′) of the final solution as indicated by a pH meter. The results indicate that full color development requires the pH′ to be within a narrow region around 4.5, attained by the use of an acetic acid–sodium acetate buffer of pH 3.5. Tests with this buffer showed that a minimum of 4 ml of buffer solution was required for full color development; to provide a margin of safety, the use of 5 ml of buffer is recommended.

Effect of foreign ions

Varying amounts of the foreign ion were taken with a fixed amount of osmium, and the color developed and measured in the usual way. The tolerance for the foreign ion was taken as the largest amount that could be present and give an absorbance differing by no more than 0.01 from that produced by osmium alone. Tolerances for various foreign ions are shown in Table III. Addition of iron(II) to the osmium solution caused darkening of the latter (presumably due to reduction of the osmium), and no blue color was produced on addition of the anil reagent. In the presence of silver(I) or gold(III), osmium gave the characteristic blue color, but a precipitate formed on standing.

TABLE III

TOLERANCE FOR FOREIGN IONS

Osmium concentration, 2.28 p.p.m.

Ion	*Tolerance (p.p.m.)*
Palladium(II)	2
Platinum(IV)	0.5
Ruthenium(III)	4
Iridium(IV)	2
Rhodium(III)	6
Iron(III)	6
Iron(II)	0
Chromium(III)	6
Copper(II)	2
Mercury(II)	4
Vanadium(V)	6
Cobalt(II)	>120
Nickel(II)	>120
Lead(II)	>120
Chloride	>200
Nitrate	>200
Sulfate	>200
Phosphate	>200

It is apparent that determination of osmium by this method (in common with most methods for osmium) would require its separation from many other elements. The separation is based upon the oxidation of osmium to its tetroxide, and distillation of the latter. If chloride is present, the stable chloroosmate is first destroyed by evaporation with nitric acid. Distillation from solution containing 10 to 40% by volume of nitric acid volatilizes osmium tetroxide without volatilizing any ruthenium tetroxide[5]. Various oxidants and absorbents have been employed[6,7]. Using an all-glass distillation apparatus designed by ALLEN AND BEAMISH[6], samples containing 3 mg of osmium and 5 mg each of ruthenium(III), rhodium(III), palladium(II), platinum(IV), silver(I), copper(II), iron(III), and chromium(III) were boiled with nitric acid solution, and the distillate was absorbed in 6 *M* hydrochloric acid. After neutralizing the combined solutions from the receivers, aliquots were analyzed for osmium by the recommended procedure. Osmium recoveries of 97–98% were obtained.

COMPOSITION OF THE REACTION PRODUCTS

Mole ratio method

For application of the mole ratio method of YOE AND JONES[8] a series of solutions was prepared containing a constant amount of osmium (3.80 p.p.m.) and varying amounts of anil reagent. A plot of absorbance at 615 mμ against the mole ratio of reagent to osmium showed a marked change of slope at a mole ratio of 2 : 1 (Fig. 2,

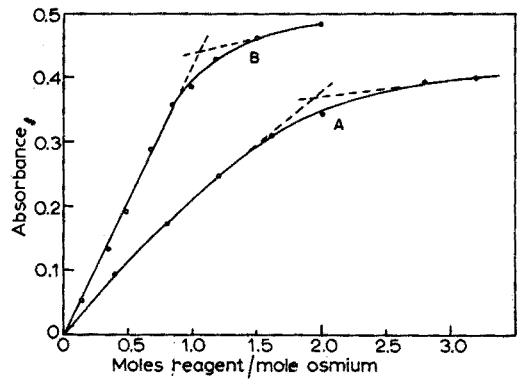


Fig. 2. Mole ratio plot; osmium concentration, 3.80 p.p.m. (A) Absorbance at 615 mμ. (B) Absorbance at 466 mμ.

curve A). For confirmation, another series of solutions was prepared in which the amount of reagent was held constant and the amount of osmium was varied; the plot of absorbance against mole ratio of osmium to reagent showed a break at a mole ratio of 0.5 : 1. In preparing these solutions it was observed that when the osmium concentration was in excess of the anil concentration, the usual blue color did not appear, even if the solutions were allowed to stand for 24 h; these solutions were dark red in color. A spectral scan of these solutions gave a sharp absorption peak at 466 mμ, and moderate general absorption over the range 500 to 650 mμ (Fig. 1, curve B), the

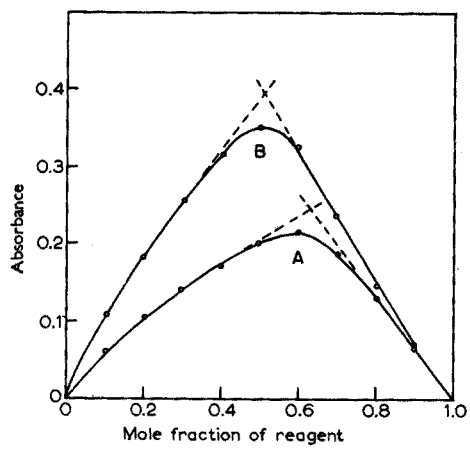


Fig. 3. Continuous variations plot; total concentration of reactants, $4.00 \cdot 10^{-5}$ *M*. (A) Absorbance at 615 mμ. (B) Absorbance at 466 mμ.

region in which the broad absorption band of the blue solutions occurs. Measurement of the mole ratio solutions at 466 mμ revealed the presence of a 1 : 1 complex (Fig. 2, curve B).

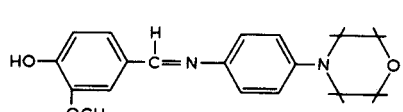
Continuous variations method

In applying the method of continuous variations[9,10] a series of solutions was prepared from equimolar concentrations of osmium and anil reagent, in which the sum of the molar concentrations was constant ($4.00 \cdot 10^{-5}$) while their ratio varied. A plot of absorbance against mole fraction of anil reagent is given in Fig. 3. Curve A, for measurements at 615 mμ, maximizes at about 0.63 mole fraction of reagent, corresponding quite closely to a 2 : 1 reaction ratio; curve B, for measurements at 466 mμ, maximizes at 0.50, representing the 1 : 1 reaction ratio.

DISCUSSION

In view of the evidence for the existence of two different complexes of osmium and anil, one absorbing strongly at 615 mμ and the other at 466 mμ, the color system was re-examined by preparing a solution by the recommended procedure, then making a spectral scan as quickly as possible, and repeating the scan at intervals of several minutes. The first scan showed a peak of moderate intensity at 615 mμ, and a more intense absorption peak at the lower wavelength. Within 5 min there was a marked increase in absorption at the longer wavelength and a marked decrease in absorption at the shorter wavelength. By the end of 30 min the absorption band at the shorter wavelength had virtually disappeared, while that at 615 mμ had further increased. Only small additional changes in the same directions had taken place in 1 h. These observations lead to the conclusion that in the presence of excess of anil reagent, both the 1 : 1 and the 2 : 1 complexes are formed initially, and that the 1 : 1 complex, which forms rapidly, is gradually converted to the 2 : 1 complex.

The structures of the complexes have not been deduced. The structure of the anil reagent,



is such that a 5- or 6-membered chelate ring would be difficult to form. Both the 1 : 1 and the 2 : 1 complexes were cationic, as shown by their behavior with Dowex 50-X cation-exchange resin. The postulation of structure is further complicated by the uncertainty of the oxidation state of the osmium. Osmium is known to be reduced from oxidation state 8 to 6 by ethanol, used as a solvent in this method; however, it seems unlikely that cationic complexes would contain osmium in oxidation state 6, and an oxidation state of 4 appears more probable.

A comparison of several methods for the spectrophotometric determination of osmium is summarized in Table IV. A simple estimate of relative sensitivities can be made by comparing the optimum concentration ranges, as given by the authors of the work or derived from data in the publications cited. The present method compares favorably with the most sensitive methods previously published. In common with all

TABLE IV

COMPARISON OF SPECTROPHOTOMETRIC METHODS FOR OSMIUM

Reagent	*Development conditions*	*Optimum range, 1-cm cell (p.p.m.)*	*Reference*
Thiourea	0.6 *M* H_2SO_4; 10 min	8–40	3
1-Naphthylamine-3,5,7-trisulfonic acid	pH 1.5; 4 h	1.5–5.5	11
1-Naphthylamine-4,6,8-trisulfonic acid	pH 2; 1 h	1–6	12
Tiron	pH 5; 15 min at boil	8–24	13
Anthranilic acid	pH 6; 1 h	2–6	14
Quinisatin oxime	pH 7; 1.5 h at boil	2–10	15
Anil (this method)	pH 4.5; 1 h	1–4	

methods for osmium, this method is subject to interference from several other elements, notably ruthenium which, if present, would require the separation of osmium by the usual distillation method.

The authors express their thanks to Dr. D. W. CARROLL of Rollins College, Winter Park, Florida, for calling the anil reagent to our attention and furnishing the initial quantity of reagent. Financial support of The University of Texas Research Institute, project R-223, and National Science Foundation grant NSF G14479 is gratefully acknowledged.

SUMMARY

A sensitive spectrophotometric determination of osmium is based on the blue color (absorption maximum at 615 mμ) formed by reaction of osmium with *p*-(morpholino)-N-(4′-hydroxy-3′-methoxy)benzylidineaniline ("anil") in acetate–buffered solution containing ethanol to prevent formation of a precipitate. Full color development is attained in 1 h at room temperature, and the color is stable for several hours. The absorbance is reproducible. The optimum concentration range for 1-cm optical path is about 1 to 4 p.p.m. of osmium. Several transition elements interfere; osmium can be separated as its tetroxide by the usual distillation method. The blue product is a cationic complex formed by reaction of anil with osmium in a 2 : 1 mole ratio. When osmium is in excess a red cationic complex (absorption maximum at 466 mμ) is formed by a 1 : 1 reaction between osmium and the reagent. The 1 : 1 complex is slowly converted to the 2 : 1 complex by excess reagent.

RÉSUMÉ

Une méthode de dosage spectrophotométrique sensible de l'osmium (1–4 p.p.m.) est basée sur la coloration bleue obtenue au moyen de la *p*-(morpholino)-N-(hydroxy-4′-méthoxy-3′)benzylidine-aniline ("anile"), en tampon acétique, renfermant de l'alcool, pour empêcher la formation d'un précipité. Plusieurs éléments de transition gênent; l'osmium peut être séparé sous forme de son tétroxyde, par la méthode de distillation habituelle. Le produit bleu est un complexe cationique formé par la réaction anile–osmium dans un rapport 2 : 1. Lorsque l'osmium est en excès, il se forme un complexe cationique rouge; le rapport osmium : réactif est alors de 1 : 1.

ZUSAMMENFASSUNG

Eine empfindliche spektralphotometrische Bestimmung von Osmium wird beschrieben. Sie beruht auf der blauen Farbe (Absorptionsmaximum bei 615 mμ), die durch Reaktion von Osmium mit Anil entsteht. Es wird eine acetatgepufferte Lösung verwendet, die Äthanol enthält, um die Bildung eines Niederschlages zu verhindern. Verschiedene Übergangselemente stören. Das Osmium kann dann durch die übliche Destillation als Tetroxid abgetrennt werden. Das blaue Produkt ist ein Kationenkomplex, der durch Reaktion von Anil mit Osmium im Molverhältnis 2 : 1 gebildet wird. Ist Osmium im Überschuss vorhanden, so wird ein roter Kationenkomplex mit dem Molverhältnis 1 : 1 gebildet, der durch einen Überschuss des Reagenzes langsam zu dem blauen Komplex umgewandelt wird.

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MICRODETERMINATION OF DISSOLVED OXYGEN IN WATER BY A RAPID SPECTROPHOTOMETRIC METHOD

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The WINKLER method[1] has long been the standard of comparison in dissolved oxygen analysis. The Winkler method requires 250 to 350 ml of water, is sensitive to interference, and has limited accuracy in dilute solutions of dissolved oxygen. Several micro-adaptations of the Winkler method have been proposed[2,3]. These methods generally require special apparatus and lengthy procedures. POTTER[4] has described a method for the determination of dissolved oxygen below 0.01 p.p.m. The procedures are exacting, and special apparatus is used. LOOMIS[5,6] has described a spectrophotometric method utilizing the dye indigo carmine. There are many practical difficulties associated with this method which limit its use.

This paper describes a further adaptation of indigo carmine to dissolved oxygen analysis. Oxygen concentration is determined by measuring the decrease in absorbance at 410 mμ of reduced indigo carmine solutions oxidized by dissolved oxygen. A 1-ml gas-tight syringe, adapted for direct placement into the Bausch and Lomb Spectronic 20 or 340 spectrophotometer, serves as a sample cell. Sample volumes of less than 1 ml are necessary and each determination requires approximately 3 min. The analysis is accurate over ranges of 0–10% to 0–100% of saturation with atmospheric oxygen. It is free of many of the interferences associated with the Winkler method.

EXPERIMENTAL

Apparatus

A gas-tight 1-ml syringe (Hamilton Microliter, Model 1001) is used to measure and mix solutions. The syringe is used as a sample cell by fitting it directly to the Bausch and Lomb Spectronic 20 or 340 spectrophotometer. Either the fixed needle or removable needle type syringe can be used. A small steel ball or lead shot is placed in the syringe barrel to aid in mixing solutions. The sample tube holder of the Spectronic 340 is altered by fastening thin aluminum plates to the top and bottom of the holder. A 1-cm hole is drilled in each plate so that the syringe is exactly centered and held firmly in the light path when inserted into the holder (Fig. 1).

If the removable needle syringe is used, a small aluminum foot is riveted to the tripping lever of the light shutter (Fig. 2a). This prevents the base of the needle from becoming wedged behind the lever. If the fixed needle syringe is used, the aluminum

foot is unnecessary. Instead, a 0.5-inch extension of epoxy resin is added to the needle end of the syringe barrel (Fig. 2b). The shutter lever is fully depressed by the extension. In either case the syringe should extend deep enough to depress the shutter fully and give an unobstructed light path. A small hole is drilled in the base of the instrument to allow the needle to pass through. A piece of black plastic tape is used to cover the hole.

Tank nitrogen such as Matheson's "Prepurified" is used in making oxygen-free

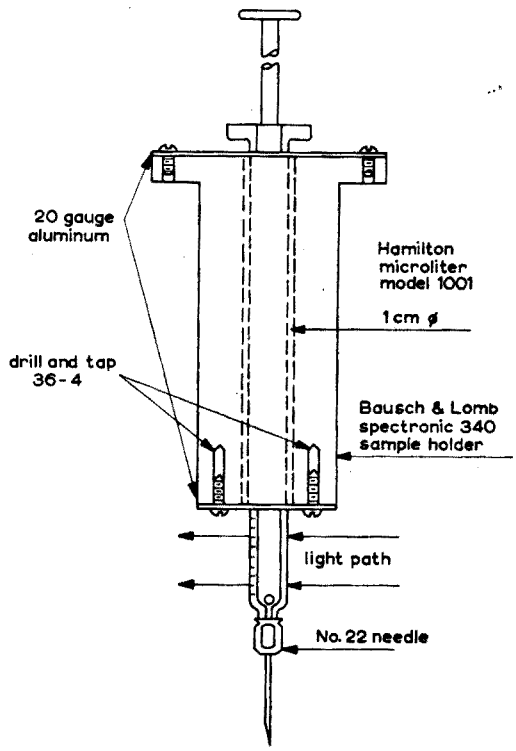

Fig. 1. Sample syringe and holder for Spectronic 340.

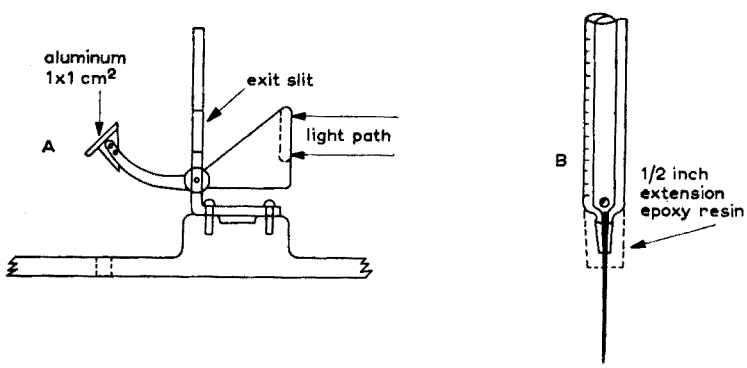

Fig. 2. (A) Modified light shutter for Spectronic 340. (B) Epoxy resin extension of syringe barrel.

water and in flushing air from reagent bottles. Lower quality nitrogen must be deoxygenated by bubbling through alkaline pyrogallol solution or freshly precipitated manganous hydroxide.

Narrow mouthed 1-l bottles or small serum bottles are used to store the reagent. The bottles are sealed with soft rubber plugs (such as Fisher Scientific Co.'s 3-225). These plugs allow repeated insertion of No. 22 or 23 hypodermic needles without gas leakage.

Reagents

The reagent is an aqueous solution of 0.045% indigo carmine, 0.8% glucose, and 1% potassium carbonate by weight. A 1-l bottle is filled half full of solution and sealed with a rubber plug. The air space is flushed with nitrogen through two No. 22 or 23 needles. The bottle should be left under a slight positive pressure of nitrogen. Dye reduction takes place in approximately 2 days at 25°. Reduction at higher temperatures causes the solution to become turbid. The solution should be allowed to stand for 1 to 2 weeks before use. Use before this aging period requires frequent re-standardization of the solution.

Oxygen-free water is made by sparging nitrogen through distilled water. A 500-ml three-necked reaction flask is used. A rubber plug, such as is used in the reagent bottles, is placed in one neck, a sintered glass sparger is placed in the center, and a flutter valve made of rubber tubing is placed in the third. The flask is supported so that the plug and sparger are well below the water surface and nitrogen escapes through the valve. The water is sparged vigorously with nitrogen for 10 min before use and is sparged gently during use. Water is withdrawn with the syringe when needed.

Procedure

All measurements are made with the spectrophotometer set at 410 mμ. The syringe is rinsed several times with oxygen-free water. It is then filled with exactly 0.5 ml of oxygen-free water and 0.5 ml of reagent and shaken for 30 sec to mix the solutions. The syringe is wiped dry, placed in the instrument, and covered with a black cloth to exclude extraneous light. The syringe barrel is carefully rotated to the point of least absorbance and the light control is adjusted to give an absorbance of 0.50. Rotating the syringe to the point of least absorbance enables the syringe to be precisely re-aligned every time it is placed in the instrument.

A working curve is constructed by mixing various volumes of oxygen-free and oxygen-saturated water directly in the syringe. For example, a sample of water of 10% oxygen saturation is made by mixing 0.1 ml of oxygen-saturated water and 0.9 ml of oxygen-free water. The syringe is discharged to 0.5 ml, 0.5 ml of reagent is added, the solutions are mixed for 30 sec and measured by the above procedure. The absorbance is read precisely 1 min after initial mixing. A stopwatch should be used to time each analysis.

Oxygen-saturated water is made by vigorously shaking a partially filled flask of water for several minutes. The water should stand several minutes before use. The temperature of the water is recorded to the nearest 0.5°, and must remain constant during construction of the working curve.

Samples are measured in the same manner as the standards used in obtaining the working curve. The syringe is rinsed with several small volumes of sample water

before filling to 0.5 ml. The temperature of the sample water must be recorded to the nearest 0.5° for correction to the standard temperature, T_{std}.

Calculations

Oxygen content in per cent saturation is read directly from the working curve. The oxygen concentration, $[O_2]$, in mg/l is obtained by multiplying the experimental per cent saturation by the dissolved oxygen concentration in mg/l corresponding to 100% saturation at the temperature of the standards, T_{std}, used to obtain the working curve. The data of WHIPPLE AND WHIPPLE[7] or the American Public Health Association[8] can be used for this purpose.

If the temperature of the sample water, T_{samp}, is different from that of the temperature of the standards used to obtain the working curve by one degree or more, the per cent saturation value read from the working curve should be corrected by use of the following equation,

$$\%_{corr} = \%_{samp} \frac{[O_2]_{at\ T_{std}}}{[O_2]_{at\ T_{samp}}}$$

where $\%_{corr}$ is the corrected per cent oxygen saturation at T_{samp}, the sample temperature, and $\%_{samp}$ is the per cent saturation read directly from the working curve.

RESULTS AND DISCUSSION

A comparison of the indigo carmine method and the modified Winkler method[8] is given in Table I. Samples are made up from stock supplies of oxygen-free and oxygen-

TABLE I

COMPARISON OF THE INDIGO CARMINE METHOD AND THE MODIFIED WINKLER METHOD

% O_2 saturated at 25°	
Indigo carmine method	*Winkler method*
1.2	0.6
1.3	1.2
7.3	9.2
9.4	8.7
9.6	10.7
10.0	9.3
10.6	12.4
10.9	11.3
12.8	13.0
13.1	12.8
13.8	13.0
14.9	15.2
15.8	15.9
16.7	15.5
20.9	21.0
21.7	19.9
22.1	21.8
22.5	21.2
25.5	26.4
28.3	30.4

saturated distilled water. The reproducibility of all measurements of dissolved oxygen in the concentration range of 1–50% saturation is in most cases better than ±0.5% oxygen saturation. The good agreement between the indigo carmine method and the modified Winkler method indicates the reliability of the method. In addition, the proposed method is much faster and less subject to error than the Winkler method.

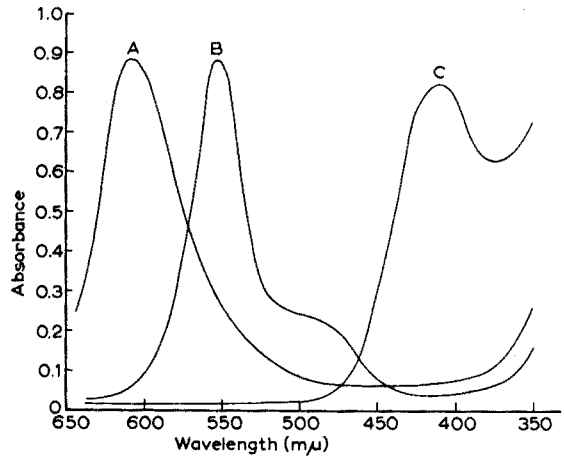

Fig. 3. Absorption spectra of indigo carmine at pH 11.5. (A) Oxidized form of indigo carmine. (B) Intermediate form of indigo carmine. (C) Reduced form of indigo carmine.

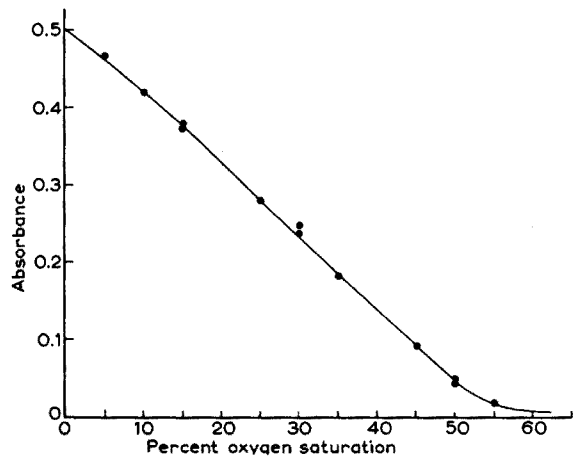

Fig. 4. Working curve of absorbance *vs.* per cent oxygen saturation.

Indigo carmine is rapidly reduced by glucose only at pH 10 or higher. The intermediate semi-quinone form of the dye is also observed only above pH 10 (Fig. 3). The oxidized dye is unstable at high pH. The reduced dye is quite stable, decomposing over a period of months. Working curves must be restandardized every 4 to 5 days, depending on the accuracy desired.

The dye is stored in a reducing solution of excess glucose to counteract oxygen

leaks in the seals. During each analysis, the glucose will slowly reduce the oxidized sample. Negligible error results if each determination is timed.

The working curve obtained by plotting the absorbance at 410 mμ (the reduced dye peak) *vs.* dissolved oxygen concentration is essentially linear (Fig. 4). Each point in Fig. 4 represents an individual determination and all points were obtained over a time interval of 1 h. The blank absorbance is arbitrarily set at any convenient value (*e.g.*, an absorbance of 0.5 in the procedure outlined). Sample volume and dye concentration determine the useful range of the analysis. A dye concentration of 0.045%, with a sample volume of 0.5 ml gives a working range of 0 to 50% oxygen saturation at 25°. Increasing the sample volume to 0.75 ml gives a working range of 0 to 25% saturation. Working curves must be constructed for each change in volume. Any desired range can be obtained by adjusting the sample volume and dye concentration.

The indigo carmine method is free from many of the interferences associated with the Winkler method. Possible interferences were investigated by comparing solutions of the substances in question with distilled water. The ionic strength of solutions has considerable effect on the solubility of oxygen, which makes comparison of solutions difficult. The following information should be considered only a general outline of interferences. Nitrite does not interfere below approximately 1000 p.p.m. Sulfite does not appear to interfere with the analysis, although sulfite rapidly reduces dissolved oxygen. Nitrate, sulfate, chloride, and carbonate do not interfere. Iron(II) interferes by precipitation of its hydroxide at 5 p.p.m. or greater. Iron(III) interferes at 200 p.p.m. Calcium, as a saturated solution of calcium carbonate, does not interfere. Soluble salts of calcium and magnesium may precipitate as carbonates. This interference can be avoided by use of a monohydrogen phosphate–hydroxide buffer at pH 11.5. The indigo carmine method should, therefore, be particularly useful in the analysis of dissolved oxygen in ground and river water samples as well as in polluted waters, boiler waters, etc.

The apparatus used in this method readily lends itself to many other types of analyses. The syringe provides a quick, efficient way of sampling closed systems. Kinetic studies, enzyme analyses, and the like, could readily be adapted to this technique.

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SUMMARY

A spectrophotometric method utilizing the dye indigo carmine has been applied to the analysis of dissolved oxygen in water samples. Oxygen concentration has been determined by the decrease in absorbance at 410 mμ of reduced indigo carmine solutions oxidized by dissolved oxygen. A simple modification of the sample compartment of a Bausch and Lomb Spectronic 20 or 340 spectrophotometer allows rapid and accurate measurements to be made within 3 min. Dissolved oxygen in the ranges of 0 to 10% and 0 to 100% saturation can be analyzed without many of the interferences inherent in the standard WINKLER method.

RÉSUMÉ

Une méthode spectrophotométrique, utilisant le colorant carmin indigo, a été appliquée au dosage de l'oxygène dissous dans l'eau. La diminution de l'absorption à 410 mμ de solutions de carmin indigo, à l'état réduit, permet de déterminer par oxydation du colorant la teneur en oxygène dissous.

ZUSAMMENFASSUNG

Es wird die Anwendung einer spektralphotometrischen Methode zur Bestimmung von gelöstem Sauerstoff in Wasser mit Hilfe von Indigocarmin beschrieben. Die Sauerstoffkonzentration wurde bestimmt durch Messen der Absorptionsverminderung einer reduzierten Indigocarminlösung bei 410 mμ, die durch Oxydation des gelösten Sauerstoffes hervorgerufen wurde. Schnelle und genaue Messungen sind innerhalb von 3 Min möglich. Der Sauerstoff kann ohne Störungen, wie sie der WINKLER-Methode anhaften, analysiert werden.

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A SIMPLE COLORIMETRIC METHOD FOR THE DETERMINATION OF AMMONIA IN SEAWATER

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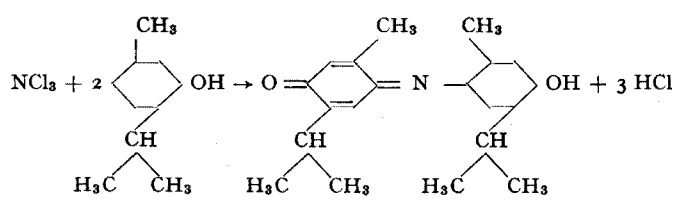
The amount of ammonia present in seawater is usually very small. During analysis this makes contamination a problem and simplicity desirable. Methods that make use of distillation, microdiffusion or extraction are not satisfactory in this respect. The phenol–hypochlorite[1-3] method is sensitive and simple, but RILEY[4] found it unsuitable for seawater, because of magnesium interference, which could not be prevented with EDTA. The method proposed here resembles the phenol–hypochlorite method. Thymol is used instead of phenol; it is much more stable and the reaction is twice as sensitive. The addition of acetone to the thymol reagent greatly enhances the sensitivity, just as in the case of phenol[5]. With seawater, however, only a limited amount of acetone can be used, otherwise the test solution becomes turbid, probably because of a salting-out effect. Magnesium interference is prevented by the use of CDTA, which forms a very stable magnesium chelate[6]. The chelating reagent should be prepared very carefully. Low results are obtained when even a slight precipitate is allowed to develop during the determination; before the other reagents are added, all the calcium and magnesium in the seawater must be completely chelated. This requires not only a sufficient excess of CDTA but also a pH value high enough to yield the CDTA in the reactive anionic form. This high pH (> 11) must be obtained without free calcium or magnesium ions being exposed locally or temporarily to a large concentration of hydroxyl ions, as would be the case if the pH were adjusted with sodium hydroxide. The tetrasodium salt of CDTA was also found to be too alkaline for the purpose. On the other hand, the trisodium salt gives too low a pH owing to the protons set free by the reaction with magnesium or calcium. The actual chelating reagent has a composition in between these.

The mechanism of the formation of the blue colour is not yet clearly understood. As a working hypothesis it is assumed that an indophenol-type compound is formed in two steps:

$$NH_3 + 3\,NaOCl \rightarrow NCl_3 + 3\,NaOH$$



It was found that addition of hypochlorite both before and after adding thymol speeds up the formation of the blue colour and enhances sensitivity and precision; however, low results are obtained if the total amount of hypochlorite is added all at once. The reason why acetone enhances the sensitivity also remains to be explained.

EXPERIMENTAL

Reagents

Thymol reagent. Dilute 5 g of thymol and 1.6 ml of acetone to 50 ml with methanol.

Hypochlorite reagent. From a commercial solution of sodium hypochlorite, measure an amount containing exactly 300 mg of active chlorine. Add 10 meq. of sodium hydroxide (for stabilisation) and dilute to 100 ml with distilled water. The reagent is stable for approximately one month if it is stored in a clean, well-stoppered glass container in the dark in a refrigerator.

Chelating reagent. Dissolve 40 g of CDTA (cyclohexyl-*trans*-1,2-diaminetetraacetic acid) and *ca.* 18.25 g of sodium hydroxide in a small amount of water and dilute to 100 ml. The exact amount of sodium hydroxide depends on the purity of the CDTA. The chelating reagent, when diluted 1+10 with distilled water, must have a pH of 11.5–11.8 and the pH must not fall below 11.0 if the reagent is diluted 1+10 with seawater.

Procedure

Add 1 ml of chelating reagent to 10 ml of seawater, mix thoroughly, add 0.2 ml of hypochlorite reagent and mix. After 1 min add 0.5 ml of a mixture of equal volumes of thymol reagent and 1 *N* sodium hydroxide. Mix and after 1 min add 0.8 ml of hypochlorite reagent; mix and after 20 min, read the extinction at 630 nm.

Subtract from the obtained value the reagent blank (in deionised distilled water) and the extinction of the seawater itself. Divide the corrected value by the extinction increment per μg NH_4^+-N obtained by adding a known amount of ammonium sulphate to the seawater under study.

RESULTS AND DISCUSSION

The sensitivity of the method is 1.3 ng NH_4^+-N/cm^2 for $\log I_0/I = 0.001$, which is equivalent to an extinction of 0.0088 per μg-at NH_4^+-N per liter of water per cm light path of the cuvette used. There is no salt effect with this method; the OD increments per 100 μg NH_4^+-N were found to be the same for seawater as for distilled water.

The precision depends of course on quite a variety of factors. The results given in Table I were obtained when the work was done in an ordinary laboratory in an industrialised area, the reaction being carried out in reagent tubes with polyethylene stoppers and the extinction being measured in a Bleeker spectrophotometer with 2-cm cuvettes and a spectral band width of 7.6 nm.

The accuracy depends mainly on the presence or absence of interfering substances. The influence of a number of substances is shown in Table II. The most powerful interfering substance, hydroxylamine, is unlikely to occur in seawater, for it is unstable[7] at the pH of *ca.* 8.4 found in the sea.

TABLE I

REPLICATE DETERMINATIONS IN SEAWATER (KNUDSEN SALINITY 35.01 ‰).

Values of $\varepsilon \begin{smallmatrix} 2\text{ cm} \\ 630\text{ nm} \end{smallmatrix}$

NH_4^+-N added (µg/l)			
0	*30*	*100*	*300*
0.023	0.059	0.149	0.388
0.024	0.060	0.149	0.390
0.025	0.059	0.148	0.388
0.024	0.061	0.149	0.389
0.025	0.060	0.150	0.388

TABLE II

ERRORS CAUSED BY ADDED INTERFERING SUBSTANCES[a]

Substance added	*Amount (µg/l)*	*Deviation* $\left(\varepsilon \begin{smallmatrix} 2\text{ cm} \\ 630\text{ nm} \end{smallmatrix}\right)$
NH_2OH	30	0.00
	100	+ 0.02
	1000	+ 0.06
$CH_3CNOHCOO^-$	1000	0.00
$N_2O_2^{2-}$	1000	0.00
NO_2^-	10000	0.00
N_2H_4	1000	0.00
$CO(NH_2)_2$	10000	0.00
$N(CH_3)_3$	10000	0.00
$CH_2NH_2COO^-$	10000	0.00
$^-OOC(CH_2)_2CHNH_2COO^-$	1000	0.00
SO_3^{2-}	1000	− 0.04
SO_3^{2-}	10000	− 0.07
Cu^{2+}	100	0.00
NaCl	3%	0.00

[a] The water used was a standard solution of 100 µg NH_4^+-N/l of deionised distilled water.

SUMMARY

A method is proposed for the determination of trace amounts of ammonia in seawater. After calcium and magnesium have been chelated with CDTA, the blue colour obtained with hypochlorite and thymol–acetone is measured at 630 nm. The sensitivity is 1.3 ng NH_4^+-N/cm².

RÉSUMÉ

Une méthode colorimétrique est proposée pour le dosage de traces d'ammoniaque dans l'eau de mer. On mesure à 630 nm l'intensité de la coloration bleue obtenue avec l'hypochlorite et la thymol–acétone. Le calcium et le magnésium gênent; ils doivent être masqués au préalable par le CDTA.

ZUSAMMENFASSUNG

Es wird eine einfache Methode zur Bestimmung von Spuren Ammoniak in Wasser vorgeschlagen. Mit Hypochlorit und Thymol–Aceton entsteht eine blaue Farbe, deren Intensität bei 630 nm photometrisch gemessen wird. Störungen durch Magnesium und Calcium werden durch Zugabe von CDTA verhindert.

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POLAROGRAPHIC DETERMINATION OF LEAD AND TIN IN STEELS

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The usual methods of determining small amounts of lead and tin in steel, very often involve a separation of the two metals from the main constituents present. In such cases polarography has often considerable advantages over photometric, potentiometric and titrimetric methods, making separations unnecessary. Both lead[1] and tin[2] can be determined polarographically from sodium formate supporting electrolyte, but the waves produced are not easy to distinguish. In 1 *M* citric acid, lead(II) and tin(II) give well-defined cathodic waves, coinciding at about −0.48 V *vs.* S.C.E. CANTACUZÈNE AND ZERMIZOGLOU[3], working with pure mixtures of lead and tin standard solutions, describe a suitable method for removing the tin wave and determining this metal by difference. When oxygen is passed through the electrolyte, tin(II) is oxidized to tin(IV), which gives no reduction wave in this area, whereas the wave due to lead(II) is unchanged.

When iron is present, iodine solution can be used as a selective oxidant for tin, in perfect agreement with the standard oxidation potentials involved. The present investigation was carried out in order to adapt this oxidant and the method proposed by CANTACUZÈNE AND ZERMIZOGLOU[3] to iron and steel analysis.

EXPERIMENTAL

Apparatus

A Sargent Model XXI recording polarograph was used to obtain the current–voltage curves. The potentials were all referred to the saturated calomel electrode (S.C.E.). Measurements were made in a thermostat at 25 ± 0.2°. The capillary characteristics were $m = 1.56$ mg/sec and $t = 4.05$ sec at −0.5 V *vs.* S.C.E. in the supporting electrolyte used. A Beckman H2 type pH meter was used for pH measurements.

Chemicals and solutions

All chemicals were reagent-grade quality.

Standard lead(II) solution. Dissolve the pure metal in warm hydrochloric acid with occasional addition of a few drops of saturated potassium chlorate solution.

Standard tin(II) solution. Dissolve the pure metal in warm hydrochloric acid, and before complete dissolution, pass purified nitrogen into the flask to prevent oxidation of tin(II). Make up to volume with oxygen-free water. Each time some of the solution is removed, bubble some more nitrogen through it, to expel the atmospheric oxygen introduced.

Standard iron(II) solution. Dissolve 17.8 g of $FeCl_2 \cdot 4\,H_2O$ in 10 ml of 6 *M* hydrochloric acid and dilute to 100 ml with distilled water (4 ml ≡ 500 mg Fe).

Iodine solution (0.25 M). Dissolve 3.17 g of iodine and 4 g of potassium iodide in 25 ml of water and dilute to 100 ml.

Procedure

Place the sample (0.500 g) in a 100-ml Erlenmeyer flask fitted with a rubber stopper with gas inlet and outlet. Add 4.0 ml of concentrated hydrochloric acid and a few ml of distilled water. Heat to complete dissolution on a small gas flame, while passing purified nitrogen through the flask to expel air. To ensure complete reduction to iron(II) and tin(II), add about 50 mg of ferrum reductum and finally boil for 1–2 min. At the same time, deaerate a mixture of 10 ml of 2.5 *M* citric acid, 5 ml of 5 *M* sodium hydroxide and 1 ml of 0.62% gelatin solution. Add the sample solution to this mixture and dilute to 25 ml with oxygen-free water. Place in a thermostat at 25° and record a polarogram between −0.3 and −0.8 V for the sum of lead and tin. Add a few drops of iodine solution until the colour becomes permanently light brown and remove the excess of iodine with a small amount of ascorbic acid. Record a new polarogram for lead only, and calculate the amounts of lead and tin present in the sample from calibration curves for the two metals.

Calibration curves

To mixtures containing the prescribed amounts of citric acid and gelatin, and different volumes of iron(II) and lead(II) solutions, about 50 mg of ascorbic acid were added to reduce traces of iron(III) present.

Deaeration was followed by addition of different volumes of standard tin(II) solution and dilution to 25 ml with distilled water. Current–voltage curves were recorded at 25° in the same way as mentioned in the procedure.

The diffusion currents of the resulting waves for the two metals separately, and for their mixture, were linear functions of the metal ion concentration present.

Diffusion current constants were determined as $I = 2.61$ for lead, and $I = 2.17$ for tin. These values are somewhat higher than those found by CANTACUZÈNE AND ZERMIZOGLOU[3]; the discrepancies are probably due to the differences in the electrolyte. At constant acidity, the diffusion currents were found to be independent of the amounts of iron(II) present.

Effect of variations in pH

The half-wave potentials for the lead(II) and tin(II) waves were about −0.48 V for pH values above zero. Raising the acidity made these potentials more negative, but did not affect the sensitivity. However, when the pH dropped to zero and below, oxidation to tin(IV) with iodine became impossible. Consequently, the pH was kept between 0.3 and 0.8. This interval gave the best reproducibility of the diffusion currents.

When present alone, the citric acid used by CANTACUZÈNE AND ZERMIZOGLOU[3] as supporting electrolyte, shows a pH of 1.54. The first results obtained were all too low for tin, probably because of an insufficient excess of hydrochloric acid during dissolution, as tin(II) is supposed to hydrolyse under such conditions. The citric acid has no buffer capacity, hence the additional quantity of hydrochloric acid necessary

will cause the pH to drop to zero or less. The prescribed acidity of the electrolyte was obtained by adding 5 *M* sodium hydroxide to the citric acid and gelatin solutions before mixing with the sample solution. This greatly improved the results.

RESULTS

The alloys used were from the National Bureau of Standards. Since tin was present in only a few samples, and since none of them contained both lead and tin, standard solutions of the two metals were added before dissolution. Table I shows the excellent agreement of the values found with the expected values.

TABLE I

LEAD AND TIN DETERMINATIONS IN STANDARD STEEL SAMPLES

Sample	*No.*	*Lead (%)*		*Tin (%)*		
		Added	*Found*	*Present*	*Added*	*Found*
Basic open-hearth	11f	0.040	0.039	0	0.040	0.040
Acidic open-hearth	20e	0.040	0.043	0.013	0.040	0.055
Bessemer	22c	0.040	0.041	0	0.040	0.039
Bessemer	22c	0.200	0.203	0	0.080	0.082
Electric	51a	0	0	0.011	0	0.009
Mangan	100a	0.040	0.039	0	0.040	0.038
Mangan	100a	0.020	0.020	0	0.020	0.019
Basic open-hearth	152	0	0	0.036	0	0.038

None of the metals present in the standard alloys interfered. For samples with high contents of carbon, however, a slight interference might be caused by carbon particles influencing the drop time of the capillary tube. None of the samples were filtered before the curves were recorded. Copper gives a single wave at about −0.2 V, so that it becomes possible to determine this metal without affecting the determinations of lead and tin.

DISCUSSION

The experimental work shows that lead and tin can be determined with sufficient accuracy by the present method, in amounts down to about 0.01%. When tin is present, the samples are dissolved under an atmosphere of purified nitrogen, and a small amount of ferrum reductum is added as reductant for traces of iron(III) and tin(IV). The polarograms then show no wave for iron(III) even in the absence of other reducing agents.

During exposure to oxygen, iron(II) and tin(II) present in the electrolyte, are both oxidized. This disadvantage is largely overcome when iodine is used as an oxidant which is selective for tin(II). Moreover, passing nitrogen becomes unnecessary after this addition, whereas bubbling with oxygen must be followed by deaeration for at least 10 min. A disadvantage of iodine is the less pronounced step for lead alone after this addition, but measurements can still be effected with satisfactory accuracy.

SUMMARY

A polarographic method is described for determining down to 0.01% lead and tin in iron and steel, using citric acid as supporting electrolyte. The sample is dissolved under purified nitrogen. Two curves are recorded for each sample solution: the first shows the sum of lead(II) and tin(II), and the second, after oxidation of tin(II) with a solution of iodine, gives a wave for lead only.

RÉSUMÉ

Une méthode polarographique est décrite pour le dosage du plomb et de l'étain (→ 0.01%) dans le fer et l'acier; on utilise l'acide citrique comme électrolyte de base. L'échantillon à analyser est dissous dans une atmosphère d'azote. Deux courbes doivent être enregistrées pour chaque échantillon: on obtient ainsi d'une part la somme plomb(II) et étain(II), d'autre part le plomb seul, l'étain(II) ayant été oxydé par l'iode.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode beschrieben, die die Bestimmung von Blei und Zinn in Eisen und Stahl bis zu 0.01% gestattet. Die Probe wird unter reinem Stickstoff gelöst. Für jede Probelösung werden 2 Kurven aufgezeichnet, die erste zeigt die Summe von Blei(II) und Zinn(II), während die zweite nach Oxydation von Zinn(II) mit Jod nur die Stufe für Blei wiedergibt.

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THE DETERMINATION OF NICKEL IN IRON AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Nickel is an important element in iron and steel and a number of procedures have been established for its determination. The nickel in ferrous alloys may be precipitated as red nickel dimethylglyoxime and subsequently determined by gravimetric[1], volumetric[1-3] or electrodeposition[1] techniques. The soluble red-brown complex of nickel dimethylglyoxime formed in an oxidising alkaline medium is used widely in spectrophotometry[1,4,5]. Other physicochemical techniques which have been used include emission spectrography, polarography and flame emission photometry. WALSH[6] has indicated that atomic absorption spectrophotometry is practically free from interference and the technique has been applied to the determination of nickel in biological[7] and agricultural materials[8]. GATEHOUSE AND WILLIS[9] used a helium-filled nickel hollow-cathode lamp and reported a sensitivity (1% absorption, 2320.1 Å) of 0.2 p.p.m.; ALLAN[10] reported a sensitivity of 0.13 p.p.m. but the gas filling of the hollow-cathode lamp was not stated. In the present study a Ransley[11] argon-filled nickel hollow-cathode lamp was used and a sensitivity of only 0.40 p.p.m. was obtained. However, atomic absorption spectrophotometry proved to be an excellent method for the determination of 0–2% nickel in both low and high alloy irons and steels.

EXPERIMENTAL AND DISCUSSION

Apparatus

The equipment used in the study consisted of a Hilger large quartz E492 spectrograph, an E.M.I. 9558-QB photomultiplier tube, a modulated argon-filled nickel hollow-cathode lamp and a tuned amplifier[11].

Reagents

AnalaR orthophosphoric (sp. gr. 1.75), sulphuric (sp. gr. 1.84) and nitric (sp. gr. 1.42) acids.

Nickel solution (1 ml ≡ 1 mg Ni). Dissolve 1.000 g of nickel (Johnson and Matthey spectrographically standardised rod) in 20 ml of 50% (v/v) nitric acid, cool, add 10 ml of sulphuric acid, heat to fumes, cool and dilute to 1 l.

Iron. Johnson and Matthey spectrographically standardised sponge (nickel 2 p.p.m.).

Recommended procedure

Transfer 1 g of iron or steel to a 125-ml conical beaker. Prepare a calibration series by making suitable additions of nickel solution to several 1-g samples of iron sponge. Add 30 ml of 15% (v/v) phosphoric–15% (v/v) sulphuric acid, simmer to dissolve and oxidise with dropwise additions of nitric acid. The dissolution of certain classes of alloyed steel may be assisted by the use of aqua regia. Evaporate to fumes and fume gently for 1 min. Extract the cooled residue with 30 ml of water and digest for 5 min to ensure dissolution of all soluble salts.

If filtration is necessary, filter through a Whatman 541 filter paper into a 100-ml volumetric flask, rinse the beaker with several washes of hot 2% (v/v) sulphuric acid and wash the filter several times with hot 2% (v/v) sulphuric acid. Allow to cool and dilute to the mark. Measure the absorbance by atomising the solution in a 10-cm slot burner using a lean air–acetylene flame and operating the nickel hollow-cathode lamp at 25 mA, with the light path 2 cm above the base of the flame. The nickel content of the sample is read directly from the calibration graph.

The 2320.1 Å[8] and 3415 Å[7] lines have been used for the determination of nickel, but the 3415 Å line was not used in this study because the sensitivity was only 25% of that obtainable at 2320.1 Å. The sensitivity of the 2320.1 Å line is markedly dependent on slit width[9], owing to difficulty in resolving this line from the non-absorbing 2319.8 Å nickel line and the resultant non-linear calibration curves[9] limit the concentration range which may be studied. Improved argon-filled lamps of higher intensity are now in the course of manufacture[12] and when these lamps are available more complete resolution of the 2320.1 Å line should be obtained. With the apparatus used in this work it is possible to compensate for the effect of non-absorbing or background radiation by the use of the dark-current balancing potentiometer. The dark-current adjustment is made while a concentrated (*ca.* 5000 p.p.m.) nickel solution is being atomised, rather than when the spectrograph shutter is closed.

An investigation of the effect of different solvent acids and iron concentration on the absorption sensitivity of nickel was carried out and the results are presented in Table I.

TABLE I

THE INFLUENCE OF SOLVENT ACIDS AND IRON CONCENTRATION ON THE ABSORPTION SENSITIVITY OF NICKEL

Lamp current: 25 mA; 10-cm burner; flame: air (10.5 l/min)–acetylene (1.5 l/min).

Solvent medium	*Absorbance*	
	30 p.p.m. Ni; 0 p.p.m. Fe	*30 p.p.m. Ni; 10,000 p.p.m. Fe*
Aqueous	0.315	—
10% (v/v) HCl	0.295	0.295
10% (v/v) HNO_3	0.310	0.295
10% (v/v) H_2SO_4	0.265	0.265
10% (v/v) H_3PO_4	0.265	0.250
4.5% (v/v) H_3PO_4–4.5% (v/v) H_2SO_4	0.275	0.255

The results indicated that any of the acids examined could be used as a solvent for iron and steel samples; a 4.5% (v/v) phosphoric–4.5% (v/v) sulphuric acid mixture was chosen because this mixture has the advantageous property of retaining tungsten

and other acid hydrolysable elements in solution; the nickel sensitivity (1% absorption) was 0.5 p.p.m. A 1-g sample dissolved in 30 ml of 15% (v/v) phosphoric acid–15% (v/v) sulphuric acid and diluted to 100 ml therefore gives a working range of 0–0.5% nickel; a calibration curve for this range was found to be linear. The absorbances were measured at 2320.1 Å with a lamp current of 25 mA, a lean air–acetylene flame and a 10-cm slot burner.

An interference study was carried out at the 0.000, 0.150 and 0.300% nickel levels, the possible interfering elements being added as spectrographically pure metals. The absorbance was not markedly dependent on flame type or on the height of the absorption path above the base of the burner and a lean air–acetylene flame (air 10.5 l/min, acetylene 1.5 l/min at S.T.P.) was used for absorption measurements. Any interference greater than 0.005% nickel was considered to be significant; under the selected conditions no interference was encountered from 30% Cr^{3+}, 20% Mn^{2+}, 20% W^{6+}, 10% Cu^{2+}, 10% Co^{2+}, 5% V^{5+}, 5% Mo^{6+} or 5% Al^{3+}. The results indicated that under the same conditions as in the interference study, nickel could be satisfactorily determined in low and high alloy irons and steels by atomic absorption spectrophotometry.

RESULTS

A series of standard irons and steels in the range 0–0.50% nickel were analysed by the proposed procedure and the results, reported to the nearest 0.005% are presented in Table II.

TABLE II

NICKEL CONTENT OF STANDARD IRONS AND STEELS IN THE RANGE 0–0.50% NICKEL

Sample	*Type*	*Nominal composition*	*% Ni*	
			Observed	*Certificate*
N.B.S. 55d	O.H. iron	—	0.010	0.009
N.B.S. 130a	Leaded steel	0.8% Mn, 0.2% Pb	0.015	0.010
N.B.S. 8h	Bessemer steel	0.4% Mn	0.020	0.019
N.B.S. 100a	Manganese steel	1.7% Mn	0.030	0.032
N.B.S. 342	Nodular iron	2.9% Si, 0.1% Cu	0.030	0.023
N.B.S. 51b	Electric steel	0.6% Mn, 0.4% Cr	0.050	0.053
N.B.S. 4i	Cast iron	0.8% Mn, 1.4% Si, 0.2% Cu	0.060	0.065
N.B.S. 50c	Tool steel	0.4% Cr, 1% V, 18% W	0.065	0.069
N.B.S. 153	Tool steel	8% Co, 8% Mo, 2% W, 2% V	0.110	0.107
N.B.S. 132a	Die steel	4% Mo, 6% W, 4% Cr, 2% V	0.145	0.137
N.B.S. 19f	O.H. steel	0.2% Cu	0.310	0.317

The accuracy obtained in the range 0–0.5% nickel was within that permissible for routine determinations. Nickel contents greater than 0.50% may be analysed by rotation of the burner to reduce the absorption path length. Standard samples in the ranges 0–1, 0–2 and 0–5% nickel were analysed in this manner by the proposed procedure and the results are presented in Table III.

The results obtained on these samples demonstrate that the method is a useful alternative to many established procedures for the determination of 0–2% of nickel in ferrous alloys. In the present state of instrumentation nickel concentrations greater than 2% can be determined better by existing standard procedures.

TABLE III

NICKEL CONTENT OF STANDARD IRONS AND STEELS IN THE RANGE 0–1%, 0–2% AND 0–5% NICKEL

Sample	*Type*	*Nominal composition*	*% Ni*		
			Observed		*Certificate*
B.C.S. 257	Alloy steel	1.4% Mn, 1.7% Cr, 0.3% Cu	0.85	(S.D. 0.006)	0.84
N.B.S. 32e	Alloy steel	0.7% Cr	1.19	(S.D. 0.015)	1.18
B.C.S. 254	Alloy steel	1% Mo, 0.5% Mn, 0.5% Cr, 0.5% V	2.03		2.08
B.C.S. 253	Alloy steel	0.4% Cr, 0.9% Mo, 0.2% V	3.08	(S.D. 0.071)	2.92
B.C.S. 251	Alloy steel	0.2% Mo	5.33		5.15

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SUMMARY

A procedure is described for the determination of 0.005 to 2% of nickel in low and high alloy irons and steels by atomic absorption spectrophotometry. The sample is dissolved in phosphoric–sulphuric acid and atomised in an atomic absorption spectrophotometer. The method is rapid and free from interferences; preliminary separations are not required and results obtained on standard samples are in good agreement with certificate values.

RÉSUMÉ

Une méthode spectrophotométrique par absorption atomique est proposée pour le dosage du nickel (0.005–2%) dans le fer et l'acier. L'échantillon est dissous dans un mélange d'acide phosphorique et d'acide sulfurique, et atomisé. La méthode est rapide; des séparations préliminaires ne sont pas nécessaires.

ZUSAMMENFASSUNG

Ein Verfahren zur Bestimmung von 0.005–2% Nickel in niedrig- und hochlegierten Stählen mit der atomaren Absorptionsspektroskopie wird beschrieben. Die Methode, bei der die Probe zum Versprühen in einem Gemisch aus Phosphor- und Schwefelsäure gelöst wird, ist schnell und frei von Störungen. Vorhergehende Trennungen sind nicht erforderlich. Die Messergebnisse für Standardproben stimmten gut mit deren bekannten Gehalten überein.

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A THEORETICAL APPROACH TO THE SOLVENT EXTRACTION OF METAL CHELATES

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Since before the turn of the present century, it has been known that metal ions could be extracted as neutral chelate compounds from an aqueous solution into an organic phase containing a suitable chelating reagent. Empirically it has been noted that a number of factors may affect the distribution of the metal between the phases. Among these factors are: (*1*) the metal ion, (*2*) the metal ion concentration, (*3*) the chelating reagent, (*4*) the chelating reagent concentration, (*5*) the pH, (*6*) the presence of an agent in the aqueous phase which complexes with the metal ion, (*7*) the complexing agent concentration, (*8*) the presence in the organic phase of substances which form adducts with the extracting chelate, (*9*) the concentration of the adduct-forming agent, (*10*) the organic solvent, (*11*) the temperature, and (*12*) the time of equilibration.

THE SYSTEM

Consider an organic solvent S (such as chloroform) pre-saturated with a 1.0 *M* aqueous sodium perchlorate solution and made up to known concentrations with a chelating reagent HR (such as oxine) and an adduct-forming agent B (such as trioctylphosphine oxide). The HR is usually one having one neutral and one acidic group arranged such that 4-, 5- or 6-membered chelate rings can form, and both the HR and B are usually only slightly soluble in water. Also consider an aqueous phase pre-saturated with the organic solvent, containing a metal ion M (such as Cd^{2+}) introduced as the perchlorate in a concentration at most 10 times less than that of the HR, a complexing or masking agent X (such as CN^-) introduced as the sodium salt, and the solution made up to an ionic strength of 1.0 with $NaClO_4$. Thus, the *simple* components of the two phases *before* contact will be (*1*) organic phase: HR, B, H_2O, (*2*) aqueous phase: M, X, H, OH, ClO_4, Na, S. Charges have been omitted for simplicity.

When the phases are placed in contact and equilibrated, a number of processes may be visualized. The B and the HR partition into the aqueous phase where the latter ionizes. The ions X, OH, and R and the molecules HR, S, and B may be seen interacting with the cation M to produce complexes. Any neutral species produced by such combinations may then partition into the organic phase.

EXPERIMENTAL RESULTS

After selection of a proper system (M, S, HR, X, B), the distribution coefficient D of the metal is determined as a function of the pH, the concentration of HR, the concentration of X, and the concentration of B over a fairly broad set of conditions. Plots of the following types are constructed: (*a*) log D against pH at constant $[HR]_o$, [X], and $[B]_o$, (*b*) log D against log $[HR]_o$ at constant pH, [X], and $[B]_o$, (*c*) log D against log [X] at constant pH, $[HR]_o$, and $[B]_o$, and (*d*) log D against log $[B]_o$ at constant pH, $[HR]_o$, and [X]. A typical set of curves of this sort is given in Fig. 1. Unsubscripted

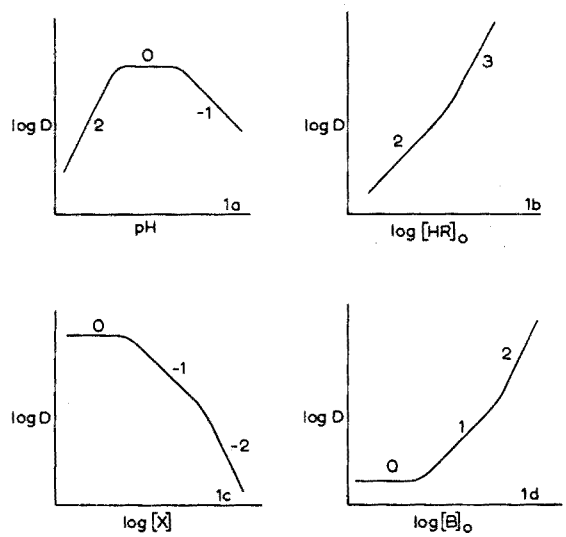

Fig. 1. Typical solvent extraction curves.

brackets indicate aqueous concentrations, whereas brackets with a subscript o indicate organic phase concentrations. The slopes of the portions of the curves having constant slope are indicated. In general, these constant-slope portions usually signify conditions under which a single species dominates each phase. Portions of the curves with changing slopes are usually indicative of the presence of several species in one of the phases.

BASIC RELATIONS

In numerous systems, it has been determined that the most likely species partitioning into the organic phase are those which may be represented by $MR_n(HR)_aB_b$ where n indicates the oxidation number of the metal ion. The most likely species in the aqueous phase may usually be represented by $MR_r(OH)_hX_x$. Cases in which there is more than one atom of M in either or both complexes, or in which HR, S, or B is included in the aqueous complexes, or in which OH or X is included in the organic species, are not too prevalent. However, more complex formulas may be written to accommodate such situations and others, if necessary.

The distribution constant D as seen in the constant-slope regions of any of the

illustrative curves may usually be approximated by an expression involving one organic-phase species and one aqueous-phase species. In general, one can write

$$D = \frac{[MR_n(HR)_aB_b]_o}{[MR_r(OH)_hX_x]} \tag{1}$$

in which n, a, b, r, h and x would have particular integer values. If one substitutes proper constants into this equation, the following expression results

$$D = \frac{K_{nab}P_{nab}[HR]_o^{n-r+a}[B]_o^b}{K_r^{n-r}P_r^{n-r+a}P_b^bC_{rhx}K_w^h[H]^{n-r-h}[X]^x} \tag{2}$$

where K_{nab} is the association constant of $MR_n(HR)_aB_b$, K_r is the acid association constant of HR, P_r is the organic/aqueous partition constant of HR, P_b is the organic/aqueous partition constant of B, C_{rhx} is the association constant of $MR_r(OH)_hX_x$, and K_w is the ion product of water. It will be noted that the slope of a log-D-against-pH plot at constant $[HR]_o$, [X], and $[B]_o$ will be $n-r-h$; the slope of a log-D-against-log-$[HR]_o$ plot at constant pH, [X], and $[B]_o$ will be $n-r+a$; the slope of a log-D-against-log-[X] plot at constant $[HR]_o$, pH, and $[B]_o$ will be $-x$; and the slope of a log-D-against-log-$[B]_o$ plot at constant pH, $[HR]_o$, and [X] will be b. These relations allow one to make reasonable decisions as to the predominating species on the constant-slope portions of the curves. (For example, in Fig. 1a, $n-r-h = 2$ or 0 or -1; these correspond to the terms $[MR_2]_o/[M]$, $[MR_2]_o/[MR_2]$, and $[MR_2]_o/[MR_3]$.)

Regions of the illustrative curves in which the slope is changing usually signify that several species are involved in one of the phases. Therefore a more complex representation is required, two or perhaps three different species appearing in either the numerator or the denominator. To describe the entire curve in any of the illustrative situations, even more terms may be required. A general relationship for such situations may be written

$$D = \frac{\sum_{o}^{a}\sum_{o}^{b}[MR_n(HR)_aB_b]_o}{\sum_{o}^{r}\sum_{o}^{h}\sum_{o}^{x}[MR_r(OH)_hX_x]} \tag{3}$$

In a large number of cases, complete systems as given by eqn. (3) can be represented as a series of terms of the form of eqn. (1). These terms can then be put into the form of eqn. (2) for analysis of the system. By proper slope analysis and curve fitting, the terms needed to write the equation for a complete system can be ascertained and often many of the constants (K_{nab}, P_{nab}, C_{rhx}) in the various terms can be estimated. A prior knowledge of these constants leads to the possibility of useful predictions.

EXAMPLES

In the illustrative curves, the plot in Fig. 1a can be quite well described by the relation

$$D = \frac{[MR_2]_o}{[M] + [MR] + [MR_2] + [MR_3]} \tag{4}$$

or by

$$\frac{1}{D} = \frac{[M]}{[MR_2]_o} + \frac{[MR]}{[MR_2]_o} + \frac{[MR_2]}{[MR_2]_o} + \frac{[MR_3]}{[MR_2]_o} \tag{5}$$

Substituting in reciprocals of expressions like those in eqn. (2), one obtains

$$\frac{1}{D} = \frac{K_r^2 P_r^2 [H]^2}{K_{200} P_{200} [HR]_o^2} + \frac{K_r P_r C_{100} [H]}{K_{200} P_{200} [HR]_o} + \frac{1}{P_{200}} + \frac{K_r^{-1} P_r^{-1} C_{300} [H]^{-1}}{K_{200} P_{200} [HR]_o^{-1}} \tag{6}$$

By recognizing that the slope relations are represented in the exponents of the [H] terms, one can see that the constant initial slope (2) is described by the first term, the succeeding changing slope by the first three terms, the plateau slope (0) by the third term, the succeeding slope change by the third and fourth terms in combination, and the constant final slope (−1) by the fourth term.

In a like manner, the plot in Fig. 1b can be quite adequately represented by the relation

$$D = \frac{[MR_2]_o + [MR_2(HR)]_o}{[M]} = \frac{[MR_2]_o}{[M]} + \frac{[MR_2(HR)]_o}{[M]} \tag{7}$$

Substituting in terms of the type of eqn. (2), this expression results

$$D = \frac{K_{200} P_{200} [HR]_o^2}{K_r^2 P_r^2 [H]^2} + \frac{K_{210} P_{210} [HR]_o^3}{K_r^2 P_r^3 [H]^2} \tag{8}$$

By realizing that the slope relations are reflected in the exponents of the $[HR]_o$ terms, it is apparent that the constant initial slope (2) is described by the first term, the constant final slope (3) by the second term, and the intermediate region of changing slope by the combination.

The plot in Fig. 1c may be considered similarly giving the following representation

$$D = \frac{[MR_2]_o}{[M] + [MX] + [MX_2]} \tag{9}$$

or

$$\frac{1}{D} = \frac{[M]}{[MR_2]_o} + \frac{[MX]}{[MR_2]_o} + \frac{[MX_2]}{[MR_2]_o} \tag{10}$$

By substituting in terms of the form of reciprocals of the relation given in eqn. (2), this results

$$\frac{1}{D} = \frac{K_r^2 P_r^2 [H]^2}{K_{200} P_{200} [HR]_o^2} + \frac{K_r^2 P_r^2 C_{001} [H]^2 [X]}{K_{200} P_{200} [HR]_o^2} + \frac{K_r^2 P_r^2 C_{002} [H]^2 [X]^2}{K_{200} P_{200} [HR]_o^2} \tag{11}$$

Recognizing the slopes as related to exponents in the [X] terms, the constant initial slope (0) is seen to be described by the first term, the succeeding region of changing slope by the first two terms, the constant-slope (−1) region appearing next by the second term, the succeeding region of changing slope by the last two terms, and the final constant-slope (−2) region by the last term.

Figure 1d may be treated analogously to give the following relation

$$D = \frac{[MR_2]_o + [MR_2B]_o + [MR_2B_2]_o}{[M]} = \frac{[MR_2]_o}{[M]} + \frac{[MR_2B]_o}{[M]} + \frac{[MR_2B_2]_o}{[M]} \qquad (12)$$

By substitution of terms of the form of eqn. (2), one obtains

$$D = \frac{K_{200}P_{200}[HR]_o^2}{K_r^2P_r^2[H]^2} + \frac{K_{201}P_{201}[HR]_o^2[B]_o}{K_r^2P_r^2P_b[H]^2} + \frac{K_{202}P_{202}[HR]_o^2[B]_o^2}{K_r^2P_r^2P_b^2[H]^2} \qquad (13)$$

Seeing that the slope relations are reflected in the exponents of the $[B]_o$ terms, the constant initial slope (0) is described by the first term, the succeeding region of changing slope by the first two terms, the constant-slope (1) region appearing next by the second term, the succeeding region of changing slope by the last two terms, and the final constant-slope (2) region by the last term.

ANALYTICAL APPLICATIONS

In the large majority of analytical applications of the solvent extraction technique, the aim is to provide for either a large or a small value of D. In many cases, the desire can be realized by the proper adjustment of variables in the system. As eqn. (2) indicates, D may be enhanced by large values of K_{nab}, P_{nab}, $[HR]_o$ and $[B]_o$, and by small values of K_r, P_r, P_b, C_{rhx}, [H] and [X].

The metal ion

The general character of the metal ion M involved in the system is very important since it enters into determining the values of K_{nab}, P_{nab}, and C_{rhx} in the basic relations. Illustrations of the extraction of many metals by a single chelating reagent are given by STARY[1], who discusses the extraction of 32 metals into chloroform containing oxine, DYRSSEN[2], who treats the extraction of 27 metals into chloroform containing β-isopropyltropolone, and POSKANZER AND FOREMAN[3], who review the extraction of 48 metals into benzene containing 2-thenoyltrifluoroacetone. Probably the most significant factor in the majority of reported instances is K_{nab}.

One of the most important possibilities with a number of metal ions is that for the formation of hydroxo species in the aqueous phase. Stability constants for a number of these have been reported by BJERRUM, SCHWARZENBACH AND SILLEN[4]. In such instances, the factors of import are C_{rhx} and [H].

Another important aspect is the metal ion concentration. As the theoretical treatment indicates, the extraction of the metal is independent of its concentration so long as the chelating reagent is in appreciable excess and so long as the dominant species in the organic and aqueous phases contain the same number of metal atoms. In most cases, the latter is the situation since the form of the metal in both phases is usually a mononuclear complex. In some instances, however, the species in one phase has more metal atoms than that in the other. This has been seen in cases in which polymerization of hydroxo species occurs in the aqueous phase and in which the extracting species dimerizes. The tendency toward aqueous-phase hydrolytic polymerization generally increases as the metal ion concentration increases. Examples are given by PANOVA, LEVIN AND BREZHNEVA[5], who encounter the hydrolytic polymerization of yttrium as well as the polymerization of the extracting species in studying the extrac-

tion of yttrium into chloroform containing oxine, and KUZNETSOV AND MING-O[6], who suppress the polynuclear hydroxo cations of zirconium with weak complexing agents when extracting zirconium into cyclohexanone containing 5,7-dinitrooxine. In cases of this sort, eqns. (1) and (2) become

$$D = \frac{[M_m R_{mn}(HR)_a B_b]}{[M_p R_r(OH)_h X_x]} \tag{14}$$

and

$$D = \frac{K_{mnab} P_{mnab} [HR]_o^{mn-r+a} [B]_o^b}{K_r^{mn+r} P_r^{mn-r+a} P_b^b C_{prhx} K_w^h [M]^{m-p} [H]^{mn-r-h} [X]^x} \tag{15}$$

SILLEN[7] has provided a survey of work on association constants and stoichiometries of numerous hydroxo polymers of the metal ions.

The general chemistry of the metallic elements is discussed in SANDELL[8], KOLTHOFF AND ELVING[9], WILSON AND WILSON[10], and COTTON AND WILKINSON[11].

The chelating reagent

The precise chelating reagent in any system will involve K_{nab}, P_{nab}, $[HR]_o$, K_r, P_r and C_{rhx}. When a reagent is structurally altered, these characteristic constants will usually change. For example, DYRSSEN[12] compares the extraction of lanthanum into benzene containing acetylacetone with that containing 2-thenoyltrifluoroacetone, and the extraction of thorium into chloroform containing five different oxine derivatives. SCHWEITZER AND MOTTERN[13] compare the extraction of uranium(VI) into chloroform containing acetylacetone, containing benzoylacetone, or/and containing dibenzoylmethane. UMLAND AND MECKENSTOCK[14] have prepared a series of 7-substituted oxines which act as tridentate reagents. They compare the extractions of magnesium and mercury into chloroform containing these various reagents. KUZNETSOV AND MING-O[6] show how tridentate reagents with two salt-forming groups prevent hydrolysis and enhance the extraction of zirconium whereas bidentate reagents with only one salt-forming group do not.

As the basic relation (2) indicates, the concentration of the chelating reagent is of considerable import. As this concentration goes up, the free R ion in the aqueous phase rises, enhancing the D value. Further, the probability of the predominant extracting species bearing one or more molecules of HR increases in many cases as this concentration rises. An illustration of concentration investigations is provided by RYDBERG[15] who has extracted uranium(VI) into chloroform containing varied quantities of acetylacetone. In many instances, the chelating reagent dimerizes in the organic phase and it is quite important that this equilibrium be included in the calculations.

Some investigations have been carried out using two chelating reagents, HQ and HR, in the organic phase. For a simple system using a divalent ion, the following equation might be expected to provide an adequate description.

$$D = \frac{[MQ_2]_o + [MQR]_o + [MR_2]_o}{[M]} \tag{16}$$

Substitution of proper constants into this relation will yield an expression which will

allow theoretical interpretation of empirical data. An example of a system of this type is provided by DYRSSEN[16], who examines the extraction of metals into chloroform containing β-isopropyltropolone and 2-thenoyltrifluoroacetone.

Good sources for the consideration of possible chelating reagents are the works of MAY AND SCHUBERT[17], WELCHER[18], HOLMES, BEAMISH AND MCBRYDE[19], and SANDELL[8].

Complexing agents

The presence of a complexing or masking agent X in the aqueous phase which forms complexes with the metal ion will also alter D. The important factors here are the constant C_{rhx} and the concentration of X. Many stability constants are available in BJERRUM, SCHWARZENBACH AND SILLEN[4], and CHENG[20] has written a review of the more familiar masking agents, which has been supplemented by an article of HOYLE, SANDERSON AND WEST[21].

An extensive study of 12 complexing agents in the extraction of indium into chloroform containing oxine has been carried out by SCHWEITZER AND COE[22]. Excellent correlation with C_{rhx} values was realized. STARY[23] reports the results obtained when 4 complexing agents are used in the extraction of uranium(VI) into benzene containing benzoylacetone. The data are employed to calculate values of C_{rhx}. PANOVA, BREZHNEVA AND LEVIN[24] studied the effects of sulfate, nitrate, and chloride ions upon the extraction of yttrium into chloroform containing oxine. Values of C_{rhx} are calculated from the results. SCHWEITZER AND MOTTERN[13] have examined the influence of 7 complexing agents on the extraction of uranium(VI) into chloroform containing dibenzoylmethane. In most instances, correlation with C_{rhx} values could be realized.

Adduct-forming agents

An adduct-forming agent B may be added to the system; this too alters D by its influence on K_{nab}, P_{nab}, and P_b plus its concentration effect. In general, most of the adduct-forming agents which have been investigated contain a basic oxygen or nitrogen and are predominantly soluble in the organic phase. Some of the more common adduct-forming agents are trialkyl phosphates, trialkyl phosphonates, trialkyl phosphinates, trialkyl phosphine oxides, amines, and alcohols. In some instances the adduct-forming agent may interact with HR to decrease the D value.

HEALY[25] has measured the distribution of lanthanides, actinides, and alkaline earth metals between aqueous solutions and organic solvents containing thenoyltrifluoroacetone and various neutral organo-phosphorus esters. DYRSSEN AND HENNICHS[26] report the effect of added quinoline or dodecylamine on the extraction of copper into chloroform containing dimethylglyoxime. UMLAND AND HOFFMANN[27] followed the influences of added alcohols and amines on the extraction of Group 2B metal ions into chloroform containing oxine.

In many cases the phenomena may be explained by assuming the replacement of coordinated waters by B. However, there are a number of instances in which rather unusual coordination numbers would have to be postulated to maintain such an assumption. Various questions have been raised, such as whether R may function as a monodentate ligand, whether B might not be attaching to the chelating reagent rather than the metal, and the precise role of attached water. In some systems the

so-called inert organic solvent seems to exercise a profound effect. For example, the effect in increasing D in the extraction of some metals into an organic solvent containing thenoyltrifluoroacetone and tributyl phosphate increases in the solvent series: chloroform, benzene, carbon tetrachloride, hexane, cyclohexane[25].

Organic solvents

The organic solvent used in a given extraction system largely affects the partition constants P_{nab}, P_r and P_b. In general, an organic solvent may be inert or it may exercise attraction for, or even attachment to, the extracting species. Often the molecular sizes, polarities, and polarizabilities of the solvents are important in such relationships.

Interesting examples of such relationships are provided by ALIMARIN AND ZOLOTOV[28]. Their work indicates that neutral chelates with waters occupying coordination positions often are extracted better by ketones, esters, and alcohols than by ethers, hydrocarbons, and halohydrocarbons. Apparently the extraction process involves replacement of the waters. The extraction of cobalt(II) thenoyltrifluoroacetonate is more effective in methyl ethyl ketone or *n*-butanol than in benzene or chloroform. Thallium(I) oxinate extracts well into isobutanol but not into diethyl ether or carbon tetrachloride. Thallium(III) oxinate, however, extracts equally well into alcohols and carbon tetrachloride.

In cases of extractions into mixed solvents, three variations may be recognized: (*1*) Both solvents are inert, that is, do not participate in the extracting complex nor exercise at least a moderate attraction for it. (*2*) One participates in the complex. (*3*) Both participate in the complex. In the first case, the major effects upon the system can be assigned to alterations in the partition constants. In the second case, relationships treating the active solvent as an adduct-forming agent generally apply. In the third case, an equation similar to (*2*) will probably apply with one solvent as the major component and the other in increasing amounts, and then with the other solvent as the major component and the first one in increasing amounts.

HONAKER AND SCHWEITZER[29] have added low molecular weight alcohols to systems involving the extraction of yttrium into chloroform containing thenoyltrifluoroacetone. The extractions are enhanced by the additions, and the effects appear to be assignable largely to alterations in the partition constants.

For consideration of various solvents, their properties, and their purifications, one should consult the works by RIDDICK AND TOOPS[30], SCHEFLAN AND JACOBS[31], and VON METZSCH[32].

Temperature

Alterations in the temperature of extractions affect all the constants involved in the extraction equation. This often makes predictions somewhat difficult. HELLWEGE AND SCHWEITZER[33] have examined the extraction of cadmium into chloroform containing oxine over the temperature range 0–50°. Extraction is better at the lower temperatures. They have ascertained the values of K_{nab}, P_{nab}, K_r and P_r at the various temperatures and have estimated the related thermodynamic constants. DYER AND SCHWEITZER[34] report the effects of temperature change in the range 25–55° on the extraction of silver into chloroform or carbon tetrachloride containing dithizone. Again better extraction is observed at lower temperatures.

Rates of extraction

Many solvent extractions of metal chelates reach equilibrium rather rapidly, the rate-determining step presumably being the transfer of the neutral chelate between the phases. However, a number of cases are known in which the rates are slow. Some of these are associated with the formation and breaking of inert complexes, such as those of Co(III) and Cr(III). Others are often those in which strong and/or multidentate aqueous complexing agents are involved. Still further cases are known in which neither of these criteria is met, and yet the reactions are still slow. In some instances, extractions may be accelerated by temporarily altering the oxidation state of the metal ion so as to produce a complex of different characteristics.

IRVING, BELL AND WILLIAMS[35] looked into the rate relationships of the extraction of zinc into chloroform and carbon tetrachloride containing dithizone. The rate of the aqueous-to-organic extraction increased with increased pH, increased HR concentration, increased M concentration and decreased chloride concentration. The rate in the case of carbon tetrachloride is faster than that with chloroform. The ionic strength apparently has marked effects since sodium nitrate alters the rate considerably. The rate of the organic-to-aqueous extraction increased with decreased pH and decreased HR concentration. These experiments suggest, as do others, that the rate is dependent upon the R and M concentrations in the aqueous phase. (P_r is smaller for carbon tetrachloride than for chloroform.) SCHWEITZER AND MOTTERN[36] report that the presence of ethylenediaminetetraacetate or fluoride ion retards the rate of the extraction of uranium(VI) into chloroform containing dibenzoylmethane. HELLWEGE AND SCHWEITZER[37] have investigated the slow rate of extraction of chromium(III) into chloroform containing acetylacetone. Passage of the aqueous phase through a Jones reductor prior to extraction markedly increased the rate. SCHWEITZER AND BENSON[38] observed a very slow rate in the extraction of cobalt from an aqueous solution of trisoxalatocobaltate(III) into chloroform containing acetylacetone. The rate was greatly increased in the presence of a freshly-abraded magnesium surface.

Other factors

Only a few experiments have been carried out to ascertain the effects of ionic strength in the aqueous phase and of the addition of inert solids to the organic phase. SCHWEITZER AND MOTTERN[13] find little ionic-strength influence on the extraction of uranium(VI) into chloroform containing dibenzoylmethane. However, in the extraction of indium into chloroform containing oxine, such effects are reported by SCHWEITZER AND COE[22] to be fairly marked, especially with aqueous complexing agents.

Literature

A number of treatments of solvent extraction of metal chelates are available in the literature. Among the more important ones are those by MORRISON AND FREISER[39], DIAMOND AND TUCK[40], FREISER AND MORRISON[41], MORRISON AND FREISER[42], IRVING AND WILLIAMS[43], DYRSSEN[12], RYDBERG[44], STARY[45], IRVING, ROSSOTTI AND WILLIAMS[46], ROSSOTTI AND ROSSOTTI[47], ZOZULYA AND PESHKOVA[48], and MARCUS[49].

SUMMARY

A simplified theory for the solvent extraction of metal chelates is presented. Factors which are taken into account include the metal ion, the chelating reagent, aqueous complexing agents,

adduct-forming substances, the organic solvent, temperature, rates of extraction, and other effects. Equations are developed for estimating the stoichiometries and the association constants of the involved species.

RÉSUMÉ

Une théorie simplifiée est présentée pour l'extraction par solvant de chélates métalliques. Les facteurs pris en considération comprennent: l'ion métallique, le réactif de chélation, les agents complexants, le solvant organique, la température, les vitesses d'extraction, etc.

ZUSAMMENFASSUNG

Eine vereinfachte Theorie für die Flüssigextraktion von Metallchelaten wird beschrieben. Dabei werden u.a. folgende Faktoren berücksichtigt: Das Metallion, das Chelat-Reagenz, verschiedene Komplexbildner, das organische Lösungsmittel, die Temperatur, der Extraktionsgrad. Gleichungen zur Abschätzung der Stöchiometrie und der Assoziationskonstanten werden entwickelt.

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THE SOLVENT EXTRACTION OF COBALT(III) FROM A TRISOXALATOCOBALTATE(III) SOLUTION INTO CHLOROFORM CONTAINING ACETYLACETONE

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The solvent extraction of metal ions from an aqueous phase into an immiscible organic phase containing a chelating reagent has been studied extensively in recent years[1]. Most of the studies have been carried out under equilibrium conditions or assumed equilibrium conditions. Only slight attention comparatively has been given to the investigation of chelate solvent extraction systems under non-equilibrium conditions.

MORRISON AND FREISER[1] point out that the rate of achievement of equilibrium depends upon the rate of the formation of the extracting species and the rate of transfer of this species from one phase to the other. Many systems reach equilibrium in a few minutes, but some systems have been reported in which the rate of attainment of equilibrium is much slower.

Investigations of the extraction rates of metal ions with dithizone have been reported by WALKLEY[2], IRVING, ANDREW AND RISDON[3], IRVING AND WILLIAMS[4] IRVING, BELL AND WILLIAMS[5], GEIGER[6] and HONAKER AND FREISER[7]. Several investigators have studied rates of extraction of metal ions with β-diketones. RUBIN AND HICKS[8] worked on the kinetics of the extraction of plutonium into benzene containing thenoyltrifluoroacetone, and TAFT AND COOK[9] have studied similar systems involving other metal ions. SUZUKI AND OKI[10] have reported on the various conditions that affect the extraction rate of cerium with acetylacetone. The extraction of chromium(III) with acetylacetone has been studied by MCKAVENEY AND FREISER[11], and the studies have been extended by HELLWEGE AND SCHWEITZER[12]. SCHWEITZER AND RIMSTIDT[13] have investigated the rates of extraction of zinc with acetylacetone, benzoylacetone, and dibenzoylmethane. The presence of very strong complexing agents in the aqueous phase has been observed to reduce the rates in several otherwise rapid extraction systems[14].

Present problem

The present work was undertaken as an attempt to study in some detail the extraction kinetics of cobalt(III) from an aqueous phase containing the trisoxalatocobaltate(III) complex ion into a chloroform phase containing acetylacetone.

Most substitution reactions in cobalt(III) complexes are known to be quite slow owing to the inert character of the cobalt(III) ion in most of its complexes[15]. Substitution reactions which involve the net replacement of one ligand by another usually proceed through either an aquation or a base hydrolysis step[16]. STEINBACH[17] has extracted cobalt(III) from sulfuric acid solutions with acetylacetone. Cobalt(II) would not extract under the acid conditions.

EXPERIMENTAL CONDITIONS

Apparatus and reagents

Extractions were performed in 125-ml glass-stoppered Erlenmeyer flasks which were placed in a tray containing water at 0.0 ± 1.0°, 30.0 ± 0.5° or 50.0 ± 0.5°. The flasks contained magnetic stirrers which were driven by motors placed beneath the water tray. Timing was done with a Nuclear T-100 Timer; pH measurements were made with a Leeds and Northrup 7662 pH Meter equipped with a Beckman 39183 Combination Electrode; and radioactivity measurements were made in a Tracerlab D-20-D Well Scintillation Detector connected to a Tracerlab Versamatic-II Scaler.

The water used in the experiments was doubly distilled; the chloroform and the acetylacetone were purified by fractional distillation. Cobalt-60 was obtained from Oak Ridge National Laboratory in 0.8 *N* hydrochloric acid solution. All other chemicals were of reagent grade.

Procedures

An aliquot of the cobalt-60 solution was converted to the perchlorate by repeated evaporations with perchloric acid. To the residue a few ml of 1 *N* sodium hydroxide was added followed by a few ml of a 3% solution of hydrogen peroxide and then enough 2 *N* oxalic acid solution to make the solution decidedly acidic. The resulting mixture was heated to 40° to drive the excess hydrogen peroxide off the solution of trisoxalatocobaltate(III). A dilution was then made such that 300 μl of this stock solution when added to 50 ml of aqueous phase gave a metal concentration of about 10^{-7} *M*. To another aliquot of the cobalt-60 solution inert cobalt was added, and it was carried through the same processes such that a final concentration of about 10^{-4} *M* could be realized.

Samples consisting of 50 ml of chloroform-saturated water 0.1 *M* in sodium perchlorate, and 50 ml of water-saturated chloroform which was $10^{0.0}$, $10^{-0.3}$, $10^{-0.5}$, $10^{-1.0}$ or $10^{-1.5}$ *M* in acetylacetone, were equilibrated at constant temperature at a predetermined constantly-maintained pH value for at least 1 h. Then 300 μl of the trisoxalatocobaltate(III) stock solution were added to the aqueous phase. The pH was rapidly readjusted with sodium hydroxide and/or perchloric acid and timing was started. Samples of 500 μl of the two phases were withdrawn at various time intervals after stopping the stirrer and allowing the phases to separate for 1 min. The samples were then counted in the scintillation counter.

To investigate the effect of a possible temporary change of oxidation state, several pieces of freshly-polished magnesium metal were placed in the extraction vessel and the rate was studied as indicated above.

RESULTS

Extractions were performed using various concentrations of acetylacetone, trisoxalato-

cobaltate(III) ion, oxalate ion and hydrogen ion. Plots of the logarithm of the ratio of the total cobalt activity to the activity in the aqueous phase against time resulted in straight lines for all extractions except the one containing the magnesium metal. The half-time period T of each reaction was calculated from the slope of the line. Table I summarizes the kinetic data obtained at 30°. The first, second, fourth, and fifth columns define the systems; the third column gives the logarithm of the concentration of the acetylacetonate ion $[R^-]$ in the aqueous phase. These values were calculated from the relationship $[R^-] = [HR]_o/K_rP_r\,[H^+]$, where $[HR]_o$ is the equilibrium concentration of the acetylacetone in the chloroform phase, $[H^+]$ is the

TABLE I

SUMMARY OF EXTRACTION RATE DATA AT 30°

pH	$log[HR]_o^a$	$log[R^-]$	$log[C_2O_4^{2-}]$	$log[Co(C_2O_4)_3^{3-}]$	$T \cdot 10^{-2}$ *(min)*
10.0	−1.0	−1.2	−3.0	−7.0	5
9.0	0.0	−1.2	−3.0	−7.0	4
9.0	−0.5	−1.7	−3.0	−7.0	4
9.0	−1.0	−2.2	−3.0	−7.0	4
9.0	−1.5	−2.7	−3.0	−7.0	4
8.0	−0.5	−2.7	−3.0	−7.0	5
8.0	−1.0	−3.2	−3.0	−7.0	4
8.0	−1.5	−3.7	−3.0	−7.0	4
7.0	0.0	−3.2	−3.0	−7.0	2
7.0	−0.5	−3.7	−3.0	−7.0	5
7.0	−1.0	−4.2	−3.0	−7.0	10
6.0	0.0	−4.2	−3.0	−7.0	4
6.0	−0.3	−4.5	−3.0	−7.0	10
6.0	−0.5	−4.7	−3.0	−7.0	20
9.0	−0.5	−1.7	−1.0	−7.0	8
6.0	−0.5	−4.7	−1.0	−7.0	—[b]
9.0	−0.5	−1.7	−3.0	−4.0	10
6.0	−0.5	−4.7	−3.0	−4.0	40

[a] All concentrations are in moles/l.
[b] No extraction in 2 h.

TABLE II

EFFECTS OF TEMPERATURE ON EXTRACTION RATE

Temp.(°)	*pH*	$log[HR]_o^a$	$log[R^-]$	$log[C_2O_4^{2-}]$	$log[Co(C_2O_4)_3^{3-}]$	$T \cdot 10^{-2}$ *(min)*
0	9.0	−0.5	−1.7	−3.0	−7.0	10
30	9.0	−0.5	−1.7	−3.0	−7.0	4
50	9.0	−0.5	−1.7	−3.0	−7.0	2
0	6.0	−0.5	−4.7	−3.0	−7.0	40
30	6.0	−0.5	−4.7	−3.0	−7.0	20
50	6.0	−0.5	−4.7	−3.0	−7.0	20

[a] All concentrations in moles/l.

hydrogen ion activity, K_r is the association constant of acetylacetone ($10^{8.9}$), and P_r is the organic/aqueous partition coefficient of the acetylacetone ($10^{1.4}$) (ref. 18).

Since the plots gave straight lines, it was assumed that the rate R would be related to the cobalt complex concentration by an expression of the type $R = K\,[Co(C_2O_4)_3^{3-}]$. Also since during any given run, the concentration of HR and the pH were held constant, it was necessary to compare different runs to ascertain any dependence on these two factors. It was assumed that at constant R^- concentration, the rate constant K was a function of $[H^+]$, that is, $K = k\,[H^+]^n$. Plots of log T against log $[H^+]$ gave slopes indicating that the rate of extraction is essentially independent of the pH. In a similar manner, the assumption was made that at constant $[H^+]$, the rate constant K was a function of $[R^-]$. Plots of log T against log $[R^-]$ gave slopes indicating independence of $[R^-]$ in the basic region and n values of 0.7 and 1.4 at pH values of 7.0 and 6.0. Increases in the concentration of oxalate ion or trisoxalatocobaltate(III) ion decreased the rate of extraction.

Table II summarizes the temperature dependence of the extraction rate. The T values were calculated as above. The rate of extraction in the presence of magnesium for a system $10^{-0.5}$ M in acetylacetone in chloroform, 10^{-3} M in oxalate, 10^{-7} M in trisoxalatocobaltate(III), at a pH of 9.0 and a temperature of 30° was determined. These results were obtained, the logarithm of the total activity over the aqueous activity appearing first followed by the time in minutes: 0.015 (5), 0.035 (10), 0.062 (15), 0.099 (20), 0.131 (25), 0.182 (30), 0.309 (40), 0.414 (50), 0.527 (60), 0.655 (75). In numerous experiments, it was demonstrated that a change in stirring rate did not alter the rate of extraction.

DISCUSSION

Since the stirring rate did not alter the rate of extraction, it was assumed that the rate of formation of the extracting species governed the system. The relative inertness of the system is what was expected[15,16]. Both the valence bond theory (inner and outer orbital considerations) and the ligand field theory (ligand field stabilization considerations) predict this behavior[19]. Since the rate-determining step in the formation of the extractable species is independent of the concentration of the hydrogen ion, it is also independent of the concentration of the hydroxide ion. This rules out the possibility of the reaction proceeding by a base hydrolysis mechanism.

The interesting dependence on the concentration of the acetylacetonate ion, particularly the difference in acidic and basic media, suggests several possibilities. One possibility is that bond breaking in the oxalato complex is predominant in basic media, with bond formation involving the cobalt–acetylacetonate bond becoming more important with increasing acidity. Another possibility is that the acetylacetonate concentration in basic media is larger than it is in acid media, and thus the rate independence of $[R^-]$ in basic media may be due to saturation effects.

The increase in the half-time of the reaction with increasing oxalate concentration might be interpreted as an indication that bond breaking in the cobalt–oxalate complex is important. The decrease in the rate of extraction with increase in the concentration of metal is in agreement with the observations of SUZUKI AND OKI[10] on the cerium acetylacetonate system.

The marked enhancement of the extraction rate in the presence of magnesium might be attributed to reduction of the cobalt(III) complex to the cobalt(II) complex.

The latter is more labile and thus ligand replacement would occur at an increased rate. After exchange of ligands, the cobalt(II) might be easily oxidized back to cobalt(III) for extraction.

SUMMARY

The rate of the extraction of cobalt(III) from aqueous solutions containing trisoxalatocobaltate(III) into chloroform containing acetylacetone has been investigated. The effects of pH, acetylacetone concentration, oxalate concentration, complex concentration, temperature, and possible change in oxidation state are reported.

RÉSUMÉ

Les auteurs ont effectué une étude sur la vitesse d'extraction du cobalt(III), à partir de solutions aqueuses de trisoxalatocobaltate(III), au moyen de chloroforme renfermant de l'acétylacétone. Ils ont examiné l'influence du pH, de la concentration en acétylacétone, en oxalate et en complexe, de la température et du changement possible du degré d'oxydation.

ZUSAMMENFASSUNG

Die Extraktion von Kobalt(III) aus Trisoxalatokobaltat(III) enthaltenden wässrigen Lösungen mit Acetylaceton in Chloroform wurde untersucht. Über den Einfluss des pH-Wertes, der Konzentration des Acetylacetons, des Oxalats und der Komplexe, der Temperatur und über einen möglichen Wechsel in der Oxydationsstufe wird berichtet.

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THE THERMAL PROPERTIES OF SOME SALICYLALDEHYDE, SALICYLALDIIMINE AND SALICYLALDEHYDE-ETHYLENEDIIMINE METAL CHELATES

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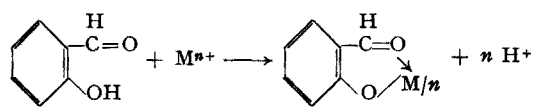
Salicylaldehyde (*o*-hydroxybenzaldehyde) readily forms coordination compounds with a number of metal ions[1-6]. The reaction for the formation of these metal chelates is:



where M^{n+} is Ca, Sr, Ba, Ni, Co(II), Zn, Cu(II), Mn(II), UO_2, Mg, Cd, Pb and other metals ions. Likewise the Schiff bases formed by the reaction of salicylaldehyde and an amine react with metal ions to give stable metal chelates[7,8].

Much work has been done on the salicylaldehyde and the Schiff base metal chelates from the standpoint of composition, structure, and stability in regard to dissociation in solution[1-3,7,9-13]. Little is known, however, concerning the thermal properties of these compounds, although the iron(II) and (III) complexes of salicylaldehyde salicyloylhydrazone have been studied by differential thermal analysis[14]. Also, the thermal properties of various Schiff base metal complexes which have polymeric structures have been investigated[15].

From the viewpoint of possible applications for analytical determinations of the various metal ions, the thermal stability of some metal complexes of salicylaldehyde, salicylaldiimine, and salicylaldehyde-ethylenediimine was studied by the techniques of thermogravimetry (TGA) and differential thermal analysis (DTA).

EXPERIMENTAL

Thermobalance

The automatic recording thermobalance has been previously described[16]. Sample sizes ranged in weight from 40 to 60 mg and were decomposed in a static air atmosphere at a heating rate of 5° per min.

Differential thermal analysis apparatus

The DTA apparatus has previously been described[17]. Sample sizes ranged in weight from 45–55 mg and were decomposed in a dynamic helium atmosphere at a heating rate of 10° per min.

Preparation of complexes

The salicylaldehyde was obtained from Eastman Organic Chemicals, Rochester, N.Y. All of the other chemicals used were of C.P. quality.

The bis(salicylaldehyde)copper(II), nickel(II) and cobalt(II) complexes and the bis(salicylaldiimine)copper(II) and nickel(II) complexes were prepared by the procedure of TYSON AND ADAMS[7]. The bis(salicylaldehyde)magnesium complex was prepared by the method of PFEIFFER *et al.*[18]. The salicylaldehyde-ethylenediimine complexes of copper(II) and nickel(II) were prepared by the method of DUBSKY AND SOKOL[8]. The precipitated complexes were all washed well with water, then alcohol and finally diethyl ether and dried in a vacuum desiccator over calcium chloride.

The complexes were analyzed for metal content by ignition of the compounds, mixed with oxalic acid, to 700° for 2 h and weighing as the metal oxides. The metal contents of the complexes are given in Table I.

RESULTS AND DISCUSSION

Weight-loss studies

The weight-loss curves for the metal chelates are given in Figs. 1 and 2.

In general, the hydrated metal complexes began to evolve water in the temperature range of 100 to 128° while the anhydrous compounds began to lose weight in the 160

TABLE I

METAL CONTENTS OF COMPLEXES

Compound	*Percent metal*	
	Theoretical	*Found*
$Cu(SAL)_2 \cdot 2H_2O$[a]	18.95	18.9
$Ni(SAL)_2 \cdot 2H_2O$	17.42	17.5
$Co(SAL)_2 \cdot 2H_2O$	17.47	18.3
$Mg(SAL)_2 \cdot 2H_2O$	8.03	8.0
$Cd(SAL)_2 \cdot 2H_2O$	28.77	28.5
$Cu(SALD)_2$[b]	20.92	21.2
$Ni(SALD)_2$	19.63	19.8
Cu(SALEN)[c]	19.26	18.8
Ni(SALEN)	18.14	17.9

[a] SAL = salicylaldehyde.
[b] SALD = salicylaldiimine.
[c] SALEN = salicylaldehyde-ethylenediimine.

to 380° temperature range. All of the complexes gave the metal oxide as the terminal decomposition product. When pertinent to the discussion, the procedural weight-loss temperatures will be used instead of the minimum weight-loss temperatures.

The weight-loss curve for $Ni(SAL)_2 \cdot 2H_2O$ showed that water of hydration began

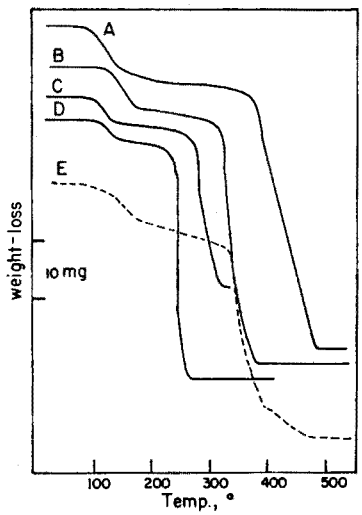


Fig. 1. Weight-loss curves of metal salicylaldehyde complexes: (A) $Mg(SAL)_2 \cdot 2H_2O$; (B) $Ni(SAL)_2 \cdot 2H_2O$; (C) $Co(SAL)_2 \cdot 2H_2O$; (D) $Cu(SAL)_2 \cdot 2H_2O$; (E) $Cd(SAL)_2 \cdot 2H_2O$.

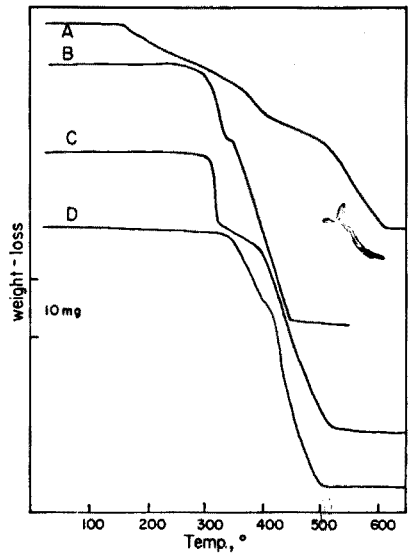


Fig. 2. Weight-loss curves of metal complexes: (A) $Cu(SALD)_2$; (B) $Ni(SALD)_2$; (C) $Cu(SALEN)_2$; (D) $Ni(SALEN)_2$.

to be evolved at about 115°, giving a break in the curve at about 175–180°. This first weight loss corresponded to the loss of two moles of water per mole of complex (11.3% H_2O found; 10.69% theor.). A horizontal weight plateau was not obtained, however, in that the anhydrous complex began to lose weight slowly up to 300°. Beyond 300° the weight loss was very rapid, giving the NiO level beginning at about 390°. Thus, the decomposition sequence appears to be:

$$Ni(SAL)_2 \cdot 2H_2O(s) \xrightarrow{115^\circ} Ni(SAL)_2(s) + 2\,H_2O(g)$$

and

$$Ni(SAL)_2 \xrightarrow[air]{300^\circ} NiO + \text{decomposition products.}$$

Similar behavior was noted for the copper(II), cobalt(II) and cadmium salicylaldehyde complexes. The dehydration reactions began at 90, 85, 80°, respectively, while rapid decomposition of the anhydrous complexes began at 190° and 230°, respectively, for the copper and cobalt complexes. The cadmium complex appeared to be much less stable than the other two listed above in that a pronounced weight loss began at about 180°. The decomposition residues were CuO, Co_3O_4, and CdO, respectively.

The weight-loss curve for $Mg(SAL)_2 \cdot 2H_2O$ was similar to that of the above transition metal complexes although it has been classified as a salt while the others were called "true" complexes[1]. As far as the thermal stability of the anhydrous metal chelate was concerned, it was the most stable of all of the complexes studied. Water of hydration began to be evolved at about 80° with the anhydrous chelate composition being attained at about 200°. Rapid decomposition of the anhydrous complex began at about 370°.

The weight-loss curves for the copper(II) and nickel salicylaldehyde-ethylenediimine complexes revealed that the first weight losses took place at 310° and 330°, respectively. A rather pronounced curve break was observed at 322° for the copper chelate and at about 400° for the nickel complex. However, from weight-loss data, no definite stoichiometries could be assigned to the curves in this region. The data suggest the evolution of one mole of ethylenediimine per mole of complex, but it is difficult to see how this could occur. As in the case of the analogous salicylaldehyde complexes, the terminal decomposition products were CuO and NiO, respectively.

The weight-loss curves obtained for the copper and nickel salicylaldiimine complexes were not very similar. The first weight losses were observed at 165° and 275°, respectively. A break was observed in the nickel complex curve at about 340° which was similar to that found in the analogous salicylaldehyde-ethylenediimine complex. Again, no definite stoichiometry could be assigned to the curve in this region.

The differential thermal analysis (DTA) curves are given in Figs. 3–5.

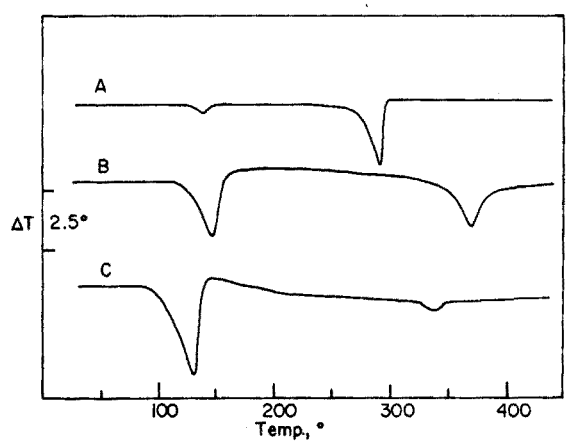


Fig. 3. DTA curves of metal salicylaldehyde complexes: (A) $Cu(SAL)_2 \cdot 2H_2O$; (B) $Ni(SAL)_2 \cdot 2H_2O$; (C) $Co(SAL)_2 \cdot 2H_2O$.

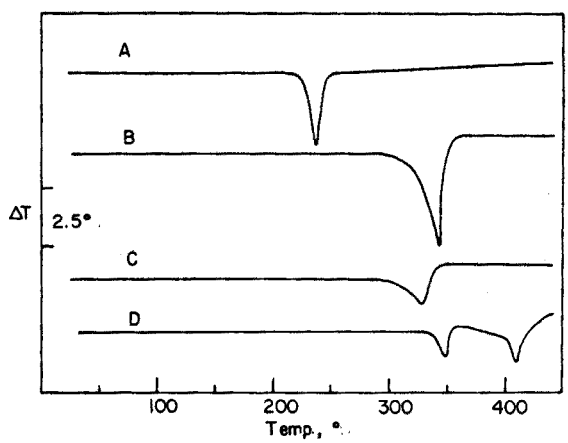


Fig. 4. DTA curves of metal complexes: (A) $Cu(SALD)_2$; (B) $Ni(SALD)_2$; (C) Cu(SALEN); (D) Ni(SALEN).

The DTA curves for the copper(II), nickel, and cobalt(II) salicylaldehyde complexes all indicated a similar decomposition pattern. The first endothermic peaks were due to the evolution of hydrate-bound water. Peak maxima temperatures found for this reaction were: Cu, 140°; Ni, 150°; and Co, 130°. It should be noted that the copper complex dehydration peak was much smaller, proportionally, than was found for the other complexes. This would indicate a much smaller thermal effect for the dehydration reaction. The second endothermic peak found in the DTA curve was due to the dissociation of the anhydrous metal complex. Since the DTA curves were obtained in a helium atmosphere, the dissociation reactions were different than those obtained on the thermobalance in an air atmosphere. Fairly large endothermic peaks were found for the copper and nickel chelates while a small peak was noted for the cobalt complex. In air, the peaks would probably be exothermic due to oxidation reactions of the decomposition intermediates or products.

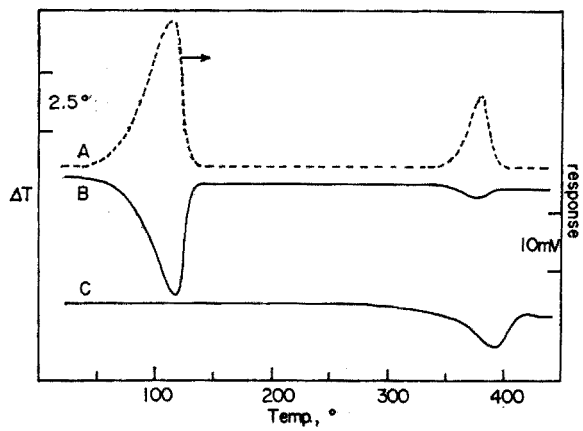


Fig. 5. DTA and GE curves of metal complexes: (A) GE curve of $Mg(SAL)_2 \cdot 2H_2O$; (B) DTA curve of $Mg(SAL)_2 \cdot 2H_2O$; (C) $Cd(SAL)_2 \cdot 2H_2O$.

The DTA and gas evolution (GE) curves for $Mg(SAL)_2 \cdot 2H_2O$ showed that each endothermic peak in the DTA curve was accompanied by the evolution of a gaseous product. The first endothermic peak, at 120°, was due to the evolution of hydrate-bound water while the second peak, at about 380°, was due to the decomposition of the anhydrous complex.

For the cadmium complex, $Cd(SAL)_2 \cdot 2H_2O$, the DTA curve contained but a single endothermic peak, with a peak maximum at about 390°. This peak was caused by the decomposition of the metal chelate.

The DTA curves for copper and nickel salicylaldiimine exhibited only single endothermic peaks. These peaks were due to the dissociation of the complexes and occurred at peak maxima temperatures of 345° and 240°, respectively. As was shown by the weight-loss curves, the nickel complex was more stable than the analogous copper compound.

The DTA curve for the copper salicylaldehyde-ethylenediimine complex contained two endothermic peaks. Both of these peaks were the result of decomposition reactions and could be correlated nicely with the weight-loss curve. The first peak, at

350°, corresponded to the first rapid weight loss while the second peak, at 415°, coincided with the second major weight loss found in the TGA curve. Only a single endothermic peak was found in the DTA curve for the nickel complex, at 325°.

Pyrolysis studies

The mass spectra of the gaseous products of the salicylaldehyde, salicylaldiimine, and salicylaldehyde–ethylenediimine chelates of copper(II) are given in Fig. 6.

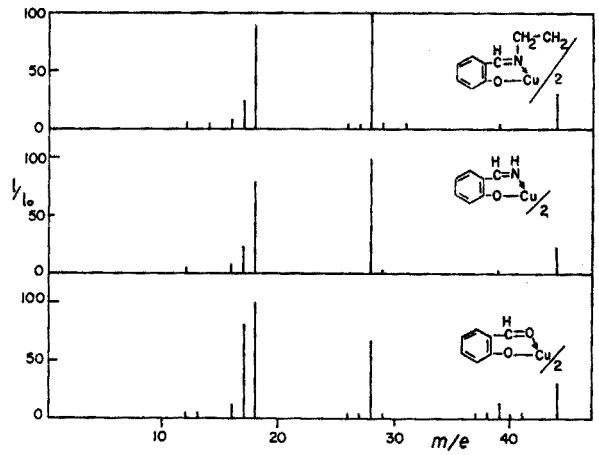


Fig. 6. Mass spectra curves of the pyrolysis decomposition products of metal complexes of copper-(II).

The mass spectra of $Cu(SAL)_2 \cdot 2H_2O$ indicated the presence of water, carbon monoxide, and carbon dioxide as the principal gaseous products. There was also some evidence for a hydrocarbon entity, but due to the *m/e* limitation of the instrument, it was not possible to determine its composition.

For the salicylaldiimine and salicylaldehyde-ethylenediimine complexes, the spectra were similar except that nitrogen was also present. Also, the latter type complexes contained a higher percentage of a hydrocarbon entity which may have originated from the fragmentation of ethylenediimine or its decomposition products.

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SUMMARY

The thermal properties of Cu(II), Ni(II), Co(II), Mg and Cd salicylaldehyde; Cu(II) and Ni(II) salicylaldiimine; and Cu(II) and Ni(II) salicylaldehyde-ethylenediimine complexes were studied by TGA, DTA, and pyrolysis techniques using the mass spectrometer. The $M(SAL)_2 \cdot 2H_2O$ type complexes dissociate by evolution of hydrate-bound water and then total disruption of the organic ligands. Only H_2O, CO, and CO_2 were detected in the pyrolysis gases of $Cu(SAL)_2 \cdot 2H_2O$ by the mass spectrometer.

RÉSUMÉ

Les auteurs ont effectué une étude des propriétés thermiques de divers chélates des composés suivants: salicylaldéhyde, salicylaldiimine et salicylaldéhyde-éthylènediimine avec le cuivre, le nickel, le cobalt, le magnésium et le cadmium, à l'aide des techniques d'analyse thermogravimétrique, d'analyse thermique différentielle et de pyrolyse.

ZUSAMMENFASSUNG

Mit Hilfe der thermogravimetrischen Analyse, der Differentialthermoanalyse und der Pyrolyse wurden die thermischen Eigenschaften folgender Komplexe mit 2-wertigen Metallen untersucht: Salicylaldehyd mit Cu, Ni, Co, Mg, Cd; Salicylaldiimin und Salicylaldehyd-äthylendiimin mit Cu, Ni. In den Pyrolyse-Gasen des $Cu(SAL)_2 \cdot 2H_2O$ konnten mit einem Massenspektrometer nur H_2O, CO und CO_2 nachgewiesen werden.

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DÜNNSCHICHTIONOPHORESE ANORGANISCHER STOFFE BEI NIEDER- UND HOCHSPANNUNG UNTER VERWENDUNG VON RADIONUKLIDEN

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(Eingegangen den 5. April, 1963)

Die Ionophorese *bzw.* Elektrophorese auf Schichten, die auf Platten aufgetragen wurden, geht auf CONSDEN *et al.*[1] zurück. SMITHIES[2] arbeitete die Elektrophorese auf Stärkeschichten aus, die mehrfach modifiziert und angewendet wurde[3-8]. HONEGGER[9] sowie PASTUSKA UND TRINKS[10,11] ersetzten die Stärke durch Kieselgel, was *z.B.* eine chromatographische Weiterverarbeitung der Platten ermöglichte.

Die im folgenden beschriebenen Methoden basieren ebenfalls auf dem SMITHIES-Verfahren, wobei sowohl bei niedriger als auch bei höherer Spannung gearbeitet wurde.

EXPERIMENTELLES

Es wurden Glasplatten mit der Abmessung 38 × 200 mm verwendet. Diese wurden mit Kieselgel (Wölm oder Merck) *bzw.* Kieselgur (Merck) entsprechend den Angaben der Herstellerfirmen beschichtet.

Die Probe wurde je nach der Laufrichtung in der Mitte oder 5 cm vom Plattenende entfernt aufgetropft. Die Platte wurde anschliessend mit der Elektrolyt(Puffer)-Lösung so besprüht, dass die Trägerschicht gerade durchsichtig erschien. Das war bei Verbrauch von etwa 1 ml Lösung der Fall.

Ionophorese bei niedriger Spannung

Bei Verwendung niedriger Spannungen wurde die SMITHIES'sche Apparatur übernommen, lediglich die Abdeckplatte wurde durch eine Glasplatte mit den gleichen Abmessungen wie die beschichtete Platte — umrandet mit 5 mm hohem und 3 mm breitem Hartgummi — ersetzt. Auf diese Weise war es möglich, die Feuchtigkeit der Kammer zu erhalten, ohne die Schicht zu beschädigen. Um das Abfallen der Kondensationstropfen und damit die Störung des Ablaufes der Ionophorese zu verhindern, wurde die Kammer an einer Seite gehoben, damit das Kondenswasser abfliessen kann.

Die meisten papierelektrophoretischen Trennungen lassen sich auf Dünnschicht übertragen. Fig. 1 zeigt das Radiodünnschichtpherogramm der Trennung von Calcium-45 und Barium-133 in 0.05 *M* Milchsäure bei 260 V Spannung (13 V/cm); Laufzeit 1 Stunde.

Hochspannungsionophorese

Da eine Erwärmung durch den elektrischen Strom zum Austrocknen der Schicht

führt, wurde nach Möglichkeiten gesucht, die hierdurch bedingte Störung zu verhindern. Das geschah nach 2 Verfahren:

(1) *Kühlung mit Wasser.* Das Schema einer solchen Anlage zeigt die Fig. 2. Die beschichtete Platte wird mit Kühlwasser unmittelbar gekühlt. Die Kühlkammer trägt oben keine Abdeckung; man legt die Platte auf die Kühlkammer, die oben an den Kanten mit 3 mm breitem Dichtungsgummi versehen ist. Die Abdeckplatte, die genau so breit ist wie die beschichtete Platte und ebenfalls Gummidichtung trägt, wird über diese gelegt und mit mehreren Klemmen nach unten gedrückt. Auf diese Weise ist die Kühlkammer abgedichtet. Bei höheren Spannungen reicht die Kühlung mit Leitungswasser nicht mehr aus. Es muss eine intensivere Kühlung mit einem Kühlelement vorgenommen werden.

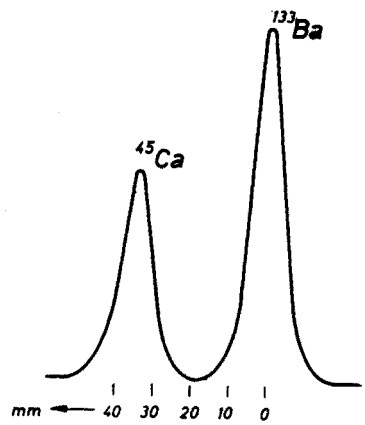

Fig. 1. Radiodünnschichtpherogramm der Trennung von Calcium und Barium in 0.05 *M* Milchsäure bei 13 V/cm in einer Stunde.

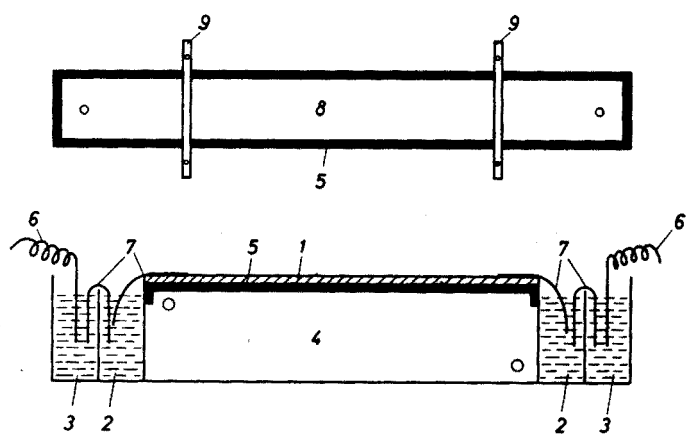

Fig. 2. Apparatur für die Hochspannungsionophorese: 1, Beschichtete Glasscheibe; 2 und 3, Behälter für die Elektrolyt (Puffer)-Lösung; 4, Kühlkammer; 5, Gummidichtung; 6, Elektroden; 7, Asbestpapier (Schleicher und Schüll); 8, Abdeckplatte aus Plexiglas; 9, Klemmen.

(2) *Ionophorese in Wasserdampfatmosphäre.* Die Ionophorese wird hier zur Vermeidung des Austrocknens der Schicht in Wasserdampfatmosphäre durchgeführt. Die Glasplatte und die Behälter für Lösungen werden in ein doppelwandiges Glasrohr gebracht, wie die Fig. 3 zeigt. Das Glasrohr enthält einige ml Wasser, die zum Teil verdampfen und die nötige Wasserdampfatmosphäre ergeben. Zwischen den beiden Glasmänteln des Rohres strömt das temperierte Wasser, das aus einem Thermostaten kommt und die gewünschte Temperatur im Glasrohr herstellt. Die vorliegenden Versuche wurden bei 90° durchgeführt. Ein Austrocknen oder eine Beschädigung der Schicht — auch bei längerem Betrieb — wurde nicht beobachtet.

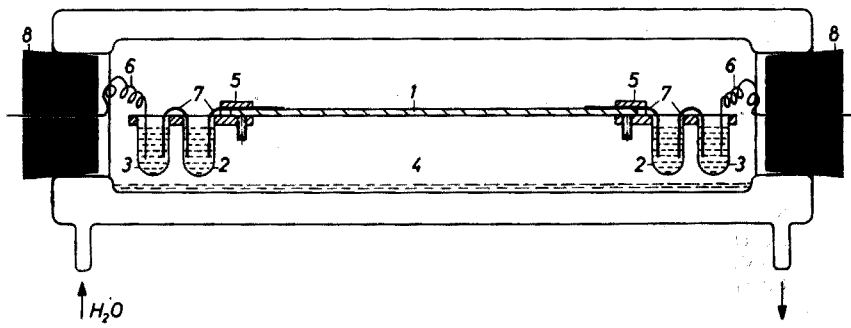

Fig. 3. Apparatur für die Hochspannungsionophorese: 1, Beschichtete Glasplatte; 2 und 3, Behälter für die Elektrolyt(Puffer)-Lösung; 4, Doppelwandiges Glasrohr; 5, Vorrichtung zur Befestigung der Glasscheibe und die Behälter 2 und 3; 6, Elektroden; 7, Asbestpapier (Schleicher und Schüll); 8, Gummistopfen.

ERGEBNISSE

Die Ergebnisse der ionophoretischen Wanderung der Anionen und Kationen sind in den Tabellen I und II zusammengefasst.

Die Fig. 4 zeigt das Radiodünnschichtpherogramm einer Phosphat/Sulfat-Trennung unter den Bedingungen, die in der Tabelle I angegeben sind.

Herrn Dr. K. HOGREBE danke ich für sein Interesse an dieser Arbeit. Fräulein H. KUSTERER und Herrn W. SCHIRMER bin ich für die Durchführung der Laboratoriumsversuche zu Dank verpflichtet.

TABELLE I

WANDERUNG DER ANIONEN IN 0.1 *N* NaOH BEI 45 V/cm UND EINER LAUFZEIT VON 2 MIN

Ion	*Wanderungsstrecke (mm)*	*Ion*	*Wanderungsstrecke (mm)*
SCN^-	35	Br^-	60
SeO_3^{2-}	30 T[a]	BrO_3^-	45
TeO_3^{2-}	22 T	NO_3^-	58
J^-	60	NO_2^-	55
JO_3^-	51	SO_4^{2-}	56
Cl^-	55	PO_4^{3-}	0
ClO_3^-	53		

[a] T = Schwanzbildung.

TABELLE II

WANDERUNG DER KATIONEN IN 0.05 *M* MILCHSÄURE BEI 46 V/cm UND EINER LAUFZEIT VON 5 MIN

Ion	*Wanderungsstrecke (mm)*	*Ion*	*Wanderungsstrecke (mm)*
Fe-III	45	Sc-III	40
Zr-IV	0	Bi-III	55 T[a]
Nb-V	40	Zn-II	85 T
Pt-IV	0 und 15	Rh-III	45
Hf-IV	50 T	Ir-IV	50
Co-II	75	Ru-III	62
Ni-II	70	Tl-I	58
Ba-II	65	Ag-I	90
Pb-II	0	Sn-II	75
Ga-III	55	Ti-IV	25
Sr-II	20	Cu-II	65
Ce-III	60	Be-II	58
La-III	50	Sb-III	60
Y-III	60 T	Al-III	50
Pd-II	35	Li-I	65
W-VI	55 T	Mg-II	70
Cd-II	75		

[a] T = Schwanzbildung.

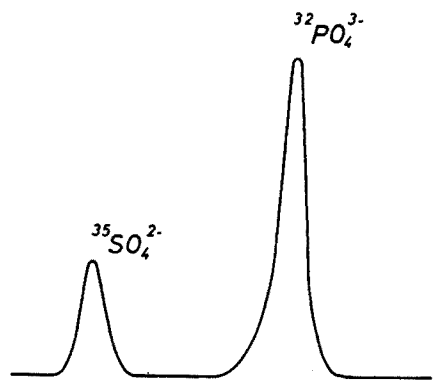

Fig. 4. Radiodünnschichtpherogramm der Trennung von Sulfat und Phosphat in 0.1 *N* NaOH bei 45 V/cm in 2 Minuten.

ZUSAMMENFASSUNG

Die Dünnschichtionophorese wurde für die Trennung anorganischer Stoffe angewandt. Es wurden Trennungen bei 13 V/cm *bzw.* 45 V/cm unter Verwendung von Radionukliden durchgeführt. Entsprechende Apparaturen zur Ausführung der Versuche wurden beschrieben. Die Hochspannungsionophorese wurde entweder unter Kühlung oder in einer Wasserdampfatmosphäre vorgenommen. Die Wanderungszeiten betrugen hierbei 2 *bzw.* 5 Minuten.

SUMMARY

Thin-layer ionophoresis was used for separating inorganic substances. Separations were carried out at 13 V/cm or 45 V/cm using radionuclides. The equipment used is described. High-voltage

ionophoresis was conducted either under cooling or in an atmosphere of water vapour. Migration times under these conditions were 2 or 5 min, respectively.

RÉSUMÉ

L'ionophorèse en couche mince a été appliquée à la séparation (à 13 V/cm ou 45 V/cm) de substances inorganiques, en utilisant des radionucléides. L'équipement est décrit. L'ionophorèse à haute tension est effectuée, soit à froid, soit dans une atmosphère de vapeur d'eau. Les temps de migration dans ces conditions sont respectivement de 2 ou 5 minutes.

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DETECTION OF SOME ALIPHATIC SATURATED LONG-CHAIN HYDROCARBON DERIVATIVES BY THIN-LAYER CHROMATOGRAPHY

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Thin-layer chromatography, a relatively new analytical technique, is often found to be superior to paper chromatography not only in speed and sensitivity but also because it is possible to employ drastic yet simple identification techniques with corrosive reagents. A rapid and sensitive method of detection of certain aliphatic saturated long-chain acids, alcohols, aldehydes, and diols in the presence of their parent hydrocarbons by thin-layer chromatography is discussed.

EXPERIMENTAL

A comprehensive thin-layer chromatographic assembly supplied by Brinkmann Instruments, Inc., Long Island, New York, U.S.A., was used in the investigations.

Preparation of chromatoplates

Glass plates (20 × 20 cm) coated with "Silica Gel G" to a thickness of 250 μ[1] were graduated to have 13 to 15 chromatocolumns (13 × 1 cm) perpendicular to the direction of coating, leaving 1 to 6 cm at the edges parallel to the columns[2]. The graduated chromatoplates were dried for maximum activity in an oven at 110° for 2 h. The dried chromatoplates were transferred to a cabinet with a desiccant ("Drierite") for immediate use or kept in a vacuum desiccator for eventual use.

Chromatoplates exposed to air for any considerable time lose their activity and must be redried to obtain full effectiveness. Such a condition is not always most desirable, however, and reduced activity is preferred for strongly adsorbed solutes[3].

Preparation of standard solutions

The following compounds were procured: decanal, dodecanal, tetradecanal, 1,10-decanediol, and 1,14-tetradecanedioic acid (Aldrich Chemical Company), 1,16-hexadecanedioic acid (Chemicals Procurement Laboratories), tetradecanol and hexadecanol (Eastman Kodak), 1,12-dodecanediol, 1,16-hexadecanediol, 1,10-hydroxydecanoic acid, and 1,15-hydroxypentadecanoic acid (K and K Laboratories), decane, dodecane, tetradecane, hexadecane, decanol, decanoic acid, dodecanoic acid, tetradecanoic acid, 1,10-decanedioic acid, and 1,12-dodecanedioic acid (Mathieson, Coleman and Bell), hexadecanoic acid (Paragon Testing Laboratories), and dodecanol

(prepared by LeBlanc of Monsanto Chemical Company). All the compounds were normal compounds unless otherwise indicated.

One per cent solutions of each of the above compounds were prepared as well as a solution of a mixture of all the compounds of a C_n series (*e.g.*, decane and its derivatives), 1% with respect to each of the compounds. The solvent for the mixtures and the acids was tetrahydrofuran; otherwise the solvent was ethanol. Also prepared was a 1% solution of aqueous sulfuric acid. Thus, 5 μl of each of the above solutions contained 50 μg of (each of) the standard(s). The reference solute was a benzene solution of Sudan Red G, indophenol and 4-dimethylaminoazobenzene, 0.001% with respect to each. Alternatively, one of the standards served as a reference.

Development of chromatograms

Five μl of each of the several solutions of standards were spotted in separate chromatocolumns 3 cm from the base ensuring a maximum solvent travel distance of 10 cm. For double or triple spotting the former spot was allowed to dry[3]. The chromatoplates were pyrex for identification by charring technique; otherwise standard glass was used.

The spotted chromatoplates were air-dried and developed in selected solvents contained to a depth of 0.5 cm in a closed rectangular developing tank. Fringe phenomena were obviated through saturation of the tank atmosphere by attaching vertically to its two broader sides, a filter paper strip (15 × 25 cm) thoroughly wetted with and immersed in the solvent. In this tank, two plates could be developed simultaneously. The developed plates could be removed from the tank at the same time since the ascent of the solvent was arrested at a distance of 10 cm from spotting[3].

Identification of spots

The developed chromatoplates were freed of the solvent before identification by heating them in an oven to a temperature of about 10° above the boiling point of the solvent for 30 min and gradually cooling to room temperature. Breaking of the standard glass plates was thus avoided.

For the detection of the compounds other than the acids, the nonspecific charring technique proved successful. Specificity of the R values of the solutes was found to be sufficient for individual identification.

Pyrosulfuric acid was found to be superior to concentrated sulfuric acid for charring. The charring of an organic compound is essentially its partial oxidation to carbon and the abstraction of water by desiccation. The desiccation was better accomplished by pyrosulfuric acid which contains 20 to 23% free sulfur trioxide — a much more vigorous scavenger of water than concentrated sulfuric acid either as such or in admixture with concentrated nitric acid or potassium dichromate.

The charring was effected by superimposing onto the developed chromatoplate a sand-blasted pyrex plate coated by means of a pad of glass wool with a thin layer of pyrosulfuric acid. These two plates were lightly pressed together and heated in an oven at a temperature of 150–180° when well-defined spots were obtained.

Bromothymol blue spray followed by exposure to ammonia was used for identifying the acid spots because charring was unsuccessful. The acids appeared as yellow spots. The spray was prepared as an 0.2% solution in ethanol brought to pH 7 (bluish green color) by the dropwise addition of 0.5 N caustic soda.

Calculation of R values

The R_F value was always a tenth of the distance traveled by the solute. The R value, which has been found to be reproducible in thin-layer chromatography, is the ratio of the R_F value of a solute to that of a reference solute and is not necessarily less than unity. For example, the R value of decanol with respect to Sudan Red G in the mobile phase, ethyl acetate–*n*-hexane (3 : 17) is 0.90 (Table I).

TABLE I

R_F VALUE TRENDS FOR THE *n*-MONO- AND 1,*n*-BIFUNCTIONAL DERIVATIVES OF C_{10}, C_{12}, C_{14} AND C_{16} ALIPHATIC SATURATED HYDROCARBONS, BASED ON —OH AND —CHO GROUPS AS SUBSTITUENTS, IN ETHYL ACETATE–*n*-HEXANE

Developing time: 30–40 min

Solute	R_F *in* EtOAc–n-hexane (v/v)			
	3:17	3:7	2:3	3:2
Sudan Red G (Reference)	0.29	0.57	0.73	0.79
Indophenol (Reference)	0.38	0.70	0.82	0.86
4-Dimethylaminoazobenzene (Reference)	0.52	0.75	0.83	0.86
Decanediol	No movement	0.06	0.15	0.29
Decanol	0.26	0.56	0.68	0.70
Decanal	0.66	0.86	0.87	0.91
Decane	Moved with solvent front			
Dodecanediol	—	—	0.17	0.35
Dodecanol	—	—	0.71	0.87
Dodecanal	—	—	0.92	0.92
Dodecane	Moved with solvent front			
Tetradecanediol[a]	—	—	0.18	—
Tetradecanol	—	—	0.73	—
Tetradecanal	—	—	0.95	—
Tetradecane	Moved with solvent front			
Hexadecanediol	—	—	0.20	0.38
Hexadecanol	—	—	0.75	—
Hexadecanal[a]	—	—	0.98	—
Hexadecane	Moved with solvent front			

[a] Compound unavailable; extrapolated value.

RESULTS AND DISCUSSION

Investigations on the standards prepared were directed towards the detection and differentiation of the derivatives of a C_n series and the parent hydrocarbons. Identification of a derivative of a C_n series from the same derivative of another C_n series was not attempted.

The C_{10} aldehyde and alcohol could be identified from the diol and all from the hydrocarbon in the developing solvent ethyl acetate–*n*-hexane (3 : 17 or 3 : 7, v/v); the diol, however, showed little or no movement. When the ratio was changed to 2 : 3, v/v the alcohols, aldehydes, and diols of all the C_n series were identified from one another and all from the hydrocarbons; however, there was the possibility of the higher aldehydes (hexadecanal, *e.g.*) moving with the solvent front like the hydrocarbons for any solvent ratio. This condition was encountered because of the relative nature of R_F values in thin-layer chromatography. For the ratio of 3 : 2 instead of 2 : 3 there was

a better movement of the more polar diols which consequently showed higher R_F values (Table I).

Separation of the alcohols, aldehydes and diols was not possible in the more polar developing solvents tried, namely, ethanol, glacial acetic acid, and a mixture of ether and glacial acetic acid. This was undoubtedly due to their R_F values being high and close to one another.

Glacial acetic acid as the developing solvent served to separate the acids broadly from sulfuric acid as well as from the alcohols, aldehydes, diols, and the parent hydrocarbons (Table II). Any developing solvents less polar than glacial acetic acid, namely, a mixture of ethyl acetate and *n*-hexane or ether and glacial acetic acid, gave rise to streaking and tailing of the acids.

TABLE II

R_F VALUE TRENDS FOR THE *n*-MONO AND 1,*n*-BIFUNCTIONAL DERIVATIVES OF C_{10}, C_{12}, C_{14} AND C_{16} ALIPHATIC SATURATED HYDROCARBONS, BASED ON —COOH AND —OH GROUPS AS SUBSTITUENTS, IN GLACIAL ACETIC ACID AND IN ETHANOL–AMMONIA (CONC.)–TETRAHYDROFURAN

Developing time: 2 h

Solute	R_F *in*	
	Glacial acetic acid	*EtOH–NH_3 (conc.)–THF as 7:3:3, v/v*
Decanedioic acid	0.79	0.40
Decanoic acid	0.84	0.72
Hydroxydecanoic acid	—	0.69
Dodecanedioic acid	0.83	0.41
Dodecanoic acid (Reference)	0.84	0.69
Tetradecanedioic acid	0.83	0.45
Tetradecanoic acid	0.87	0.69
Hydroxypentadecanoic acid	—	0.73
Hexadecanedioic acid	0.84	0.52
Hexadecanoic acid	0.87	0.65
Sulfuric acid	No movement	

Identification of the more polar dicarboxylic acids from the less polar mono- or hydroxycarboxylic acids was possible in a developing solvent of ethanol–ammonia (conc.)–tetrahydrofuran as 7:3:3, v/v (Table II). Increasing the content of the relatively nonpolar tetrahydrofuran for the same added volume of ethanol and ammonia (conc.) did not result in the separation of the more polar hydroxy acid from the less polar monocarboxylic acid. Eliminating tetrahydrofuran, as such, and substituting *n*-butanol (and water) or *n*-propanol for ethanol did not produce better results even upon varying the alcohol : ammonia volume ratio. Further, there was the disadvantage of a much longer developing time (6 to more than 8 h).

CONCLUSION

Compounds like aldehydic alcohols, dialdehydes, and the aldehydic acids of the C_n series besides the hydroxy acids of the C_{12}, C_{14}, and C_{16} series, the C_{14} diol and the C_{16} aldehyde could not be procured. However, from the R_F values obtained with the available compounds, the R_F values of the unprocured compounds can be derived as follows: —COOH > —OH > —CHO in polarity; the reverse is true for R_F values in a given C_n series, other conditions being the same. For the same functional group

(alcohol, aldehyde, diol, or dicarboxylic acid) the R_F value sequence is $C_{10} < C_{12} < C_{14} < C_{16}$. For the monocarboxylic (and the hydroxycarboxylic) acids, however, the trend has been reversed, *i.e.*, $C_{10} > C_{12} > C_{14} > C_{16}$ (Table II) which is explained perhaps by differences in solubility.

Based on the above trends, the following generalizations are possible for the R_F values of the derivatives of a C_n series under identical conditions of chromatoplate development:

(*1*) Aldehydic acid > hydroxy acid > dicarboxylic acid.

(*2*) Aldehyde > dialdehyde > hydroxyaldehyde > diol.

(*3*) Alcohol > hydroxyaldehyde > diol.

From such generalizations the R_F values of the C_{16} aldehyde and the C_{14} diol were obtained (Table I).

The authors wish to thank Dr. W. A. DARLINGTON, Central Research Department, Monsanto Chemical Company, St. Louis, Missouri, U.S.A., for supplying most of the compounds listed.

SUMMARY

The aliphatic saturated long-chain alcohols, aldehydes, and diols were identified to a sensitivity of 50 μg from the parent hydrocarbons (C_{10}, C_{12}, C_{14} and C_{16}) by thin-layer chromatography using "Silica Gel G"-coated pyrex chromatoplates for the fixed phase and ethyl acetate–*n*-hexane mixtures as the mobile phase. Identification of the developed spots was made by a modified charring technique employing ground glass pyrex plates coated with pyrosulfuric acid. Identification of the 1,*n*-dicarboxylic acid from the *n*-mono- or the 1,*n*-hydroxycarboxylic acid derived from the same parent hydrocarbon was effected in a mobile phase of 7 : 3 : 3 v/v ethanol–ammonia (conc.)–tetrahydrofuran. The indicator spray employed was an ethanolic solution of bromothymol blue. The spray was followed by exposure to ammonia vapor for intensification of the yellow acid spots.

R_F value trends for the *n*-mono- and 1,*n*-bifunctional derivatives of the C_{10}, C_{12}, C_{14} and C_{16} aliphatic saturated hydrocarbons based on the —OH, —COOH and —CHO groups as the possible substituents are outlined.

RÉSUMÉ

Une méthode a été mise au point pour l'identification d'alcools, d'aldéhydes et de diols aliphatiques saturés, à longues chaînes, en présence des hydrocarbures correspondants. On procède par chromatographie en couches minces, en utilisant comme phase solide des plaques de pyrex revêtues de gel de silice G et, comme phase mobile, des mélanges acétate d'éthyle–*n*-hexane. Pour l'identification d'acides dicarboxyliques, en présence d'acides mono- ou hydroxycarboxyliques, on emploie un mélange éthanol–ammoniaque–tétrahydrofurane comme phase mobile. Comme réactif révélateur, on utilise le bleu de bromothymol en solution alcoolique.

ZUSAMMENFASSUNG

Mit Hilfe der Dünnschichtchromatographie wurden die aliphatischen, gesättigten, langkettigen Alkohole, Aldehyde und Diole in den analogen Kohlenwasserstoffen (C_{10}, C_{12}, C_{14}, C_{16}) bis zu einer Empfindlichkeit von 50 μg nachgewiesen. Dazu wurden mit Silicagel G überzogene Chromatographierplatten für die stationäre Phase und Äthylacetat–*n*-Hexan-Mischungen als mobile Phase benutzt. Zur Identifizierung der sich von den analogen Kohlenwasserstoffen ableitenden 1,*n*-Dicarbonsäure neben der *n*-mono- oder der 1,*n*-Hydroxycarbonsäure wurde mit einer mobilen Phase von Äthanol–Ammoniak–Tetrahydrofuran (7 : 3 : 3, v/v) gearbeitet. Indikator war eine äthanolische Lösung von Bromthymolblau. Zur Verstärkung des Nachweises wurde Ammoniakdampf genommen. Die R_F-Werte der verschiedenen Verbindungen sind tabellarisch aufgeführt.

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SALTING-OUT CHROMATOGRAPHY OF SERUM PROTEINS

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Salting-out chromatography on beds of ion-exchange resins has proved useful in the separation of complex mixtures of alcohols, polyglycols, amines, etc.[1]. An aqueous mixture of the nonionic solutes is placed on a bed previously equilibrated with a concentrated solution of an electrolyte such as ammonium sulfate, and eluted with eluants of decreasing electrolyte concentration. Hydrophobic solutes are salted out of the solution phase into the resin phase and are retained on the bed while the hydrophilic solutes are more rapidly eluted.

This technique has had limited success in the separation of proteins. Unpublished work by the authors indicates that conventional ion-exchange resins are usually unsuitable for the separation of proteins because of low capacities and irreversible sorption. Low capacities arise from the small effective surface areas of such resins (< 0.1 m^2/g) and irreversible sorption probably occurs owing to a physical bonding with the hydrophobic polystyrene resin matrix. Bacterial alkaline phosphatase, however, was successfully isolated from E. Coli cells by salting-out chromatography on beds of a special highly-porous cation exchanger having pores of 0.05 μ and a surface area of 300 m^2/g. Most proteins are held so tightly by this resin that hydrolysis to smaller fragments was required for removal. For example, the recovery of blood serum proteins ranged between 15 and 30% from the porous resins.

Recently "gel filtration"[2] on beds of Sephadex cross-linked dextran has been successfully used to separate high molecular weight species from those of lower molecular weight. The larger molecules are excluded from the pores of the gel and are eluted more rapidly than those which are small enough to enter the gel structure. Both Sephadex and cellulose have been aminated to produce anion exchangers capable of high resolution of complex biological mixtures. DEAE-Sephadex was used to separate peptides and amino acids[3] and DEAE-cellulose was employed for the fractionation of blood serum proteins[4]. Unlike the irreversible sorption observed with the polystyrene-based resins, full recovery of the solutes was possible from beds of these hydrophilic carbohydrate gels. Protein molecules of similar size can not be separated from each other by gel filtration on beds of Sephadex with water as eluant. It appeared logical, therefore, to combine the advantages of complete recovery with the high resolving power of salt eluants to develop a technique whereby similar proteins could be separated on a bed with no ion-exchange properties.

EXPERIMENTAL

Sephadex G-50, 100–250 mesh, was slurried in water and poured into glass columns. The beds were then equilibrated with a buffered 1.5 *M* sodium sulfate solution that was to be used as the first eluant. A sample of blood serum was pipetted onto the bed and eluted with the buffered salt eluant at a controlled rate of flow. A gradient salt eluant was produced by feeding buffered 0.5 *M* sodium sulfate at 0.05 cm per min to a 500-ml round-bottom flask containing 500 ml of 1.5 *M* buffered sodium sulfate and a magnetic stirring bar. The effluent from the stirred mixer was fed directly to the bed. The molarity of the salt entering the bed was calculated using the equation[5]

$$[Na_2SO_4] = M_2 - (M_2 - M_1)\, e^{-\varphi/V_r}$$

where M_1 and M_2 are the molarities in the mixer and in the solution fed to the mixer, respectively, φ is the volume of column effluent, V_r is the volume of the mixer, and e is the base of natural logarithms. Fractions of column effluent were analyzed for protein by measuring the spectrophotometric absorbance at 280 mμ. Recovery was calculated by summation of the products of fraction volume and absorbance and compared with a diluted sample of the original serum. Qualitative confirmation of eluted protein peaks was attempted by ultracentrifugation and electrophoresis.

RESULTS

Two runs are described below to illustrate the method. In the first run, 1.5 *M* sodium sulfate buffered with 0.1 *M* phosphate at pH 7.0 was used to equilibrate the column of Sephadex before the addition of sample. As shown in Fig. 1, the eluant was changed abruptly to 0.08 *M* phosphate at pH 7.0, which caused the remaining globulins to be eluted in a sharp band. Some precipitation of the globulins occurred at this point and resulted in increased pressure drop across the bed. Recovery was not computed on this run.

In the second run shown in Fig. 2, the eluant was changed from a constant to a gradient sodium sulfate concentration while maintaining a constant pH of 5.5 with

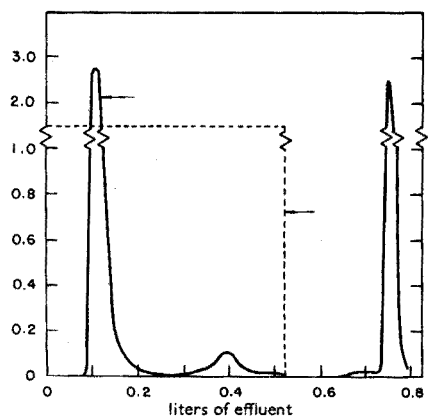

Fig. 1. Salting-out chromatography of serum with stepwise eluant change. Bed: 15.5 cm × 16.76 cm^2 = 260 ml, Sephadex G-50, 100–250 mesh. Sample: 3.0 ml fresh pooled human blood serum. Eluants: 520 ml 1.50 *M* Na_2SO_4 buffered with 0.1 *M* phosphate at pH 7.0 followed by 0.08 *M* phosphate buffer at pH 7.0. Flow rate: 0.05 cm per min. Temperature: 30°. (left←: A_{280}; right←: $[Na_2SO_4]$.)

0.1 *M* phosphate buffer. Lowering the pH toward the isoelectric point of the α-globulins resulted in better resolution, as a component (peak 2 of Fig. 2) which was not visible in Fig. 1 was partially resolved at this pH. The gradient produced a partial separation of the remaining globulins which might be improved further by use of a deeper bed and a more gradual gradient.

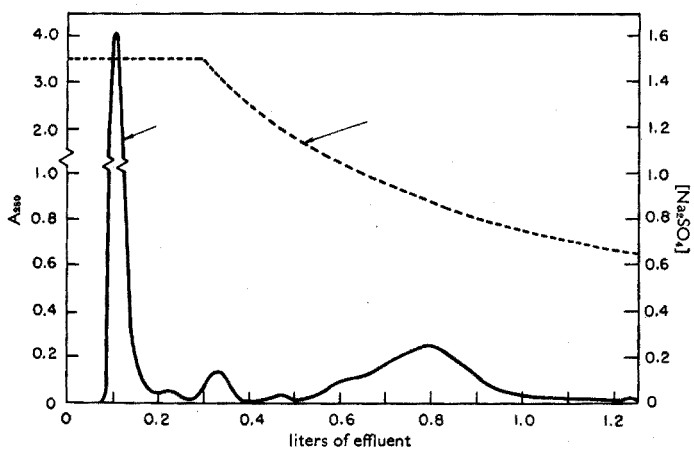

Fig. 2. Salting-out chromatography of serum with a gradient eluant change. Bed: 14.3 cm × 16.76 cm^2 = 240 ml, Sephadex G-50, 100–250 mesh. Sample: 3.0 ml fresh pooled human blood serum. Eluants: 300 ml 1.50 *M* Na_2SO_4 buffered with 0.1 *M* phosphate at pH 5.5 followed by a gradient approaching 0.5 *M* Na_2SO_4 buffered with 0.1 *M* phosphate at pH 5.5. Volume of mixer was 500 ml. Flow rate: 0.05 cm per min. Temperature: 30° (left←: A_{280}; right←: $[Na_2SO_4]$.)

The order of elution reflects the solubility of the protein in sodium sulfate solutions and the general shape of the elution graph is similar to the pattern obtained in electrophoresis except for higher resolution in the earlier fractions. The order of elution is, in general, the reverse of that obtained by anion exchange on DEAE-cellulose columns. The straw-colored component of the serum could be observed as it passed through the bed coincident with the first (albumin) peak. Up to about 600 ml of effluent, the less soluble globulins were observed as a white precipitate uniformly distributed at the top of the bed. Albumin in the first effluent peak was readily precipitated by adjusting the pH to 3.85. Filtration yielded a straw-colored precipitate and a colorless filtrate from which no further precipitation occurred when the pH was varied over wide limits. This pH was probably close to the isoelectric point of albumin in the presence of 1.5 *M* sodium sulfate. The proteins in the third (probably α_1-globulin) and the sixth (γ-globulin) peaks were partially precipitated by lowering the pH to 4.0 and 5.0, respectively and adding sodium sulfate if necessary to bring the concentration up to 1.5 *M*. Better yields of the globulin could probably have been obtained by dialysis against water as they are quite insoluble in solutions of low ionic strength.

Because albumin (peak 1 of Fig. 2) was eluted at high concentration and could be dialyzed without precipitation, it was easily identified by both ultracentrifugation and electrophoresis. Qualitative identification of the remaining peaks could not be

obtained by the above methods. However, the amount of protein recovered under the various peaks of Fig. 2 matches very well the published percentages of the serum proteins as indicated below.

Peak number	*Per cent of sample*	*Component*	*Literature value (%)*
1	56.8	Albumin	56.0
2	1.28		
3	4.97 } 6.81	α_1-Globulin	7.2
4	0.56		
		α_2-	8.8
5 and 6	36.7	β- } Globulin	13.1 } 36.6
		γ-	14.7
Total	100.31		

If this analogy is correct, chromatographic separation of blood serum proteins on columns of Sephadex offers the advantage of a preparative method for the isolation of albumin and α_1-globulin from the remaining globulins. Elaborate schemes have been devised[7] for the selective precipitation of proteins from blood serum by the addition of salts or ethanol at carefully controlled temperature and pH. These methods yield fractions rich in a particular protein but are always contaminated with others. Chromatographic separations are capable of clean-cut isolation of components and may replace precipitation methods if conditions for separation are found. A major stumbling block — that of dilution which makes identification of the components difficult — might be overcome by a combination of the precipitation and chromatographic techniques wherein one or two impurities of a precipitated fraction could be removed from the desired component by a simple chromatographic procedure.

SUMMARY

The usefulness of salting-out chromatography is demonstrated by the separation of blood serum proteins on Sephadex. Conventional and highly porous ion exchangers generally can not be used because of irreversible sorption of protein.

RÉSUMÉ

Les auteurs ont démontré l'utilité de la chromatographie "salting-out" par la séparation des protéines du sérum sanguin sur Sephadex. Des échangeurs d'ions habituels et très poreux ne peuvent pas être utilisés, en raison de la sorption irréversible de la protéine.

ZUSAMMENFASSUNG

Die Brauchbarkeit der Aussalzchromatographie wird an der Trennung von Blutserumproteinen an Sephadex gezeigt. Konventionelle und hochporöse Ionenaustauscher können im allgemeinen wegen der irreversiblen Sorption des Proteins nicht benutzt werden.

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Short Communication

Quantitative separation of iron, nickel and chromium from magnesium using ammonium pyrrolidinedithiocarbamate in partially methanolic medium

Extraction of chromium(III) pyrrolidinedithiocarbamate

The precipitation of chromium(III) pyrrolidinedithiocarbamate from an aqueous medium is not quantitative at any pH[1]. A new technique using a partially methanolic medium effects a quantitative precipitation in the pH range 7–9.

Procedure. Add 1 ml of methanol to 1 ml of a solution containing 1 mg of chromium(III). Add solid ammonium pyrrolidinedithiocarbamate in a 6–7 *M* excess (20 to 30 mg) and leave the mixture to stand for 5 min in a separatory funnel. Then shake the mixture with 1 ml of chloroform. The chloroform and aqueous layers separate quickly and sharply and no chromium(III) can be detected in the aqueous layer on testing with ammonium hydroxide and evaporating to dryness.

During the reaction ammonium hydroxide is formed and the pH changes to 8–9; however, no chromium(III) hydroxide is formed under these conditions. Chromium(III) hydroxide is insoluble in methanol and chloroform, even in the presence of ammonium pyrrolidinedithiocarbamate. If chromium(III) hydroxide is formed first in a purely aqueous medium, then it cannot be converted into the carbamate with or without the addition of methanol. Chromium(III) pyrrolidinedithiocarbamate can only be formed quantitatively in a partially methanolic medium in the pH range 7–9.

Extraction of chromium, iron and nickel pyrrolidinedithiocarbamates

The extraction of the chromium, iron and nickel complexes is accomplished quantitatively with chloroform, but only by multiple extractions. However, if methanol is added to the aqueous phase before or after the formation of the chromium, iron or nickel complex, then a quick and complete separation of the phases is effected and all the carbamate precipitate dissolves in the chloroform layer. The approximate limiting ratios of methanol, water and chloroform were established for an aqueous volume of 1.0 ml containing 1 mg of metal ion precipitated out as the carbamate, and shaken with 1.0 ml of chloroform.

Chromium. Only methanol allows a quantitative precipitation. The alcohol must be added before carbamate precipitation is effected at pH 7–9. The lower and upper limits of methanol are 0.75 and 3 ml, respectively; the best ratio is approximately 1 : 1 : 1 of ionic solution, methanol and chloroform.

Iron and nickel. More than 0.75 ml of methanol is necessary to effect complete dissolution of the carbamate in the chloroform layer and sharp separation of the chloroform and aqueous layers; above 3 ml of methanol a single phase is obtained. For methanol, the lower and upper limits are 0.5 and 2 ml respectively. In both cases the alcohol is just as effective if added before or after carbamate precipitation. The best ratio of water, methanol and chloroform is approximately 1 : 1 : 1.

Quantitative separation of magnesium from chromium, iron and nickel

Procedure. Add 1 ml of methanol to 1.00 ml of a neutral solution containing 1 mg of chromium(III) and 0.0623 mg of magnesium ion in a separatory funnel. Add a 2–3-fold excess of solid ammonium pyrrolidinedithiocarbamate and allow the mixture to stand at room temperature for 5 min. Extract the chromium(III) complex with six 1-ml portions of chloroform and wash the contents of the separatory funnel — the aqueous layer and a small quantity of precipitate-free chloroform — into a titration flask. Titrate the magnesium content of the solution with 0.001 *M* EDTA solution using eriochrome black T as indicator after buffering to pH 11–12.

In the pH range 7–9 in a 50% methanolic medium, the iron and nickel carbamates — and not the hydroxides — are formed quantitatively. When the above procedure was repeated with a solution containing 1 mg each of iron, nickel and chromium, and 0.0623 mg of magnesium, very satisfactory results were obtained (Table I).

TABLE I

SEPARATION OF MAGNESIUM

Separation from	*Magnesium taken (mg)*	*Magnesium found (mg)*	*Number of 1.00-ml samples taken*
1 mg chromium	0.0623 ± 0.0003	0.0623 ± 0.0005	15
1 mg chromium 1 mg nickel 1 mg iron	0.0623 ± 0.0003	0.0623 ± 0.0005	15

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1 H. MALISSA AND H. KOTZIAN, *Talanta*, 9 (1962) 991.

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Book reviews

Official, Standardised and Recommended Methods of Analysis, Compiled and edited by S. C. JOLLY, published for the Society for Analytical Chemistry by W. Heffer & Sons Limited, Cambridge, England, 1963, xx + 577 pp., price 126/—.

This publication, compiled and edited for the Analytical Methods Committee of the Society for Analytical Chemistry, is in two parts. The first, under the main heading, *Standardised Methods of Analysis*, details methods that have been extensively examined

cooperatively by leading analytical chemists in the United Kingdom, and approved by their various sub-committees. It deals with subjects such as Metallic Impurities in Organic Matter, the determination of Vitamins and of Fluorine in Foods, the examination of Essential Oils, Milk Products (liquid and condensed), Flour, Meat Extracts, Oils and Fats, Soaps, Trade Effluents, Pesticide Residues and the assay of Crude Drugs. To illustrate the depth of coverage under these headings: the section on Pesticide Residues deals with items such as the Determination of Malathion Residues in Cereals and Oilseeds, and in the section on Crude Drugs, provision is made for the Assay of Aconite, the Determination of Capsaicin in Capsicum and its Preparations, and the Assay of Ephedra, Gelsemium, Rauwolfia, etc. From this random selection of headings, and the subsequent brief expansion, it may appear that this part of the book will have a limited appeal to analysts engaged in the inorganic field, but this is not so.

The detailed section on the Destruction of Organic Matter, with a view to the quantitative recovery of elements such as As, Cu, Pb and Zn, occupies 17 pages, and Perchloric Acid and Its Uses in Analytical Work also receives special attention. It is noteworthy that the section on Trade Effluents occupies 134 pages and will have a special appeal not only to analysts associated with the growing importance of trade effluent problems, but to anyone interested in the determination of small amounts of many elements.

The second part (234 pp.), under the main heading, *Bibliography of Official, Standardised, Tentative and Recommended Methods of Analysis*, is an up-to-date version of a 1951 publication (now out of print) of the Society for Public Analysts and Other Analytical Chemists. In the original bibliography, only British and American sources were quoted, but in this revised version all readily available publications, irrespective of the language, provided that English translations are available, have been included. This second part, containing over 40 separate sections (each written by experts in the particular field) includes subjects arranged alphabetically from Acids, Alkalis and Antibiotics, through Miscellaneous Foodstuffs, Gums, Hormones and Ferrous Metals to Vitamins, Water and Wood.

The condensed method of presenting the information in this second part is of the same acceptable pattern throughout. The lists of references are given first under each heading, and these have obviously been carefully selected and kept to a minimum. Over half of the subjects contain less than 20 references although, understandably, there are exceptions; under Pesticides, for example, 563 references are given. The method of dealing with these numbered references is commendable, because it gives the reader an immediate simple guide in his quest for analytical information on the numerous sub-headings. The methods given in the references are classified as Official and Standardised, Tentative, and/or Recommended.

It is usual in these reviews to recommend the book, where this is justified, to analysts engaged in some particular field, but this is difficult on this occasion, because the Analytical Methods Committee has clearly aimed at a very wide coverage of subjects, and has carried out the immense task extremely well. To the analyst who thinks in terms of more sophisticated analytical procedures, *e.g.* neutron activation, mass spectroscopy or even polarography, the book will have a limited appeal, because the emphasis has been placed on the attainment of desirable orders of accuracy and precision without resort to the use of expensive equipment.

The credit to all concerned with the preparation, presentation and production of this book, is well earned, and the busy analyst, not knowing what problem is next in line of succession, should be grateful for having this reliable source of authoritative information made available at a reasonable price.

W. T. ELWELL (Birmingham)

Treatise on Analytical Chemistry, Edité par I. M. KOLTHOFF ET P. J. ELVING avec l'assistance de E. B. SANDELL, Part II, *Chimie analytique des éléments*, Vol. 8, *Terres rares, bismuth, vanadium, chrome et les métaux du platine*, Interscience, New York, 1963, 556 pp., prix £ 7.10/—.

Spécialistes universitaires et chimistes de l'industrie ont collaboré à ce volume.

La première partie concerne l'analyse des terres rares (146 pages): c'est l'oeuvre de M. M. WOYSKI ET R. E. HARRIS. Les terres rares, étant donné la difficulté des séparations, sont traitées en groupes, sauf celles présentant plusieurs valences.

Après un court historique, suivi de tableaux donnant la concentration des terres rares dans diverses substances naturelles et les procédés industriels mis en oeuvre pour les obtenir, les auteurs traitent de leur propriétés physiques et chimiques et singulièrement celles utiles à l'analyse. Des tableaux fort subjectifs en résument les données essentielles.

La séparation des terres rares et de l'yttrium fait l'objet du chapitre 3. On y traite de la mise en solution des échantillons: composés inorganiques, verres et céramiques, métaux, etc., des séparations des terres rares d'avec les autres éléments, selon les méthodes les plus modernes, puis de l'analyse quantitative de celles ci. Après l'identification des terres rares, les auteurs donnent les méthodes de dosage du cérium et de l'europium par diverses méthodes, dont la fluorimétrie X et celle basée sur les rayons infra-rouges.

On pourrait faire quelques petits reproches aux auteurs, par exemple celui de fournir quelquefois des renseignements sur des sujets qui ne nous semblent pas fondamentaux. D'autre part il nous semble que les auteurs n'insistent pas suffisamment, au cours de leurs exposés, sur les bases théoriques de l'analyse chimique.

Ce volume, comme les précédents, est présenté de façon parfaite, les exposés sont fort clairs, et l'étudiant, comme le chimiste chevronné, trouvera sans peine toutes les méthodes dont il a besoin, tant pour l'identification que pour le dosage des éléments traités.

D. MONNIER (Genève)

STEROID CHROMATOGRAPHY

BY ROBERT NEHER

Pharmaceutical Research Department

CIBA Ltd., Basel, Switzerland

Chromatographic methods are today indispensable aids in the isolation, separation and determination of the various classes of steroids. In this English Edition of his highly successful "Chromatographie von Sterinen, Steroiden und verwandten Verbindungen" (Elsevier, 1958), the author has completely revised the original material and taken into account the most recently published results in the field. He provides a detailed exposition of the techniques best suited to the analysis of steroids, sterols and related compounds, describes apparatus specially adapted for this purpose, presents typical examples of applications, and discusses the relationship between chemical structure and chromatographic behaviour. Reference is also made to paper electrophoresis of ionized steroids and derivatives, in the development of which success has been recently noted.

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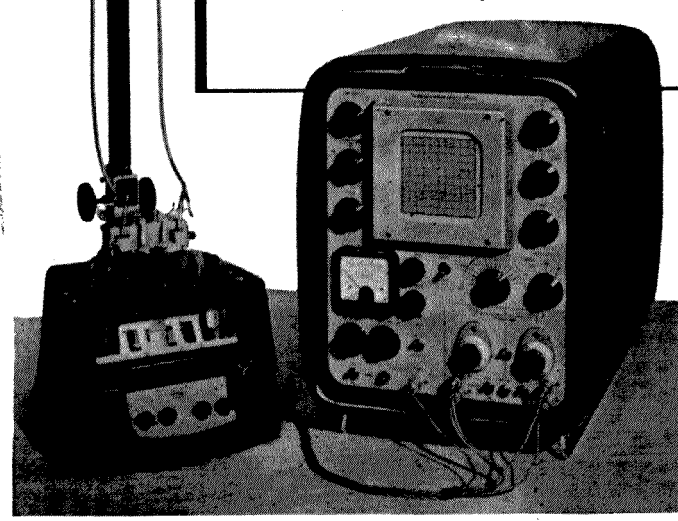

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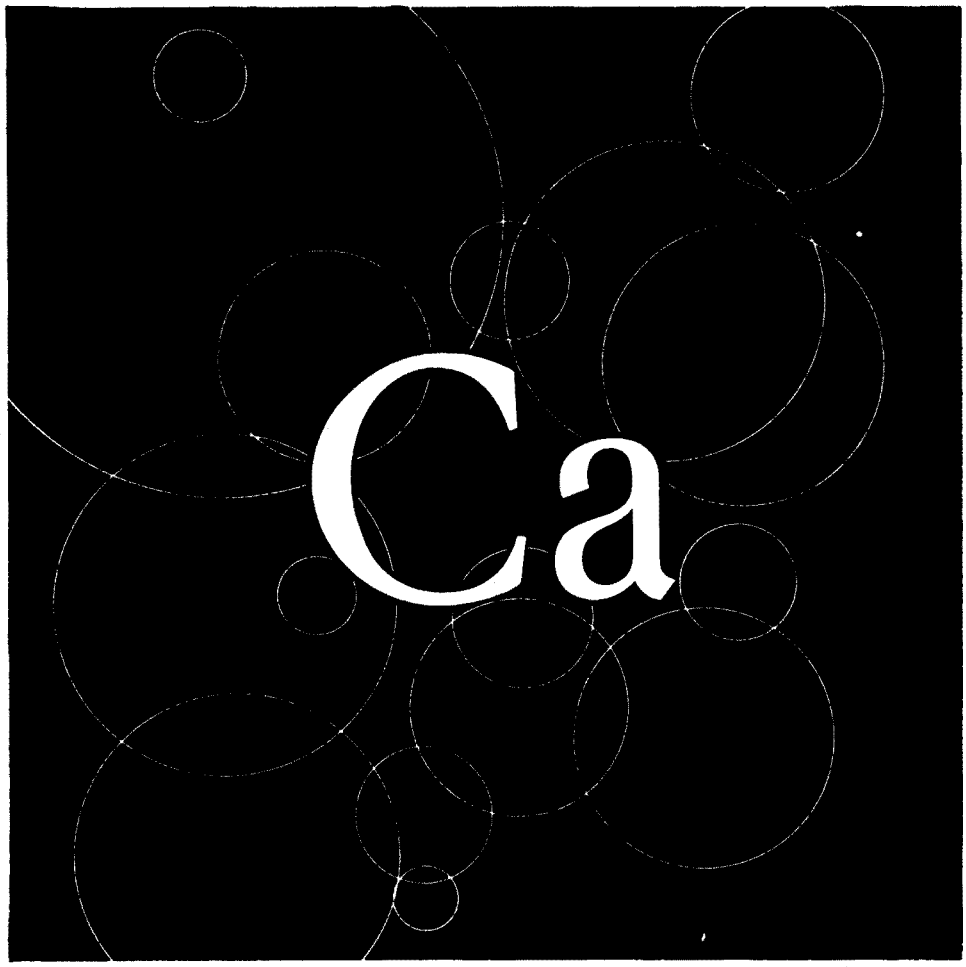

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