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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 33, No. 5, November 1965

STUDIES ON THE PRECISE DIFFERENTIAL POLAROGRAPHIC DETERMINATION OF ELEMENTS OF NUCLEAR INTEREST

PART I. DETERMINATION OF EUROPIUM AND YTTERBIUM IN LITHIUM CHLORIDE AND LITHIUM IODIDE ELECTROLYTES

Differential polarographic determinations of the europium content of solutions of LiI and LiCl can be made within the concentration ranges of 50 to 500 μg Eu/g with varying precision. Comparative techniques can give precisions of the order of 0.1% or even better; the accuracy depends on the reference material used for the standardisation of the method.

V. VERDINGH AND K. F. LAUER,
Anal. Chim. Acta, 33 (1965) 469–480

DETERMINATION OF NANOGRAM AMOUNTS OF CESIUM BY A CONCENTRATION-DEPENDENT DISTRIBUTION METHOD

Paper impregnated with Prussian blue sorbs cesium in low concentration to a different extent if varying initial concentrations of cesium are present. This dependence can be employed for the determination of submicrogram amounts of cesium. The selectivity and precision of the method are discussed. The method is applied to the determination of specific activity in "carrier-free" ^{137}Cs samples.

M. KYRŠ AND L. KADLECOVÁ,
Anal. Chim. Acta, 33 (1965) 481–486

COMPLEX FORMATION THERMODYNAMICS OF SOME METAL(II) PHENYL-2-PYRIDYLKETOXIMATES

The formation of phenyl-2-pyridylketoximates of nickel(II), zinc(II), cadmium(II), mercury(II) and lead(II) was studied potentiometrically in a medium of 40% (w/w) acetone and 60% (w/w) water. The values of step formation constants, free energy, entropy and enthalpy of complex formation were calculated. The formation of the mercury chelate was found to be entropy driven. The formation of phenyl-2-pyridylketoximates of other metals of the first transitional series could not be studied owing to experimental difficulties.

D. C. SHUMAN AND B. SEN,
Anal. Chim. Acta, 33 (1965) 487–496

SPECTROGRAPHIC DETERMINATION OF ULTRAMICRO AMOUNTS OF BORON IN HIGH-PURITY SILICON TETRACHLORIDE AND TRICHLOROSILANE

A new sensitive method is proposed for the determination of boron in high-purity silicon tetrachloride and trichlorosilane. The method consists of complexing boron with triphenylchloromethane, removal of excess silicon tetrachloride, hydrolysis of the complex, and improved spectrographic excitation of liberated boric acid. The best sensitivity attainable is 0.03 μg B, which corresponds to 0.06 p.p.b. B for a 500-g sample.

K. Kawasaki and M. Higo,
Anal. Chim. Acta, 33 (1965) 497–502

APPLICATIONS OF THE POLAROVOLTRIC METHOD

THE DETERMINATION OF MALEIC ACID BY ORGANIC BASES IN N,N-DIMETHYLFORMAMIDE MEDIA

(in French)

The determination of the voltammetric curves, $I = f(E)$, of maleic acid and of a basic titrant in N,N-dimethylformamide using 3 electrodes allowed interpretation of the polarovoltric titration curves of the neutralization of this acid by sodium methylate and tetrabutylammonium hydroxide. The different variations of the potential between 2 polarized platinum electrodes observed in such a neutralization reaction were identified and a notation was developed so that the origin of the observed potential variations could be established. The signal $E_C^{H^+\to S}$, which is related to the initial acidity, is given by the cathode and corresponds to a jump from the potential of the H^+ reduction curves to that of the solvent reduction curves. The signal $E_A^{S\to OH^-}$, characteristic of the second acidity, is given by the anode and is related to a jump from the potential of the solvent oxidation curves to that of the titrant oxidation curves.

The effect of the use of unsymmetrical polarized electrodes (a rotating filament electrode and a large-surface, stationary electrode) on the shape of the titration curve was also examined: a rotating cathode gave rise to a curve resembling an inverted U, whereas a rotating anode gave rise to a curve resembling a deformed M.

J. E. Dubois et P. C. Lacaze,
Anal. Chim. Acta, 33 (1965) 503–513

ADDUCT FORMATION IN THE EXTRACTION OF ZINC OXINATE INTO VARIOUS ORGANIC SOLVENTS

The extraction of zinc oxinate into 10 different organic solvents was investigated. By studying the dependence of the distribution upon pH, reagent concentration, and solvent concentration (in an inert medium), the species were identified and the extraction constants estimated. Correlations between the species type and the efficiency of extraction are postulated. The species extracting into 4-methyl-2-pentanone, 1-butanol, and 4-methyl-2-pentanol is ZnR_2S_2, that extracting into benzene and chloroform is $ZnR_2(HR)S$, that extracting into butyl and pentyl ethers is ZnR_2S, that extracting into carbon tetrachloride is $ZnR_2(HR)$, and that extracting into hexane and cyclohexane is $ZnR_2(H_2O)_2$. In these formulas, R is the oxinate ion, HR is oxine, and S is the organic solvent. It is suggested that the extraction behavior can be explained by assuming a water molecule to be attached to the ZnR_2S and $ZnR_2(HR)$ species.

G. K. Schweitzer, R. B. Neel and F. R. Clifford,
Anal. Chim. Acta, 33 (1965) 514–521

THE EFFECT OF ARSENATE, AND OF TRANSITION-METAL IONS, ON THE PRECIPITATION OF PHOSPHATE AS AMMONIUM 12-MOLYBDOPHOSPHATE

The radionuclides phosphorus-32, arsenic-74, iron-59 and molybdenum-99 were used to determine the effect of arsenate and some transition-metal ions on the precipitation of phosphorus as ammonium 12-molybdophosphate. Under the conditions necessary for the quantitative precipitation of phosphorus, arsenic is also precipitated by ammonium molybdate. The presence of iron(III) nitrate inhibits the precipitation of phosphorus and, particularly, arsenic, although the precipitates contain more molybdenum, and are heavier, than when iron is absent. Chromium(III) nitrate, nickel(II) nitrate and manganese(II) nitrate do not inhibit the precipitation of phosphorus and arsenic to the same extent as iron(III) nitrate.

R. B. Heslop and E. F. Pearson,
Anal. Chim. Acta, 33 (1965) 522–531

THE RAPID ANALYSIS OF COPPER–PALLADIUM ALLOYS BY CONTROLLED POTENTIAL ELECTROLYSIS

(in French)

The optimum conditions for separation by controlled potential electrolysis were determined by linear chronoamperometry. This method can be applied to any alloy which can be deposited on platinum electrodes. For Cu–Pd alloys, the palladium was deposited at 50° in *N* sulphuric acid medium at +640 mV (with respect to the normal hydrogen electrode). Copper was deposited in several stages at ambient temperature after adding hydroxylammonium chloride. For *ca.* 100 mg of deposited metal, the errors were less than 1%; they could be reduced by using bigger samples. The two successive electrolyses required less than 3 h.

Tran Van Danh et J. C. Viguie,
Anal. Chim. Acta, 33 (1965) 532–537

THE TEMPERATURE DEPENDENCE OF THE FADING EFFECT IN SEMIQUANTITATIVE AUTORADIOGRAPHY BY THE RING-OVEN METHOD

(in German)

In semiquantitative autoradiography used in conjunction with the ring-oven method, a fading effect was found to cause erroneous results, especially for long exposure times. The dependence of this effect on the temperature was studied for several examples (^{45}Ca, ^{204}Tl and ^{90}Sr/^{90}Y). It was shown that the exposure and storage of the undeveloped autoradiogram at low temperature ($< 4°$) practically eliminated the fading effect.

H. Weisz und D. Klockow,
Anal. Chim. Acta, 33 (1965) 538–542

GENERAL CONSIDERATIONS IN THE ACID–BASE TITRATIONS IN GLACIAL ACETIC ACID

AN EXTENSION OF THE CONCEPT OF LIGAND BUFFER

Some continuous expressions are derived for potentiometric as well as photometric acid–base titrations in anhydrous acetic acid. Various methods of end-point location are discussed and the titration error is calculated.

M. Tanaka and G. Nakagawa,
Anal. Chim. Acta, 33 (1965) 543–553

DETERMINATION OF ORGANIC HYDROXYL AND AMINO COMPOUNDS WITH *o*-SULPHOBENZOIC ANHYDRIDE

The determination of alcoholic hydroxyl groups by acylation with *o*-sulphobenzoic anhydride in dioxane medium is proposed. Quantitative esterification was generally obtained by refluxing for 2–3 h. No interferences were found from water, aldehydes, ketones, ethers, esters and phenols; the reagent appeared to be of the phthalic anhydride type. Results for 26 hydroxyl and some amino compounds by the proposed reagent are given.

V. Iyer and N. K. Mathur,
Anal. Chim. Acta, 33 (1965) 554–558

FREEZE CONCENTRATION OF DILUTE SOLUTIONS

(Short Communication)

G. H. Smith and M. P. Tasker,
Anal. Chim. Acta, 33 (1965) 559–560

REACTIONS OF ORGANIC COMPOUNDS WITH HETEROPOLY ACIDS

PART III. COLORIMETRIC DETERMINATION OF CARBONYL COMPOUNDS WITH 12-MOLYBDOSILICIC ACID

(Short Communication)

J. H. Billman and A. W. Seiling,
Anal. Chim. Acta, 33 (1965) 561–563

AMPEROMETRIC DETERMINATION OF PALLADIUM, SILVER AND COPPER WITH 2-MERCAPTOBENZOXAZOLE

(Short Communication)

B. C. Bera and M. M. Chakrabartty,
Anal. Chim. Acta, 33 (1965) 564–566

DETERMINATION OF SILICON IN MINERALS BY MICRO-DIFFUSION TECHNIQUE

(Short Communication)

C. Hozdic,
Anal. Chim. Acta, 33 (1965) 567

A NEW EDTA METHOD FOR THE DETERMINATION OF CALCIUM IN BLOOD SERUM

(Short Communication)

W. R. Douglas,
Anal. Chim. Acta, 33 (1965) 567–570

DETERMINATION OF MAGNESIUM IN NEEDLE-BIOPSY SAMPLES OF MUSCLE TISSUE BY MEANS OF NEUTRON ACTIVATION ANALYSIS

(Short Communication)

D. Brune and H. E. Sjöberg,
Anal. Chim. Acta, 33 (1965) 570–572

STUDIES ON THE PRECISE DIFFERENTIAL POLAROGRAPHIC DETERMINATION OF ELEMENTS OF NUCLEAR INTEREST

PART I. DETERMINATION OF EUROPIUM AND YTTERBIUM IN LITHIUM CHLORIDE AND LITHIUM IODIDE ELECTROLYTES

V. VERDINGH AND K. F. LAUER
Euratom, Central Bureau for Nuclear Measurements, Geel (Belgium)

(Received March 3rd, 1965)

Because of their high neutron cross-section the elements of the rare earth group are of considerable interest in nuclear science. Their accurate determination is a problem that interests many scientists doing nuclear measurements or using doped scintillation crystals. Polarographic methods are rapid and have already been used for the determination of europium and other rare earths[1–10]. As the quantity of the element available is very often quite small and as the accuracies required are becoming higher, it was thought that a comparative method for the determination of rare earths might give accurate results.

A study of the polarographic determination of europium was made, so as to allow a clear evaluation of the analytical possibilities of the method. The instruments and the general technique used resemble closely those described by DAVIES and SHALGOSKY[11,12]. It is clear that the best working conditions are to be found with diluted electrolytes. One of the objectives was however the determination of small quantities of europium in lithium halide monocrystals, and in view of obtaining as high an absolute europium concentration as possible, it was decided to work with a high electrolyte concentration.

EXPERIMENTAL

Apparatus

Throughout the studies the Davis Differential Cathode Ray Polarograph type A. 1660 from Southern Analytical Limited, was used with cells and stand as delivered. The whole stand was enclosed in a gas-tight box that was kept under a slight nitrogen overpressure. Potentials were measured against a mercury pool anode or against a separated, saturated calomel electrode.

The capillary characteristics were: m = 0.345 mg/sec flowing weight of mercury; t = 7.27 sec/drop at the applied potentials 0.363 V to −0.854 V *vs.* S.C.E.

All measurements were made at 25°.

Reagents

Eu_2O_3 (Pechiney), 99.9% pure ref. 14572.

Yb_2O_3, Johnson + Matthey Specpure JM.319.

LiI pure, Merck: 5688; and LiCl p.a. Merck: 1418. Mercury tridistilled (99.99999% Le Mercure Distillé). Water was demineralized and tridistilled from quartz apparatus. Buffer $\mathrm{pH} = 3$ (Merck Titrisol).

Gelatin solution (0.05 ml 10^{-3} M) when used as maximum suppressor was freshly prepared.

The europium standard solution was prepared by weighing Eu_2O_3 which had been calcined for 1 h at 700°. The Eu concentration of this standard can not be regarded as absolute. All the europium concentrations cited in this article, however, are based on and calculated with this standard solution as a reference. All measurements were done on cell-fillings of about 5 ml. The oxide was dissolved in a minimum amount of distilled hydrochloric acid.

Dilutions were made by weighing or by pipetting with a Metrohm precision buret.

(I) DETERMINATION OF Eu IN 1 M LiI (1–1000 μg Eu/ml)

(a) Single cell operation

Experimental procedure. Before each measurement the cells were degassed by passing a slow stream of oxygen-free nitrogen or hydrogen through the solution. For concentrations above 1 μg Eu/ml, a 10-min degassing period was sufficient; at lower concentrations this time was prolonged to at least 15 min.

The capillaries were adjusted as described in the manual of the instrument.

Calibration. A series of standard solutions (Table I) was prepared and the base line of the electrolyte used was measured along with the polarograms of the different standards. All peak heights given in this paper are calculated for maximum sensitivity and are arbitrary values of the instrument, so amplification factors, "shunt scale

TABLE I

DETERMINATION OF Eu IN 1 M LiI

µg Eu/ml	*Single cell operation*		*Subtractive operation*	
	Peak height	*Peak height at maximum sensitivity*	*Peak height*	*Peak height at maximum sensitivity*
988.9	66.5	399,000	66.0	396,000
494.5	80.0	200,000	79.5	198,750
197.8	72.0	72,000	72.0	72,000
98.89	89.0	35,600	89.5	35,800
59.53	60.0	24,000	94.5	23,625
39.56	68.0	17,000	66.0	16,300
29.71	73.5	11,025	81.5	12,225
9.88	94.0	3,760	94.0	3,760
7.93	46.5	1,860	75.0	3,000
5.94	73.6	1,104	62.0	2,480
3.96	65.8	658	52.0	1,300
1.99	40.1	160.4	59.1	591
0.99	27.6	27.6	73.2	292

factor", and the "amplificator scale factor" are eliminated from the discussions.

The curvature shown in Fig. 1 is due to the compensation of background signals of the supporting electrolyte.

The measurements showed that the signal obtained at maximum sensitivity for 1000 μg Eu/ml is about 400,000 scale divisions.

Results. The calibration graph obtained is given in Fig. 1. The reproducibility of the measurements depends mainly on the reproducibility of the drop mechanism and start potential. This was checked by measuring the peak height of a standard solution and adjusting the conditions until the arbitrarily chosen value of 400,000 scale divisions for a concentration of 1000 μg Eu/ml was obtained. The reproducibility of the determination could then be limited to the accuracy of the oscilloscope reading. The trace of the polarogram was very stable and the reading could be estimated to about ± 0.5 scale division.

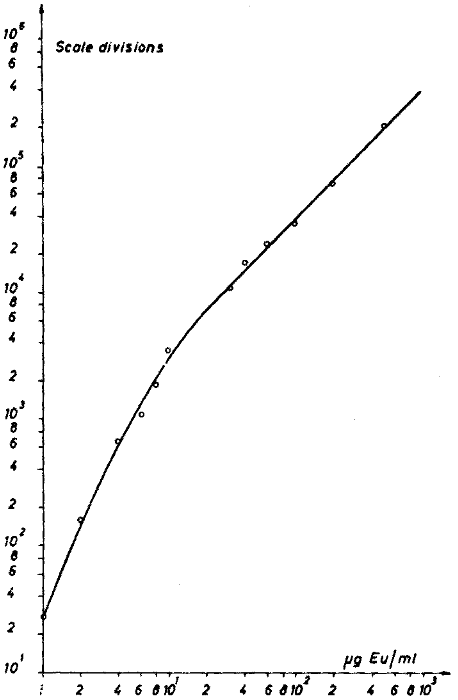

Fig. 1. Eu in 1 *M* LiI. Single cell operation.

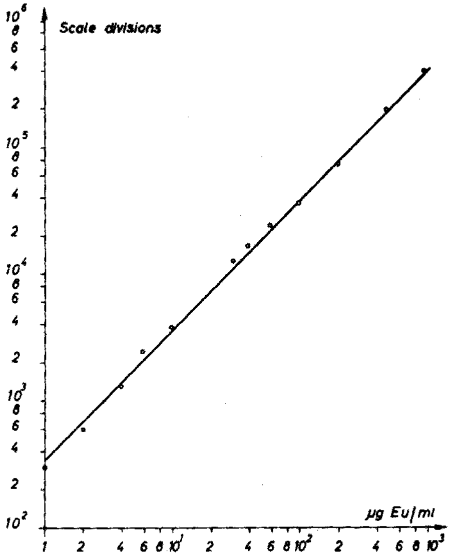

Fig. 2. Eu in 1 *M* LiI. Subtractive operation.

To reach about 2–3% reproducibility it was best to work in the linear range of the calibration graph above 10 μg Eu/ml and to make at least 5 measurements on separate cell fillings for each concentration. The peak potential of the measured peak, relative to a saturated calomel electrode[1,3] is -0.70 ± 0.01 V.

(b) Subtractive operation

Effects due to reagent blanks and impurities are compensated by opposing the signals obtained for a blank solution in cell 1 and the unknown solution in cell 2. The adjustment of capillaries was done according to the manual. Cadmium solutions were used for primary balancing.

Results. A series of standard solutions was measured by the subtractive technique (Table I). The fluctuations of the base line were the same as in the case of the single cell determination but were compensated because of the subtractive working. All other working conditions were as described in the case of the single cell operation.

The calibration graph is given in Fig. 2. This calibration graph was linear for concentrations from 1 to 1000 μg/ml, so that the reproducibilities cited before were improved and reproducibilities of 2–3% could also be obtained for concentrations below 10 μg Eu/ml.

(II) DETERMINATION OF Eu IN LiCl (1–100 μg Eu/ml)

Influence of LiCl electrolyte concentration

Figure 3 shows the influence of the electrolyte concentration on the peak height of the Eu polarograms.

Single cell operation

All working conditions were the same as in method Ia. Table II gives the values found for the standard solutions used in the measurements. Figure 4 shows the calibration graph for the standards analysed. The reproducibilities were still limited by the accuracy of the readings of the oscilloscope. Subtractive working increased this reproducibility only very slightly. The determination of small quantities of europium in lithium chloride was rather complicated because of the presence of impurities.

TABLE II

DETERMINATION OF Eu IN LiCl: SINGLE CELL OPERATION

μg Eu/ml	*Peak height*	*Peak height at maximum sensitivity*
98.9	70.2	28,100
59.3	70.0	17,500
39.6	74.0	11,100
19.8	56.5	5,650
9.9	82.5	3,300
5.9	59.5	1,487
3.96	62.3	934
1.98	52.7	527
0.99	20.7	51.7

(III) DETERMINATION OF Yb IN 0.1 *M* LiCl (1–50 μg Yb/ml)

Single cell operation

Calibration. All working conditions were as described in method Ia. Figure 5 shows the calibration graph obtained. Here also the reproducibility was limited by the accuracy of reading the oscilloscope. The peak potential of the measured peak, relative to a saturated calomel electrode was −1.52 V.

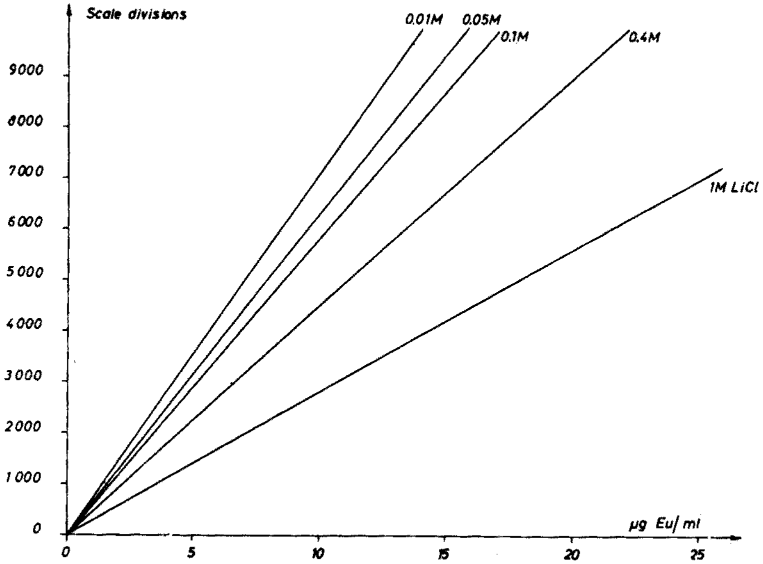

Fig. 3. Eu in LiCl. Influence of electrolyte concentration.

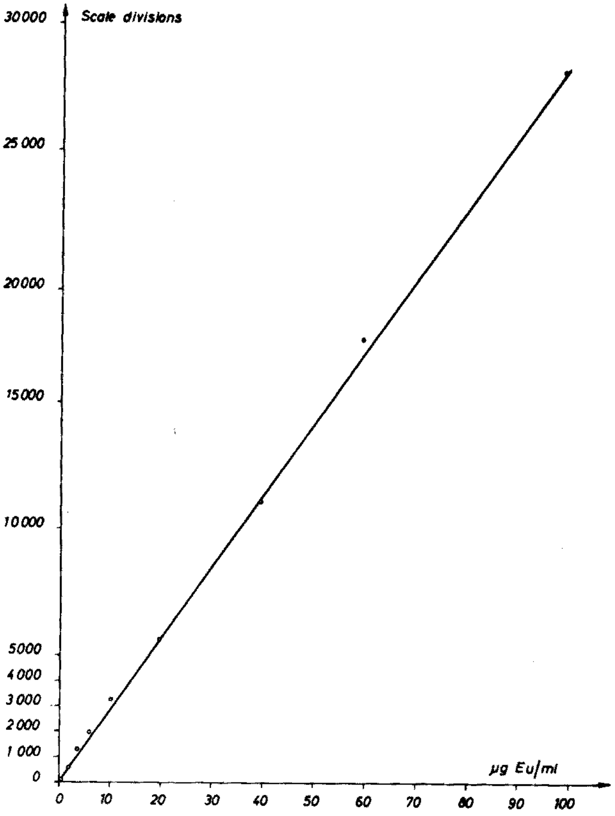

Fig. 4. Eu in 1 M LiCl. Single cell operation.

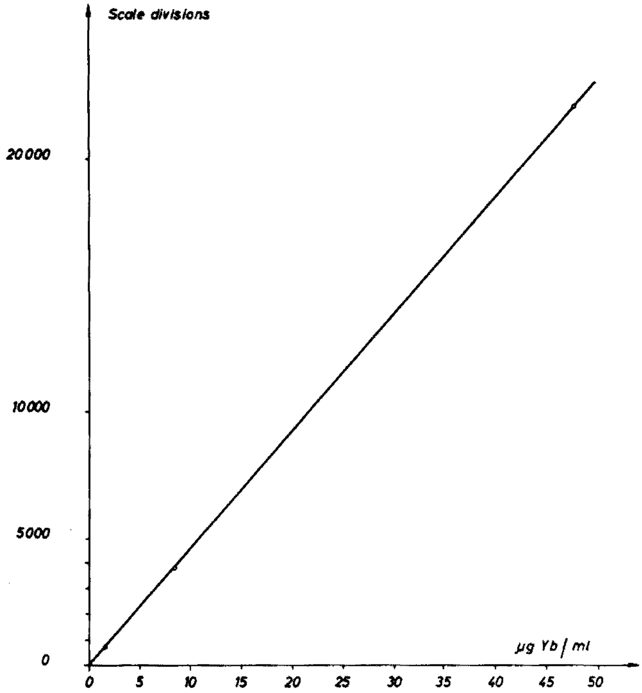

Fig. 5. Yb in 0.1 *M* LiCl. Single cell operation.

(IV) HIGH PRECISION COMPARATIVE ANALYSIS OF Eu IN 1 *M* LiCl

Stability of the base line

The reproducibility of comparative measurements depends largely on the deviations of the balance of the two cells to be compared[11,12]. A series of reproducibility tests was made each time with 10 pairs of cells containing the same solution (100 µg Eu/g). These measurements were made at different electronic settings of the instrument. In Table III the relative standard deviations are given for these measurements. All solutions cited in this paragraph were prepared by weighing.

TABLE III

REPRODUCIBILITY OF THE BALANCE

Amplification	*Relative standard deviation*[a]
1 × 4 × 10	0.12
1 × 2.5 × 10	0.10
1 × 1.5 × 10	0.07
1 × 1 × 10	0.08
1 × 6 × 1	0.07
1 × 4 × 1	0.10

[a] Calculated each time from 10 pairs of cells containing a solution of 107.2 µg Eu/g. The measurements were spread over 24 h.

For accurate and reproducible results it was essential that the start potential was maintained constant over a series of determinations; all measurements were made at a start potential of −0.45 V *vs.* Hg anode. The peak should always occur at the same spot of the X axis of the oscilloscope screen. In order to reach the maximum obtainable reproducibilities, it was of the greatest importance to recheck the exact setting of the whole instrument frequently with standards of suitable concentration. If the peak heights for these standards changed, either the settings of the mercury heights had to be changed or the values had to be corrected accordingly. For highest precision a complete standardisation had to be made frequently.

Range of applicability. The method was applicable for differences of 0.10–10 μg Eu/g in concentrations of two solutions containing 50–500 μg Eu/g. The best operational conditions prevailed if the reference solution had a concentration of 100–200 μg Eu/g.

Procedure

Degassing, balancing of capillaries and all other conditions of operating the instrument had to be carried out with the greatest care possible. The potential balance was rechecked before each reading. The height of the mercury columns was adjusted after and before each second measurement.

The standard and the unknown were filled into their respective cells. The standard was measured under single cell conditions to check the operation and standardisation of the equipment, and the difference between the two cells was measured. The peak height was read every 3 min until there were at least 10 values, the mean of which was used for further calculations. The peak height was corrected for possible existing changes of the peak height of the standard measurement in single cell mode. At least 10 such series were made for each point of the calibration curve as well as for the measurement of each unknown.

Results

Table IV contains the results of one such series of measurements. The calibration graph for this type of operation is given in Fig. 6. From this graph a mean factor of 0.00219 μg Eu/g/scale division was obtained; this factor was used to calculate unknown concentrations from measured scale divisions. Figure 7 shows an expanded portion of the calibration graph at very low europium concentrations. From the corrected peak heights at maximum sensitivity given in Table IV a mean value $\bar{x}=2.475/11=225$ was obtained with a standard deviation of $s=6.1$ and a relative standard deviation of $s/\bar{x}=2.7\%$.

The value $\bar{x}$ (from Table IV) multiplied by the above cited mean factor gave the difference in concentration between standard and unknown. The total concentration of the unknown was then obtained by adding or subtracting this difference in concentration to the concentration of the standard. Table V gives the values found by this method for concentrations of unknown Eu solutions containing ±100 μg Eu/ml.

DISCUSSION

Considerations about the comparative technique allow one to make the following generalisations.

TABLE IV

REPRODUCIBILITY MEASUREMENT FOR A COMPARATIVE DETERMINATION

Peak for the standard single cell	*Differential peak heights: readings*	*Differential peak height mean*	*Differential peak height at max. sensitivity*	*Corrected peak height at max. sensitivity*
87.0	64, 66, 64.5, 62, 62, 67, 70, 58, 64, 66, 64	64.3	257	222
86.0	62, 64.5, 66, 65, 65, 64.5, 63.5, 66, 63.5, 63, 63.5	64.2	257	224
86.0	65, 63, 65, 64.5, 66, 65, 63.5, 63, 65, 64.5, 65	64.5	258	225
85.0	64, 63, 61.5, 62, 63, 64, 62, 63, 62, 60, 64	62.6	250	221
85.0	63, 64, 65.5, 64.5, 65, 63.5, 64.5, 63, 63, 64.5	64.1	256	226
76.5	55.5, 54, 55.5, 56, 56, 57, 56, 55, 56, 54, 56	55.5	222	218
74.0	52, 53, 53.5, 53, 54, 52.5, 54, 52, 53, 52, 54	53.0	212	215
74.0	58, 57, 57.5, 58.5, 57, 56, 58.5, 59, 58, 56.5, 56	57.4	230	233
74.5	56, 58, 55, 57, 56, 58, 57.5, 55, 57.5, 54.5, 57	56.5	226	227
76.0	58.5, 57, 57.5, 59, 57, 56, 59, 58, 59.5, 58, 56	57.8	231	228
75.0	59, 60, 58, 58.5, 59, 60, 58, 59, 60, 58	58.9	236	236

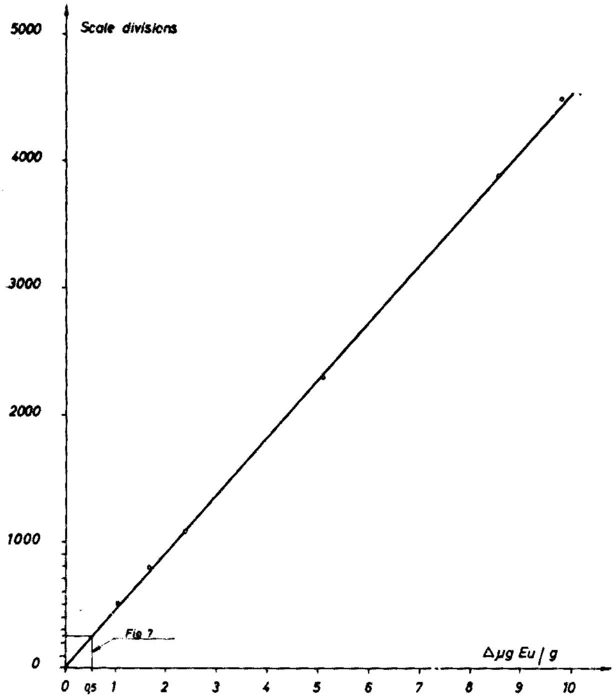

Fig. 6. Eu in 1 *M* LiCl. Comparative operation.

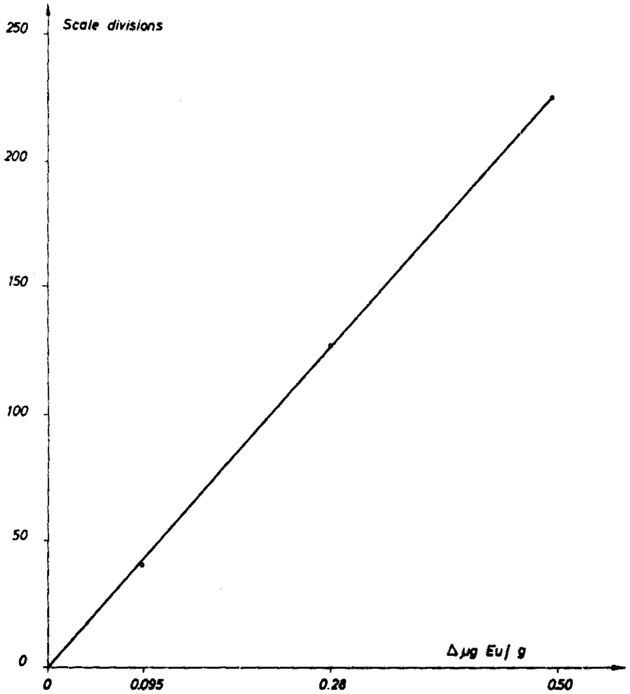

Fig. 7. Eu in 1 *M* LiCl. Comparative operation.

TABLE V

ANALYSIS OF UNKNOWN SAMPLES

Standard total concn. (μg Eu/g in cell 1)	*Calcd. total concn. (μg Eu/g in cell 2)*	*Found total concn. (μg Eu/g in cell 2)*	*Difference in concn.*		*Deviation from the calcd. value (μg Eu/g)*
			Calcd.	*Found*	
107.20	116.99	117.02	9.79	9.82	+0.03
107.20	115.72	115.70	8.52	8.50	−0.02
107.20	112.27	112.27	5.07	5.07	0.00
107.20	109.59	109.60	2.39	2.40	+0.01
107.20	108.86	108.92	1.66	1.72	+0.06
107.20	108.25	108.29	1.05	1.09	+0.04
107.20	107.71	107.69	0.51	0.49	−0.02
107.20	107.48	107.48	0.28	0.28	0.00
107.20	107.30	107.29	0.10	0.09	−0.01

In Fig. 8 the relative standard deviations for about 10 determinations on separate cell fillings of the same solutions are given for different concentrations of μg Eu/g, and for the differences in concentration *Δ* μg Eu/g (comparative technique). From these curves it can be seen that below 100 μg Eu/g the single cell method was about 10 times less reproducible than the comparative method.

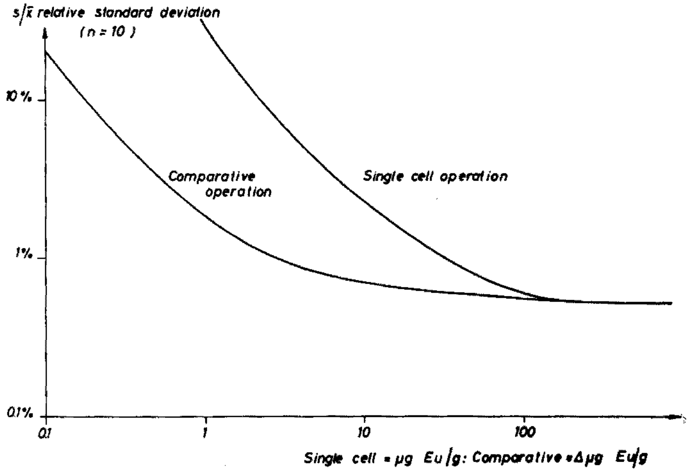

Fig. 8. Relative standard deviations for single cell and comparative techniques.

The comparative values for the analysis of unknowns proved that even for differences of about 0.1 μg Eu/g between the standard and the unknown solution, deviations from the assumed theoretical value were less than 10%. If these values are used for a calculation involving the total content of the unknown, *e.g.* 100 + difference measured (expressed in μg Eu/g), the overall reproducibility of the method can be represented by the curves given in Fig. 9. The ordinate shows the total content of the solutions used as standard, or as unknown (in μg Eu/g) and the abscissa shows the attainable relative standard deviation for measurements of 10 different cell fillings.

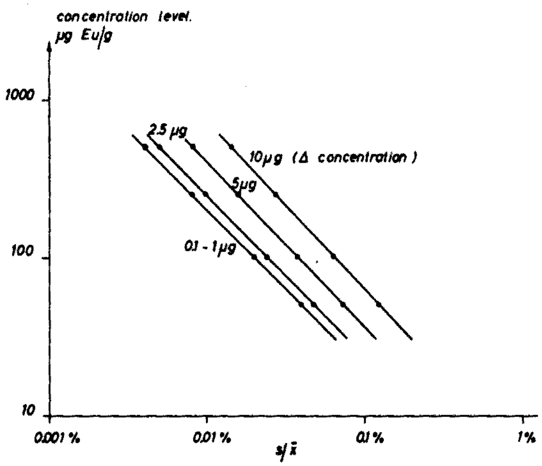

Fig. 9. Relative standard deviation attainable.

A straight line was obtained for each specific difference in concentration of the unknown and the standard and using this figure one can easily predict the reproducibilities that can be obtained for these specific differences in concentration at all concentration levels for which the method has been tested (50–500 µg Eu/g). It can be seen that overall precisions of better than 0.1% can be obtained.

The final accuracy of the method will, of course, depend on the accuracy with which the standard solutions can be prepared. The absolute value for the europium concentration of these standard solutions depends on our knowledge of the purity and stoichiometry of the europium compound used for the preparation. With very exact weighing techniques and with solely gravimetric techniques, final accuracies in preparing aliquots of the order of 0.01–0.001% can be achieved. All accuracies will therefore depend on the reliability of the values given for the europium content of the sample used for preparing the starting solution of the standard series.

We thank Mr. VAN BOUWEL for his valuable technical assistance.

SUMMARY

Differential polarographic determinations of the europium content of solutions of LiI and LiCl can be made within the concentration ranges of 50 to 500 µg Eu/g with varying precision. Comparative techniques can give precisions of the order of 0.1% or even better; the accuracy depends on the reference material used for the standardisation of the method.

RÉSUMÉ

Les auteurs ont effectué le dosage de l'europium (50 à 500 µg) dans des solutions de LiI et LiCl, par polarographie différentielle. Des techniques comparatives peuvent donner des précisions de l'ordre de 0.1 % ou même mieux. L'exactitude dépend du matériel de référence utilisé pour la standardisation de la méthode.

ZUSAMMENFASSUNG

Mit der Differentialpolarographie wurden Europiumgehalte von LiI- und LiCl-Lösungen im Konzentrationsbereich von 50–500 µg Eu/g mit variierender Genauigkeit bestimmt. Die Vergleichsanalyse ergibt Genauigkeiten in der Grössenordnung von 0.1% oder sogar besser. Die Richtigkeit hängt vom Vergleichsmaterial ab, das für die Eichung der Methode benutzt wurde.

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DETERMINATION OF NANOGRAM AMOUNTS OF CESIUM BY A CONCENTRATION-DEPENDENT DISTRIBUTION METHOD

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(Received March 1st, 1965)

The principle of the method of concentration-dependent distribution, some examples of its application in the literature and some calculated calibration curves were described in a previous paper[1]. The object of the work described here was to apply this method for the development of as sensitive a determination as possible for cesium by means of ^{137}Cs tracer. Only sorption systems were considered, because there are no suitable extraction reagents for cesium at low reagent concentrations, nor are there any satisfactory masking agents for cesium.

A suitable sorbent for the determination must satisfy the following requirements: (*1*) relatively high distribution coefficients K_d (amount of cesium in the sorbent: amount of cesium in the solution after sorption); (*2*) as low a capacity as possible; (*3*) selective sorption; (*4*) easy separation from the solution; (*5*) a reasonably short time of contact between the phases; (*6*) reproducible sorption values.

Compliance with points (*1*), (*3*) and (*6*) would clearly be achieved in systems where sorption is not a purely surface effect, but cesium is built into the crystal lattice of the sorbent, owing to its ionic dimensions. The use of very small sorbent amounts and fine granulation may ensure the fulfilment of conditions (*2*) and (*5*), but this would probably make satisfying conditions (*4*) and (*6*) more difficult. Accordingly, the method chosen was based on impregnating paper with a precipitate which was capable of sorbing cesium. Prussian blue was selected for the impregnation, since it sorbs cesium efficiently, forming mixed crystals[2,3]; moreover, sorption is relatively selective, the precipitate is only very slightly soluble, and its colour allows the quality of the impregnation to be judged visually.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. A carrier-free preparation of the fission product ^{137}Cs of Russian origin was used for tracing cesium.

Preparation of the sorbent

(*A*) A disc (diameter *ca.* 10 cm) of Schleicher Blue Band filter paper was immersed several times in a fresh solution of "colloidal" Prussian blue (1 part 0.010 M $FeCl_3$ in 0.01 N HCl and 30 parts 0.0010 M $K_4Fe(CN)_6$). The paper was immediately washed by submerging in a 5% sodium nitrate solution and dried in air. If the paper was homogeneously colored after drying, pieces of exactly the same area (9 × 15 mm) were cut out of the parts which had been in the same horizontal strips while drying.

(*B*) Pieces of the above-mentioned shape were cut from the filter paper. Exactly equal amounts of colloidal Prussian blue were transferred to the centre of each piece by a calibrated capillary (0.005–0.01 ml) and the paper was air-dried.

(*C*) A procedure similar to the preceding ones was followed, except that the Prussian blue spot was formed in the centre of paper discs 26 mm in diameter and a Prussian blue solution approximately 3 times diluted was used.

Procedure

A solution containing inactive cesium was labelled with ^{137}Cs of a negligible concentration, the pH was adjusted with an acetate buffer to 4.4, and sodium nitrate was added to give a final concentration of 0.40 *M*. The total volume of the aqueous phase was 1.5 ml. A type *A* or *B* sorbent was added and the solution was shaken for 1 h. Excess of solution was removed by sharp suction on a sintered glass filter, and the radioactivity of the paper, as well as that of the aqueous phase was measured. The value of α (% Cs on the paper /% Cs in solution) was then calculated.

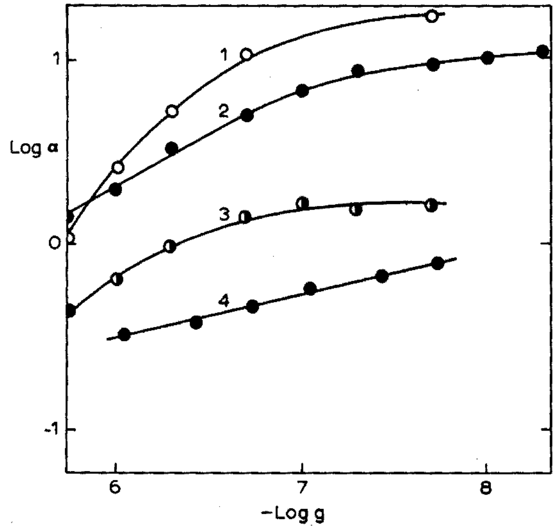
With the type *C* sorbent, 0.060 ml of the labelled cesium solution (pH 4.4) was placed exactly on the centre of the paper disc. All the liquid was dispersed by capillary forces within 1 min, wetting the whole disc area. After the paper had been dried, the centre part of the disc containing the Prussian blue, was cut out and its activity, as well as that of the remaining ring, was measured. The ratio of both activities *r* was then evaluated.

RESULTS AND DISCUSSION

Typical calibration curves obtained with a 1.5-ml volume of aqueous phase are shown in Fig. 1; curves obtained with a volume of 0.06 ml are given in Fig. 2. The Figs. indicate that the results are sufficiently reproducible for these curves to be used as calibration graphs for the determination. A comparison of Figs. 1 and 2 shows that the method with sorbent *C* is more sensitive; a concentration of $3 \cdot 10^{-7}$ *M* Cs could be readily detected in this way, corresponding to $2 \cdot 10^{-9}$ g Cs. Similar sensitivity by other methods is only achieved with activation analysis, which, however, requires incomparably more expensive equipment; moreover, activation analysis poses very great difficulties in determining cesium which is already radioactive, *e.g.* in determining the amount of the carrier in "carrier-free" radioactive preparations.

The corresponding sorption isotherms are shown in Fig. 3. It can be seen that the sorbent is never saturated with cesium, but sorption can be expressed satisfactorily (in the range which allows the determination) by Freundlich's isotherm with a value of *n* close to 2. Therefore, the proposed method does not involve the isolation of equal amounts (the "substoichiometric principle").

The left-hand side of the isotherm is a straight line, indicating the validity of Henry's law in the region of the lowest concentrations. The decrease of K_d values with increasing cesium concentration in such a wide concentration range (validity of Freundlich's isotherm) is probably caused by the existence of sorption sites with various affinities for cesium sorption. When the sites with the greatest affinity for cesium are filled, further ions are sorbed on less favourable sites, and the K_d value



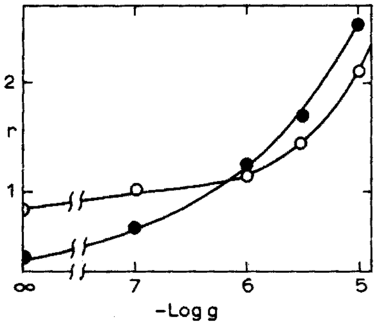
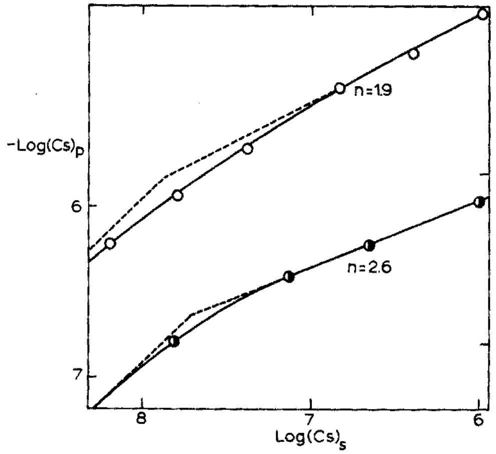


Fig. 1. Dependence of α on the amount of cesium carrier added. g, concentration of inactive cesium in 1.5 ml (moles/l); 1,3 = sorbent A; 1,2 = sorbent used immediately after drying; 2,4 = sorbent B; 3,4 = sorbent used 10 days after drying.

Fig. 2. Dependence of r on the amount of cesium carrier added. g, concentration of inactive cesium in 0.06 ml (moles/l); ○ = impregnation with fresh Prussian blue solution; ● = impregnation with solution aged for 3 days.



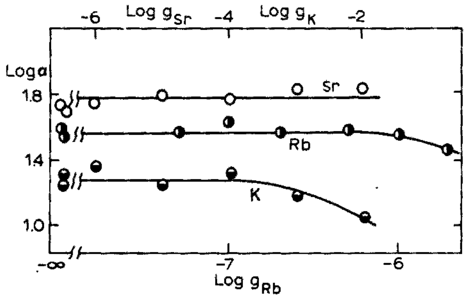


Fig. 3. Typical sorption isotherms. $[Cs]_p$ = amount of cesium sorbed; $[Cs]_s$ = equilibrium cesium concentration in the aqueous phase (moles/l); ○ = sorbent A; ◑ = sorbent B.

Fig. 4. Influence of salts on the values of α. g_{Me}, concentration of contaminant in 1.5 ml (moles/l) Sorbent A.

decreases, although the sorbent capacity is far from exhausted. The affinity towards cesium clearly involves thermodynamic, as well as kinetic, factors.

The isotherms mentioned are only formal in that they do not correspond to the actual equilibrium; if shaking is continued, sorption may be further increased.

Such prolonged shaking, however, causes a marked deterioration in the reproducibility of the results for cesium. This can probably be explained by changes undergone by the sorbent with time (partial dissolution, or mechanical liberation of Prussian blue).

In order to test the selectivity of the determination, the influence of some ions on the α and r values was studied. The results for the 2 methods of determination are given in Figs. 4 and 5. As might have been expected, the selectivity of the determination was satisfactory. Sodium (present in the determination as the buffer and as $NaNO_3$) did not interfere at ratios, with respect to cesium, of about $10^5:1$, calcium at $10^6:1$, strontium at $10^5:1$, potassium at $100:1$ and rubidium at $50:1$.

The precision of the determination was also studied. Four independent calibration curves were used to determine the cesium content in a synthetic sample. It was found for a type *A* sorbent, that when 0.2 μg Cs was determined the standard deviation of an individual determination was 20%; when an amount of 0.02 μg was determined, the mean of 4 determinations had to be taken to achieve the same precision. When amounts of 0.008 μg were determined by means of sorbent *C*, the standard deviation of the average value of 3 determinations was ±40%. It was also found that an increase in the rubidium content, in the concentration range where it did not lower the sorption of cesium, had an unfavourable effect on the reproducibility of the experiments (Fig. 5).

The method was applied to determine the contamination of a radioactive ^{137}Cs preparation ("carrier-free") by a carrier. The principle of this determination was described earlier[1]. The dependence of α (or r) on the amount of inactive cesium added in a known concentration, and on the amount of radioisotope used was investigated. A comparison of these 2 relationships allowed the determination in question to be achieved by means of the equation:

$$k \cdot a_1 + g_1 = a_2 \cdot k$$

relating to the 2 points of the 2 curves which have equal α values. In this equation,

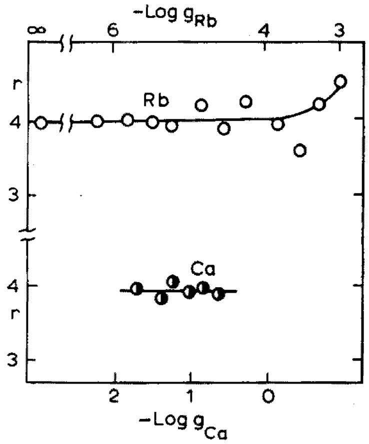


Fig. 5. Influence of salts on the values of r. g_{Me}, concentration of contaminant in 0.06 ml (moles/l) Sorbent *C*; "Ca", synthetic contaminants solution (Rb:K:Ca = $1:10^3:2\cdot10^4$).

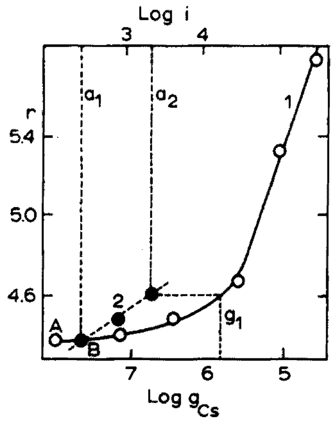


Fig. 6. Determination of specific activity. g_{Cs}, concentration of inactive cesium added in 0.06 ml (moles/l); *i*, cesium radioactivity in the given sorption experiment (counts/min). 1 r = f(log g_{Cs}); 2 r = f(log i).

k denotes the required quantity (weight of the element corresponding to a unit of the recorded radioactivity); the subscript 1 denotes values on the curve showing α *vs.* the amount of inactive cesium added (g); the subscript 2 denotes the values on the curve showing α *vs.* the amount of radioactivity added; and a indicates the overall radioactivity present at a given distribution (counts/min for the given manner of measuring).

A typical determination is illustrated in Fig. 6. The determination was repeated 3 times, and a mean value of specific activity of $1/k = (0.4 \pm 0.15) \cdot 10^6$ counts/min/μg Cs was found. It is interesting to compare this value (which may be regarded rather as the lower limit with respect to the possible decrease of cesium sorption by other effects) and the value theoretically calculated for ^{137}Cs on the assumption that the preparation is absolutely free of inactive cesium and that the total efficiency in recording the radioactivity is 1%. A theoretical (maximum) specific activity of $1/k_{\text{th}} = 1.92 \cdot 10^6$ counts/min/μg ^{137}Cs is readily found by means of known equations. From this point of view the value of $1/k$ which was obtained in practice appears quite acceptable. It is probably impossible completely to avoid contamination of the preparation with inactive cesium in isolating ^{137}Cs from other fission products. However, the actual specific activity differs from the maximum attainable value by less than one order of magnitude, which can be regarded as satisfactory for most radiochemical studies.

The method described is suitable for checking the specific activity of cesium preparations in any radiochemical laboratory, because of its speed and experimental simplicity. An erroneous determination would be possible, however, if the cesium salt added contained large amounts of rubidium. If there is any suspicion of such contamination, rubidium should be determined spectroscopically. This determination is more sensitive than that of cesium, and the permissible rubidium concentration in the radiochemical method exceeds by several orders of magnitude the concentrations of cesium determined. Accordingly, if the rubidium content is known, in case of interference, calibration curves may be constructed in the presence of corresponding concentrations of rubidium salts.

SUMMARY

Paper impregnated with Prussian blue sorbs cesium in low concentration to a different extent if varying initial concentrations of cesium are present. This dependence can be employed for the determination of submicrogram amounts of cesium. The selectivity and precision of the method are discussed. The method is applied to the determination of specific activity in "carrier-free" ^{137}Cs samples.

RÉSUMÉ

Les auteurs proposent une méthode pour le dosage du césium, en faible quantité (de l'ordre du nanogramme), à l'aide d'un papier imprégné de bleu de Prusse. La sélectivité et la précision de ce procédé sont examinées. Cette méthode est appliquée à la détermination de l'activité spécifique d'échantillons de ^{137}Cs, sans traceur.

ZUSAMMENFASSUNG

Mit Berliner Blau imprägniertes Papier sorbiert geringe Konzentrationen

Cäsium in verschiedenem Ausmass, wenn unterschiedliche Anfangskonzentrationen des Cäsiums vorliegen. Diese Abhängigkeit kann zur Bestimmung von Submikromengen Cäsium verwendet werden. Die Selektivität und Genauigkeit der Methode wird diskutiert. Die Methode wird zur Bestimmung spezifischer Aktivitäten trägerfreier ^{137}Cs-Proben angewendet.

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Anal. Chim. Acta, 33 (1965) 481–486

COMPLEX FORMATION THERMODYNAMICS OF SOME METAL(II) PHENYL-2-PYRIDYLKETOXIMATES*

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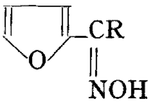
(Received March 29th, 1965)

The purpose of this research program was to study the structure of chelates and the thermodynamics of formation of chelates with ligands of very similar intramolecular environment as is represented by structures I–IV.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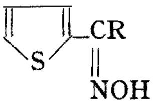
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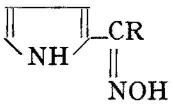
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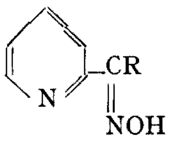
IV

R = H, or an alkyl group, or an aryl group.

This paper describes the thermodynamic formation constants, free energy, enthalpy and entropy of formation of a number of chelates with the ligand phenyl-2-pyridylketoxime (IV, R = phenyl).

Chelate formation was studied potentiometrically in a solvent 40% by weight of acetone and 60% by weight of water (hereafter this mixed solvent will be referred to as 40% acetone system). The use of mixed aqueous–organic solvent was found necessary in order to keep the metal phenyl-2-pyridylketoximates in solution. For a number of reasons acetone was deliberately selected as the organic component of the mixed solvent system. First there is considerable structural similarity between acetone and water, secondly the dielectric constant (approximately 20 at moderate temperatures) of acetone is comparatively high among the organic solvents. The 40% acetone system has a dielectric constant approximately 42. Barring any chemical interaction, the medium effect in such a system will be much smaller than in, say, water–dioxane system of comparable composition. In this work we have assumed the infinitely dilute solution in 40% acetone system as the thermodynamic reference state. Therefore, the values of chelate formation thermodynamics reported in this paper will have to be corrected by a quantity which corresponds to the transfer of a mole of the chelate from the infinitely dilute aqueous solution to the infinitely dilute 40% acetone system. The nature of this correction has been discussed elsewhere[1,2]. In order to apply these

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* Taken from the Ph.D. dissertation of DAVID C. SHUMAN. Presented at the 20th Southwest Regional Meeting of the American Chemical Society, December 3–5, 1964, at Shreveport, Louisiana.
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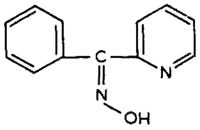
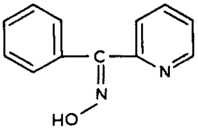
corrections, the complex formation thermodynamics in infinitely dilute mixed solvent system, and the primary and the secondary medium effects must be known.

In a subsequent publication we intend to demonstrate the computational technique of applying these corrections. Work is under way in our laboratory to determine the primary and the secondary medium effects of various mixed solvent systems.

Phenyl-2-pyridylketoxime (*PPK*). TSCHITSCHIBABIN[3] first observed the two stereoisomers of phenyl-2-pyridylketoxime:

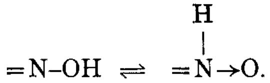


anti- m.p. 165–167°



syn- m.p. 150–152°

The correct assignment of the configuration was first made by HUNTRESS AND WALKER[3]. The reactivity of the syn-form towards metals has been ascribed to the nitrone function which has been assumed to exist in tautomeric equilibrium[4],



$$=\text{N–OH} \rightleftharpoons =\overset{\text{H}}{\overset{|}{\text{N}}}\rightarrow\text{O}.$$

Phenyl-2-pyridylketoxime reacts with several metals to form colored chelates which are soluble in several organic solvents. Methods for spectrophotometric determination of a number of metals have been developed[5–7].

EXPERIMENTAL

syn-Phenyl-2-pyridylketoxime was prepared by a variation of the method described by DIEHL AND SMITH[4]. Hydroxylamine hydrochloride (150 g) dissolved in 200 ml of water was added to 350 ml of an ethanolic (95%) solution of benzoylpyridine (200 g). To the above mixture was then slowly added a hot solution of sodium hydroxide (100 g) dissolved in 200 ml of water. The magenta colored solution* was refluxed for 1 h on a steam bath and then cooled to room temperature. A mixture of *anti*- and *syn*-isomers separated out on lowering the pH by the addition of dry ice. The precipitate was allowed to stand for several hours at room temperature, and then filtered, washed and dried at room temperature. The lower melting isomer (*syn*-) was retrieved by crystallization from chloroform. The crude product was purified by repeated crystallization from ethanol. The pure product had a melting point range 150–152°. *syn*-Phenyl-2-pyridylketoxime is unstable towards light and heat, but is indefinitely stable when stored in a brown bottle and kept in a refrigerator.

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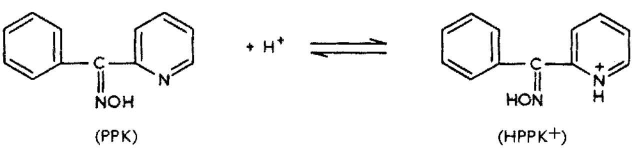
* We have noticed in the literature that the production of the magenta color at this stage is observed not only during the preparation of phenyl-2-pyridylketoxime but also during the preparation of other R-2-pyridylketoximes. The color has been attributed to the presence of iron as impurity. In our case, only benzoylpyridine contained any detectable amount of iron. The intensity of the magenta color was much higher than that which could be attributed to iron alone.

Glass electrode correction

The necessity of using mixed solvent required the determination of glass electrode corrections for the entire range of pH and ionic strength of experimental interest. A Beckman pH-meter, model G, with a Beckman general purpose electrode (No. 4990-80) and a saturated calomel electrode (S.C.E.) was standardized against 0.05 M solution of potassium acid phthalate in water (pH = 4.01) at 25°. pH meter readings at small intervals, covering the pH range 2–12 were taken. Each such reading was taken at ionic strengths 0.025 M, 0.05 M, 0.075 M and 0.100 M and at temperatures 20°, 30° and 40°. The solvent was 40% acetone system. The EMF of the hydrogen electrode *vs.* the same S.C.E. using each of the above solutions was also measured. The hydrogen electrode was designed after HILLS AND IVES[8]. The EMF values, after correcting for junction potential, were converted to pH. The pH meter readings were then corrected on the basis of pH values calculated from EMF measurements. The values of junction potential were taken from BATES[9]. It was shown in an earlier communication[2] that the junction potential due to the interface of aqueous phase and mixed solvent phase is without any consequence in this procedure of calibration. Further, the junction potential attributable to two solvent interfaces is most probably negligible because of the fairly high dielectric constant of the 40% acetone system. The solutions for the glass electrode calibration were prepared as follows: a 0.010 M perchloric acid solution in 40% acetone and an appropriate amount of neutral salt ($NaClO_4$) in order to obtain the proper ionic strength, were placed in a specially designed titration cell. The solution was then saturated with ultra-pure hydrogen (Matheson Co.). Before introducing into the titration cell, hydrogen was passed through "Deoxo" catalyst and a bubbler containing 40% acetone. The pH of the solution was varied by adding small increments of sodium hydroxide solution in 40% acetone. The ionic strength of the sodium hydroxide solution was the same as that of the perchloric acid solution; therefore, there was no change of ionic strength during titration.

Protonation constant of phenyl-2-pyridylketoxime

Phenyl-2-pyridylketoxime is a weak base due to the pyridyl nitrogen and it is extensively protonated at low pH.



By definition

$$K_{NH} = \frac{(PPK)\,(H^+)}{(HPPK^+)} \qquad (1)$$

It is essential to know the value of K_{NH} at the relevant ionic strengths in order to be able to calculate the formation constants of the chelates. Two solutions were prepared, solution B, containing a known amount of standard perchloric acid and solution A, containing the same amount of acid and a known amount of phenyl-2-pyridylketoxime. The hydrogen ion concentrations of the two solutions were measured and were designated as (H_i^+) and (H_f^+). All solutions were prepared with 40% acetone, but ionic strengths and temperatures were varied. The protonation constant K_{NH} was calculated as follows:

T_{PPK} = total analytical concentration of phenyl-2-pyridylketoxime
(H_i^+) = hydrogen ion concentration of the system before the addition of PPK (solution B)
(H_f^+) = hydrogen ion concentration of the system after the addition of PPK (solution A)
$(HPPK^+)$ = concentration of the protonated base
$= (H_i^+) - (H_f^+)$ (2)
(PPK) = concentration of the base
$= T_{PPK} - (HPPK^+)$
$= T_{PPK} - [(H_i^+) - (H_f^+)]$ (3)

Substitution of (2) and (3) into (1) yields

$$K_{NH} = \frac{[T_{PPK} - \{(H_i^+) - (H_f^+)\}](H_f^+)}{(H_i^+) - (H_f^+)}$$

Dividing throughout by (H_f^+) gives

$$K_{NH} = \frac{T_{PPK} - \{(H_i^+) - (H_f^+)\}}{\dfrac{(H_i^+)}{(H_f^+)} - 1} \tag{4}$$

All quantities except K_{NH} in eqn. (4) are either known or measurable, hence K_{NH} can be evaluated. Table I summarizes the values of K_{NH}.

TABLE I

IONIZATION CONSTANT (K_{NH}) OF PROTONATED PHENYL-2-PYRIDYLKETOXIME

Ionic strength (M)	K_{NH} $(\cdot 10^4)$ 20°	30°	40°
0.100	14.5	11.3	9.7
0.075	14.4	10.8	9.4
0.050	14.3	10.1	8.7
0.025	14.2	9.3	7.4
0.000	14.0	7.3	5.3

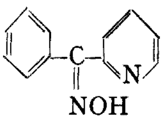
Phenyl-2-pyridylketoxime behaves as a weak acid in basic solution due to the process:

$$>C{=}NOH \rightleftharpoons C{=}NO^- + H^+$$

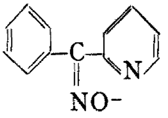
The ionization constant K_a, of this process is given by

$$K_a = \frac{(H^+)(A^-)}{(HA)} \tag{5}$$

where HA =



A⁻ =



The ionization constant K_a, was determined by measuring the hydrogen ion concentration of the half neutralized acid at relevant ionic strengths and temperatures. Again all measurements were made in the 40% acetone system. The values of K_a are given in Table II.

TABLE II

IONIZATION CONSTANT (K_a) OF PHENYL-2-PYRIDYLKETOXIME

Ionic strength (M)	$K_a \cdot 10^{13}$		
	20°	*30°*	*40°*
0.100	6.52	12.90	24.60
0.075	6.20	12.00	22.30
0.050	5.90	10.90	20.40
0.000	4.47	7.20	13.50

Formation constants

CALVIN AND MELCHIOR's titration technique[10] was used to measure the extent of complex formation. Progressive complex formation was followed by measuring the pH with the calibrated glass electrode. Computation of formation constants from experimental data was performed by using BJERRUM's method[11,12].

TABLE III

NICKEL(II)-PPK FORMATION CONSTANTS

Ionic strength (M)	*∞ dil.*	*0.025*	*0.050*	*0.075*	*0.100*
Temp. = 30°					
Log K_1	9.21	9.15	8.90	8.81	8.75
Log K_2	7.05	7.00	6.70	6.61	6.52
Log K_{ov}[a]	16.30	16.15	15.60	15.45	15.28
Log $(K_1^0 \cdot K_2^0)$[b]	16.26				
Temp. = 40°					
Log K_1	9.10	9.00	8.70	8.62	8.52
Log K_2	7.03	6.95	6.66	6.54	6.45
Log K_{ov}	16.03	15.85	15.35	15.15	14.98
Log $(K_1^0 \cdot K_2^0)$	16.13				

[a] K_{ov} is the value directly obtained from the degree of formation curve[11,12].
[b] K_n^0 refer to the value of K_n at infinite dilution obtained by extrapolation.

Details of titration technique, titration vessel and preparation of solution were described in an earlier communication[2]. However, the solvent used in the present work was 40% acetone.

The shape of the titration curves and the formation curves were normal and are not reproduced. Tables III–VII summarize the results. Plots of log K^0 *vs.* $1/T$ were straight lines, and in the case of mercury the plots had negative slopes making ΔH^0 for the formation of mercury(II) chelates positive. The ΔF^0 and ΔS^0 values are given in Table VIII. The values of ΔH^0 are given in Table IX. The method of computation of these thermodynamic quantities is too well known to require any elaboration. The subscripts and superscripts used in these Tables are self-explanatory.

TABLE IV

ZINC(II)–PPK FORMATION CONSTANTS

Ionic strength (M)	*∝ dil.*	*0.025*	*0.050*	*0.075*	*0.100*
Temp. = *20°*					
Log K_1	8.44	8.40	8.20	8.15	8.11
Log K_2	6.90	6.86	6.75	6.70	6.66
Log K_{ov}	15.37	15.25	14.98	14.89	14.78
Log $(K_1^0 \cdot K_2^0)$	15.34				
Temp. = *30°*					
Log K_1	8.40	8.34	8.15	8.08	8.04
Log K_2	6.95	6.89	6.70	6.66	6.62
Log K_{ov}	15.30	15.23	14.90	14.79	14.72
Log $(K_1^0 \cdot K_2^0)$	15.35				
Temp. = *40°*					
Log K_1	8.14	8.08	7.91	7.85	7.78
Log K_2	6.92	6.85	6.70	6.63	6.58
Log K_{ov}	15.04	14.95	14.64	14.50	14.48
Log $(K_1^0 \cdot K_2^0)$	15.06				

TABLE V

CADMIUM(II)–PPK FORMATION CONSTANTS

Ionic strength (M)	*∝ dil.*	*0.025*	*0.050*	*0.075*	*0.100*
Temp. = *20°*					
Log K_1	7.24	7.20	7.14	7.11	7.08
Log K_2	6.65	6.64	6.60	6.56	6.55
Log K_{ov}	13.84	13.80	13.72	13.70	13.66
Log $(K_1^0 \cdot K_2^0)$	13.89				
Temp. = *30°*					
Log K_1	6.95	6.92	6.84	6.82	6.80
Log K_2	6.44	6.42	6.38	6.35	6.34
Log K_{ov}	13.38	13.34	13.25	13.22	13.20
Log $(K_1^0 \cdot K_2^0)$	13.39				
Temp. = *40°*					
Log K_1	6.65	6.62	6.54	6.53	6.50
Log K_2	6.45	6.40	6.33	6.31	6.30
Log K_{ov}	13.00	12.98	12.90	12.89	12.86
Log $(K_1^0 \cdot K_2^0)$	13.10				

TABLE VI

MERCURY(II)–PPK FORMATION CONSTANTS

Ionic strength (M)	*∝ dil.*	*0.025*	*0.050*	*0.075*	*0.100*
Temp. = *20°*					
Log K_1	9.80	9.74	9.52	9.44	9.40
Log K_2	7.12	7.15	6.94	6.90	6.88
Log K_{ov}	16.90	16.80	16.46	16.36	16.30
Log $(K_1^0 \cdot K_2^0)$	16.92				
Temp. = *30°*					
Log K_1	10.12	10.06	9.84	9.78	9.74
Log K_2	7.40	7.36	7.20	7.20	7.12
Log K_{ov}	17.92	17.88	17.70	17.64	17.60
Log $(K_1^0 \cdot K_2^0)$	17.54				
Temp. = *40°*					
Log K_1	10.44	10.38	10.16	10.10	10.00
Log K_2	8.04	8.00	7.82	7.78	7.72
Log K_{ov}	18.50	18.44	18.20	18.10	18.04
Log $(K_1^0 \cdot K_2^0)$	18.48				

TABLE VII

LEAD(II)–PPK FORMATION CONSTANTS

Ionic strength (M)	*∝ dil.*	*0.025*	*0.050*	*0.075*	*0.100*
Temp. = *20°*					
Log K_1	7.74	7.72	7.68	7.66	7.65
Log K_2	7.20	7.18	7.10	7.07	7.04
Log K_{ov}	14.95	14.90	14.75	14.70	14.65
Log $(K_1^0 \cdot K_2^0)$	14.94				
Temp. = *30°*					
Log K_1	7.52	7.50	7.47	7.45	7.43
Log K_2	7.11	7.08	7.01	6.98	6.96
Log K_{ov}	14.70	14.65	14.46	14.41	14.35
Log $(K_1^0 \cdot K_2^0)$	14.63				
Temp. = *40°*					
Log K_1	7.41	7.39	7.33	7.30	7.29
Log K_2	7.01	6.97	6.90	6.88	6.85
Log K_{ov}	14.40	14.35	14.20	14.15	14.10
Log $(K_1^0 \cdot K_2^0)$	14.41				

DISCUSSION

Because of experimental difficulties, the formation constants for all metals of the first transition series could not be determined. The manganese(II) chelate was insoluble even in pure acetone. The copper(II), cobalt(II) and iron(II) chelates were too stable and complex formation was virtually complete even at a very low pH. Consequently their complex formation could not be followed by the present technique. Nickel(II) chelate at 20° and platinum(II) and paladium(II) chelates at all temperatures precipitated too early in the titration.

The order of stability of the metal chelates studied deserves some comments. Published data[13] on the stability of the chelates of Ni(II), Zn(II), Pb(II), Cd(II), with ligands containing similar functional groups, such as α,α'-dipyridyl, dimethyl-

TABLE VIII

THERMODYNAMIC VALUES OF FORMATION OF METAL PHENYL-2-PYRIDYLKETOXIMATES AT DIFFERENT TEMPERATURES

	Ni(II)	*Zn(II)*	*Cd(II)*	*Hg(II)*	*Pb(II)*
At 20°					
Log K_1^0	—	8.44	7.24	9.80	7.74
Log K_2^0	—	6.90	6.65	7.12	7.20
Calcd. log K^0 [a]	—	15.34	13.89	16.92	14.94
Exptl. log K^0 [b]	—	15.37	13.84	16.80	19.95
$-\Delta F_1^0$, kcal/mole	—	11.25	9.66	13.07	10.32
$-\Delta F_2^0$	—	9.20	8.87	9.50	9.60
—Calcd. ΔF^0	—	20.45	18.53	22.57	19.92
—Exptl. ΔF^0	—	20.50	18.46	22.54	19.94
ΔS_1^0, e.u.	—	16.83	−9.28	high positive	11.52
ΔS_2^0	—	29.16	15.88	high positive	19.07
Calcd. ΔS^0	—	45.99	6.60	high positive	30.59
Exptl. ΔS^0	—	46.14	2.79	high positive	28.53
At 30°					
Log K_1^0	9.21	8.40	6.95	10.12	7.52
Log K_2^0	7.05	6.95	6.44	7.40	7.11
Calcd. log K^0	16.26	15.35	13.39	17.52	14.63
Exptl. log K^0	16.30	15.30	13.38	17.88	14.70
$-\Delta F_1^0$, kcal/mole	12.77	11.65	9.64	14.04	10.43
$-\Delta F_2^0$	9.78	9.64	8.93	10.26	9.86
—Calcd. ΔF^0	22.55	21.29	18.57	24.30	20.29
—Exptl. ΔF^0	22.61	21.22	18.56	24.85	20.39
ΔS_1^0, e.u.	33.47	17.12	−8.80	high positive	11.20
ΔS_2^0	29.95	28.83	15.14	high positive	18.78
Calcd. ΔS^0	63.42	45.95	6.34	high positive	29.98
Exptl. ΔS^0	54.20	45.72	2.94	high positive	28.29
At 40°					
Log K_1^0	9.10	8.14	6.65	10.44	7.41
Log K_2^0	7.03	6.92	6.45	8.04	7.01
Calcd. log K^0	16.13	15.06	13.10	18.48	14.42
Exptl. log K^0	16.03	15.04	13.00	18.44	14.40
$-\Delta F_1^0$, kcal/mole	13.04	11.66	9.53	14.96	10.62
$-\Delta F_2^0$	10.07	9.91	9.24	11.52	10.04
—Calcd. ΔF^0	23.11	21.57	18.77	26.48	20.66
—Exptl. ΔF^0	22.97	21.55	18.63	26.50	20.63
ΔS_1^0, e.u.	34.23	17.10	−9.12	high positive	11.77
ΔS_2^0	30.78	29.60	16.78	high positive	19.30
Calcd. ΔS^0	55.01	46.70	7.66	high positive	31.07
Exptl. ΔS^0	55.19	46.64	3.16	high positive	28.97

[a] Calcd. $X^0 = X_1^0 + X_2^0$.

[b] Exptl. X^0 is computed from exptl. K^0. Exptl. K^0 is the value of K_{0v} at infinite dilution obtained by extrapolation (*cf.* Tables III–VII).

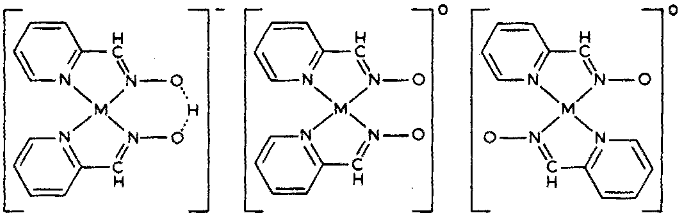
TABLE IX

STANDARD ENTHALPY OF FORMATION OF METAL PHENYL-2-PYRIDYLKETOXIMATES

	Ni(II)	*Zn(II)*	*Cd(II)*	*Hg(II)*	*Pb(II)*
$-\Delta H_1^0$, kcal/mole	2.31	6.30	12.39	high negative	6.93
$-\Delta H_2^0$	0.42	0.63	4.20	high negative	3.99
—Calcd. ΔH^0	2.73	6.93	16.59	high negative	10.92
—Exptl. ΔH^0	5.67	6.93	17.64	high negative	11.55

glyoxime, 1,10-phenanthroline and 8-hydroxyquinoline indicate the order of stability Ni > Zn > Pb > Cd. This is also the order of stability of phenyl-2-pyridylketoximates. The unusual stability of Hg(II)–PPK is consistent with other chelates of mercury(II)[14]. IRVING AND WILLIAMS[15] have attributed this characteristic of mercury(II) chelates to the "soft" polarizable outer shell. The chelate formation of mercury(II) appeared to be entropy-driven.

The generalization that the chelates of oxime have nitrone structure was based largely on the proof that this was the structure of nickel dimethylglyoximate or very closely related chelates[16]. The nitrone structure seemed reasonable since only the *syn*-oxime was reactive[3]. It has been assumed by FEIGL[16] and DIEHL AND SMITH[4], because the oxygen of *syn*-oxime is not in a position to form an oxygen–metal bond. We believe that the proposed structure of phenyl-2-pyridylketoximates requires further experimental evidence. The stability of five-membered rings is usually characterized by saturation, *i.e.*, absence of double bonds. The stability of the unsaturated five-membered ring in nickel dimethylglyoximate may be largely due to the 2 six-membered rings formed through hydrogen bonding. Recently LIU AND LIU[17] postulated the following five-membered rings for pyridine-2-aldoxime complexes of Cu(II), Pd(II) and Pt(II).



Such a structure is also possible for phenyl-2-pyridylketoximates. However, it would seem that such a structure would render these complexes sparingly soluble in non-polar solvents, except in the case of the *trans* isomer; but this is not the case at least with the phenyl-2-pyridylketoximates.

We believe that the existence of a nitrogen–metal bond in all oximates has not been conclusively proved. Nitrogen–metal bonding is not typical for oximates. In β-furfuraldoximates, the metal is bound to the oxygen. There are certain indications that metal might be bound to the oxygen in phenyl-2-pyridylketoximates. X-ray and IR data should be revealing and we intend to carry out studies with these techniques. However, if it is shown that the oxygen–metal bond exists, a mechanism will be required to explain the *syn-* → *anti*-isomerization of phenylketoxime. The extreme stability of the iron and cobalt complexes might be attributed to oxidation to the trivalent state. The values of the chelate formation entropies for the mercury(II) chelate computed from our experimental data turned out to be incredibly high (positive). For this reason these values were not included in the Tables. One explanation is possible polymerization. The chelate formation was also endothermic. The only conclusion that can be safely made regarding mercury(II) is that the ligation is entropy-driven.

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SUMMARY

The formation of phenyl-2-pyridylketoximates of nickel(II), zinc(II), cadmium(II), mercury(II) and lead(II) was studied potentiometrically in a medium of 40% (w/w) acetone and 60% (w/w) water. The values of step formation constants, free energy, entropy and enthalpy of complex formation were calculated. The formation of the mercury chelate was found to be entropy driven. The formation of phenyl-2-pyridylketoximates of other metals of the first transitional series could not be studied owing to experimental difficulties.

RÉSUMÉ

Les auteurs ont examiné la formation de phényl-2-pyridylcétoximates de nickel, zinc, cadmium, mercure(II) et plomb, par potentiométrie, en milieu acétone (40%)-eau (60%). On a calculé les valeurs des constantes de formation, énergie libre, entropie et enthalpie. La formation de phényl-2-pyridylcétoximates d'autres métaux de transition n'a pas pu être étudiée, en raison de difficultés expérimentales.

ZUSAMMENFASSUNG

Es wurde die Bildung von Phenyl-2-pyridylketoximaten von Nickel(II), Zink(II), Cadmium(II), Quecksilber(II) und Blei(II) in einem Medium aus 40 Gew. % Aceton und 60 Gew. % Wasser potentiometrisch untersucht. Die Werte für die Bildungskonstanten der einzelnen Stufen, der freien Energie, Entropie und Enthalpie der Komplexbildung wurden berechnet. Die Bildung von Phenyl-2-pyridylketoximaten anderer Metalle der ersten Übergangsreihe konnten wegen experimenteller Schwierigkeiten nicht untersucht werden.

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SPECTROGRAPHIC DETERMINATION OF ULTRAMICRO AMOUNTS OF BORON IN HIGH-PURITY SILICON TETRACHLORIDE AND TRICHLOROSILANE

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Several methods have been reported for the determination of traces of boron in silicon tetrachloride. However, effective methods sensitive enough for determining boron down to 0.01 p.p.b. are still lacking. MIYAMOTO[1] first concentrated boron by N,N-dimethylaniline as a complexing agent, and then determined 1 p.p.b. level of boron spectrophotometrically with curcumin as colour reagent. VELEKAR AND MEHALCHICK[2] attempted to determine ultramicro amounts of boron ranging from 0.8 to 50 p.p.b. in silicon tetrachloride spectrochemically after concentration of boron into silicic acid formed by a partial hydrolysis of the sample with methyl cyanide solution. HASS *et al.*[3] also developed a colorimetric procedure for up to 2000 p.p.b. of boron in silicon tetrachloride using quinalizarin. Recently PEHELINTSEVA *et al.*[4] have reported a spectrographic method for the determination of boron, down to 4 p.p.b., in which boron was preliminarily concentrated by complexing with triphenylchloromethane which forms a stable coordination compound with boron trichloride[5]. However, their method was limited to the use of a small sample size (8 ml) to which 2 mg of triphenylchloromethane was added as the collecting agent. The use of increasing amounts of the reagent for larger amounts of the sample to increase the sensitivity, results in liberation of large quantities of organic carbon during the subsequent arcing process in an argon chamber; this hinders the transmittance of emitted light through the quartz window, makes the excitation quite unstable and hence lowers the spectrochemical sensitivity of boron.

Because of the increasing requirements for the extreme purity for silicon tetrachloride or trichlorosilane, we have developed a combined chemical–spectrographic method for determining boron, down to 0.06 p.p.b. of boron; this is a satisfactory sensitivity for semiconductor analysis. The method consists of complexing boron with triphenylchloromethane, removal of excess of silicon tetrachloride by evaporation, hydrolysis of the complex by sodium hydroxide solution to remove the resulting carbinol, and improved spectrographic excitation of the liberated boric acid. Because of the inclusion of the hydrolysis step, substantially larger quantities of sample can be handled and extreme sensitivity is obtained without any difficulty in the subsequent spectrographic analysis.

EXPERIMENTAL

Reagents

Triphenylchloromethane (TPCM), slightly yellow crystalline powder, b.p. 230–235°/20 mm, analytical grade.

All chemicals were of analytical grade, unless otherwise mentioned. Boron was not detected in any of these reagents by the spectrographic method with the amounts used for the present study.

Procedure

Place up to 500 g of sample in a 500-ml quartz beaker. Add 100 mg of TPCM and mix. Let stand 30 min in a cool place. Evaporate off excess $SiCl_4$ on an oil bath heated to 90–100°. Add 5 ml of 0.1 M sodium hydroxide solution to the residue and rinse the wall of the vessel with a small amount of water. Filter through a small filter paper placed on a quartz weighing bottle, without using a funnel. Wash the filter paper with a small amount of water. All the work above must be carried out in an air-tight glove box through which a continuous slow flow of pure nitrogen gas is supplied. Add 100 mg of a 1:1 mixture of carbon powder and Sb_2O_3 to the filtrate and evaporate to dryness. Pack the residue into a graphite electrode and arc in an argon atmosphere; the detailed excitation conditions and equipment are given in Table I.

TABLE I

EXCITATION CONDITION AND EQUIPMENTS

Excitation source	330-V Se rectifier with 30-A maximum d.c. current output. A high-frequency igniter and series resistance to control the arc
Working current	17 A
Pre-exposure period	None
Exposure period	60 sec
Spectrograph	R. Fuess Model 110-H Four quartz spectrograph
Spectral region	2300–2850 Å
Dispersion	Reciprocal linear dispersion 2.3 Å/mm for 2500 Å region
Slit illumination	Intermediate image system
Filter	6 step
Electrode system	High-purity graphite rods, 6.15 mm diam. Lower electrode: cupped 8 mm deep with wall thickness 1.0 mm. Upper electrode: sharp end to a 90° cone. Analytical gap, 3 mm
Slit	30 μ
Intensity recorder	Rigakudenki comparater microphotometer Type CM-1A
Emulsion	Fuji process type
Development	4–6 min at 20° in Fuji FD-131
Argon chamber	A conventional type: argon flow-rate 5 l/min

Preparation of standard samples

Place less than 1000 ml of high-purity silicon tetrachloride in a 1000-ml quartz volumetric flask, and add 0.65 ml of boron bromide from a 1-ml syringe (graduated at 0.02-ml intervals), inserting the injection needle into the silicon tetrachloride. Dilute to the mark with silicon tetrachloride; 1 g of this liquid contains 50 μg of boron. Dilute further with silicon tetrachloride to obtain a solution which contains

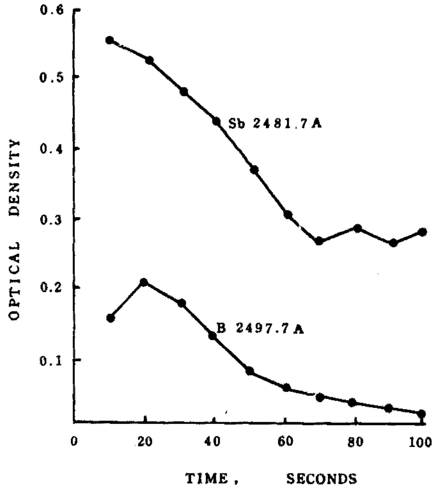
0.05 μg B/g. Take aliquots containing 0.05, 0.15, 0.20, 0.30, 0.50, 1.50, and 2.50 μg B, respectively, place in quartz beakers and treat as described in the procedure. All the above work must be carried out in the inert atmosphere.

Preparation of analytical curve

Transmittances were measured on a recording microphotometer Rigakudenki, CM-1A type, for an analysis line pair of B I 2497.7 Å and Sb I 2481.7 Å. Background corrections were made and values were converted to intensities on a calibration curve previously constructed by a two-step method[6]. The relative intensity ratio B I 2497.7 Å/Sb I 2481.7 Å *vs.* micrograms of boron was plotted on logarithmic paper. The analytical curve thus obtained was linear over the concentration range 0.03 μg–2.50 μg B.

RESULTS AND DISCUSSION

To obtain the highest sensitivity for the spectrographic determination of boron, it is of prime importance to select a suitable matrix material for boron. For this purpose a number of metal oxides, metal salts and carbon were checked. Of these, the most effective was found to be a 1 : 1 mixture of carbon and antimony trioxide. A detection limit of 0.25 μg B was obtained when carbon was used as a matrix material, while a 1 : 1 mixture of carbon and antimony trioxide gave a sensitivity limit of 0.03 μg B. When antimony trioxide was used without any carbon, the sensitivity was further extended down to 0.01 μg B, but poor reproducibility resulted. The antimony line Sb 2481.7 Å served as a good internal standard line. Plate moving techniques showed that antimony behaved like boron in its volatilization trend during the exposure period 0–100 sec (Fig. 1).



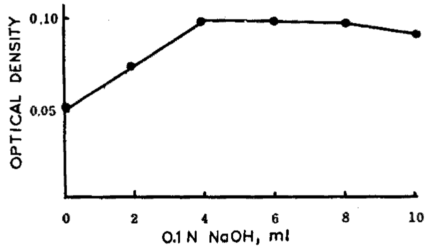


Fig. 1. Volatilization of boron and antimony during excitation.

Fig. 2. Effect of added amounts of triphenylchloromethane on the recovery of boron from silicon tetrachloride.

The amount of TPCM to be added to the sample was of primary importance to obtain good recovery of boron from silicon tetrachloride. To give a quantitative recovery of boron, at least 50 mg of TPCM had to be added to each 500 g of silicon tetrachloride as shown in Fig. 2. However, the use of a large excess of TPCM had to be avoided, because hydrochloric acid liberated through the hydrolysis of TPCM reacted with sodium hydroxide to give sodium chloride which seriously lowered the spectrographic sensitivity of boron. The quantity of sodium hydroxide to neutralize hydrochloric acid was rather critical. Insufficient quantities of sodium hydroxide resulted in free hydrochloric acid which reacted with boric acid to give volatile boron trichloride during the evaporation process. Excess of sodium hydroxide, just like sodium chloride, lowered the temperature of the arc and so decreased the spectral sensitivity for boron. In Fig. 3 the variation of the intensity of B I 2497.7 Å is plotted against the varying amounts of sodium hydroxide solution for each 100 mg of TPCM used. Although approximately 4 ml of sodium hydroxide solution is theoretically sufficient to hydrolyse 100 mg of TPCM, somewhat larger quantities of sodium hydroxide solution were required to obtain good sensitivity.

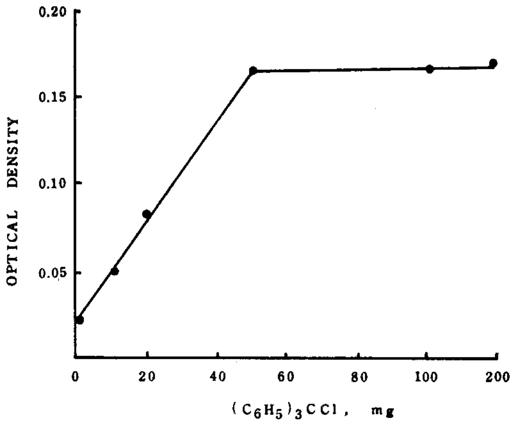


Fig. 3. Effect of added amount of sodium hydroxide on the intensity of boron.

In the procedure above, the best sensitivity attainable was 0.03 μg B, which corresponds to 0.06 p.p.b. B on the basis of a 500-g sample. When the excitation was carried out in an air atmosphere, the sensitivity figure altered to 0.16 p.p.b. on the same basis of sample size.

To check any inaccuracy, another series of independent standard samples was prepared, which consisted of 1:1 carbon–antimony trioxide matrices containing varying amounts of boron as sodium borate. A series of spiked standards was then analysed for boron by the procedure given above. The results based on the independently prepared analytical curve are shown in Table II. As can be seen, the agreement between values calculated and those found was good. Consequently, one can conveniently use the borate-based analytical curve for determining boron in silicon tetrachloride. The results also gave an indication of the accuracy of the present

TABLE II

RELIABILITY OF A SERIES OF SPIKED STANDARDS FOR BORON

Standard (g)	*Boron (µg)*				
	Added	*Found*			*(Average)*
0.5	0.03	0.04	0.03	0.03	(0.03)
1.0	0.06	0.06	0.07	0.08	(0.07)
2.0	0.13	0.17	0.12	0.11	(0.13)
5.0	0.32	0.29	0.29	0.32	(0.30)
10.0	0.63	0.63	0.55	—	(0.59)

TABLE III

DETERMINATION OF BORON IN SILICON TETRACHLORIDE AND TRICHLOROSILANE

Sample taken (g)		*Boron (µg)*				
		Added	*Found*		*(Average)*	*Net*
$SiCl_4$	500	—	0.15	0.15	(0.15)	—
	500	0.15	0.30			0.15
	500	0.30	0.45			0.30
$SiCl_4$	500	—	0.07	0.07	(0.07)	—
	500	0.07	0.14			0.07
	500	0.15	0.23			0.16
$SiHCl_3$	500	—	0.06	0.06	(0.06)	—
	500	0.03	0.10	0.09	(0.10)	0.04
	500	0.06	0.15	0.18	(0.17)	0.11
	500	0.32	0.40	0.35	(0.38)	0.32
	500	0.63	0.70	0.62	(0.66)	0.60
$SiHCl_3$	500	—	0.85	0.85	(0.85)	—
	500	0.50	1.35	1.40	(1.38)	0.53
	500	1.00	1.85	1.85	(1.85)	1.00

procedure. In Table III several duplicate determinations of boron in actual samples are quoted, along with the results for addition tests on the basis of a 500-g sample. Agreement between duplicate determinations was good and satisfactory recoveries of added boron from 500-g samples were also achieved.

In the present method the chances of introducing a boron blank from reagent chemicals were kept to a minimum, because the least number, and smallest amounts, of reagents possible were used to concentrate boron from large quantities of sample. In addition, the use of the spectrographic technique excluded the possibility of introducing further contamination of boron.

Thanks are due to Professor HIROSHI HAMAGUCHI of the University of Tokyo, Dr. ROKURO KURODA of Tokyo Kyoiku University, and to Mr. RYOKICHI NEGISHI of the Industrial Research Institute of Kanagawa Prefecture.

SUMMARY

A new sensitive method is proposed for the determination of boron in high-purity silicon tetrachloride and trichlorosilane. The method consists of complexing boron with triphenylchloromethane, removal of excess silicon tetrachloride, hydrolysis of the complex, and improved spectrographic excitation of liberated boric acid.

The best sensitivity attainable is 0.03 µg B, which corresponds to 0.06 p.p.b. B for a 500-g sample.

RÉSUMÉ

Une nouvelle méthode sensible est proposée pour le dosage du bore dans du tétrachlorure de silicium et du trichlorosilane de grande pureté. Elle consiste à complexer le bore au moyen de triphénylchlorométhane, à éliminer l'excès de tétrachlorure de silicium, à hydrolyser le complexe et à procéder à un dosage spectrographique de l'acide borique. La meilleure sensibilité est de 0.03 µg B, correspondant à 0.06 p.p.b. B pour un échantillon de 500 g.

ZUSAMMENFASSUNG

Es wird eine neue empfindliche spektrographische Methode zur Bestimmung von Bor in hochreinem Siliciumtetrachlorid und Trichlorsilan vorgeschlagen. Die Methode beruht auf der Komplexbildung des Bors mit Triphenylchlormethan, Beseitigung des Überschusses an Siliciumtetrachlorid, Hydrolyse des Komplexes und einer verbesserten spektrographischen Anregung der freien Borsäure. Die grösste Empfindlichkeit lag bei 0.03 µg B, das entspricht 0.06 p.p.b. B in einer Probe von 500 g.

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APPLICATION DE LA METHODE POLAROVOLTRIQUE

INTERPRÉTATION DU DOSAGE DE L'ACIDE MALÉIQUE PAR DES BASES ORGANIQUES EN MILIEU N,N-DIMÉTHYLFORMAMIDE

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De nombreuses méthodes peuvent être mises en œuvre pour les dosages du type acide–base. En particulier, dans le cas de titrages de monoacides ou de diacides organiques, en solution dans des solvants non aqueux et par l'emploi de réactifs basiques, différentes techniques de complexité plus ou moins grande sont connues.

Parmi les méthodes les plus souvent employées, nous signalerons celle de la conductimétrie[1-3], la méthode aux indicateurs colorés[4-9], la méthode potentiométrique de mesure de pH, qui est la plus utilisée[10-22], et enfin la méthode de haute fréquence qui a également suscité dans ce domaine quelques applications[23-26].

A notre connaissance, très peu d'auteurs utilisent dans ces types de dosages les propriétés des systèmes d'électrodes bimétalliques polarisées[27], dont l'application ne présente pourtant aucune difficulté, si ce n'est l'interprétation des formes de courbes de dosages.

La courbe de titrage obtenue au moyen d'un couple d'électrodes de platine polarisées, est en effet plus complexe que celle obtenue en potentiométrie classique par mesure de pH.

Dans un cas on mesure des variations de potentiel qui ont pour origine des phénomènes d'oxydo-réduction d'entités diverses, alors que dans le dernier cas le potentiel de l'électrode de verre indicatrice ne dépend que de l'activité des ions H^+.

Ceci explique qu'une courbe polarovoltrique de neutralisation d'un diacide organique par un réactif basique puisse présenter au voisinage de chaque acidité, des variations de potentiel de signes opposés, contrairement à une courbe acidimétrique de pH où le potentiel varie toujours dans le même sens.

Aussi, afin de donner une interprétation de ces résultats expérimentaux, nous avons choisi d'étudier la courbe de dosage de l'acide maléique par une base organique, ce qui nous a conduit à analyser le réseau voltammétrique de cet acide pour différentes valeurs du degré d'avancement Z de la réaction de neutralisation (Z est égal au rapport de la concentration de solution titrante versée à la concentration de corps à titrer).

Les déductions tirées de cette étude permettront par la suite d'analyser et de classer en plusieurs types les courbes de dosages d'autres diacides organiques obtenues dans les mêmes conditions opératoires.

INTERPRÉTATION DE LA COURBE DE DOSAGE DE L'ACIDE MALÉIQUE PAR LE TRACÉ DES COURBES VOLTAMMÉTRIQUES $I = f(E)$

Les courbes courant-tension dans le N,N-diméthylformamide (DMF) sont obtenues à l'aide d'un montage à 3 électrodes.

L'électrode de travail, dont on mesure le potentiel par rapport à une électrode de référence Ag–AgCl modifiée, est une électrode tournante filiforme, alors que l'électrode auxiliaire est constituée par une grille cylindrique fixe de platine, coaxiale à l'électrode tournante et de très grande surface par rapport à l'électrode à fil.

L'exploration préalable des courbes voltammétriques de l'acide maléique au cours de la réaction de neutralisation par une base, montre que les variations de potentiel se produisent tour à tour en zone cathodique pour $0 < Z < 1$, et en zone anodique pour $Z > 1$. Ceci nous permet alors de diviser l'étude du réseau des courbes de neutralisation en 2 parties complémentaires: d'une part les courbes de réduction de l'acide maléique $0 < Z < 1$ et d'autre part les courbes d'oxydation pour $Z > 1$.

(a) Courbes cathodiques de l'acide maléique neutralisé par l'hydroxyde de tétrabutylammonium (TBA-OH) pour $0 < Z < 1$

Nous avons représenté sur la Fig. 1 les courbes de réduction de l'acide maléique

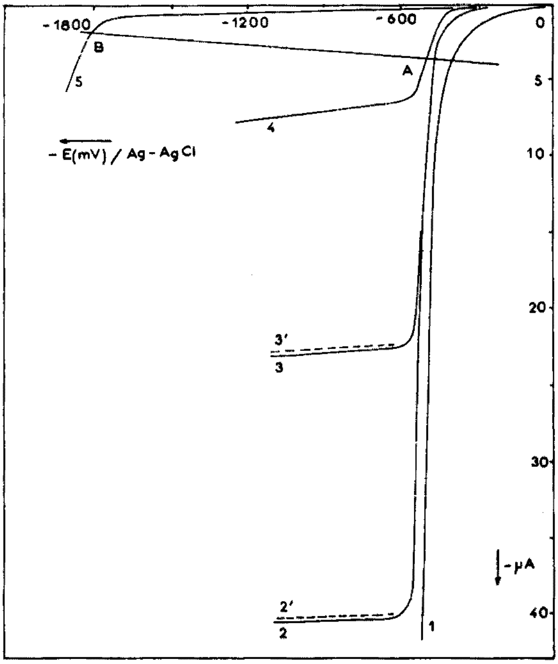


Fig. 1. Courbes de réduction voltammétriques de l'acide maléique au cours de sa demi-neutralisation par le réactif TBA-OH. Solvant, 40 ml DMF + $NaClO_4$ 0.5 N; titrant, TBA-OH 0.1 N; concentrations d'acide maléique: $C_1 = 4.74 \cdot 10^{-3}\,N$; $C_2 = 3.74 \cdot 10^{-3}\,N$ (C_1 + 0.4 ml TBA-OH); $C_3 = 3.24 \cdot 10^{-3}N$ (C_1 + 0.6 ml TBA-OH); $C_4 = 2.74 \cdot 10^{-3}N$ (C_1 + 0.8 ml TBA-OH); $C_5 = 2.35 \cdot 10^{-3}N$ (C_1 + 0.96 ml TBA-OH); les courbes 2' et 3' représentent la reproductibilité des électrodes de platine par rapport aux courbes 2 et 3.

à divers degrés d'avancement de la réaction de neutralisation par le réactif TBA-OH.

La courbe 1 représente l'acide maléique à la concentration $4.7 \cdot 10^{-3}$ N dans le DMF et en présence de $NaClO_4$ 0.5 N.

Les courbes 2, 3 et 4 représentent la disparition progressive de l'acide, neutralisé par TBA-OH, et montrent ainsi la proportionnalité entre la hauteur du palier du courant limite et la quantité d'acide qui reste en solution.

La neutralisation de la première acidité, c'est à dire $Z = 1/2$, est représentée par la courbe 5, qui n'est autre que la courbe de réduction du solvant, située à -1800 mV, alors que la courbe de réduction de l'acide a un potentiel de 1/2 vague de -480 mV.

Pendant toute la durée d'addition du réactif correspondant à la neutralisation de la deuxième acidité ($1/2 < Z < 1$), aucune vague de réduction n'apparaît, de même par ailleurs qu'aucune vague d'oxydation nouvelle. Le potentiel de l'électrode tournante est déterminé par la courbe de réduction du solvant.

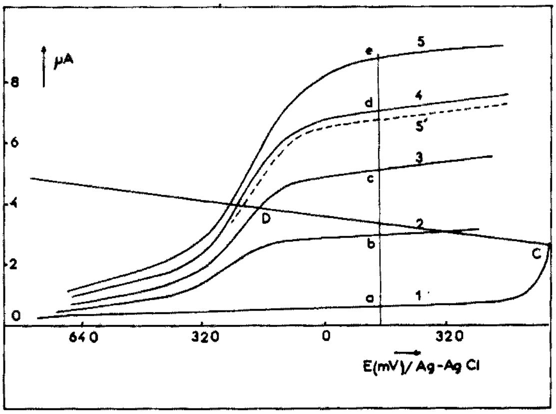
(b) Courbes anodiques du titrant méthylate de sodium en présence de perchlorate de tétrabutylammonium

Nous avons indiqué précédemment qu'il n'y a pas de variation de potentiel anodique tant que $Z < 1$, c'est à dire tant que les deux acidités ne sont pas entièrement neutralisées. Le domaine anodique est alors limité à $+600$ mV par la courbe d'oxydation du solvant.

Pour $Z > 1$ nous avons en solution un excès de réactif, du perchlorate de sodium et un sel d'acide organique.

Le domaine cathodique reste inchangé tandis qu'apparaît une nouvelle vague anodique ayant pour origine l'oxydation électrochimique de la solution titrante.

Lorsque celle-ci est le TBA-OH, les courbes voltammétriques d'oxydation en présence de $NaClO_4$ 0.5 N ont peu de signification.



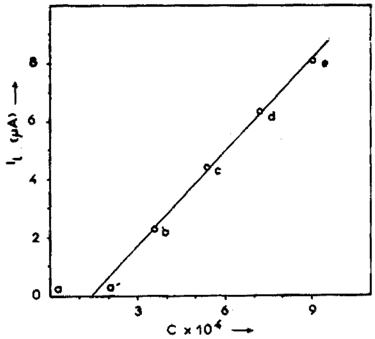


Fig. 2. Courbes voltammétriques d'oxydation du méthylate de sodium. Solvant, 40 ml DMF + $N(Et)_4ClO_4$ 0.4N; concentrations de méthylate de sodium: $C_1 = 0$; $C_2 = 3.6 \cdot 10^{-4}$ N; $C_3 = 5.4 \cdot 10^{-4} N$; $C_4 = 7.2 \cdot 10^{-4} N$; $C_5 = 9.0 \cdot 10^{-4} N$. La courbe 5' est la courbe de reproductibilité obtenue 10 min après l'obtention du tracé de la courbe 5.

Fig. 3. Variation du courant limite du réactif MeONa en fonction de sa concentration. Les points a,b,c,d et e ont été obtenus à partir du réseau de la Fig. 2. Le point a' représente la concentration en impuretés acides du solvant.

En effet, le tracé de chacune de ces courbes exige une durée de 5 à 6 min, or le réactif est instable dans le DMF et se décompose dans les mêmes intervalles de temps, si bien qu'on n'observe pas de proportionnalité entre la hauteur du palier du courant limite et la concentration de la base ajoutée.

Aussi nous avons préféré remplacer ce réseau par celui des courbes d'oxydation du méthylate de sodium (MeONa) en présence de perchlorate de tétraéthylammonium. Ce dernier réactif est en effet moins instable que le TBA-OH et donne sensiblement les mêmes valeurs du potentiel de 1/2 vague (—180 mV par rapport à l'électrode de référence utilisée précédemment).

Les courbes voltammétriques de la Fig. 2, obtenues pour diverses concentrations de méthylate de sodium et en l'absence de sel d'acide maléique, montrent une bonne proportionnalité entre l'intensité du courant limite et la concentration du réactif.

Cependant, la droite de la Fig. 3 (I_1 en fonction de C_{MeONa}), obtenue à partir du réseau de la Fig. 2, montre qu'une quantité de MeONa équivalente à $1.5 \cdot 10^{-4}$ N, est nécessaire pour neutraliser les impuretés acides du solvant, ce qui explique que cette droite ne passe pas par l'origine.

En résumé, à la neutralisation des 2 acidités, pour $Z=1$, ce qui équivaut ici à la courbe 1 ($\mathrm{DMF}+\mathrm{N(Et)_4ClO_4}$), nous sommes limités en zone anodique par l'oxydation du solvant à +600 mV.

Pour $Z > 1$ c'est la vague d'oxydation du réactif, représentée par les courbes 2, 3 et 4 qui détermine le potentiel de l'anode, dont le potentiel de 1/2 vague est alors égal à —180 mV.

Ces dernières indications jointes aux précédentes permettent alors de donner une interprétation de la courbe de dosage polarovoltrique de l'acide maléique.

(c) Identification des différentes variations de potentiel. Notation symbolique

Les renseignements obtenus par l'étude des réseaux précédents des courbes voltammétriques $I=\mathrm{f}(E)$, ne sont valables que pour l'électrode tournante de platine. Au cours d'un dosage, les deux électrodes dissymétriques deviennent tour à tour indicatrices.

La déduction rigoureuse de la courbe de dosage ne peut être faite qu'au moyen du tracé des réseaux $I=\mathrm{f}(V)$ ou $V=\mathrm{f}(U)$, obtenus directement entre les deux électrodes indicatrices, et dont nous avons montré l'application sur des cas particuliers dans l'article précédent[28].

Cependant dans le cas présent nous savons que pour $0<Z<1$ la cathode est indicatrice alors que l'anode se comporte comme une référence, et que pour $Z > 1$ c'est l'inverse qui se produit. Cette particularité permet alors une utilisation simple du réseau précédent.

La tension aux électrodes V est en effet égale à E_A-E_C+rI, où E_A et E_C représentent respectivement les potentiels de l'anode et de la cathode, et r la résistance de la solution. Celle-ci est inférieure à 100 ohms, ce qui nous permet de négliger le terme rI pour les faibles valeurs de l'intensité, et d'écrire plus simplement $V=E_A-E_C$.

Dans les conditions d'emploi du polarovoltmètre standard, où la tension U appliquée aux électrodes est égale à 3 V, la résistance extérieure égale à 0.5 mégohm, et pour un dosage où la cathode est électrode tournante, la première variation de potentiel est alors représentée sur la Fig. 1 par la projection sur l'axe des tensions du segment AB. Ce segment correspond à l'intersection de la droite $U-E_A=\Delta(-E_C)+R\Delta I$ (valable pour $0<Z<1$), et des courbes 4 et 5 de la Fig. 1.

Le point figuratif du dosage effectue donc la transition du point A au point B, sur la droite précédemment définie. Ceci correspond, avec les valeurs indiquées sur la Fig. 1, à un saut de potentiel de 1200 à 1300 mV, que nous retrouvons sur la courbe de la Fig. 4, pour $Z=1/2$.

Cette première variation de potentiel est d'ailleurs indépendante de la base utilisée, car elle ne fait intervenir que la courbe cathodique du solvant et celle des ions H^+ (ou des protons solvatés SH^+) de la première acidité.

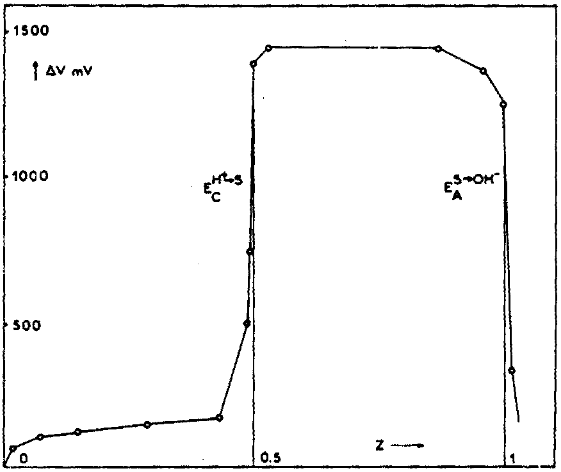


Fig. 4. Courbe de dosage polarovoltrique de l'acide maléique par le réactif MeONa 0.1 *N*. Solvant, 40 ml DMF + $NaClO_4$ 0.5 *N*; la cathode est une électrode tournante de platine, l'anode est une électrode fixe de grande surface en platine irridié.

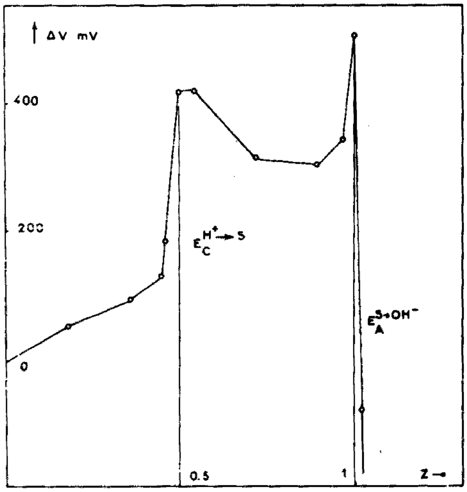


Fig. 5. Courbe de dosage polarovoltrique de l'acide maléique par le réactif MeONa 0.1 *N*. Solvant 40 ml DMF + $NaClO_4$ 0.5 *N*; les polarités des électrodes sont opposées à celles de la Fig. 4.

Aussi nous proposons pour cette variation de potentiel la notation symbolique $E_C{}^{H^+ \to S}$, pour rappeler que c'est la cathode C qui est indicatrice, et que le saut de potentiel E_C est dû au passage des courbes de réduction des ions H^+ à celle du solvant S.

Pour la deuxième variation de potentiel correspondant à $Z > 1$, nous considérons cette fois le dosage de la Fig. 5 où l'anode est l'électrode tournante.

En supposant que le potentiel de la cathode reste constant, la droite de résistance précédente devient:

$$U + E_C = \Delta(E_A) + R\Delta I$$

et le saut de potentiel est alors représenté par la projection sur l'axe de tensions du segment CD, soit par une valeur de 700 à 800 mV (Fig. 2).

Cette dernière variation de potentiel, notée symboliquement $E_A{}^{S \to OH^-}$, est donc provoquée par le passage du potentiel de l'anode de la courbe d'oxydation du solvant à celle du réactif titrant.

(d) Remarques sur la stabilité de la solution titrante. Conséquences sur les courbes de dosage

Nous avons indiqué dans le paragraphe (*b*) que la stabilité des réactifs est faible dans le DMF, et se traduit par une mauvaise reproductibilité de la partie anodique des courbes voltammétriques.

Ceci n'intéresse cependant que la partie du dosage correspondant à $Z > 1$, car pour $Z < 1$, la base étant neutralisée par le diacide, sa stabilité n'intervient pas, comme le montrent les courbes de reproductibilité 2′ et 3′ de la Fig. 1.

Le réseau tracé représente donc un cas idéal. Il reste cependant valable, car les mesures de la tension V, pour $Z > 1$ sont faites rapidement, et il est peu vraisemblable que le réactif ait le temps de se décomposer. Les valeurs de potentiel obtenues pour le signal $E_A{}^{S \to OH^-}$ dans le cas de la Fig. 4 confirment cette hypothèse. Cependant, dans le cas d'une réaction de décomposition, on constate que le domaine cathodique évolue également pour $Z > 1$ et se déplace vers les valeurs plus positives.

Ceci a pour effet de compenser l'affaiblissement du signal $E_A{}^{S \to OH^-}$, et parfois même de donner un signal apparent plus élevé que celui normalement attendu, provoqué par l'apparition de produits nouveaux, parmi lesquels se trouverait l'amine $NH(CH_3)_2$ provenant de la décomposition du DMF.

MODIFICATIONS APPORTÉES AUX COURBES DE DOSAGES PAR LE CHOIX DES POLARITÉS APPLIQUÉES À DEUX ÉLECTRODES DE PLATINE DISSYMÉTRIQUES

La comparaison des courbes de dosage de la Fig. 4 à celles de la Fig. 5 nous amène à envisager l'influence du choix des polarités appliquées aux électrodes.

Le signal cathodique $E_C{}^{H\ \to S}$ est en effet meilleur dans le cas où l'électrode tournante est cathode, alors que la signal $E_A{}^{S \to OH^-}$ est sensiblement équivalent dans les 2 cas, comme le montre le Tableau ci-dessous.

	Electrode tournante	*Electrode fixe*
Cathode	$E_C{}^{H^+ \to S} = 1300$ mV	$E_C{}^{H^+ \to S} = 300$ mV
Anode	$E_A{}^{S \to OH^-} = 1000$ mV	$E_A{}^{S \to OH^-} = 1200$ mV

De plus des différences secondaires apparaissent dans la morphologie de ces 2 courbes.

La courbe de la Fig. 4, où l'électrode tournante est cathode a la forme d'un U renversé, la courbe 5 avec anode tournante celle d'un M dissymétrique, avec un pic très aigu au voisinage de $Z=1$.

Cette brusque remontée de potentiel pour $Z=1-\varepsilon$ (ε très petit), que ne laisse pas prévoir le réseau de courbes voltammétriques précédent peut être interprétée comme un signal résiduel $E_C{}^{H^+\rightarrow S}$. L'électrode de grande surface pour laquelle la densité de courant est très faible comparée à celle de l'électrode tournante, est sensible à de plus faibles concentrations d'ions H^+ que l'électrode précédente.

Ainsi pour $Z=1/2$, le potentiel de la cathode n'est pas déterminé par la réduction du solvant (comme dans le cas de l'électrode tournante), mais par celle des ions H^+ résiduels, provenant de la dissociation très faible de la deuxième acidité, ce qui explique ainsi la valeur peu élevée de 300 mV du signal $E_C{}^{H^+\rightarrow S}$ pour $Z=1/2$.

En toute rigueur, ce signal résulte du passage des courbes de réduction des ions $H_{(1)}$ de la première acidité à ceux $H^+{}_{(2)}$ de la deuxième acidité, et devrait être noté $E_C{}^{H^+(1)\rightarrow H^+(2)}$.

Pour plus de simplicité, nous continuerons cependant de le noter $E_C{}^{H^+\rightarrow S}$, en ne tenant pas compte de ce phénomène secondaire.

Lorsque $Z=1$, la concentration des ions $H^+{}_{(2)}$ disparaît et le potentiel de l'électrode est alors déterminé par la courbe de réduction du solvant, ce qui provoque cette remontée de potentiel de l'ordre de 200 mV pour $Z=1-\varepsilon$, signal qui dans notre symbolique serait noté $E_C{}^{H^+(2)\rightarrow S}$.

Afin de profiter des avantages de l'électrode tournante on pourrait alors concevoir un dosage effectué avec 2 systèmes d'électrodes indépendants identiques au précédent, chacun d'eux étant utilisé par l'intermédiaire de l'électrode tournante à la détermination d'une seule acidité. Comme cela entraîne cependant des complications

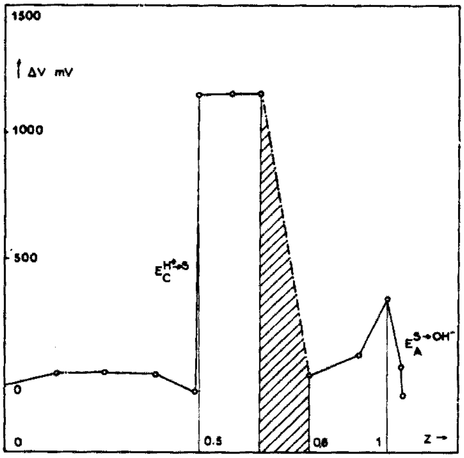


Fig. 6. Courbe de dosage polarovoltrique de l'acide maléique par le réactif TBA-OH 0.1 *N*. Solvant, 40 ml + $NaClO_4$ 0.5 *N*. Les polarités des électrodes sont inversées en cours de dosage de manière à ce que les signaux $E_C{}^{H^+\rightarrow S}$ et $E_A{}^{S\rightarrow OH^-}$ se produisent à l'électrode tournante. La partie hachurée de la courbe correspondant à l'inversion des polarités n'a pas été mesurée et les variations de potentiel pour Z supérieur à 0.8 sont mesurées par rapport à une origine nouvelle et arbitraire.

matérielles de montage, nous avons pensé intervertir les polarités des 2 électrodes après neutralisation de la première acidité, et utiliser ainsi l'électrode tournante tour à tour comme cathode, puis comme anode.

La Fig. 6 montre cependant que le résultat espéré n'est pas atteint. En effet, si le premier signal $E_C^{H^+ \rightarrow S}$ est aussi élevé que celui de la Fig. 3 (1200 mV), le deuxième signal $E_A^{S \rightarrow OH^-}$ n'est plus que de l'ordre de 350 mV au lieu de 800 mV.

En conclusion, il apparaît préférable de conserver les mêmes polarités tout au long d'un dosage. Dans le cas où la première acidité peut être détectée, comme dans l'exemple de l'acide maléique, on aura avantage à polariser cathodiquement l'électrode tournante; si on ne peut doser que la somme des deux acidités, comme pour d'autres diacides, il est alors préférable de choisir l'électrode tournante comme anode.

PARTIE EXPÉRIMENTALE

Préparation et purification des produits

Réactifs titrants. L'hydroxyde de tétrabutylammonium a été préparé par la méthode de CUNDIFF ET MARKUNAS[13], dans le mélange 10 : 1 benzène–méthanol, à partir de l'iodure de tétrabutylammonium Merck.

Le méthylate de sodium est préparé dans le même mélange. Le sodium métallique, en quantité calculée est préalablement décapé dans du méthanol purifié et sec puis transvasé rapidement dans 25 ml de méthanol; lorsque tout le sodium a été transformé en méthylate, on ajoute 250 ml de benzène rigoureusement anhydre.

Solvant. Le N,N-diméthylformamide pur Prolabo a été purifié et séché suivant la méthode indiquée par THOMAS ET ROCHOW[29].

Sels. Le perchlorate de sodium pur Prolabo est recristallisé dans l'eau puis séché à 140° dans l'étuve. Il doit être parfaitement blanc, et sans traces de décomposition.

Le perchlorate de tétraéthylammonium est préparé à partir du bromure de tétraéthylammonium Prosynor. On dissout une mole de ce sel dans le minimum de méthanol, et on ajoute la quantité stoechiométrique d'acide perchlorique dissous également dans un peu de méthanol. L'addition est faite lentement et à la température de 0°. On obtient un précipité blanc immédiat, qui est lavé abondamment, jusqu'à l'obtention d'un test négatif au nitrate d'argent.

Acides. L'acide maléique pur Prolabo a été recristallisé avant utilisation.

L'acide benzoïque, pur pour analyses Prolabo a été utilisé pour l'étalonnage des réactifs titrants.

Appareillage

Toutes les mesures sont faites au moyen d'une électrode de platine tournante (1000 tours/min), de 5 mm de long et de 8/10 mm de diamètre, associée à une électrode fixe constituée par une grille de fil de platine irridié de 16/100 mm de diamètre, de grande surface, cylindrique et coaxiale à la première (diamètre 2 cm, hauteur 12 mm).

L'électrode de référence est une électrode Ag–AgCl, au contact d'une solution de méthanol saturée en NaCl.

L'appareil utilisé pour les dosages est le polarovoltmètre différentiel standard[28], désigné commercialement sous le nom de Titravit Universel Prolabo; le réactif est délivré par une burette à piston Ströhlein de capacité 6 ml, et est protégé de la carbonatation par des tubes de garde contenant de la chaux sodée.

Pour le tracé des courbes voltammétriques $i=\mathrm{f}(E)$, nous avons utilisé un potentiostat Tacussel, type PRT 500 L, équipé d'un moteur Synchrovolt, assurant une vitesse de balayage du potentiel de 20 V/h et comme enregistreur, un XY Sefram Luxytrace, pourvu de calibres de tensions supplémentaires de 2 et 3 V.

Nettoyage des électrodes. Avant d'effectuer le tracé d'un réseau de courbes voltammétriques, l'électrode tournante est préalablement nettoyée à l'acide nitrique concentré et bouillant pendant 2 min, rincée à l'eau permutée puis séchée.

Avant de tracer une courbe de réduction il faut cependant prépolariser l'électrode pendant 3 à 5 min au potentiel de −600 mV par rapport à l'électrode de référence, dans le cas du solvant et du perchlorate de sodium, à 0 mV dans le cas où l'acide est en solution.

Les courbes anodiques peuvent être tracées sans prépolarisation.

Dans le cas des dosages, les électrodes peuvent être utilisées un grand nombre de fois sans nettoyage. On risque cependant d'observer des variations secondaires des formes des courbes ainsi qu'un affaiblissement des sauts de potentiel au point équivalent.

Il est alors nécessaire de traiter les électrodes à l'acide nitrique et de les prépolariser dans une solution de DMF + $NaClO_4$ en les connectant pendant 5 min aux bornes du polarovoltmètre.

RÉSUMÉ

L'établissement des réseaux voltammétriques $I=\mathrm{f}(E)$ de l'acide maléique et d'un réactif basique à l'aide d'un montage à 3 électrodes en milieu N,N-diméthylformamide permet d'interpréter la courbe de dosage polarovoltrique de cet acide par le méthylate de sodium ou l'hydroxyde de tétrabutylammonium. Les différentes variations de potentiel obtenues dans une telle analyse à 2 électrodes de platine polarisées sont identifiées, et une notation symbolique pour chaque signal permet de préciser l'origine des variations de potentiel. Le signal $E_C{}^{H^+ \to S}$ correspondant à la première acidité est provoqué par la cathode, et correspond au saut de potentiel des courbes de réduction des ions H^+ à celles du solvant. Le second signal $E_A{}^{S \to OH^-}$, caractéristique de la deuxième acidité, est dû à l'anode, et correspond au saut de potentiel des courbes d'oxydation du solvant à celles du réactif titrant.

Les conséquences sur la morphologie des courbes de dosage du choix des polarités de 2 électrodes dissymétriques (électrode tournante à fil et électrode fixe de grande surface) ont été également étudiées; dans un cas (électrode tournante en cathode) la courbe rappelle la forme d'un U renversé, dans l'autre (électrode tournante en anode) celle d'un M déformé.

SUMMARY

The determination of the voltammetric curves, $I=\mathrm{f}(E)$, of maleic acid and of a basic titrant in N,N-dimethylformamide using 3 electrodes allowed interpretation of the polarovoltric titration curves of the neutralization of this acid by sodium methylate and tetrabutylammonium hydroxide. The different variations of the potential between 2 polarized platinum electrodes observed in such a neutralization reaction were identified and a notation was developed so that the origin of the observed potential variations could be established. The signal $E_C^{H^+ \rightarrow S}$, which is related to the initial acidity, is given by the cathode and corresponds to a jump from the potential of the H^+ reduction curves to that of the solvent reduction curves. The signal $E_A^{S \rightarrow OH^-}$ characteristic of the second acidity, is given by the anode and is related to a jump from the potential of the solvent oxidation curves to that of the titrant oxidation curves.

The effect of the use of unsymmetrical polarized electrodes (a rotating filament electrode and a large-surface, stationary electrode) on the shape of the titration curve was also examined: a rotating cathode gave rise to a curve resembling an inverted U, whereas a rotating anode gave rise to a curve resembling a deformed M.

ZUSAMMENFASSUNG

Die Aufnahme der Titrationskurven $I = f(E)$ der Maleinsäure mit einem basischen Reagenz in N,N-Dimethylformamid mittels 3 Elektroden gestattet es, die polarovoltrischen Titrationskurven dieser Säure mittels Natriummethylat oder Tetrabutylammoniumhydroxyd zu erklären. Die Potentialänderungen an den 2 polarisierten Platinelektroden sind identifiziert worden. Eine Symbolgebung erlaubt es, den Ursprung der Potentialänderung anzugeben. Das Signal $E_C^{H^+ \rightarrow S}$, welches zur ersten Dissoziationsstufe gehört, wird an der Kathode hervorgerufen und entspricht einem Potentialsprung der Reduktionskurven des H^+-Ions zu denen des Lösungsmittels. Das zweite Signal $E_A^{S \rightarrow OH^-}$, charakteristisch für die zweite Dissoziationsstufe, wird an der Anode erzeugt und entspricht einem Potentialsprung der Oxydationskurven des Lösungsmittels zu denen des Titrationsmittels.

Der Einfluss der Polarität der beiden unsymmetrischen Elektroden (eine rotierende Elektrode besteht aus einem Draht und eine feste Elektrode besitzt eine grosse Oberfläche) auf die Titrationskurven wurden ebenfalls untersucht. Eine rotierende Elektrode als Kathode ergibt für die Form der Titrationskurve ein umgekehrtes U, während eine rotierende Elektrode als Anode ein deformierten M ergibt.

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ADDUCT FORMATION IN THE EXTRACTION OF ZINC OXINATE INTO VARIOUS ORGANIC SOLVENTS

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In many metal chelate solvent extraction systems the propensity for adduct formation has been observed. The neutral metal chelate may hold one or more molecules of water, organic solvent, neutral chelating agent, or an intentionally-introduced adducting agent. In general, the attachment of water tends to decrease the organic distribution of the chelate, whereas the attachment of the others fosters this distribution. The overall subject of adduct formation has been surveyed by several authors[1].

Such adduct formation in the solvent extraction of neutral zinc chelates ZnR_2 might be expected since a number of adduct compounds of zinc chelates have been isolated. Among those giving the stoichiometry ZnR_2L, LI *et al.*[2] report zinc thenoyltrifluoroacetonate with trioctyl- or triphenylphosphine oxide and zinc hexafluoroacetylacetonate with water. LIPPERT AND TRUTER[3] report the acetylacetonate–water compound and show by X-ray analysis that it is five-coordinate. GRADDON AND WEEDEN[4] have prepared zinc acetylacetonate with one water or pyridine or 4-methylpyridine or 2-methylpyridine and zinc benzoylacetonate with one methanol or ammonia or pyridine or 4-methylpyridine or 2-methylpyridine. Among compounds of the type ZnR_2L_2, UMLAND AND HOFFMANN[5] report zinc oxinate with methanol or water, and LI *et al.*[2] have prepared zinc thenoyltrifluoroacetonate with water or 4-methylpyridine and zinc hexafluoroacetylacetonate with water or trioctyl phosphine oxide. On the basis of X-ray studies, MERRITT[6] concludes that the oxinate–water compound has an octahedral geometry with the waters occupying *trans* positions. DWYER AND SARGESON[7] report zinc acetylacetonate with two ammonias or one *o*-phenanthroline or one bipyridyl (the latter two presumably bidentate). GRADDON AND WEEDEN[4] have prepared zinc acetylacetonate with pyridine or 4-methylpyridine and zinc benzoylacetonate with pyridine or 4-methylpyridine. Compounds of the type ZnR_2LQ have been prepared by UMLAND AND HOFFMANN[5]. Included are zinc oxinate with water–methylamine or water–ethylamine or water–butylamine and zinc oxinate with alcohol–amine.

This array of adduct compounds indicates that zinc in the crystalline state seems capable of showing coordination numbers of 5 or 6. It is thus not unreasonable to expect these to be shown in the liquid state; in fact, the higher one might be more prevalent. It is possible, however, for an adducting agent to attach to a neutral metal chelate in several ways: (*i*) it may bond directly to the metal filling a coordination site, (*ii*) it may bond to the atoms of the chelating anion which attach the chelating anion to the metal, or (*iii*) it may affix itself to outer regions of the attached chelate anions. In many instances, the first of these explanations is quite adequate to explain solvent extraction behavior[8]. In some cases, however, non-metallic sites of attachment have been considered by the investigators[9]. A survey of the field indicates that no satisfactory all-inclusive theory is as yet available.

Indications from previous work are that zinc is not usually coordinatively saturated by two monobasic bidentate groups. Thus it is to be expected that the extraction of such zinc chelates into various organic solvents ought to be different, and there should be a good possibility that the properties of the solvents could be related to these differences. To these ends, the extraction of zinc into several solvents containing oxine was chosen for this study.

THEORETICAL CONSIDERATIONS

All the data realized in this study can be interpreted by assuming the predominant organic species to be $ZnR_2(HR)_aS_s$ and the predominant aqueous species to be zinc(II). Herein the S represents the organic solvent, R represents the oxinate ion, and HR represents undissociated oxine. Under these conditions the distribution coefficient D of the total metal will be given by

$$D = [ZnR_2(HR)_aS_s]_0/[Zn] \qquad (1)$$

where the brackets with the subscript o represent an organic phase concentration and the unsubscripted brackets indicate an aqueous phase concentration. When proper equilibrium constants are introduced into this expression, the following relation results

$$D = K_{2as}P_{2as}[HR]_0^{2+a}[S]_0^s/K^2P^{2+a}P_s^s[H]^2 \qquad (2)$$

In this equation, K_{2as} is the aqueous association constant of $ZnR_2(HR)_aS_s$, P_{2as} is its organic–aqueous distribution constant, K is the aqueous acid association constant of the HR, P is its organic–aqueous distribution constant, and P_s is the organic–aqueous distribution constant of S.

When a simple two-phase system (H_2O and S) is used, the term $[S]_0$ becomes invariant and it along with P_s may be adsorbed into K_{2as}, P_{2as} converting them to K_{2a} and P_{2a}, and causing (2) to read

$$D = K_{2a}P_{2a}[HR]_0^{2+a}/K^2P^{2+a}[H]^2 \qquad (3)$$

This relation indicates that a plot of log D against pH at constant $[HR]_0$ will show a slope of 2, and a plot of log D against log $[HR]_0$ at constant pH will show a slope of $2+a$. These relationships allow decisions as to the possible stoichiometries of predominating species, and often calculations of the constants K_{2a} and P_{2a}. When experimental curves with regions of changing slope are obtained, a reflection of changing species, a series of terms or inverted terms of the above type is often applicable.

When the organic phase consists of an inert solvent (that is, one which does not add to the metal chelate) plus an active or adducting solvent S, eqn. (2) may be used as it is. Here a plot of log D against pH at constant $[HR]_0$ and $[S]_0$ should give a slope of 2, a plot of log D against log $[HR]_0$ at constant pH and $[S]_0$ should evidence a slope of 2 + a, and a plot of log D against log $[S]_0$ at constant pH and $[HR]_0$ should yield a slope of s. These relations again allow determinations of stoichiometries and sometimes calculations of K_{2as} and P_{2as}. Experimental plots with changing slopes can often be treated, as above, by a series of terms of this general type.

EXPERIMENTAL

Zinc-65 in hydrochloric acid as obtained from Oak Ridge National Laboratory was converted to the perchlorate by successive evaporations with perchloric acid, after which it was diluted to provide a stock solution. Oxine as obtained from Eastman Chemical Company was purified by double recrystallization from hot ethanol–water solution. Organic solvents were purified by distillation and/or acidic and basic washes plus redox reagent washes in some cases. All other chemicals were analytical reagent grade.

Ten-ml samples of organic phases presaturated with 0.1 M sodium perchlorate solution were stirred at 30.0° ± 0.5° with 10-ml samples of aqueous phases presaturated with the appropriate organic solvent until equilibrium was attained (usually less than 5 h required). The initial aqueous phases were $10^{-6.3}$ M in zinc perchlorate labelled with zinc-65 and were adjusted to an ionic strength of 0.1 with sodium perchlorate (unless indicated otherwise). Adjustments in pH were made with sodium hydroxide and perchlorate acid solutions and pH determinations were made on a Leeds and Northrup 7663-Al pH Meter equipped with a 124138 miniature electrode assembly. This instrument was calibrated at every pH unit from 2 to 12 with Coleman buffers. After equilibration and high-speed centrifugation, appropriate aliquots were taken from each phase and placed in small vials. The radioactivities were determined with a Tracerlab Scintillation Well Detector.

The solubilities of oxine in the various organic solvents were determined at 30.0° ± 0.5° by adding a known weight of oxine to a known volume of organic solvent which had been presaturated with a 0.1 M sodium perchlorate solution. After equilibration for at least 8 h, the supernatant liquid was filtered off and the weight of the remaining oxine determined.

EXPERIMENTAL DATA

Presented in Table I are extraction data as determined by the foregoing procedures. Three major types of data are presented: log D as a function of pH, log D as a function of log $[HR]_0$, and log D as a function of log $[S]_0$ in cyclohexane. Following the presentation of the data for each system, the slopes through which the points

TABLE I

EXPERIMENTAL EXTRACTION RESULTS

System number–Experimental parameters–Data
1. 0.10 M HR in chloroform: pH(log D), 3.3(−2.31), 4.0(−1.00), 4.5(0.00), 5.0(0.73), 5.1(0.83), 6.0(1.89), 7.1(1.90), 7.2(1.94); slopes 2, 1, 0
2. Variable HR in chloroform at pH 5.0: log$[HR]_0$(log D), −2.00(−1.10), −1.50(0.31), −1.00 (1.73); slope 3

TABLE I (continued)

System number–Experimental parameters–Data

3. Variable chloroform and 0.10 *M* HR in cyclohexane at pH 4.3: log[S]$_0$(log *D*), −2.00(−1.96), −1.50(−2.00), −1.30(−1.92), −1.00(−1.85), −0.75(−1.74), −0.50(−1.42), −0.25(−1.42), 0.00(−1.00), 0.50(−0.41); slopes 0, 1
4. 0.10 *M* HR in benzene: pH(log *D*), 3.2(−2.39), 3.4(−1.66), 3.8(−1.55), 4.2(−0.70), 4.6(0.26), 5.0(0.48), 5.3(0.43), 5.3(0.43), 6.1(0.18), 6.7(−0.74); slopes 2, 1, 0, −1
5. Variable HR in benzene at pH 3.7: log[HR]$_0$(log *D*), −1.50(−2.92), −1.00(−1.48), −0.50 (0.08); slope 3
6. Variable benzene and 0.10 *M* HR in cyclohexane at pH 4.4: log[S]$_0$(log *D*), −2.00(−2.27), −1.50(−2.25), −1.25(−2.27), −1.00(−2.28), −0.75(−2.22), −0.50(−2.33), −0.25(−1.96), 0.00(−1.92), 0.25(−1.92), 0.50(−1.62); slopes 0, 1
7. Variable HR and 0.30 *M* benzene in cyclohexane at pH 4.4: log[HR]$_0$(log *D*), −1.00(−1.52), −0.90(−0.96), −0.70(−0.36); slope 3
8. 0.10 *M* HR in carbon tetrachloride: pH(log*D*), 3.7(−3.25), 4.3(−2.36), 4.5(−1.51), 4.6(−1.19), 4.7(−1.28), 5.5(−0.30), 6.4(−0.26); slopes 2, 1, 0
9. Variable HR in carbontetrachloride at pH 4.3: log[HR]$_0$(log *D*), −1.50(−3.02), −1.00(−1.82), −0.50(−0.38); slope 2.5
10. Variable carbon tetrachloride and 0.10 *M* HR in cyclohexane at pH 4.4: log[S]$_0$(log *D*), −2.50(−2.30), −2.00(−2.20), −1.50(−2.28), −1.30(−1.96), −1.08(−1.89), −0.75(−1.96), −0.50(−1.74), −0.25(−1.83), 0.00(−1.92); slopes 0, 0.3
11. 0.10 *M* HR in pentyl ether: pH(log *D*), 3.2(−2.80), 3.5(−2.57), 3.9(−1.52), 4.5(−0.44), 4.8(−0.25), 5.5(0.04); slopes 2, 1, 0
12. Variable HR in pentyl ether at pH 4.0: log[HR]$_0$(log *D*), −1.50(−1.89), −1.00(−1.34), −0.50(−0.34); slopes 1, 2
13. Variable pentyl ether and 0.10 *M* HR in cyclohexane at pH 4.4: log[S]$_0$(log *D*), −2.50(−2.38), −2.00(−2.13), −1.50(−2.15), −1.25(−2.14), −1.00(−2.05), −0.75(−2.10), −0.50(−1.85), −0.25(−1.64), 0.00(−1.64); slopes 0, 1
14. 0.10 *M* HR in butyl ether: pH(log *D*), 4.2(−1.51), 4.3(−1.17), 4.4(−1.10), 4.7(−0.96), 4.7(−0.89), 4.8(−0.68), 5.1(−0.49), 5.3(−0.57), 5.8(−0.54); slopes 2, 1, 0
15. Variable HR in butyl ether at pH 4.3: log[HR]$_0$(log *D*), −2.00(−2.85), −1.50(−2.48), −1.00(−1.34), −0.50(−0.82); slopes 1, 2
16. Variable butyl ether and 0.10 *M* HR in cyclohexane at pH 4.4: log[S]$_0$(log *D*), −2.50(−2.55), −2.00(−2.40), −1.50(−2.33), −1.25(−2.28), −0.50(−2.24), −0.25(−2.17), 0.00(−1.92); slopes 0, 1
17. 0.10 *M* HR in 4-methyl-2-pentanone: pH(log *D*), 3.2(−1.58), 3.5(−1.00), 4.0(−0.12), 4.7(1.04), 5.3(1.34), 6.0(1.43), 6.4(1.15); slopes 2, 1, 0
18. Variable HR in 4-methyl-2-pentanone at pH 3.6: log[HR]$_0$(log *D*), −1.50(−1.70), −1.00 (−0.72), −0.50(0.57); slope 2
19. Variable 4-methyl-2-pentanone and 0.10 *M* HR in cyclohexane at pH 4.3: log[S]$_0$(log *D*), −2.00(−0.82), −1.25(−0.72), −0.75(−0.44), −0.25(0.11), 0.00(0.36); slopes 1, 2
20. 0.10 *M* HR in 1-butanol: pH(log *D*), 3.5(−0.35), 3.6(−0.18), 3.8(0.67), 3.9(0.80), 4.2(1.38), 4.7(1.97), 4.9(2.11), 5.5(2.15), 5.6(2.05), 5.8(2.10), 6.5(2.12); slopes 2, 1, 0
21. Variable HR in 1-butanol at pH 3.6: log[HR]$_0$(log *D*), −1.50(−0.74), −1.00(0.08), −0.50 (1.00); slope 2
22. Variable 1-butanol and 0.10 *M* HR in cyclohexane at pH 4.4: log[S]$_0$(log *D*), −2.50(−2.35), −2.00(−2.27), −1.50(−2.30), −1.00(−1.36), −0.50(−0.58), −0.25(0.45), 0.00(0.60), 0.07 (0.88), 0.25(1.23), 0.46(1.46); slopes 0, 1, 2
23. 0.10 *M* HR in 4-methyl-2-pentanol: pH(log *D*), 3.5(−0.36), 3.8(0.46), 4.3(1.30), 4.4(1.57), 5.5(2.06), 5.9(2.20), 6.3(2.23); slopes 2, 1, 0
24. Variable HR in 4-methyl-2-pentanol at pH 3.7: log[HR]$_0$(log *D*), −1.50(−0.85), −1.00(0.15), −0.50(1.04); slope 2
25. Variable 4-methyl-2-pentanol and 0.10 *M* HR in cyclohexane at pH 4.3: log[S]$_0$(log *D*), −2.50(−1.80), −2.00(−1.64), −1.50(−1.49), −1.25(−1.42), −1.00(−0.89), −0.75(−0.48), −0.50(−0.10), −0.25(0.34); slopes 0, 1, 2
26. Variable 4-methyl-2-pentanol and 0.10 *M* HR in benzene at pH 4.2: log[S]$_0$(log *D*), −2.50 (−0.80), −2.00(−0.72), −1.50(−0.89), −1.25(−0.72), −1.00(0.64), −0.75(−0.55), −0.50 (−0.37), −0.25(−0.13), 0.00(0.20); slopes 0, 1, 2
27. Variable HR and 0.30 *M* 4-methyl-2-pentanol in benzene at pH 4.2: log[HR]$_0$(log *D*), −1.25 (−1.11), −1.00(−0.64), −0.50(0.23); slope 2

TABLE II

EXTRACTION DATA

Solvent	*HR Soly. (M)*	*Log P*	*Species*	*Log K_e*	*Log $K_{2as}P_{2as}$*	*Log K_1*	*Log K_2*
n-Hexane	0.11	1.5	$ZnR_2(H_2O)_2$				
Cyclohexane	0.34	2.0	$ZnR_2(H_2O)_2$				
Carbon tetrachloride	0.81	2.3	$ZnR_2(HR)$	−7.8	18.5		
Butyl ether	0.52	1.1	ZnR_2S	−8.8	15.0	0.3	
Pentyl ether	0.45	1.1	ZnR_2S	−8.4	16.1	0.5	
Benzene	2.25	2.7	$ZnR_2(HR)S$	−7.1	23.7	1.0	
Chloroform	2.20	2.6	$ZnR_2(HR)S$	−7.2	22.8	1.9	
4-Methyl-2-pentanone	0.23	1.8	ZnR_2S_2	−7.2	18.8	1.0	1.2
1-Butanol	0.84	2.4	ZnR_2S_2	−7.2	19.0		2.7
4-Methyl-2-pentanol	0.53	2.2	ZnR_2S_2	−7.0	20.2	1.8	2.8

pass when log D is plotted against the pH or log $[HR]_0$ or log $[S]_0$ are indicated.

Table II gives the solubility values of oxine in the various solvents employed in this study. In addition, the log P values in these solvents were estimated by dividing these solubilities by the solubility of HR in water ($3.8 \cdot 10^{-3}$ M) and taking the logarithm of the result.

Data analysis

Experiments involving 0.01, 0.03, 0.1, and 0.3 M HR in hexane and cyclohexane indicated that only very little extraction of zinc occurred between pH values of 2.0 and 7.0. The log D at all these pH values appeared to be about -2.3 ± 0.3. Since it would be expected that neither of these non-polar solvents would add to the zinc chelate, the lack of appreciable extraction can probably be assigned to the species $ZnR_2(H_2O)_2$. This compound is known from previous experiments on the solid material to be quite insoluble in organic media[5].

System 1 consists of a series of data points which rise with a slope of 2, pass quickly through a slope of 1, and then plateau at a slope of 0 when log D is plotted as a function of pH. The slope on the initial rising portion of the curve (from pH 3.3 to 5.0) is 2 and indicates the extracting species to be $ZnR_2(HR)_aS_s$, where a and s remain as yet unknown, provided that the assumption is made that zinc(II) is the predominant aqueous species. In view of the general chemical behavior of zinc this latter assumption is probably justified. The data in system 2 yield a plot of log D against log $[HR]_0$ at a constant pH of 5.0 which shows a slope of 3. An examination of eqn. (3) indicates that this should be set equal to the exponent of $[HR]_0$ which is $2+a$. Thus $2+a=3$, and $a=1$, identifying the extracting species as $ZnR_2(HR)S_s$, where only s now remains undetermined. System 3 gives a series of data points run at pH 4.3 with 0.1 M HR in cyclohexane as increasing amounts of chloroform are added. The curve of log D against log $[S]_0$ shows an initial slope of 0, gradually rising to a slope of 1 when $[S]_0$ reaches a value of 3 M. This would indicate the attachment of one molecule of S to the chelate species under these circumstances. Thus it could be concluded that at least one S adds to the extracting species in pure chloroform, perhaps giving the species $ZnR_2(HR)S$. Log D against pH plots at HR concentrations of 0.01, 0.03, and 0.3 M agreed with the data in systems 1 and 2. In addition, runs similar to the one shown in system 1 were made at zinc concentrations of 10^{-5} and 10^{-4} M. Essentially the same curve was seen indicating no metal ion concentration dependence and thus giving confidence that no appreciable metal ion polymerization was occurring.

Systems 4–7 present data on extractions into benzene. These data can be interpreted in much the same way as those for chloroform yielding again an extracting species $ZnR_2(HR)S$. The data of systems 8–10 for carbon tetrachloride indicate little or no addition of the solvent to the chelate since the slope of the log D against log $[S]_0$ plot is 0. However, the slope of the log D against log $[HR]_0$ plot is 3, identifying an extracting species of $ZnR_2(HR)$. In systems 11–13 for pentyl ether and systems 14–16 for butyl ether, $2+a=2$ as can be seen from the log D against log $[HR]_0$ plots and $s=1$ as can be discerned from the log D against log $[S]_0$ plots, indicating an extracting species ZnR_2S. In systems 17–19 for 4-methyl-2-pentanone, systems 20–22 for 1-butanol, and systems 23–25 for 4-methyl-2-pentanol, the extracting species turns out to be ZnR_2S_2 since $2+a=2$ (from the log D against log $[HR]_0$ plots) and $s=2$ (from the final slopes of the log D against log $[S]_0$ plots). In system 26, the inert solvent cyclohexane is replaced by the active solvent benzene and the concentration of 4-methyl-2-pentanol is varied. As the alcohol concentration rises it appears that both the HR and the benzene of the species $ZnR_2(HR)S$ are replaced by alcohol molecules since the final slope is 2. The data of system 27 give assurance that the HR molecule has been replaced by the alcohol since $2+a=2$ and thus $a=0$.

Summarized in the 4th column of Table II are the species which are suspected of being the extracting compounds according to the preceding analysis. Employing these species identifications and utilizing eqn. (2) the values of $K_{2as}P_{2as}/K^2P^{2+a}P_s^s$ (called the extraction constant K_e) were calculated and placed in column 5 of Table II. By employing known values of K, P, and P_s, the product $K_{2as}P_{2as}$ may be computed. The log K is taken as 9.7, and log P_s values calculated from aqueous solubilities of S are: carbon tetrachloride (3.3), butyl ether (2.4), pentyl ether (2.9), benzene (3.1), chloroform (2.3), 4-methyl-2-pentanone (1.7), 1-butanol (1.0), 4-methyl-2-pentanol (1.7). $K_{2as}P_{2as}$ is the equilibrium constant for the reaction

$$Zn+2R+aHR+sS \rightarrow ZnR_2(HR)_aS_s \text{ (org)}$$

The values appear in column 6 of Table II.

The curves of log D against log $[S]_0$ as seen in systems 3, 6, 10, 13, 16, 19, 22, and 25 may be analyzed as transformations from the species $ZnR_2(H_2O)_2$ to the species listed in column 4 of Table II. By writing a series of terms corresponding to eqn. (2), the adduction of the molecules may be described as $D=D'(1+K_1[S]_0[HR]_0^a+K_2[S]_0^2[HR]_0^a)$. Here the D represents any given value of the distribution coefficient at a corresponding value of $[S]_0$ whereas D' represents the distribution coefficient when $[S]_0$ is very low, that is, when S is not adding to the chelate. The values of K_1 and K_2 are reported in the 7th and 8th columns of Table II. These are of the same order of magnitude as given by somewhat similar adductions[10].

The role of water in these extractions is an extremely interesting one. It has been postulated that the very small extractions seen in the hydrocarbons are due to the predominance of $ZnR_2(H_2O)_2$. The somewhat better extractions shown by carbon tetrachloride, butyl ether, and pentyl ether are probably due to the replacement of one of these waters by a solvent molecule, the extracting species being $ZnR_2S(H_2O)$. The attachment of only one S molecule and the low values of K_1 can be related to the small dielectric constants and dipole moments of these solvents. In the case of the

6 remaining solvents, the extractions are seen to be very good, probably indicating the absence of any water molecules on the extracting species. In the cases of the ketone and the two alcohols, the S molecules probably occupy coordination positions of the zinc ion, positions which are occupied by waters in the hydrocarbon systems. The sites of attachment of the benzene and the chloroform molecules are more problematical. The chloroform could possibly hydrogen bond to the oxygen and/or nitrogen of the oxinate ions or the neutral oxine of the chelate. The benzene may be associated with the oxinate or oxine also.

If these postulates are valid, one possibility for explaining the trends in extraction is presented. The species containing two waters extract poorly, those containing one moderately, and those containing none excellently. It must be borne in mind that P changes as the concentration of S in cyclohexane increases and that P has been assumed constant in calculating K_1 and K_2. Nonetheless, since the differences in P are not too marked, the slopes of these curves are probably meaningful even though the values of K_1 and K_2 would appear somewhat differently if the precise P values were investigated and used.

An examination of columns 3 and 6 of Table II indicates that there is a rough approximate relation between P and $K_{2as}P_{2as}$, a situation noted in other systems by Omori *et al.*[11].

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SUMMARY

The extraction of zinc oxinate into 10 different organic solvents was investigated. By studying the dependence of the distribution upon pH, reagent concentration, and solvent concentration (in an inert medium), the species were identified and the extraction constants estimated. Correlations between the species type and the efficiency of extraction are postulated. The species extracting into 4-methyl-2-pentanone, 1-butanol, and 4-methyl-2-pentanol is ZnR_2S_2, that extracting into benzene and chloroform is $ZnR_2(HR)S$, that extracting into butyl and pentyl ethers is ZnR_2S, that extracting into carbon tetrachloride is $ZnR_2(HR)$, and that extracting into hexane and cyclohexane is $ZnR_2(H_2O)_2$. In these formulas, R is the oxinate ion, HR is oxine, and S is the organic solvent. It is suggested that the extraction behavior can be explained by assuming a water molecule to be attached to the ZnR_2S and $ZnR_2(HR)$ species.

RÉSUMÉ

Les auteurs ont examiné l'extraction du zinc, au moyen de 10 solvants organiques différents, en fonction du pH, de la concentration du réactif et de la concentration du solvant (en milieu inerte). Les composés extraits sont les suivants: dans la 4-méthyl-2-pentanone, le 1-butanol et le 4-méthyl-2-pentanol: ZnR_2S_2; dans le benzène et le chloroforme: $ZnR_2(HR)S$; dans les butyl- et pentyléthers: ZnR_2S; dans le tétrachlorure de carbone: $ZnR_2(HR)$; dans l'hexane et le cyclohexane: $ZnR_2(H_2O)_2$. Dans ces formules: R = ion oxinate, HR = oxine et S le solvant organique.

ZUSAMMENFASSUNG

Die Extraktion von Zinkoxinat mit 10 verschiedenen organischen Lösungsmitteln wurde untersucht. Dabei wurde die Abhängigkeit der Verteilung vom pH-Wert, der Reagenzkonzentration und der Lösungsmittelkonzentration (in einem inerten Medium) verfolgt; die Spezies wurden identifiziert und die Extraktionskonstanten geschätzt. Es werden Beziehungen zwischen dem Typ der Spezies und der Extraktionswirksamkeit aufgestellt.

Es wurden extrahiert mit 4 Methyl-2-Pentanon, 1-Butanol, 4-Methyl-2 Pentanol ZnR_2S_2, mit Benzol und Chloroform $ZnR_2(HR)S$, mit Butyl- und Pentyläther ZnR_2S, mit Tetrachlorkohlenstoff $ZnR_2(HR)$ und mit Hexan und Zyklohexan $ZnR_2(H_2O)_2$. In diesen Formeln bedeutet R das Oxinat-Ion, HR das Oxin und S das organische Lösungsmittel. Es wird vorgeschlagen, das Extraktionsverhalten durch die Annahme eines Wassermoleküls, das mit dem ZnR_2S und $ZnR_2(HR)$ verbunden ist, zu erklären.

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THE EFFECT OF ARSENATE, AND OF TRANSITION-METAL IONS, ON THE PRECIPITATION OF PHOSPHATE AS AMMONIUM 12-MOLYBDOPHOSPHATE

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While it is known that a number of elements, notably arsenic and iron, interfere in the precipitation of phosphorus as ammonium 12-molybdophosphate, little is known about the extent of the interference. A radiochemical study has therefore been carried out using phosphorus-32, arsenic-74, iron-59 and molybdenum-99, in an attempt to determine the effect of arsenic and a number of transition metals on the precipitation of ammonium 12-molybdophosphate.

It has long been known, and CANNON[1] has recently demonstrated, that 12-molybdophosphates are formed much more easily than 12-molybdoarsenates. However, arsenic can interfere in the quantitative precipitation of phosphate as ammonium 12-molybdophosphate, and in the BRITISH STANDARD method[2] it is removed as the volatile bromide.

STOCKDALE[3] investigated the effect of iron on the precipitation of ammonium 12-molybdophosphate, and KITAHARA[4] the effect of both iron and arsenic. KITAHARA noted that the amount of molybdoarsenate precipitated depended upon the temperature of precipitation, and suggested 45° as the best temperature for the quantitative precipitation of ammonium 12-molybdophosphate with minimum interference from arsenic. He also found that the presence of iron(III) nitrate substantially reduced the amount of arsenic precipitated. STOCKDALE[3] noted that in the presence of iron the precipitate was too heavy to be only ammonium 12-molybdophosphate, but the increase in weight was not due only to the iron present. STOCKDALE suggested that the precipitate is richer than duodeca in molybdenum.

EXPERIMENTAL

General procedure

(a) Phosphate and molybdate solutions. Solutions of potassium dihydrogen phosphate labelled with phosphorus-32, and of nitric acid/ammonium molybdate reagent were prepared as described previously[5]. The radioisotope molybdenum-99, which was obtained as ammonium molybdate, was added to the stock ammonium molybdate solution in some experiments, while in others an unlabelled solution containing 1.28 g of dried A.R. grade potassium dihydrogen phosphate per litre was used.

(b) Arsenate solutions. Disodium hydrogen arsenate heptahydrate (0.293 g) and

about 40 μc of the radioisotope arsenic-74, which was obtained as sodium arsenate, were diluted to 100 ml with distilled water. An unlabelled solution containing 2.93 g of disodium hydrogen arsenate per litre was also used in some experiments.

(c) Solutions containing transition-metal ions. Six solutions of iron(III) nitrate were prepared, each containing, per litre, 1.28 g of dried A.R. grade potassium dihydrogen phosphate and sufficient iron(III) nitrate to give solutions containing Fe^{3+} and PO_4^{3-} in the molar ratios of 10, 25, 50, 75, 100 and 150 to 1, respectively. In some experiments the radioisotope iron-59, which was obtained as iron(III) chloride, was added to the stock solutions.

Six solutions of chromium(III) nitrate were also prepared, each containing, per litre, 1.28 g of dried A.R. grade potassium dihydrogen phosphate and sufficient chromium(III) nitrate to give solutions containing Cr^{3+} and PO_4^{3-} in the molar ratios of 10, 25, 50, 75, 100 and 150 to 1, respectively.

Solutions containing manganese(II) nitrate or nickel(II) nitrate were prepared in the same way as the chromium(III) solutions.

(d) Wash solutions. Acid ammonium nitrate solution: 20 g of A.R. grade ammonium nitrate and 12.5 ml of nitric acid (s.g. 1.42) were made up to 2.5 l with distilled water. A 1% (w/v) solution of nitric acid was also prepared.

(e) Counting equipment. The β-emission from phosphorus-32 and the β- and γ-emissions from arsenic-74 were counted with a Mullard MX 124 liquid counter and an ECKO N530F or PANAX D657 scaler. The γ-emissions from molybdenum-99 and iron-59 were counted using an IDL 663A counter and an IDL 1700 scaler. In most experiments more than 10,000 counts were obtained, so that the standard deviation should not exceed 1%.

(f) Temperature control. The temperature was controlled in an external water bath heated by a 1kV "Techne Tempunit" thermostatic head. The selected temperature was maintained to within ±0.05°.

(g) Sintered glass filters of porosity 4 were used.

All four radiochemicals used in these experiments were obtained from the Radiochemical Centre, Amersham.

The effect of arsenate and transition-metal ions on the precipitation of ammonium 12-molybdophosphate

The following general procedure was used in all experiments except as otherwise stated.

Ammonium molybdate was added to potassium dihydrogen phosphate in a series of experiments at different temperatures. The solution, which was stirred every 15 min with a glass rod, was maintained at the selected temperature for 1 h and for the same period of time at room temperature. The ammonium 12-molybdophosphate was filtered, washed with acid ammonium nitrate solution, and given a final wash with 1% nitric acid solution. A count was taken on the combined filtrate and washings and on the ammoniacal extract of the ammonium 12-molybdophosphate. The percentage precipitation was calculated from the corrected count-rates.

The effect of arsenate on the precipitation of ammonium 12-molybdophosphate. Ammonium molybdate was added to potassium dihydrogen phosphate (2 ml) containing about 0.5 μc phosphorus-32 and sodium arsenate. The percentage of phosphorus precipitated was calculated (Table I).

TABLE I

THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM 12-MOLYBDOPHOSPHATE IN THE PRESENCE OF ARSENATE

Amount of ammonium molybdate added		*Amount of arsenate added*		*Phosphorus precipitated (%)*				
ml	*Stoichiometric ratio (12Mo:1P = 1)*	*ml*	*Stoichiometric ratio (1As:1P = 1)*	*30°*	*40°*	*50°*	*60°*	*70°*
2.3	2.0	Nil	Nil	98.28	99.37	99.74	99.87	99.91
2.3	2.0	0.25	0.125	98.28	99.37	99.74	99.87	99.91
2.3	2.0	0.5	0.25	98.27	99.36	99.72	99.86	99.89
2.3	2.0	1.0	0.50	98.27	99.36	99.72	99.84	99.87
2.3	2.0	1.5	0.75	98.26	99.35	99.70	99.82	99.84
2.3	2.0	2.0	1.00	98.24	99.34	99.69	99.81	99.81
4.0	3.5	Nil	Nil	99.71	99.80	99.93	99.95	99.96
4.0	3.5	0.25	0.125	99.71	99.80	99.93	99.95	99.96
4.0	3.5	0.5	0.25	99.71	99.80	99.93	99.95	99.96
4.0	3.5	1.0	0.50	99.71	99.80	99.92	99.94	99.94
4.0	3.5	1.5	0.75	99.70	99.79	99.91	99.92	99.92
4.0	3.5	2.0	1.00	99.69	99.79	99.90	99.91	99.91

TABLE II

THE PRECIPITATION OF ARSENIC AS AMMONIUM 12-MOLYBDOARSENATE IN THE PRESENCE OF PHOSPHATE

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of arsenate added Stoichiometric ratio (1As:1P = 1)*	*Moles of AsO_4^{3-} precipitated as a percentage of PO_4^{3-} present*				
		30°	*40°*	*50°*	*60°*	*70°*
2.0	0.125	1.4	1.6	1.8	3.6	6.2
2.0	0.25	2.5	3.1	3.7	7.2	12.4
2.0	0.375	3.6	4.8	5.7	10.7	17.0
2.0	0.50	4.8	6.3	7.5	14.1	19.9
2.0	0.75	6.8	9.0	10.7	18.7	24.2
2.0	1.00	9.0	11.0	12.9	23.4	28.2
3.5	0.125	1.4	1.9	2.7	4.9	8.2
3.5	0.25	3.1	4.1	5.2	9.6	16.5
3.5	0.375	4.9	6.2	7.9	14.3	23.4
3.5	0.50	6.6	8.3	10.4	19.0	29.8
3.5	0.75	10.0	11.2	15.7	26.7	37.0
3.5	1.00	12.8	15.9	19.5	31.0	42.0

The amount of arsenate precipitated. Ammonium molybdate was added to potassium dihydrogen phosphate (2 ml) and sodium arsenate containing about 0.5 μc arsenic-74/ml. The percentage of arsenic precipitated was calculated (Table II).

The effect of arsenate on the gravimetric determination of phosphate as ammonium 12-molybdophosphate. Ammonium molybdate was added to potassium dihydrogen phosphate (2 ml) and sodium arsenate. The precipitate was filtered, washed and dried at 270° for 24 h before weighing[3]. The weights of the precipitate are shown in Table III.

TABLE III

THE GRAVIMETRIC DETERMINATION OF PHOSPHATE AS AMMONIUM 12-MOLYBDOPHOSPHATE IN THE PRESENCE OF ARSENATE

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of arsenate added Stoichiometric ratio (1As:1P = 1)*	*Weight of the precipitate*[a] *(mg)*				
		30°	*40°*	*50°*	*60°*	*70°*
3.5	0.125	35.7	36.1	36.4	37.1	38.1
3.5	0.25	36.2	37.0	37.2	38.8	41.4
3.5	0.375	36.7	37.9	38.1	40.8	44.0
3.5	0.50	37.1	38.7	38.9	42.5	46.6
3.5	0.75	38.1	39.5	40.2	44.8	49.2
3.5	1.00	39.0	40.1	41.7	46.3	50.6

[a] Theoretical weight of ammonium 12-molybdophosphate 35.3 mg.

The effect of arsenate and iron(III) nitrate on the gravimetric determination of phosphorus as ammonium 12-molybdophosphate. Ammonium molybdate was added to an active phosphate solution (2 ml) containing sufficient iron(III) nitrate to give a Fe^{3+}/PO_4^{3-} ratio of 100. Sodium arsenate was present in some experiments (Table IV).

TABLE IV

THE GRAVIMETRIC DETERMINATION OF PHOSPHORUS AS AMMONIUM 12-MOLYBDOPHOSPHATE IN THE PRESENCE OF ARSENATE AND IRON(III) NITRATE

(Fe^{3+}/PO_4^{3-} ratio = 100)

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of arsenate added Stoichiometric ratio (1As:1P = 1)*	*Weight of the precipitate*[a] *(mg)*	
		50°	*70°*
2.0	Nil	36.6	37.8
3.5	Nil	37.7	40.9
2.0	1.00	40.9	40.7
3.5	1.00	41.6	45.8

[a] Theoretical weight of ammonium 12-molybdophosphate 35.3 mg.

The effect of arsenate and iron(III) nitrate on the precipitation of phosphorus as ammonium 12-molybdophosphate. Ammonium molybdate was added to a solution (2 ml) containing radioactive phosphate and inactive ferric nitrate. In a series of experiments the Fe^{3+}/PO_4^{3-} ratio varied from 10 to 150. Sodium arsenate, equimolar with the phosphate, was added in some of the experiments (Table V).

The effect of iron on the amount of molybdenum in the precipitate. Ammonium molybdate containing 0.5 μc molybdenum-99 was added to an iron(III) nitrate solution (2 ml) containing phosphate. In a series of experiments the Fe^{3+}/PO_4^{3-} ratio varied from 10 to 150. The count-rate was compared with a standard obtained from a similar set of experiments carried out simultaneously, in which radioactive ammonium molybdate (from the same stock solution as that used in the first part of

TABLE V

THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM 12-MOLYBDOPHOSPHATE IN THE PRESENCE OF ARSENATE AND IRON(III) NITRATE

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of iron(III) nitrate added Stoichiometric ratio (1Fe:1P = 1)*	*Phosphorus precipitated in the absence of arsenate (%)*		*Phosphorus precipitated in the presence of arsenate (equimolar with the phosphorus) (%)*	
		50°	*70°*	*50°*	*70°*
2.0	10		99.86		99.85
2.0	25		99.78		99.59
2.0	50		99.70		99.20
2.0	75		99.42		98.51
2.0	100		95.22		86.24
2.0	150		84.25		51.20
3.5	10	99.90	99.91	99.88	99.94
3.5	25	99.88	99.90	99.81	99.87
3.5	50	99.83	98.80	99.46	99.63
3.5	75	99.62	99.41	99.17	99.11
3.5	100	99.29	98.95	98.75	98.57
3.5	150	98.87	98.12	97.22	95.29

TABLE VI

THE EFFECT OF IRON ON THE AMOUNT OF MOLYBDENUM IN A MOLYBDOPHOSPHATE PRECIPITATE

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of iron(III) nitrate present Stoichiometric ratio (1Fe:1P = 1)*	*Mo in precipitate (iron present)/ Mo in precipitate (iron absent)*	
		50°	*70°*
3.5	10	1.00	0.99
3.5	50	1.03	1.05
3.5	100	1.16	1.21
3.5	150	1.50	1.56

the experiment) was added to potassium dihydrogen phosphate (2 ml). To eliminate the need for a decay correction, the solutions containing iron were counted alternately with standards (Table VI).

The amount of iron in the precipitate. Ammonium molybdate was added to an active iron(III) nitrate solution (2 ml) (*ca.* 0.5 μc iron-59) containing inactive phosphate. In a series of experiments the Fe^{3+}/PO_4^{3-} ratio varied from 10 to 150. Any residue remaining on the filter after the precipitate had been extracted with dilute ammonia solution was dissolved in a few drops of concentrated nitric acid and these washings were added to the ammoniacal extract. The amount of iron in the precipitate was calculated (Table VII).

The effect of phosphate and iron(III) nitrate on the precipitation of arsenic as ammonium 12-molybdoarsenate. (*1*) Ammonium molybdate was added to an iron(III)

TABLE VII

THE AMOUNT OF IRON IN THE PRECIPITATE OF AMMONIUM 12-MOLYBDOPHOSPHATE

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of iron(III) nitrate added Stoichiometric ratio (1Fe:1P = 1)*	*Moles of Fe^{3+} in the precipitate/moles of PO_4^{3-} present 70°*
3.5	10	0.14
3.5	25	0.22
3.5	75	0.57
3.5	150	0.94

TABLE VIII

THE PRECIPITATION OF ARSENIC AS AMMONIUM 12-MOLYBDOPHOSPHATE IN THE PRESENCE OF PHOSPHATE AND IRON(III) NITRATE

(AsO_4^{3-}/PO_4^{3-} ratio = 1)

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of iron(III) nitrate added Stoichiometric ratio (1Fe:1P = 1)*	*Moles % of AsO_4^{3-} precipitated 70°*
2.0	10	25.4
2.0	25	18.6
2.0	50	12.0
2.0	75	6.3
2.0	100	3.9
2.0	150	2.0
3.5	10	38.9
3.5	25	33.6
3.5	50	27.9
3.5	75	20.8
3.5	100	15.8
3.5	150	9.3

nitrate solution (2 ml) containing inactive phosphate and active sodium arsenate (2 ml) (*ca.* 0.5 μc arsenic-74). A series of experiments was carried out at 70° in which the Fe^{3+}/PO_4^{3-} ratio was varied from 10 to 150. The percentage of arsenic in the precipitate was calculated (Table VIII). (*2*) Part (*1*) was repeated with iron(III) nitrate/phosphate solutions in which the Fe^{3+}/PO_4^{3-} ratio was 100 and to which various amounts of sodium arsenate were added (Table IX).

The effect of arsenate with chromium(III) nitrate, manganese(II) nitrate or nickel(II) nitrate, on the precipitation of phosphorus as ammonium 12-molybdophosphate. Ammonium molybdate was added to a chromium(III) nitrate solution (2 ml) containing active phosphate (*ca.* 0.5 μc phosphorus-32). Sodium arsenate was present in a number of experiments. A series of experiments was carried out in which the Cr^{3+}/PO_4^{3-} ratio varied from 10 to 150.

The experiment was repeated with manganese(II) nitrate/phosphate and with nickel nitrate/phosphate solutions. The results are shown in Table X.

TABLE IX

THE PRECIPITATION OF ARSENIC AS AMMONIUM 12-MOLYBDOARSENATE IN THE PRESENCE OF AN EQUIMOLAR AMOUNT OF PHOSPHATE AND IRON(III) NITRATE

(Fe^{3+}/PO_4^{3-} = 100)

Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)	*Amount of arsenate added Stoichiometric ratio (1As:1P = 1)*	*Moles of AsO_4^{3-} precipitated as a percentage of PO_4^{3-} present*				
		30°	*40°*	*50°*	*60°*	*70°*
2.0	0.125	0.3	0.3	0.4	0.4	0.5
2.0	0.25	0.5	0.6	0.7	0.8	1.0
2.0	0.375	0.8	1.0	1.1	1.3	1.4
2.0	0.50	1.2	1.3	1.5	1.7	1.9
2.0	0.75	1.7	2.0	2.2	2.6	2.9
2.0	1.00	2.3	2.7	3.0	3.4	3.9
3.5	0.125	1.3	1.5	1.7	1.8	2.0
3.5	0.25	2.7	3.1	3.5	3.7	4.0
3.5	0.375	4.1	4.5	5.3	5.6	5.9
3.5	0.50	5.6	6.2	7.0	7.5	8.0
3.5	0.75	8.2	9.3	10.6	11.2	11.8
3.5	1.00	11.1	12.2	14.0	15.1	15.8

TABLE X

CHE PRECIPITATION OF PHOSPHORUS AS AMMONIUM 12-MOLYBDOPHOSPHATE IN THE PRESENCE OF THROMIUM(III) NITRATE, MANGANESE(II) NITRATE OR NICKEL(II) NITRATE. THE EFFECT OF ADDITIONAL ARSENATE

Element added as the nitrate	*Amount of ammonium molybdate added Stoichiometric ratio (12Mo:1P = 1)*	*Amount of arsenate present Stoichiometric ratio (1As:1P = 1)*	*Phosphorus precipitated at 50° (%) Parts of element*					
			10	*25*	*50*	*75*	*100*	*150*
Cr	3.5	1.00	99.89	99.84	99.71	99.43	99.01	98.12
	3.5	Nil	99.90	99.85	99.75	99.47	99.24	98.97
Mn	3.5	1.00	99.90	99.86	99.79	99.58	99.30	98.94
	3.5	Nil	99.90	99.87	99.81	99.69	99.54	99.32
Ni	3.5	1.00	99.90	99.84	99.73	99.49	99.23	98.71
	3.5	Nil	99.90	99.86	99.80	99.65	99.49	99.12
			Phosphorus precipitated at 70° (%) Parts of element					
			10	*25*	*50*	*75*	*100*	*150*
Cr	2.0	1.00	99.76	99.70	99.35	98.70	97.98	96.56
	3.5	1.00	99.91	99.90	99.75	99.39	99.00	98.31
	2.0	Nil	99.88	99.81	99.66	99.37	98.92	97.87
	3.5	Nil	99.95	99.92	99.79	99.63	99.49	99.01
Mn	2.0	1.00	99.78	99.76	99.72	99.45	99.02	98.21
	3.5	1.00	99.90	99.88	99.80	99.65	99.54	99.07
	2.0	Nil	99.91	99.86	99.75	99.59	99.41	98.96
	3.5	Nil	99.96	99.92	99.80	99.71	99.57	99.43
Ni	2.0	1.00	99.76	99.70	99.63	99.31	98.79	97.77
	3.5	1.00	99.90	99.86	99.62	99.50	99.31	98.80
	2.0	Nil	99.90	99.86	99.71	99.48	99.17	98.65
	3.5	Nil	99.94	99.91	99.75	99.59	99.43	99.26

TABLE XI

THE PRECIPITATION OF ARSENIC AS AMMONIUM 12-MOLYBDOARSENATE IN THE PRESENCE OF PHOSPHATE WITH CHROMIUM(III) NITRATE, MANGANESE(II) NITRATE OR NICKEL(II) NITRATE

Element added as the nitrate	*Amount of ammonium molybdate added Stoichiometric ratio ($12Mo:1P = 1$)*	*Amount of arsenate present Stoichiometric ratio ($1As:1P = 1$)*	*Moles of AsO_4^{3-} precipitated (as a percentage of the PO_4^{3-} present) 50° Parts of element*					
			10	*25*	*50*	*75*	*100*	*150*
Cr	3.5	0.125	2.7	2.5	2.4	2.4	2.2	2.1
	3.5	1.00	19.5	19.3	19.2	19.0	18.7	18.4
Mn	3.5	0.125	2.7	2.6	2.5	2.5	2.4	2.4
	3.5	1.00	19.5	19.3	19.2	19.1	18.8	18.6
Ni	3.5	0.125	2.7	2.6	2.5	2.4	2.4	2.4
	3.5	1.00	19.5	19.4	19.3	19.2	19.1	18.9
			Moles of AsO_4^{3-} precipitated (as a percentage of the PO_4^{3-} present) 70° Parts of element					
			10	*25*	*50*	*75*	*100*	*150*
Cr	2.0	0.125	6.2	6.2	6.1	6.0	5.9	5.7
	3.5	0.125	8.2	8.1	8.0	7.9	7.8	7.7
	2.0	1.00	28.2	28.0	27.9	27.7	27.5	27.3
	3.5	1.00	42.0	41.8	41.6	41.4	41.2	40.9
Mn	2.0	0.125	6.2	6.2	6.2	6.1	6.0	6.0
	3.5	0.125	8.2	8.2	8.1	8.1	8.0	8.0
	2.0	1.00	28.2	28.1	28.0	28.0	27.9	27.8
	3.5	1.00	42.0	41.9	41.8	41.8	41.7	41.6
Ni	2.0	0.125	6.2	6.2	6.1	6.0	5.9	5.9
	3.5	0.125	8.2	8.1	8.1	8.1	8.0	7.9
	2.0	1.00	28.2	28.1	27.9	27.9	27.8	27.7
	3.5	1.00	42.0	41.9	41.7	41.5	41.5	41.4

The effect of phosphate with chromium(III) nitrate, manganese(II) nitrate or nickel(II) nitrate, on the precipitation of arsenic as ammonium 12-molybdoarsenate. Ammonium molybdate was added to a chromium(III) nitrate solution (2 ml) containing phosphate and active sodium arsenate (*ca.* 0.5 μc arsenic-74/ml). A series of experiments was carried out in which the Cr^{3+}/PO_4^{3-} ratio varied from 10 to 150.

The experiment was repeated with manganese(II) nitrate/phosphate and with nickel nitrate/phosphate solutions. The percentage of arsenic precipitated was calculated (Table XI).

DISCUSSION

At any temperature in the range 50–70°, phosphorus can be quantitatively precipitated with 3.5 times the stoichiometric amount of ammonium molybdate, even in the presence of an equivalent amount of arsenic. When the same amount of arsenic is present and twice the stoichiometric amount of ammonium molybdate, quantitative precipitation of phosphorus is achieved from 60–70°. It has been shown both gravimetrically and radiometrically, however, that arsenic is also precipitated, the amount depending upon the excess of ammonium molybdate and the temperature of precipitation.

The effect of iron(III) nitrate is to reduce the amounts of phosphorus and arsenic precipitated, the reduction being greater at higher temperatures. In the absence of arsenic, phosphorus may be quantitatively precipitated, provided that the Fe^{3+}/PO_4^{3-} ratio does not exceed 50, by using a 3.5-fold excess of ammonium molybdate and a precipitation temperature of 50–70°. If arsenate is also present (equimolar with the phosphate), phosphorus may be quantitatively precipitated provided that the Fe^{3+}/PO_4^{3-} ratio is less than 25. When a 2-fold excess of ammonium molybdate is used, phosphorus can be quantitatively precipitated provided that the Fe^{3+}/PO_4^{3-} ratio does not exceed 10. The temperature of precipitation in this case should be 70°.

Large Fe^{3+}/PO_4^{3-} ratios considerably reduce the amount of arsenic precipitated, but since phosphorus is not quantitatively precipitated under these conditions, this is of no practical value. However, smaller Fe^{3+}/PO_4^{3-} ratios which do allow quantitative precipitation of phosphorus, still reduce the amount of arsenic precipitated by significant amounts.

Although the effect of iron(III) nitrate is to reduce the amounts of phosphorus and arsenic precipitated, the weight of precipitate increases. The increase in weight is due to an increase in the amounts of molybdenum in the precipitate. When the Fe^{3+}/PO_4^{3-} ratio reaches 50, the amount of molybdenum in the precipitate is no longer consistent with a duodeca formula and increases markedly at higher Fe^{3+}/PO_4^{3-} ratios. The precipitate also contains iron, but the amount of iron present could account for only a fraction of the increase in weight.

Inhibitory effects due to the presence of chromium(III) nitrate, manganese(II) nitrate and nickel(II) nitrate are less marked than those caused by iron(III) nitrate. However, the conditions required for quantitative precipitation of phosphorus in their presence are similar to those required in the presence of iron(III) nitrate. In order to obtain quantitative precipitation of phosphorus in the absence of arsenic the Cr^{3+}/PO_4^{3-}, Mn^{2+}/PO_4^{3-} or Ni^{2+}/PO_4^{3-} ratio should not exceed 50, using a 3.5-fold excess of ammonium molybdate and precipitation temperatures from 50–70°. In the presence of arsenic (equimolar with the phosphate) with the same excess of ammonium molybdate, the metal ion/phosphate ratio must not exceed 25. When a 2-fold excess of ammonium molybdate is used, in order to obtain quantitative precipitation of phosphorus, the metal ion/phosphate ratio should not be greater than 25 in the absence of arsenic, and 10 in the presence of arsenic (equimolar with phosphate). The temperature of precipitation should be 70°.

Chromium(III) nitrate, manganese(II) nitrate and nickel(II) nitrate inhibit the precipitation of arsenic by ammonium molybdate to about the same extent, but none of them reduces the precipitation by the same amount as iron(III) nitrate.

In all the experiments the solutions were maintained at the precipitation temperature for 1 h and afterwards at room temperature for the same period of time. It would probably be possible to reduce both of these times to 30 min and achieve quantitative precipitation of phosphorus[5], with rather less interference from arsenic. However, in the presence of transition-metal ions no advantage could be expected from a shorter precipitation time.

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SUMMARY

The radionuclides phosphorus-32, arsenic-74, iron-59 and molybdenum-99 were used to determine the effect of arsenate and some transition-metal ions on the precipitation of phosphorus as ammonium 12-molybdophosphate. Under the conditions necessary for the quantitative precipitation of phosphorus, arsenic is also precipitated by ammonium molybdate. The presence of iron(III) nitrate inhibits the precipitation of phosphorus and, particularly, arsenic, although the precipitates contain more molybdenum, and are heavier, than when iron is absent. Chromium(III) nitrate, nickel(II) nitrate and manganese(II) nitrate do not inhibit the precipitation of phosphorus and arsenic to the same extent as iron(III) nitrate.

RÉSUMÉ

Les radionuclides: phosphore-32, arsenic-74, fer-59 et molybdène-99 ont été utilisés pour déterminer l'influence de l'arséniate et de quelques métaux de transition sur la précipitation du phosphore comme molybdophosphate d'ammonium. L'arsenic précipite également avec le molybdate d'ammonium. Le nitrate de fer(III) gêne la précipitation. Les nitrates de chrome(III), de nickel(II) et de manganèse(II) gênent également, mais pas autant que le nitrate de fer(III).

ZUSAMMENFASSUNG

Die Radionuklide ^{32}P, ^{74}As, ^{59}Fe und ^{99}Mo wurden benutzt, um den Einfluss des Arsenats und der Ionen einiger Übergangsmetalle auf die Fällung des Phosphors als Ammonium-12-molybdophosphat zu bestimmen. Unter den Bedingungen, die zur quantitativen Fällung des Phosphors notwendig sind, wird Arsen ebenfalls durch das Ammoniummolybdat gefällt. Die Gegenwart von Eisen(III)-nitrat verhindert die Fällung des Phosphors und besonders des Arsens, obwohl die Niederschläge mehr Molybdän enthalten und schwerer sind als bei Abwesenheit von Eisen. Chrom(III)-nitrat, Nickel(II)-nitrat und Magnesium(II)-nitrat verhindern die Fällung des Phosphors und Arsens nicht in demselben Ausmass wie Eisen(III)-nitrat.

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DOSAGE RAPIDE DES ALLIAGES CUIVRE–PALLADIUM PAR ELECTROLYSE A TENSION CONTROLEE

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L'électrogravimétrie étant sûrement la plus simple et, dans bien des cas, la plus rapide des méthodes de dosage des métaux peu oxydables, nous avons envisagé d'appliquer cette technique à l'analyse d'alliages à peu près équimolaires de cuivre et de palladium. Les conditions classiques de dosage électrolytique du cuivre[1,2] conduisent au dépôt simultané des deux métaux. Il est donc nécessaire de contrôler la tension cathodique[3] pour déposer d'abord le palladium seul, puis le cuivre. Le dépôt du premier métal à tension contrôlée sur une cathode de platine et dans différents milieux a déjà été étudié par TSUCHI[4]. D'autre part, TANAKA[5] a réalisé la séparation du cuivre et du palladium en présence de diphosphate ($Na_4P_2O_7$) ou de triéthanolamine, mais l'ensemble des deux électrolyses dure 12 h. Nous avons cherché un milieu et des conditions qui permettraient de réaliser un dosage plus rapide.

PRINCIPE

Le palladium se dépose quantitativement dans un grand nombre de milieux[4]; en fixant la tension de la cathode à une valeur suffisamment élevée, il est possible de le déposer seul. Le choix de la tension de contrôle E_c, facteur essentiel de la séparation, se fait en utilisant la chronoampérométrie linéaire[6]. La courbe (Fig. 1) est tracée en moins d'une minute et dans la solution même qui doit être électrolysée. On voit que E_c doit être supérieure à 600 mV/E.N.H. Dans un milieu H_2SO_4 N à 50° pour $E_c = +640$ mV/E.N.H. le rendement en palladium varie de 99.9 à 100.3%*.

Par contre, le cuivre ne peut être déposé dans la même solution de façon satisfaisante. En fixant la tension entre +100 et −100 mV/E.N.H. le dépôt de métal est, en effet, grossier. Il se ternit et noircit quand on prolonge l'électrolyse. Il est vraisemblable que de petites quantités d'oxydes de cuivre CuO et Cu_2O se forment sur l'électrode**.

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* Si le dépôt du palladium est effectué en dessous de +600 mV, par exemple à 550 mV, le poids du dépôt devient nettement supérieur au poids de palladium introduit, alors que dans la même solution, le cuivre est dosé par défaut. Les écarts sont de l'ordre de 5%. Ce fait est à rapprocher de l'existence sur le chronoampérogramme (Fig. 1) d'un léger accident en dessous de 600 mV. Il est peut-être dû à la formation d'un oxyde de cuivre.

** Il y a lieu de noter d'ailleurs que ce phénomène n'apparaît pas dans l'électrolyse d'une solution sulfurique de sulfate de cuivre pur. Il semble donc lié, d'une façon que nous n'avons pas cherché à approfondir, à la présence de traces de palladium restant après le dépôt de ce métal.

Pour obtenir un dépôt mieux défini, nous avons cherché à éviter l'apparition d'oxydes en complexant le cuivre. Parmi les réactifs que l'on peut envisager, les ions chlorure présentent l'avantage de former des complexes dont le coefficient de diffusion est sans doute voisin de celui des ions Cu^{2+} hydratés, la durée de l'électrolyse restera alors comparable. Dans ces conditions, il faudra évidemment ajouter une substance oxydable anodiquement pour éviter l'attaque de l'anode en platine. Le chlorure d'hydroxylammonium donne de bons résultats, il réduit partiellement les ions Cu^{2+} sans précipitation de composés cupreux. C'est lui en même temps qui fournira les ions chlorure nécessaires à la complexation du cuivre.

Après séparation du palladium et addition de chlorure d'hydroxylammonium, le pH restant toujours voisin de 0, le cuivre se trouve alors à la fois aux degrés d'oxydation(I) et (II), peut-être sous la forme de complexes $CuCl_2^-$ et $CuCl^+$ respectivement. Les données de LINGANE[3] et CHARLOT[7] permettent d'envisager les réactions suivantes:

$$CuCl^+ + Cl^- + e \rightarrow CuCl_2^- \quad E_1{}^0 = 0.45 \text{ V/E.N.H.}$$

et

$$CuCl_2^- + e \rightarrow Cu + 2Cl^- \quad E_2{}^0 = 0.24 \text{ V/E.N.H.}$$

Pour des concentrations 10^{-1} *M* en Cl^- et 10^{-2} *M* en Cu^{2+} les tensions d'équilibre sont: $E_1 = 0.39$ V et $E_2 = 0.24$ V/E.N.H. Le chronoampérogramme linéaire de la Fig. 2 confirme la succession de deux réactions approximativement aux tensions indiquées sans permettre d'affirmer, toutefois, que les espèces réduites sont bien les complexes envisagés.

En fixant la tension de la cathode à +250 mV/E.N.H., une partie du cuivre(II)

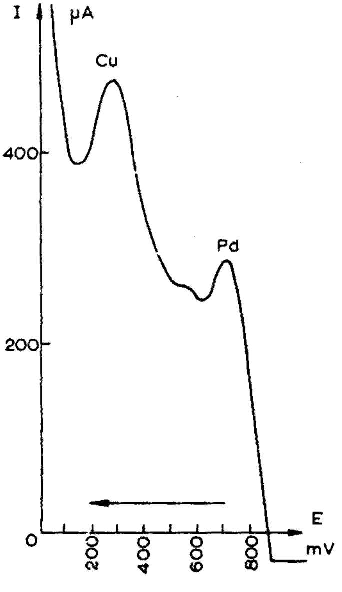

Fig. 1. Chronoampérométrie d'un alliage Cu–Pd sur cathode de platine recouverte de Pd. Milieu H_2SO_4 *N*. T = 50°. Balayage 4.2 V/min.

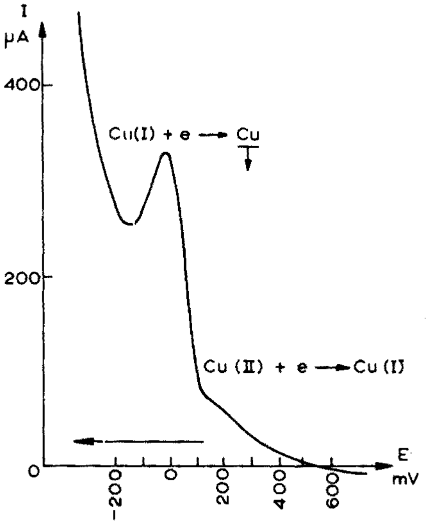

Fig. 2. Chronoampérométrie du cuivre après séparation du palladium. Milieu H_2SO_4 *N* et ClH, NH_2OH. T = 20°. Balayage 4.2 V/min.

présent est réduit à l'état de cuivre(I); le courant d'électrolyse décroît (Fig. 3)puis se stabilise à une valeur élevée. Celle-ci traduit l'existence d'un cycle formé par l'oxydation du cuivre(I) à l'anode et la réduction du cuivre(II) à la cathode par suite de l'agitation de la solution. A 100 mV/E.N.H. le cuivre(I) est réduit et le métal se dépose.

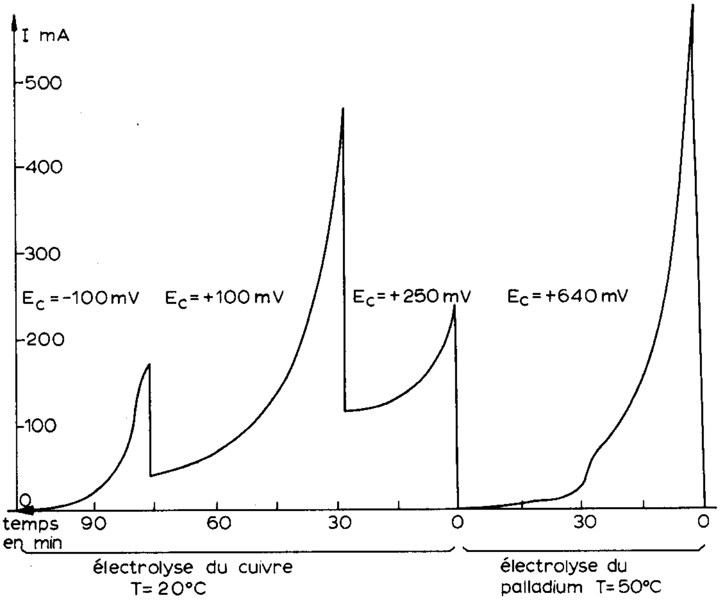

Fig. 3. Electrolyse de 115.5 mg de palladium et 110.7 mg de cuivre. Décroissance du courant d'électrolyse en fonction du temps pour les différentes valeurs du potentiel de contrôle E_c. La vitesse d'agitation est constante.

Dans ces conditions, le dépôt est parfaitement satisfaisant pour un dosage gravimétrique. On terminera à -100 mV/E.N.H. pour réduire les dernières traces de $CuCl_2^-$.

PARTIE EXPÉRIMENTALE

Appareillage

La cellule d'électrolyse est constituée par un bécher de 250 ml à enceinte thermostatée; les deux électrodes sont du type classique. La tension de référence est donnée par une électrode au calomel saturée. Un agitateur magnétique permet de brasser la solution à volonté. La tension est fournie par un potentiostat Tacussel du type ASA 10. Un suiveur de spot Séfram est utilisé pour contrôler la tension entre l'électrode de référence et l'électrode de travail; un appareil identique enregistre le courant d'électrolyse en fonction du temps. Dans le cas de la chronoampérométrie linéaire, un système de commande en tension constitué par un moteur synchrone entraînant un potentiomètre hélicoïdal permet de faire varier régulièrement la tension imposée.

Mode opératoire

Un gramme d'échantillon est attaqué par un mélange de 10 ml d'acide chlorhydrique concentré et de 10 ml d'acide nitrique concentré. Après dissolution, on ajoute 60 ml d'acide sulfurique 6 *N*. La solution est évaporée puis chauffée aux fumées blanches jusqu'à ce qu'il ne reste plus que 4 ou 5 ml de liquide. On refroidit puis on reprend par de l'acide sulfurique normal. Il faut chauffer pour achever la dissolution du sulfate de palladium. Lorsque la totalité est passée en solution, on dilue avec de l'acide sulfurique normal et on ajuste le volume en flacon jaugé. Les parties aliquotes seront fixées de manière à obtenir des dépôts supérieurs à 100 mg. Un gramme d'alliage équimolaire Cu–Pd permet de faire 3 ou 4 déterminations.

La portion de solution prélevée est portée à environ 160 ml par addition d'un volume convenable d'acide sulfurique normal. La cellule d'électrolyse étant maintenue à 50°, on laisse se stabiliser la température de l'électrode de référence. Comme il n'est pas utile de définir la tension de contrôle à mieux de 5 mV près, on retiendra comme tension de l'électrode au calomel dans l'intervalle de température 30–40° la valeur +0.24 V/E.N.H. Après avoir fixé la tension de la cathode à une valeur élevée, on ferme le circuit d'électrolyse, puis on fait décroître la tension jusqu'à +640 mV/E.N.H., le palladium se dépose. Pour avoir un dépôt fin, il faut éviter que la densité de courant dépasse 5 mA/cm^2. L'agitation permet de limiter très simplement sa valeur. On commence l'électrolyse avec une agitation faible puis on augmente progressivement la vitesse de rotation du barreau magnétique jusqu'à sa valeur maximale. L'électrolyse est arrêtée dès que le courant est tombé à une valeur faible et constante. On retire alors le vase rapidement, on rince l'électrode et enfin on coupe le circuit. L'électrode est de nouveau rincée à l'alcool, séchée et pesée.

La solution est refroidie jusqu'à la température ordinaire. Pour un dépôt de 100 mg environ de cuivre, on ajoute 2 g de chlorure d'hydroxylammonium. On ferme le circuit d'électrolyse et on fixe la tension à la valeur +250 mV/E.N.H.: le cuivre(II) est réduit à l'état de complexe cupreux. Il ne doit pas y avoir de cuivre déposé sur la cathode. Quand le courant est stabilisé, la tension est amenée à +100 mV/E.N.H. Le courant croît alors brutalement et il est nécessaire d'attendre qu'il ait diminué de nouveau avant d'amener la tension de contrôle à −100 mV pour laquelle toutes les espèces ioniques sont réduites. On termine l'électrolyse comme dans le cas du palladium. Les variations d'intensité sont représentées sur la Fig. 3.

RÉSULTATS ET CONCLUSIONS

Une solution synthétique a été constituée en attaquant des quantités connues de cuivre et de palladium. Les résultats sont rassemblés dans le Tableau I.

TABLEAU I

Essai no.	*Pd introduit (mg)*	*Pd trouvé (mg)*	*Ecart (mg)*	*Erreur relative (%)*	*Cu introduit (mg)*	*Cu trouvé (mg)*	*Ecart (mg)*	*Erreur relative (%)*
1	115.5	115.7	+0.2	+0.2	110.7	111.4	+0.7	+0.6
2	115.5	115.6	+0.1	+0.1	110.7	110.6	−0.1	−0.1
3	115.5	115.7	+0.2	+0.2	110.7	110.7	0	0
4	115.5	115.4	−0.1	−0.1	110.7	110.3	−0.4	−0.4
5	115.5	115.8	+0.3	+0.3	110.7	110.7	0	0

Quatre déterminations sur un alliage inconnu ont donné les résultats suivants, exprimés sous forme de rapport de masses.

62.8% de Pd et 37.4% de Cu
62.2% de Pd et 37.7% de Cu
62.5% de Pd et 37.2% de Cu
62.5% de Pd et 37.2% de Cu

soit en moyenne:

62.5 ± 0.3% de Pd et 37.4 ± 0.3% de Cu.

Le même alliage a été analysé en déterminant le palladium sous la forme de diméthylglyoximate et le cuivre par électrolyse classique à courant constant. Les résultats sont les suivants:

62.2 ± 0.3% de Pd et 37.6 ± 0.2% de Cu.

Les deux méthodes se recoupent donc de manière satisfaisante; dans les deux cas, les écarts enregistrés sont nettement inférieurs à 1%. L'avantage de l'électrolyse à tension contrôlée réside dans la simplicité et la rapidité des manipulations qui rendent cette méthode particulièrement adaptée aux dosages de séries.

D'autre part, la difficulté signalée plus haut d'obtenir un bon dépôt de cuivre si celui-ci a été précédé du dépôt d'un autre métal n'est sans doute pas particulier au cas étudié ici. On peut espérer pallier cette difficulté par l'emploi de complexant bien choisi. Dans tous les cas, l'emploi préalable de la chronoampérométrie linéaire permettra de fixer rapidement les meilleurs conditions expérimentales.

RÉSUMÉ

Les conditions optimales de séparation par électrolyse à tension contrôlée sont déterminées par chronoampérométrie linéaire. La méthode peut être appliquée à n'importe quel mélange susceptible d'être déposé sur des électrodes de platine. Dans le cas des alliages Cu–Pd, on déposera le palladium à 50° en milieu H_2SO_4 N à une tension de +640 mV/E.N.H. Le cuivre est déposé en plusieurs étapes à la température ordinaire, après addition de chlorure d'hydroxylammonium. Pour 100 mg environ de métal déposé, les écarts sont inférieurs à 1%. Ils peuvent encore être réduits en opérant sur de plus grandes quantités. Les deux électrolyses successives sont réalisées en moins de 3 h.

SUMMARY

The optimum conditions for separation by controlled potential electrolysis were determined by linear chronoamperometry. This method can be applied to any alloy which can be deposited on platinum electrodes. For Cu–Pd alloys, the palladium was deposited at 50° in N sulphuric acid medium at +640 mV (with respect to the normal hydrogen electrode). Copper was deposited in several stages at ambient temperature after adding hydroxylammonium chloride. For *ca.* 100 mg of deposited metal, the errors were less than 1%; they could be reduced by using bigger samples. The two successive electrolyses required less than 3 h.

ZUSAMMENFASSUNG

Die optimalen Verhältnisse für die Elektrolyse bei kontrollierter Spannung werden durch lineare Chronoamperometrie bestimmt. Die Methode kann auf jede Legierung angewandt werden, die sich auf Platinelektroden niederschlagen lässt. Im Falle von Cu–Pd-Legierungen wird das Palladium bei 50°, in einer Lösung von 0.5 M H_2SO_4, bei einer Spannung von +640 mV (Wasserstoff-Normalelektrode) niedergeschlagen. Das Kupfer wird, nach der Zugabe von Hydroxylammoniumchlorid bei Zimmertemperatur in mehreren Stufen niedergeschlagen. Bei einer Menge von 100 mg niedergeschlagenen Metalls liegen die Messschwankungen unter 1%. Sie können durch Verwendung grösserer Mengen noch weiter herabgesetzt werden. Die beiden aufeinanderfolgenden Elektrolysen nehmen drei Stunden in Anspruch.

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UNTERSUCHUNGEN ZUR TEMPERATURABHÄNGIGKEIT DES "FADING"-EFFEKTES BEI DER HALBQUANTITATIVEN AUTORADIOGRAPHIE MIT HILFE DER RINGOFENMETHODE

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In einer früheren Mitteilung[1] beschrieben wir ein halbquantitatives Verfahren zur autoradiographischen Bestimmung geringster Mengen radioaktiver Substanzen, bei welchem kein spezielles Expositionsgerät erforderlich ist. Es wurde in diesem Zusammenhang bereits auf die Erscheinung des Latenzbildschwundes, des sogenannten "Fading"-Effektes hingewiesen, der sich besonders dann störend bemerkbar machte und zu starken Minusfehlern führte, wenn das Verhältnis Aktivitätskonzentration der Probelösung : Aktivitätskonzentration der Standardlösung $\ll 1$ war und deshalb die Proberinge bedeutend länger exponiert werden mussten als die Standardringe (Expositionszeit für die Standardringe = 20 Stunden). Es konnte gezeigt werden, dass sich diese "Fading"-Fehler durch Exposition bei tiefen Temperaturen (−21°) vermeiden lassen.

In Ergänzung hierzu wurden systematische Untersuchungen über die Temperaturabhängigkeit des "Fading" sowie dessen Einfluss auf die halbquantitative Autoradiographie mit Hilfe der Ringofenmethode durchgeführt. Einige Ergebnisse dieser Untersuchungen werden im folgenden mitgeteilt.

Ohne noch einmal auf die bereits beschriebene Methodik[1,2] einzugehen, sei an dieser Stelle erwähnt, dass die Auswertung der erhaltenen Autoradiogramme wie in der halbquantitativen Ringofentüpfelkolorimetrie üblich, nach dem Rechenverfahren des "gewogenen" Mittels[3] erfolgte, also unter Anwendung der Gleichung

$$\frac{a_p}{a_s} = \frac{\sum z_s}{\sum z_p} \cdot \frac{t_s}{t_p}$$

t_s = Expositionszeit für die Standardringe
t_p = Expositionszeit für die Proberinge
a_s = Aktivität eines Tropfens der Standardlösung (45–90 pC/μl)
a_p = Aktivität eines Tropfens der Probelösung
$\sum z_s$ ($\sum z_p$) = Summe der Tropfenzahlen derjenigen Standardringe (Proberinge), deren Autoradiogramme zur Berechnung herangezogen werden.

Um die Temperaturabhängigkeit des "Fading" für die bei allen Autoradiographie-Versuchen verwendeten ADOX-DONEO-Röntgenfilme (Hersteller: ADOX-Fotowerke, Dr. C. Schleusner GmbH; Frankfurt/Main) zu demonstrieren, wurden Proben der Isotopen ^{45}Ca (β_{max} = 0.254 MeV), ^{204}Tl (β_{max} = 0.764 MeV) und ^{90}Sr/^{90}Y (β_{max} =

0.545/2.26 MeV) mit $a_p/a_s = 1.000$ (also Probelösung identisch mit Standardlösung) unter verschiedenen Voraussetzungen halbquantitativ bestimmt. Zunächst wurden Standardfilm (9 Standardringe auf einem Filmstreifen von 3.6 × 24 cm) und Probefilme (5 Proberinge auf je einem Film vom Format 3.4 × 3.6 cm) jeweils 20 Stunden in der üblichen Weise unter den gleichen äusseren Bedingungen bei Raumtemperatur exponiert*. Hierbei befanden sich die Röntgenfilme in Schutzhüllen aus schwarzer Supronylfolie (Flächengewicht *ca.* 6.6 mg/cm²; Hersteller: Kalle & Co. AG., Wiesbaden). Nach beendeter Exposition lagen die Probefilme bis zum Entwickeln 20 Stunden oder 7 Tage bei drei verschiedenen Temperaturen, nämlich +4° (Kühlschrank), Raumtemperatur oder +35° (Trockenschrank), während der zugehörige Standardfilm in jedem Fall die gleiche Zeit bei −21° (in einer Tiefkühltruhe) aufbewahrt wurde.

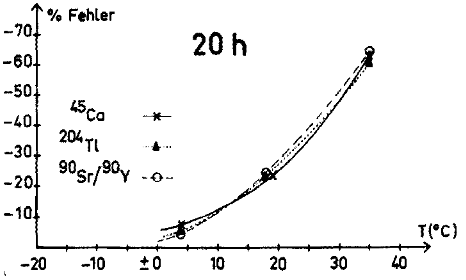

Fig. 1. Temperaturabhängigkeit des "Fading" für ^{45}Ca, ^{204}Tl und ^{90}Sr/^{90}Y. Die Probefilme liegen bis zum Entwickeln 20 Stunden bei 3 verschiedenen Temperaturen.

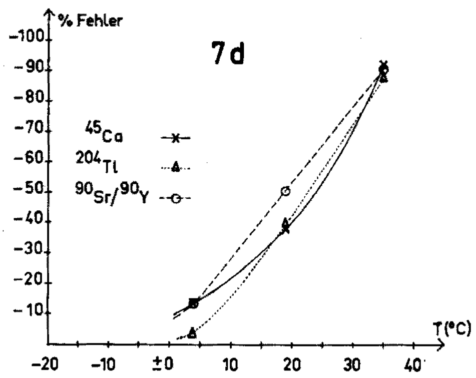

Fig. 2. Temperaturabhängigkeit des "Fading" für ^{45}Ca, ^{204}Tl und ^{90}Sr/^{90}Y. Die Probefilme liegen bis zum Entwickeln 7 Tage bei 3 verschiedenen Temperaturen.

Die Figuren 1 und 2, in denen die bei der Auswertung erhaltenen Minusfehler gegen die Lagerungstemperatur der Probefilme aufgetragen sind, zeigen deutlich, wie bei konstanter Zeitdauer zwischen Expositionsende und Entwickeln diese Abweichungen (sie enthalten arbeitstechnisch bedingte Fehler und "Fading"-Fehler) mit steigender Temperatur zunehmen. Ein Einfluss der β-Energie auf das "Fading" liess sich mit derartigen Versuchen nicht feststellen.

Die in die graphischen Darstellungen eingetragenen Messpunkte sind jeweils Mittelwerte aus zwei halbquantitativen Bestimmungen. Es wurde hier nur das "Fading" der Probefilme berücksichtigt. Man kann jedoch auch die Probefilme bei −21° aufbewahren und den Standardfilm bei +4°, Raumtemperatur oder +35° liegen lassen und erhält dann entsprechende Plusfehler. Alle Versuche wurden ohne Kontrolle der jeweils herrschenden Luftfeuchtigkeit durchgeführt**, da deren in der Literatur[4–6] erwähnter Einfluss auf den Rückgang latenter Autoradiogramme nicht

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* Wegen $a_p/a_s = 1.000$, also $t_p = t_s = 20$ h, war es hier nicht notwendig, jedes Filter durch *zwei* Röntgenfilme einzuschliessen, wie dies bei unbekannten Proben ($50\ a_s \geq a_p \geq 1/50\ a_s$) erforderlich ist[1,2].

** Im Kühlschrank und in der Tiefkühltruhe ist der Wasserdampf-Partialdruck selbstverständlich definiert.

nachgewiesen werden konnte. So wurde z.B. kein signifikanter Unterschied in den Minusabweichungen festgestellt, wenn die Probefilme nach der Exposition 20 Stunden bei Raumtemperatur lagen, und zwar einmal bei ≈70% relat. Luftfeuchtigkeit und einmal in einem Exsikkator über Phosphorpentoxid (jeweils mit und ohne Schutzhülle).

Die Temperatur der Tiefkühltruhe (−21°) wurde für die hier geschilderten Versuche als Bezugstemperatur gewählt. Die Annahme, dass bei −21° ein "Fading" nur noch in sehr geringem Umfang oder überhaupt nicht mehr stattfindet, konnte durch eine Reihe von halbquantitativen Bestimmungen gestützt werden: Die Fehler beim Vergleich von Probeautoradiogrammen, die bis zum Entwickeln 7 Tage bei

TABELLE I

BESTIMMUNG VON ^{204}Tl-PROBEN GERINGER AKTIVITÄTSKONZENTRATION ($a_p/a_s = 0.100$) NACH EXPOSITION BEI VERSCHIEDENEN TEMPERATUREN

Nr.	*Probe*		*Standard*		a_p/a_s		*Relat. Fehler (%)*	*Temperatur (°)*
	Isotop	t_p *(h)*	*Isotop*	t_s *(h)*	*Sollwert*	*Gefunden*		
1	^{204}Tl	143.3	^{204}Tl	20	0.100	0.063	−37	+35
2	^{204}Tl	145	^{204}Tl	20	0.100	0.087	−13	+17
3	^{204}Tl	99	^{204}Tl	20	0.100	0.089	−11	+17
4	^{204}Tl	143.25	^{204}Tl	20	0.100	0.092	− 8	+ 4
5	^{204}Tl	143	^{204}Tl	20	0.100	0.112	+12	−21

TABELLE II

BESTIMMUNG VON ^{90}Sr/^{90}Y-PROBEN GERINGER AKTIVITÄTSKONZENTRATION ($a_p/a_s = 0.100$) NACH EXPOSITION BEI VERSCHIEDENEN TEMPERATUREN

Nr.	*Probe*		*Standard*		a_p/a_s		*Relat. Fehler (%)*	*Temperatur (°)*
	Isotop	t_p *(h)*	*Isotop*	t_s *(h)*	*Sollwert*	*Gefunden*		
6	^{90}Sr/^{90}Y	162	^{90}Sr/^{90}Y	19	0.100	0.041	−59	+35
7	^{90}Sr/^{90}Y	137	^{90}Sr/^{90}Y	20	0.100	0.071	−29	+20
8	^{90}Sr/^{90}Y	99	^{90}Sr/^{90}Y	20	0.100	0.090	−10	+17
9	^{90}Sr/^{90}Y	164	^{90}Sr/^{90}Y	20.3	0.100	0.085	−15	+ 4
10	^{90}Sr/^{90}Y	167	^{90}Sr/^{90}Y	20	0.100	1.080	+ 8	−21

TABELLE III

BESTIMMUNG VON VERSCHIEDENEN PROBEN GERINGER AKTIVITÄTSKONZENTRATION ($0.400 \geqq a_p/a_s \geqq 0.0625$) NACH EXPOSITION IM KÜHLSCHRANK (+4°) BZW. IN DER TIEFKÜHLTRUHE (−21°)

Nr.	*Probe*		*Standard*		a_p/a_s		*Relat-Fehler (%)*	*Temperatur (°)*
	Isotop	t_p *(h)*	*Isotop*	t_s *(h)*	*Sollwert*	*Gefunden*		
11	^{45}Ca	88.17	^{45}Ca	22	0.400	0.340	−15	+ 4
12	^{110m}Ag	148	^{110m}Ag	20	0.0625	0.0664	+ 6.2	+ 4
13	^{204}Tl	168	^{204}Tl	20	0.100	0.093	− 7	−21
14	^{90}Sr/^{90}Y	168	^{90}Sr/^{90}Y	20	0.100	0.095	− 5	−21
15	^{90}Sr/^{90}Y	68.2	^{90}Sr/^{90}Y	20.5	0.200	0.194	− 3	−21
16	^{90}Sr/^{90}Y	90.5	^{90}Sr/^{90}Y	20	0.200	0.206	+ 3	+ 4

−21° aufbewahrt wurden, mit unmittelbar nach der Exposition entwickelten Standardskalen (Exposition von Probe- und Standardfilmen in diesen Fällen jeweils in der Tiefkühltruhe) lagen innerhalb des Streubereiches $Q_{(95)} = \pm 15\%$. (Zur Statistik vgl. GOTTSCHALK[7].)

Um zu zeigen, welchen Einfluss das "Fading" auf die halbquantitative Autoradiographie nach Art der "Sandwich"-Technik[1,2] (Filter mit Probering jeweils zwischen zwei Röntgenfilmen) hat, wurden Proberinge von ^{204}Tl- und ^{90}Sr/^{90}Y-Proben geringer Aktivitätskonzentration ($a_p/a_s = 0.100$) längere Zeit (99–167 Stunden) bei verschiedenen Temperaturen exponiert. Die bei den jeweils gleichen Temperaturen durchgeführten Expositionen der Standardskalen wurden so geleitet, dass am Ende der Expositionszeit t_p für eine Probe auch die Expositionszeit t_s für die Standardskala abgelaufen war, so dass Probefilme und zugehöriger Standardfilm unmittelbar nach Expositionsende gemeinsam entwickelt werden konnten.

Die Tabellen I und II zeigen als Ergebnis dieser Versuche, dass das "Fading" unterdrückt werden kann, wenn man Standard- und Probefilme in der Kälte (−21°; +4°) exponiert, dass jedoch sein Einfluss mit zunehmender Expositionstemperatur (Raumtemperatur; +35°) immer stärker in Erscheinung tritt.

In Tabelle III sind noch einige Ergebnisse halbquantitativer Bestimmungen zusammengestellt, welche nach Exposition von Standard- und Probefilmen bei +4° oder −21° erhalten wurden.

Die Figuren 1 und 2 sowie die Daten der Tabellen I–III zeigen deutlich, dass die halbquantitative Autoradiographie mit Hilfe der Ringofenmethode[1,2] wegen des "Fading"-Effektes nur dann brauchbare Resultate zu liefern vermag, wenn man Standard- und Probefilme bei tiefen Temperaturen exponiert (vgl. auch bei LAUDA[5]). Die Expositionstemperatur spielt lediglich in den Fällen keine Rolle, in denen t_p und t_s wenig voneinander verschieden sind (vgl.[1,2]). Obwohl die Temperatur eines Kühlschrankes bereits ausreichend sein würde, so erlaubt doch eine Tiefkühltruhe wegen der Grösse des zur Verfügung stehenden Raumes ein bequemeres Arbeiten. Zudem lassen sich in einer Tiefkühltruhe (Temperaturen um −20°) latente Autoradiogramme ohne merkliches "Fading" bis zum Entwickeln mehrere Tage (mindestens 1 Woche) aufbewahren.

ZUSAMMENFASSUNG

Bei der bereits früher beschriebenen Methode zur halbquantitativen Autoradiographie mit Hilfe der Ringofentechnik wurde auf das Auftreten des "Fading"-Effektes hingewiesen, welcher namentlich bei längeren Expositionszeiten zu Fehlresultaten führen kann. In der vorliegenden Arbeit wird die Abhängigkeit dieses Effektes von der Temperatur an einigen Beispielen (^{45}Ca, ^{204}Tl, ^{90}Sr/^{90}Y) untersucht. Es konnte gezeigt werden, dass Exposition und Aufbewahren der latenten Autoradiogramme bei tiefen Temperaturen (+4° oder tiefer) den "Fading"-Fehler praktisch ausschalten.

SUMMARY

In semiquantitative autoradiography used in conjunction with the ring-oven method, a fading effect was found to cause erroneous results, especially for long exposure times. The dependence of this effect on the temperature was studied for several examples (^{45}Ca, ^{204}Tl and ^{90}Sr/^{90}Y). It was shown that the exposure and storage of the undeveloped autoradiogram at low temperature ($< 4°$) practically eliminated the fading effect.

RÉSUMÉ

Lors de l'autoradiographie semiquantitative combinée à la méthode du "ring-oven", on a constaté qu'un effet de fading était la cause de résultats erronés, spécialement pour des expositions de longue durée. On a examiné l'influence de la température dans plusieurs cas (^{45}Ca, ^{204}Tl et ^{90}Sr/^{90}Y). L'exposition et la conservation d'autoradiographies non développées, à basse température ($< 4°$), suppriment pratiquement l'effet du fading.

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GENERAL CONSIDERATIONS IN THE ACID-BASE TITRATIONS IN GLACIAL ACETIC ACID

AN EXTENSION OF THE CONCEPT OF LIGAND BUFFER

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Titrations of bases in glacial acetic acid have been used for various analytical purposes. However, the treatment of the subject was for long of an empirical nature, until the thorough treatment by KOLTHOFF AND BRUCKENSTEIN[1,2] placed acid-base titrations in anhydrous acetic acid on a sound theoretical basis. Recently CHARLOT AND TRÉMILLON[3] have also discussed various acid-base equilibria in non-aqueous solvents by means of the acidity and basicity scales proposed by themselves.

In the present paper, continuous expressions for potentiometric and photometric titration curves in anhydrous acetic acid are given and various factors influencing the titration are discussed. The proposed expressions hold over an entire range of titration, and the sharpness of a titration can be calculated as in compleximetric titrations[4]. An extension of the concept of ligand buffer[5] is attempted and it is shown that the effect of a second base, in particular that of water, can be quantitatively accounted for in much the same way as in compleximetric titrations.

POTENTIOMETRIC TITRATIONS

In solvents of low dielectric constant such as anhydrous acetic acid, HAc, an acid HX exists as ionized species $H_2Ac^+X^-$ and non-ionized species HX, and a base B as BH^+Ac^- and B. In the titration of B with HX in anhydrous acetic acid, the following stoichiometric relationships hold (omitting the solvated solvent molecules for simplicity)*:

$$C_B = [BH^+Ac^-] + [B] + [BH^+X^-] + [BH^+] \tag{1}$$

$$C_{HX} = [BH^+X^-] + [HX] + [H^+X^-] + [X^-] \tag{2}$$

where C_B and C_{HX} refer to the total concentrations of the base B and the acid HX respectively. In anhydrous acetic acid dissociation constants of most acids, bases and

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* In the following no volume change during the titration is assumed. In acetic acid an activity coefficient of unity may be assumed[2].

salts are less than 10^{-5}, and $[BH^+]$ and $[X^-]$ can be reasonably neglected when we are concerned with concentrations not lower than $10^{-3}\,M$. Then from eqns. (1) and (2) we have

$$C_{HX} = C_B - ([BH^+Ac^-] + [B]) + ([H^+X^-] + [HX]) \tag{3}$$

Overall dissociation constants of B and HX are defined as follows:

$$K_B = \frac{[BH^+][Ac^-]}{[BH^+Ac^-] + [B]} \tag{4}$$

$$K_{HX} = \frac{[H^+][X^-]}{[H^+X^-] + [HX]} \tag{5}$$

Combining eqns. (4) and (5), the formation constant of BH^+X^-, $K_f^{BH^+X^-}$, is given by the following:

$$K_f^{BH^+X^-} = \frac{[BH^+X^-]}{([BH^+Ac^-] + [B])([H^+X^-] + [HX])} = K_{HX}K_B/K_d^{BH^+X^-}K_{HAc} \tag{6}$$

where $K_d^{BH^+X^-}$ denotes the dissociation constant of BH^+X^- and K_{HAc} the autoprotolysis constant of anhydrous acetic acid. Substituting eqn. (6) into eqn. (3), we have

$$a = C_{HX}/C_B = 1 - \frac{[BH^+X^-]}{C_B K_f^{BH^+X^-}([H^+X^-] + [HX])} + \frac{[H^+X^-] + [HX]}{C_B} \tag{7}$$

Now the side-reaction coefficient taking into account the presence of the non-ionized species HX is defined as:

$$\alpha_{n.i.(HX)} = 1 + (K_i^{HX})^{-1} \tag*{(8)*}$$

where $K_i^{HX} = [H^+X^-]/[HX]$. Then

$$[HX]' = [H^+X^-] + [HX] = [H^+X^-]\alpha_{n.i.(HX)} \tag{9}$$

where $[HX]'$ represents the total concentration of the acid HX not combined with B. From eqns. (7) and (9) we get

$$a = 1 - \frac{[BH^+X^-]}{C_B K_f^{BH^+X^-}\alpha_{n.i.(HX)}[H^+X^-]} + \frac{\alpha_{n.i.(HX)}[H^+X^-]}{C_B} \tag{10}$$

Equation (10) holds for the entire range of titration. In the vicinity of the equivalence point, $[BH^+X^-] \approx C_B$, then we have:

$$a = 1 - \frac{1}{K_f^{BH^+X^-}\alpha_{n.i.(HX)}[H^+X^-]} + \frac{\alpha_{n.i.(HX)}[H^+X^-]}{C_B} \tag*{(10)$'$}$$

Equation (10) or (10)′ enables one to construct the a–p$[H^+X^-]$ diagram in the absence of a second base (Fig. 2).

Now in the presence of a second base B_{II}, the side-reaction coefficient, taking into account its presence, is defined as:

$$\alpha_{B_{II}(HX)} = \frac{[H^+X^-] + [HX] + [B_{II}H^+X^-]}{[H^+X^-]} = (1 + K_f^{B_{II}H^+X^-}[B_{II}]')\alpha_{n.i.(HX)} \tag*{(11)**}$$

---

* $\alpha_{n.i.(HX)}$ is a constant for a given acid in a given solvent. For perchloric acid in anhydrous acetic acid, $\alpha_{n.i.(HClO_4)}$ may be regarded as unity, *i.e.* perchloric acid may be assumed to be fully ionized in this solvent.

** In the absence of B_{II}, $\alpha_{B_{II}(HX)} = \alpha_{n.i.(HX)}$.

where $[B_{II}]'$ refers to the total concentration of the base B_{II} not combined with HX, namely $[B_{II}]' = [B_{II}H^+Ac^-] + [B_{II}]$. Then eqn. (12) relates a with $[H^+X^-]$ in the presence of a second base B_{II}:

$$a = 1 - \frac{[BH^+X^-]}{C_B K_f^{BH^+X^-} \alpha_{n.i.(HX)} [H^+X^-]} + \frac{\alpha_{B_{II}(HX)} [H^+X^-]}{C_B} \tag{12}$$

This expression is valid for the whole range of titration. Near the equivalence point, $[BH^+X^-] \approx C_B$, then:

$$a = 1 - \frac{1}{K_f^{BH^+X^-} \alpha_{n.i.(HX)} [H^+X^-]} + \frac{\alpha_{B_{II}(HX)} [H^+X^-]}{C_B} \tag{12$'$}$$

In eqns. (10), (10)′, (12) and (12)′ the second term on the right side is mainly concerned with the transition before the equivalence point and the third term is mainly concerned with that after the equivalence point. Thus it can be concluded that the presence of a second base hardly affects the transition before the equivalence point.

It may be noted that eqns. (10), (10)′, (12) and (12)′ are similar to the expressions for [Y] in compleximetric titrations[4]. Before the equivalence point, we are concerned with a "ligand buffer" with respect to $[H^+X^-]$, BH^+X^- being considered as a complex. And in the presence of excess of B_{II}, the solution can be regarded as a "ligand buffer" after the equivalence point[5]. In such a ligand buffer, $p[H^+X^-]$ is buffered at a higher level, and correspondingly pH is also buffered at a higher level than in the absence of excess B_{II} (*cf.* Figs. 2 and 3).

Now $[H^+X^-]$ will be related with $[H^+]$. From the rule of electroneutrality, in the absence of a second base,

$$[BH^+] + [H^+] = [X^-] + [Ac^-] \tag{13}$$

Substituting various constants into eqn. (13), we have

$$[H^+] = ([H^+X^-] K_{HX} \alpha_{n.i.(HX)} + K_{HAc})^{\frac{1}{2}} \times \left(\frac{K_d^{BH^+X^-} [BH^+X^-]}{K_{HX} \alpha_{n.i.(HX)} [H^+X^-]} + 1\right)^{-\frac{1}{2}} \tag{14}$$

Then in the presence of a second base B_{II}, analogously to the preceding case, we have:

$$[BH^+] + [B_{II}H^+] + [H^+] = [X^-] + [Ac^-] \tag{15}$$

which leads to:

$$[H^+] = ([H^+X^-] K_{HX} \alpha_{n.i.(HX)} + K_{HAc})^{\frac{1}{2}} \times \left\{\frac{K_d^{BH^+X^-} [BH^+X^-]}{K_{HX} \alpha_{n.i.(HX)} [H^+X^-]} + \frac{K_d^{B_{II}H^+X^-}}{K_{HX}} \left(\frac{\alpha_{B_{II}(HX)}}{\alpha_{n.i.(HX)}} - 1\right) + 1\right\}^{-\frac{1}{2}} \tag{16}$$

Equations (14) and (16) enable one to trace pH–p$[H^+X^-]$ diagrams in the presence as well as in the absence of a second base (Fig. 1). It is evident from Fig. 1 (of course from eqns. (14) and (16)) that the pH–p$[H^+X^-]$ relationship is not always linear and that the linear portion decreases with increasing concentration of a second base (for example, water). Diagrams as given in Fig. 1 are very useful in the construction of potentiometric titration curves as given in Fig. 3: firstly the a–p$[H^+X^-]$ curve (Fig. 2) is drawn by the use of eqns. (10) or (12), and then the a–pH diagram can be easily drawn by consulting one of the curves given in Fig. 1.

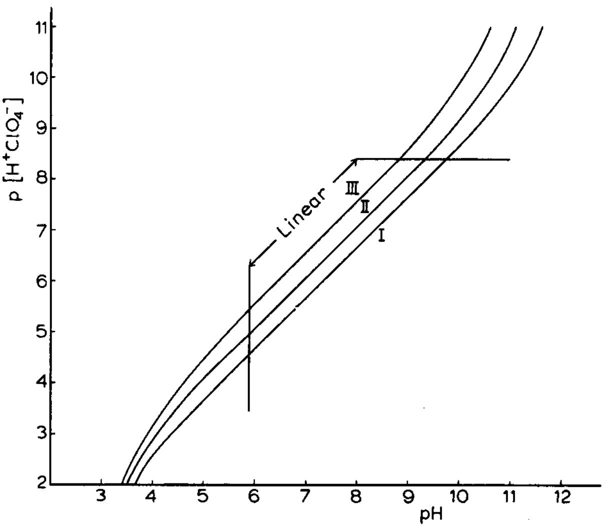
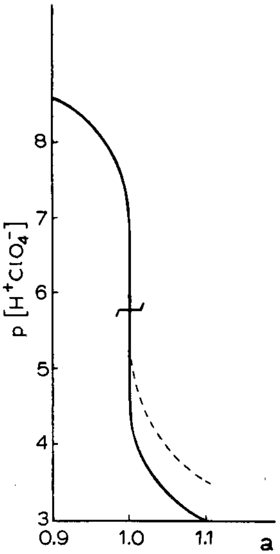


Fig. 1. p[$H^+ClO_4^-$]–pH diagram. Curve I: [$BH^+ClO_4^-$]$K_d^{BH^+ClO_4^-}$ = 10^{-7}; curve II: [$BH^+ClO_4^-$]-$K_d^{BH^+ClO_4^-}$ = 10^{-8}; curve III: [$BH^+ClO_4^-$] $K_d^{BH^+ClO_4^-}$ = 10^{-9}; pK_{HClO_4}; 4.87; pK_{HAc} = 14.45.



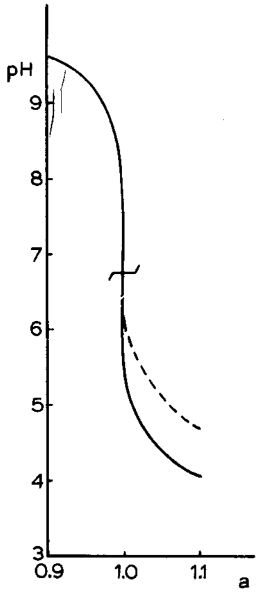


Fig. 2. p[$H^+ClO_4^-$]–a diagram for the titration of diethylaniline with perchloric acid in glacial acetic acid. $C_B = 10^{-2}$; $K_f^{BH^+ClO_4^-} = 10^{9.58}$; —— in the absence of a second base; ---- in the presence of water.

Fig. 3. Potentiometric titration curve of diethylaniline with perchloric acid in glacial acetic acid. $K_d^{BH^+ClO_4^-} = 10^{-5.79}$; —— in the absence of a second base; ---- in the presence of water.

[H^+X^-] and [H^+] at the equivalence point

As is mentioned above, eqns. (10) and (14) or eqns. (12) and (16) allow one to calculate [H^+X^-] and [H^+] at any point of titration (Figs. 2 and 3).

Now it may be useful to calculate $[H^+]$ at the equivalence point. In the absence of a second base,

$$[H^+X^-]_{e.p.} = \frac{1}{\alpha_{n.i.(HX)}}\sqrt{\frac{C_B}{K_f^{BH^+X^-}}} \tag{17}$$

$$[H^+]_{e.p.} = \left(K_{HX}\sqrt{\frac{C_B}{K_f^{BH^+X^-}}} + K_{HAc}\right)^{\frac{1}{2}}\left(\frac{K_d^{BH^+X^-}\sqrt{C_B K_f^{BH^+X^-}}}{K_{HX}} + 1\right)^{-\frac{1}{2}} \tag{18}$$

When $K_{HX}\sqrt{C_B/K_f^{BH^+X^-}} \gg K_{HAc}$ and $K_d^{BH^+X^-}\sqrt{C_B K_f^{BH^+X^-}} \gg K_{HX}$, *i.e.* $[H^+]_{e.p.}$ falls on the linear portion of Fig. 1, eqn. (18) simplifies to:

$$[H^+]_{e.p.} = K_{HX}/(K_f^{BH^+X^-}K_d^{BH^+X^-})^{\frac{1}{2}} \tag{19}$$

This expression conforms with the formula presented by KOLTHOFF AND BRUCKENSTEIN[1].

In the presence of B_{II},

$$[H^+X^-]_{e.p.} = \sqrt{\frac{C_B}{K_f^{BH^+X^-}\alpha_{n.i.(HX)}\alpha_{B_{II}(HX)}}} \tag{20}$$

$$[H^+]_{e.p.} = \left(K_{HX}\sqrt{\frac{C_B\alpha_{n.i.(HX)}}{K_f^{BH^+X^-}\alpha_{B_{II}(HX)}}} + K_{HAc}\right)^{\frac{1}{2}}$$

$$\times\left\{\frac{K_d^{BH^+X^-}}{K_{HX}}\sqrt{\frac{C_B K_f^{BH^+X^-}\alpha_{B_{II}(HX)}}{\alpha_{n.i.(HX)}}} + \frac{K_d^{B_{II}H^+X^-}}{K_{HX}}\left(\frac{\alpha_{B_{II}(HX)}}{\alpha_{n.i.(HX)}} - 1\right) + 1\right\}^{-\frac{1}{2}} \tag{21}$$

When only the first terms in the numerator and denominator of eqn. (21) have to be taken into account, eqn. (21) can be rewritten as:

$$[H^+]_{e.p.} = K_{HX}\left(\frac{\alpha_{n.i.(HX)}}{K_d^{BH^+X^-}K_f^{BH^+X^-}\alpha_{B_{II}(HX)}}\right)^{\frac{1}{2}} \tag{22}$$

Potentiometric sharpness index

Under conditions where only the first terms in the numerator and denominator of eqns. (14) and (16) are important compared with the other terms, *i.e.* in the linear range of Fig. 1, potentiometric titration curves may be expressed by the following equation:

$$a = 1 - \frac{K_{HX}[BH^+X^-]^{\frac{1}{2}}}{C_B K_f^{BH^+X^-}(K_d^{BH^+X^-})^{\frac{1}{2}}[H^+]} + \frac{\alpha_{B_{II}(HX)}(K_d^{BH^+X^-}[BH^+X^-])^{\frac{1}{2}}[H^+]}{\alpha_{n.i.(HX)}K_{HX}C_B} \tag{23}$$

In the vicinity of the equivalence point where $[BH^+X^-]$ can be regarded as C_B, we have:

$$a = 1 - \frac{K_{HX}}{K_f^{BH^+X^-}(C_B K_d^{BH^+X^-})^{\frac{1}{2}}[H^+]} + \frac{\alpha_{B_{II}(HX)}(K_d^{BH^+X^-})^{\frac{1}{2}}[H^+]}{\alpha_{n.i.(HX)}K_{HX}(C_B)^{\frac{1}{2}}} \tag{24}$$

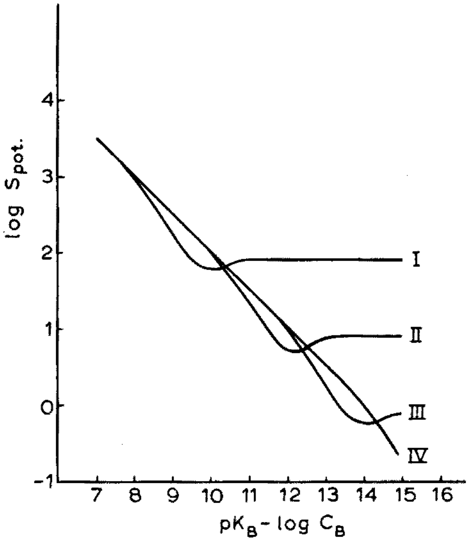
Equations (23) and (24) can be generalized as:

$$a = 1 - \frac{p_1}{[H^+]} + p_2[H^+] \tag{25}$$

where p_1 and p_2 are the constants dependent upon various constants of the species involved and experimental conditions such as C_B, and the presence or the absence of a second base. The similarity of eqn. (25) to eqn. (30) in ref. 4 may be noted. The lower p_1 and p_2, the more distinct the potential break at the end-point. The potentiometric sharpness index, $S_{\text{pot.}}$ is given by:

$$S_{\text{pot.}} = (\pi_{\text{pH}})^{-1}_{\text{e.p.}} = (\text{dpH}/\text{d}a)_{\text{e.p.}} \tag{26}$$

where π_{pH} denotes the buffer capacity of the solution. Further discussions can be made in the same way as in compleximetric titrations[4]. Calculated values of $S_{\text{pot.}}$ for various cases are given in Figs. 4 and 5.



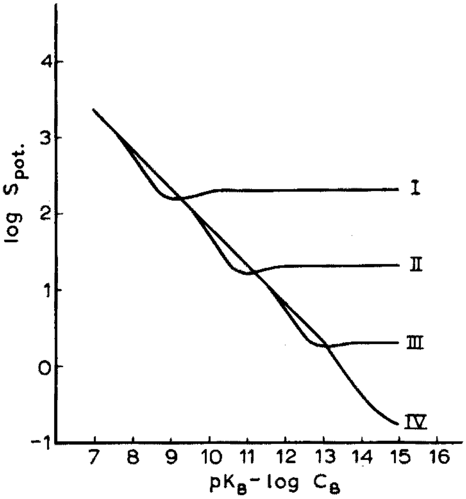


Fig. 4. $S_{\text{pot.}}$ in the absence of a second base. Curve I: $K_d^{BH^+ClO_4^-} = 10^{-8}$; curve II: $K_d^{BH^+ClO_4^-} = 10^{-7}$; curve III: $K_d^{BH^+ClO_4^-} = 10^{-6}$; curve IV: $K_d^{BH^+ClO_4^-} = 10^{-5}$.

Fig. 5. $S_{\text{pot.}}$ in the presence of water (0.5 M). Curve I: $K_d^{BH^+ClO_4^-} = 10^{-8}$; curve II: $K_d^{BH^+ClO_4^-} = 10^{-7}$; curve III: $K_d^{BH^+ClO_4^-} = 10^{-6}$; curve IV: $K_d^{BH^+ClO_4^-} = 10^{-5}$.

Titration errors involved in the potentiometric titration

So far as the dissociation of any species involved can be neglected, in the $p[H^+X^-]$–a diagram (titration curve for $p[H^+X^-]$), a point with a maximal value of $d(p[H^+X^-])/da$ coincides with the equivalence point regardless of the presence or the absence of a second base (see eqns. (10) and (12)). However, as is evident from eqns. (14) and (16), the $p[H^+X^-]$–pH relationship is not always linear (*cf.* Fig. 1). Thus it may be concluded that, although the end-point is usually located to a point with a maximal value of dpH/da in the potentiometric titration (pH–a curve), this end-point *does not always* coincide with the equivalence point*.

Such end-point location leads always to a negative theoretical error, which can be calculated by an electronic computor by means of the combined use of eqns. (10)

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* In the linear range of the pH–$p[H^+X^-]$ diagrams given in Fig. 1, the difference between the potentiometric end-point and the equivalence point can be practically neglected.

and (14) or eqns. (12) and (16). Some of the results are given in Fig. 6. When C_BK_B is higher than 10^{-10}, the theoretical error of the end-point with $(\mathrm{dpH}/\mathrm{d}a)_{\max}$. is given by the following:

$$\text{Titration error (\%)} = -\frac{10^{-12}}{K_BC_B}(1 + 10^2C_{H_2O}) \tag{27}$$

When an error of ΔpH is introduced in the potential measurement, the relative error is given by:

$$\text{Titration error (\%)} = \frac{\Delta \mathrm{pH}}{S_{\mathrm{pot.}}} \times 100 \tag{28}$$

If the titration error given by eqn. (27) is in the same order of magnitude as that given by eqn. (28), the error will be the sum of the two.

PHOTOMETRIC TITRATIONS*

The indicator is designated as I and the formation constant of IH^+X^-, $K_f^{IH^+X^-}$, is usually defined as:

$$K_f^{IH^+X^-} = \frac{[IH^+X^-]}{[I]\,[H^+X^-]} \tag{29}$$

Designating the indicator transition as ϕ,

$$\phi = \frac{[IH^+X^-]}{C_I} \tag{30}$$

and combining eqns. (29) and (30), we have

$$[H^+X^-] = \frac{\phi}{1-\phi}\,\frac{1}{K_f^{IH^+X^-}} \tag{31}$$

Thus, when $\phi = 0.5$:

$$[H^+X^-]_{\phi=0.5} = (K_f^{IH^+X^-})^{-1} \tag{32}$$

$[H^+X^-]_{\mathrm{e.p.}}$ in the absence and in the presence of a second base are given in eqns. (17) and (20) respectively. Then in order to realize that $\phi = 0.5$ at the equivalence point, the formation constant of IH^+X^- should be as follows (compare eqns. (17) and (20) with (32)): in the absence of a second base,

$$K_f^{IH^+X^-} = \alpha_{\mathrm{n.i.(HX)}}(K_f^{BH^+X^-}/C_B)^{\frac{1}{2}} \tag{33}$$

and in the presence of a second base,

$$K_f^{IH^+X^-} = (\alpha_{\mathrm{n.i.(HX)}}\alpha_{\mathrm{B_{II}(HX)}}K_f^{BH^+X^-}/C_B)^{\frac{1}{2}} \tag{34}$$

Now the indicator transition during the titration will be considered. Substituting eqn. (31) into eqns. (10) and (12), we have, in the absence of a second base,

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{K_f^{IH^+X^-}[BH^+X^-]}{C_BK_f^{BH^+X^-}\alpha_{\mathrm{n.i.(HX)}}} + \frac{\phi}{1-\phi}\,\frac{\alpha_{\mathrm{n.i.(HX)}}}{C_BK_f^{IH^+X^-}} \tag{35}$$

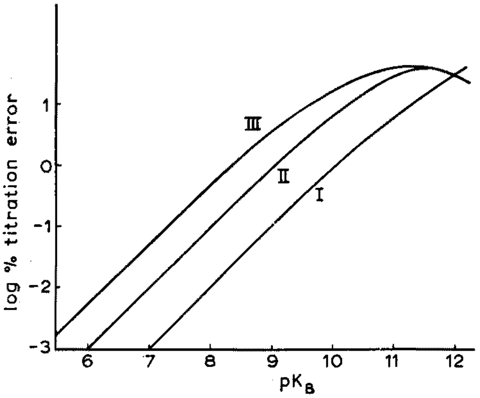
---

* In the following it is assumed that the total concentration of indicator is negligibly small as compared with C_{HX} and C_B.

and in the presence of a second base B_{II},

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{K_f^{IH^+X^-}[BH^+X^-]}{C_B K_f^{BH^+X^-}\alpha_{n.i.(HX)}} + \frac{\phi}{1-\phi}\,\frac{\alpha_{B_{II}(HX)}}{C_B K_f^{IH^+X^-}} \tag{36}$$

Equations (35) and (36) hold over the entire range of titration. The second terms in these equations are mainly concerned with the indicator transition before the equivalence point and the third terms are mainly concerned with that after the equivalence point. Typical photometric titration curves are drawn by means of eqns. (35) and (36), and given in Fig. 7. The theoretical plots agree well with the experimental results given by KOLTHOFF AND BRUCKENSTEIN[6].



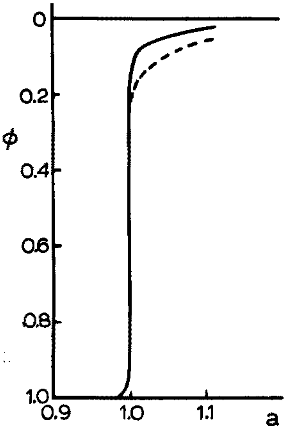


Fig. 6. Titration error in potentiometric titration. Curve I: water absent; curve II: presence of 0.1 M of water; curve III: presence of 0.5 M of water; $C_B = 10^{-2}$ M.

Fig. 7. Photometric titration curve of diethylaniline with perchloric acid in the presence of *p*-naphtholbenzein as an indicator. Log $K_f^{IH^+ClO_4^-} = 5.00$; $C_B = 10^{-2}$ M; —— in the absence of a second base; ---- in the presence of water.

It may be useful to note that $\alpha_{n.i.(HX)}$ in the last term on the right side of eqn. (35) is replaced by $\alpha_{B_{II}(HX)}$ in eqn. (36) and that the presence of a second base hardly affects the indicator transition before the equivalence point. In the vicinity of the equivalence point where $[BH^+X^-] \approx C_B$, eqns. (35) and (36) simplify to:

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{K_f^{IH^+X^-}}{K_f^{BH^+X^-}\alpha_{n.i.(HX)}} + \frac{\phi}{1-\phi}\,\frac{\alpha_{n.i.(HX)}}{C_B K_f^{IH^+X^-}} \tag{37}$$

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{K_f^{IH^+X^-}}{K_f^{BH^+X^-}\alpha_{n.i.(HX)}} + \frac{\phi}{1-\phi}\,\frac{\alpha_{B_{II}(HX)}}{C_B K_f^{IH^+X^-}} \tag{38}$$

respectively.

As in the consideration of compleximetric titrations[4], eqns. (35), (36), (37) and (38) can be written in the following general expression:

$$a = 1 - \frac{1-\phi}{\phi} f_1 + \frac{\phi}{1-\phi} f_2 \tag{39}$$

where f_1 and f_2 are the constants dependent upon various constants of the species involved and the experimental conditions. The product $f_1 f_2$ is independent of the indicator characteristics and is given as:

$$f_1 f_2 = \frac{\alpha_{B_{II}(HX)}}{K_t^{BH^+X^-} C_B \alpha_{n.i.(HX)}} \tag{40}$$

Sometimes precipitation of BH^+X^- occurs during the titration. In such a case we notice an unexpectedly sharp end-point. This can be well understood comparing eqns. (35) and (36) with eqn. (37): precipitation of BH^+X^- will control the concentration of BH^+X^- at a lower level, and a correspondingly lower f_1 will result. Thus we can say that precipitation of BH^+X^- improves the indicator transition before the equivalence point*. When the base B_{II} is sufficiently weak or in the absence of B_{II}, $\alpha_{B_{II}(HX)} = \alpha_{n.i.(HX)}$, and then eqn. (40) simplifies to:

$$f_1 f_2 = (K_t^{BH^+X^-} C_B)^{-1} \tag{41}$$

Visual titration is generally possible with an error not exceeding 1% when f_1 and f_2 are both lower than 10^{-3}. And the lower the values of f_1 and f_2, the more distinct is the end-point[4]. When $f_1 f_2$ is greater than 10^{-5}, it is difficult to find the end-point visually, and photometric titration is preferable. As to the end-point location and the titration error involved in the photometric titration, ref. 4 should be consulted.

Now some considerations will be made on the method of linear extrapolation in end-point detection[7,8]. Designating the ratio [basic indicator color]/[acidic indicator color] as R, we have from eqn. (39):

$$a = 1 - f_1 R + f_2/R \tag{42}$$

Suppose a straight line is drawn through $R = 1$ and $R = 2$ (AB in Fig. 8). If the intersection of this line with the horizontal line at $R = 0$ (C in Fig. 8) is taken as the end-point, the titration error is given by:

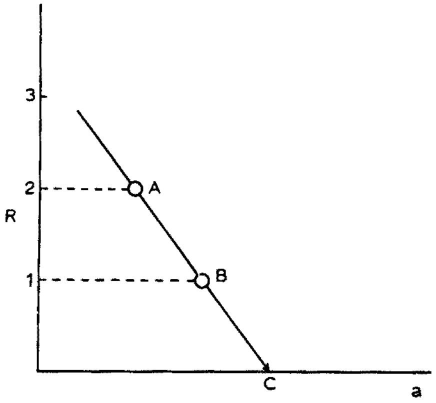


Fig. 8. Method of linear extrapolation for end-point location.

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* Referring to the expressions given in the section on potentiometric titrations one can easily account for the greater potential break observed when precipitation of BH^+X^- occurs.

$$\text{Titration error } (\%) = +1.5 f_2 \times 100 \tag{43}$$

The titration error is always positive. With a value of f_2 lower than 10^{-3} the titration is successful. Then the third term on the right side of eqn. (42) may be neglected and the slope of AB is about $-f_1$. It may be worth noting that the error involved in the extrapolation will be greater if f_1 is greater than 10^{-1}*. Therefore it is desirable to use an indicator with which f_1 will be smaller than 10^{-1} and f_2 smaller than 10^{-3}. If the extrapolation is made through $R = 0.1$ and $R = 0.2$, the titration error will be ten times as large as that given by eqn. (43). Thus in order to reduce titration error it is preferable to extrapolate through as high a value of R as practical in the linear range of plot.

An alternative method is possible by means of the plot of R^{-1} against a. If we locate the end-point to the intersection of the horizontal line $R^{-1} = 0$ and the straight line drawn through $R^{-1} = 1$ and $R^{-1} = 2$, the titration error is given by:

$$\text{Titration error } (\%) = -1.5 f_1 \times 100 \tag{44}$$

Here the error is always negative, contrary to the preceding case. In this case it is preferable to employ an indicator which makes f_1 smaller than 10^{-3} and f_2 smaller than unity, as in the method of $a^{-1} \sim R$ plot[7].

Above all, this method is advantageous because a titration can be performed with an error less than 1% even when $f_1 f_2$ is as high as $10^{-3} \sim 10^{-4}$ (provided that an appropriate selection of indicator is made). Finally it may be useful to note that the presence of a second base, for example that of water, does not affect f_1 but makes f_2 high. Thus the plot of R^{-1} against a is advantageous, because the error involved remains unchanged regardless the presence of a second base.

The theory given in the present paper is applicable not only to acid–base titrations in anhydrous acetic acid, but also to titrations in other solvents with low dielectric constants. It is assumed in this paper only that the dissociation constants of all the species involved are not much greater than 10^{-5}, and that no polymerization occurs during the titration.

SUMMARY

Some continuous expressions are derived for potentiometric as well as photometric acid–base titrations in anhydrous acetic acid. Various methods of end-point location are discussed and the titration error is calculated.

RÉSUMÉ

Quelques expressions continues sont dérivées pour des titrages potentiométriques, de même que pour des titrages photométriques acide–base, en milieu acide acétique anhydre. Diverses méthodes de fixation du point final sont discutées; l'erreur de titration est calculée.

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* When f_2 is lower than 10^{-3}, it may be important to note that: (*i*) it is preferable, in the method of $a^{-1} \sim R$ plot[7], to have f_1 smaller than unity (*ii*) with $f_1 < 10^{-1}$ $a \sim R$ plot gives a good result (*iii*) with $f_1 < 10^{-2}$ photometric titration is successful[3] by means of the plot ϕ—a; (*iv*) with $f_1 < 10^{-3}$ visual titration is possible.

ZUSAMMENFASSUNG

Es wurden einige Ausdrücke sowohl für die potentiometrische wie für die photometrische Säure–Basen-Titration in Essigsäureanhydrid abgeleitet. Einige Methoden der Endpunktsbestimmung werden diskutiert und der Titrationsfehler berechnet.

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DETERMINATION OF ORGANIC HYDROXYL AND AMINO COMPOUNDS WITH *o*-SULPHOBENZOIC ANHYDRIDE

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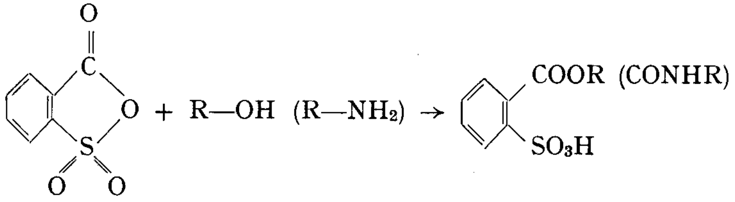
The commonest methods for the determination of hydroxyl groups in organic compounds are based on acylation reactions. A review of the methods available up to 1952 has been published[1], but since that time many new acylation methods have been developed and earlier methods have been reinvestigated and modified. This is because the hydroxy compounds occupy a very important position among naturally occurring organic compounds as well as industrial organic products.

Hydroxyl compounds differ considerably in the ease with which they undergo esterification and while it is desirable to find an acylating reagent that serves for general purposes, modifications become mandatory when difficulty arises. Acetylation and phthalation are the most widely used esterification procedures for determining hydroxyl compounds, but 3,5-dinitrobenzoyl chloride in pyridine[2], stearoyl chloride in chloroform[3], pyromellitic acid dianhydride (PMDA) in tetrahydrofuran–pyridine mixture[4], propionic anhydride[5], 3-nitrophthalic anhydride (NPA)[6], succinic anhydride in pyridine[7], and stearic anhydride in xylene[8] have recently been used successfully for the determination of hydroxyl compounds. Of these acylating reagents, pyromellitic dianhydride[4] and 3-nitrophthalic anhydride[6] are similar to phthalic anhydride in that they do not react with phenols and are free from interference from water, lower aldehydes, ketones, esters, ether[5], etc.; they are, however, more like acetic anhydride in being faster in their reactions. SIGGIA has classified PMDA as a fast-reacting phthalic anhydride-type reagent and the same is true for NPA.

In the present paper *o*-sulphobenzoic anhydride (SBA) is proposed as an acylating reagent for determining hydroxyl or amino compounds. *o*-Sulphobenzoic anhydride reacts with alcohols and primary or secondary amines to give exclusively carboxy ester and carboxy amides respectively[9],



and this reaction was used in the work described below. The original acetylation and phthalation methods were carried out in a base-catalysed pyridine medium, but recently perchloric or *p*-toluenesulphonic acid-catalysed acetylations[10] have also been reported. No acid-catalysed phthalation-type procedures have been reported and in the absence of solvents such as pyridine, these reactions are extremely slow. With SBA it was observed that many alcohols underwent complete reaction in 2–3 h even in a neutral solvent such as dioxane; thus the proposed acylating reagent appears to be highly reactive.

EXPERIMENTAL

Reagents

Preparation, standardization and stability of o-*sulphobenzoic anhydride–dioxane reagent solution.* *o*-Sulphobenzoic anhydride is commercially available for the preparation of sulphonphthalein dyes. The reagent used in the present investigation was prepared as described in the literature[11]. The recrystallized compound from benzene was obtained as a pure white product, but even the pale yellow uncrystallized product could be used for making the reagent solution. An *o*-sulphobenzoic anhydride sample obtained from Fluka was also found to be satisfactory. The dioxane used as the solvent was purified to remove acetals and finally distilled over sodium metal. A stock solution of the reagent was prepared by dissolving 10 g of SBA in 100 ml of dioxane. The solution remained colourless for 15–20 days and the only change in the concentration of the solution during that time was due to slight evaporation of the solvent. The total anhydride and the free acid contents of the solution were determined by hydrolysis followed by titration with alkali solution using phenolphthalein as indicator. The presence of 2–4% acid in the anhydride did not affect the rate of acylation.

Other reagents and solutions. An approximately 0.5 *N* aqueous (carbonate-free) sodium hydroxide solution was prepared and standardized against potassium hydrogen phthalate. The alcohol and amino samples used were of A.R. grade or C.P. quality; wherever necessary, these samples were further purified by distillation over calcium oxide or by recrystallization. The purity of the samples was frequently checked by physical methods as well as by an acetylation method[12]. Synthetic mixtures of ethanol and water were also prepared and analysed in order to study the tolerance of the method towards water.

Procedure

A sample containing 2–3 meq. of hydroxy (or amino) compound was weighed accurately in a 150-ml conical flask with standard ground neck, and 5.0 ml of the SBA–dioxane reagent was added by means of an automatic pipet. The flask was then connected to a reflux condenser and refluxed on a hot plate for 2–3 h. After the flask had been cooled, about 20 ml of water was added through the condenser and the mixture was again heated for about 5 min to hydrolyse the excess of the anhydride. The condenser was rinsed into the flask and the acid concentration was finally determined by titration with standard 0.5 *N* alkali using phenolphthalein as indicator. A blank was determined similarly. The amount of alcohol was calculated from the difference in the volume of alkali consumed in the test and the blank.

When amines were determined, the reaction was generally complete in 20–30 min by heating the mixture in a stoppered flask on a water bath.

RESULTS AND DISCUSSION

The choice of indicator was based on the pH titration of *o*-sulphobenzoic acid in a blank determination as well as in mixtures with its ester after the acylation reaction. Typical titration curves are shown in Fig. 1; the curves show two inflexions corresponding to the neutralization of the strong sulphonic acid group and the weaker carboxyl group. The mid-point of the maximum slope of the final inflexion corresponds to pH 7–9.5 which justifies the choice of phenolphthalein; the visual end-point checked very well with the potentiometric end-point.

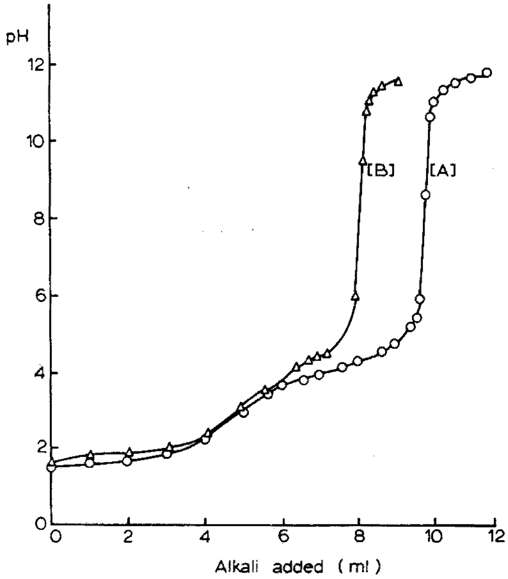


Fig. 1. pH-Titration curves of [A], *o*-sulfobenzoic acid in blank and [B], with its monoester.

The results of some typical determinations of hydroxyl and amino groups are given in Table I.

In the determination of alcohols and amines with *o*-sulphobenzoic anhydride, no interference was found from water, aldehydes, esters or ethers present in the sample. Phenols also did not react with the reagent which was therefore like phthalic anhydride from the point of view of reactivity. Unlike acetylation and phthalation, however, acylation with SBA could be carried in a neutral solvent such as dioxane, benzene, toluene, etc.; dioxane was preferred because it is miscible with water and thus more convenient for the titration with aqueous alkali solutions. The SBA–dioxane reagent solution was more stable than any of the acylating reagents in pyridine and did not require frequent standardization. Most of the alcohols reacted quantitatively in 2–3 h.

Since the reactions proceeded quantitatively at a reasonable rate even in a neutral solvent, it seems likely that they were acid-autocatalysed by the sulphonic acid liberated during acylation. The acylation reactions of hydroxyl compounds are cases of nucleophilic substitution at an unsaturated carbon atom. The reactivity of acylating agents thus depends on the reactivity of the various groups which are

TABLE I

DETERMINATION OF HYDROXYL AND AMINO COMPOUNDS BY ACYLATION WITH *o*-SULPHOBENZOIC ANHYDRIDE

Compound	*Percentage purity*		*Recovery (%)*	*Compound*	*Percentage purity*		
	Present method	*Other method*			*Present method*	*Other method*	*Recovery %*
Hydroxyl compounds							
Methanol	98.30	99.56	98.74	Glycerol	96.25	97.54	98.68
Ethanol	98.40	98.65	99.74	Butane-2,3-diol	98.60	99.38	99.24
2-Propanol	99.60	99.48	100.3	Butane-1,4-diol	98.24	99.52	98.72
1-Butanol	99.70	100.00	99.70				
2-Butanol	99.50	99.82	99.68	Pentane-1,5-diol	97.00	98.12	98.86
				Glycolic acid	99.60	99.85	99.77
2-Methyl-1-propanol	99.50	100.65	98.91	Lactic acid	86.46	85.85	100.70
2-Propen-1-ol	99.05	98.84	100.2	Malic acid	100.20	100.54	99.72
3-Methyl-1-butanol	99.50	100.10	99.38	Tartaric acid	98.20	97.86	100.30
1-Hexanol	100.00	100.00	100.00				
1-Octanol	100.00	100.05	100.00	*Amino compounds*			
				Aniline	100.00	100.20	99.80
2-Octanol	99.80	100.02	99.79	*p*-Toluidine	99.40	98.50	100.90
1-Hexadecanol	98.40	98.85	99.54	2-Naphthylamine	98.60	99.40	99.20
Cyclohexanol	99.80	100.00	99.79	*m*-Nitroaniline	100.10	100.10	100.00
2-Methylcyclohexanol	100.04	99.88	100.2	Benzylamine	99.80	100.00	99.80
Benzyl alcohol	97.55	97.85	99.70				
				Cyclohexylamine	99.70	99.80	100.00
2-Methoxyethanol	99.54	100.03	99.54	Ethylenediamine	96.90	97.80	99.10
Diethyleneglycol monoethylether	100.02	100.20	99.79	Piperidine	99.40	99.50	100.00
Menthol	99.80	98.52	101.30	Dimethylamine (aq. soln.)	32.10	32.40	99.1
				Diethylamine	97.20	97.50	99.70

replaced in the reagent during the course of nucleophilic substitution at the carbonyl carbon atom[13]. In general, the reactivity of acylating reagents increases when the replaced group is more electronegative. This would also explain the greater reactivity of a carboxy-sulphonic mixed anhydride compared to a simple carboxy anhydride. The end-point of the titration is also sharp because of the presence of the strongly acidic sulphonic acid in the reaction mixture.

The authors express their sincere thanks to Prof. R. C. KAPOOR and Dr. K. KANT for their keen interest in the work and for extending laboratory facilities.

SUMMARY

The determination of alcoholic hydroxyl groups by acylation with *o*-sulphobenzoic anhydride in dioxane medium is proposed. Quantitative esterification was generally obtained by refluxing for 2–3 h. No interferences were found from water, aldehydes, ketones, ethers, esters and phenols; the reagent appeared to be of the phthalic anhydride type. Results for 26 hydroxyl and some amino compounds by the proposed reagent are given.

RÉSUMÉ

On propose une méthode de dosage des groupes-OH alcooliques au moyen d'anhydride *o*-sulfobenzoïque, en milieu dioxane. Une estérification quantitative est généralement obtenue par chauffage à reflux pendant 2–3 h. L'eau, les aldéhydes, les cétones, les éthers, les esters et les phénols ne gênent pas. Les résultats obtenus avec 26 composés hydroxylés et quelques composés aminés sont donnés.

ZUSAMMENFASSUNG

Es wird die Bestimmung alkoholischer Hydroxylgruppen durch Acylierung mit *o*-Sulfobenzosäureanhydrid in Dioxan vorgeschlagen. Eine quantitative Veresterung wurde allgemein durch 2–3-stündiges Kochen am Rückfluss erhalten. Wasser, Aldehyde, Ketone, Äther, Ester und Phenole störten nicht. Das Reagenz schien vom Phthalsäureanhydridtyp zu sein. Es werden die Ergebnisse mit dem vorgeschlagenen Reagenz für 26 Hydroxyl- und einige Amino-verbindungen angegeben.

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SHORT COMMUNICATIONS

Freeze concentration of dilute solutions

The determination of traces of inorganic ions in de-ionized water, natural waters and various solutions suspected to contain micro amounts of contaminants becomes ever more exacting in the demands for precision at extremely low levels of concentration. The difficulties associated with the determination of ions at solution concentrations of less than 1 p.p.m. are frequently due to uncertainties concerning the purity and reproducibility of reagents. A method by which these very dilute solutions could be concentrated was sought so that they might then be brought within the range of more accurate analysis without incurring the hazards due to contamination, and possible losses resulting from volatility or chemical reaction.

The method of freeze concentration developed by SHAPIRO[1] seemed to provide an attractive answer to the problem. This method, shown by KOBAYASHI AND LEE[2] to be effective for the determination of NaCl at concentrations down to 1 p.p.m., stimulated an investigation into its application to the determination of a variety of inorganic substances, present in solution at concentrations of less than 1 p.p.m.

Essentially, the method consists of the transfer of the solution to be concentrated to a suitable container, allowing room for expansion on freezing; it is then shaken mechanically in a freezing chamber. After a few hours most of the solution is frozen leaving a small oval cavity in the centre which contains the concentrated solution.

The equipment used for the present investigation consisted of a Microid flask shaker, with which 4 samples could be concentrated simultaneously, placed inside a Frigidaire freezer cabinet. The optimum operating temperature was found to be $-20° \pm 2°$, and the shaking rate was adjusted to be just insufficient to cause splashing of the solutions.

The volume of solution taken was always 100 ml, contained in polythene bottles (of *ca.* 120-ml capacity) which were found to be the best containers for this volume. Larger bottles introduced the danger of some loss of solute, probably because the larger surface area induced too rapid freezing. The samples could be left to shake in the freezer for 3 h without attention, after which frequent inspection was necessary to ensure that the samples could be removed from the freezer when the volume of solution remaining unfrozen had reached about 5 ml. Occasionally it was necessary to make a hole in the ice before the concentrated solution could be poured off, but more usually a small hole remained through the top of the ice. After draining off the concentrate, the cavity in the ice was rinsed out twice by pouring in about 1 ml of water at room temperature, and rapidly swirling this around before adding it to the concentrated solution. The final volume of solution was never more than 10 ml, representing a 10-fold concentration of the solute.

The results derived from these studies are shown in Table I, together with the method of determination used for each solute. Triple-distilled water was used throughout, and, as necessary, its purity was checked by blank determination.

We wish to thank Mr. H. FOSTER for experimental assistance.

TABLE I

CONCENTRATION OF VARIOUS SALTS

Solute	*Concentration of solute (μg/100 ml)*	*Recovery (μg)*	*Calculated %age recovery*	*Method of determination*
NaH_2PO_4	20.0	19.7	98.5	Counting of ^{32}P labelled NaH_2PO_4
	20.0	19.2	96.0	
	20.0	20.0	100.0	
	20.0	19.9	99.5	
	5.0	4.5	90.0	
	5.0	4.9	98.0	
	5.0	5.0	100.0	
	5.0	4.8	96.0	
	5.0	4.9	98.0	
	5.0	4.7	94.0	
NaF	22.0	21.8	99.1	Colorimetric determination of F^-
	22.0	21.6	98.2	
NaCl	45.0	45.2	100.4	Flame photometry
	45.0	45.0	100.0	
	15.0	15.0	100.0	
	15.0	14.8	98.7	
	15.0	15.3	102.0	
	15.0	15.0	100.0	
$Mg(NO_3)_2$	61.0	61.0	100.0	Mg by atomic-absorption spectrophotometry
	61.0	61.0	100.0	
	61.0	59.8	98.0	
	24.4	23.8	97.5	
	24.4	24.4	100.0	
	12.2	12.2	100.0	
	12.2	12.2	100.0	
SiO_2 (as Na_2SiO_3)	10.0	10.0	100.0	Colorimetric
	10.0	10.0	100.0	
	5.0	5.0	100.0	
	5.0	5.0	100.0	
	3.0	3.0	100.0	
	1.0	1.0	100.0	
	1.0	1.0	100.0	
	0.5	0.55	110.0	
	0.5	0.50	100.0	

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Reactions of organic compounds with heteropoly acids. Part III. Colorimetric determination of carbonyl compounds with 12-molybdosilicic acid

Recently, some data on color reactions of some heteropoly acids with organic compounds in basic solution were reported[1]. It was found that 12-molybdosilicic acid and its sodium salt are effective color reagents for the qualitative determination of aldehydes and cyclic ketones containing at least one α-hydrogen atom. 12-Molybdophosphoric acid, sodium 12-molybdophosphate, and sodium 18-molybdo-2-phosphate were found to be less specific in that they react with several non-carbonyl compounds. Under the conditions investigated, 12-tungstosilicic acid failed to react with most of the compounds studied.

Although the investigation has not been extended to complex mixtures, the determinations of individual carbonyl-containing compounds have been carried out in the range of 15–800 p.p.m. of the organic compound. In view of the qualitative results in which it was shown that very few non-carbonyl-containing compounds interfere with the test, under the specified conditions, it appears that the method may be extended to mixtures containing non-carbonyl compounds without too much difficulty.

Of the heteropoly acids tested, it was found that the molybdosilicates were the most practical to use because of the stability of the blue color. The molybdophosphates were unsatisfactory owing to the rapid fading of the blue color.

Reagents

An aqueous stock solution of 200 mg of 12-molybdosilicic acid/ml was prepared using the material prepared by the process of STRICKLAND[2] or obtained from the Climax Molybdenum Company.

The sodium hydroxide solutions were prepared from reagent-grade sodium hydroxide and standardized against potassium hydrogen phthalate. These solutions were protected from atmospheric carbon dioxide during storage.

Eastman white-label samples of acetaldehyde and propionaldehyde were distilled under an atmosphere of nitrogen 3 times immediately before use. In each distillation a narrow center fraction was reserved. The final distillate was stored in a dry-ice–acetone bath and protected from light until the solutions were prepared.

The isobutyraldehyde and cyclohexanone were purified by decomposition of their sodium hydrogen sulfite addition compounds as described by VOGEL[3]. The resulting products were distilled 3 times under a nitrogen atmosphere with a small center fraction being retained each time. The pure samples were stored in a dry-ice–acetone bath until use.

Procedures

Distilled water was used as the solvent for acetaldehyde and propionaldehyde while absolute ethanol was the solvent for isobutyraldehyde and cyclohexanone. Dry nitrogen was bubbled through the solvents for 30 min before use to free them of dissolved gases which might react with the carbonyl compounds. The solvent was placed in a rubber-capped serum bottle, which was flushed with nitrogen and then sealed. The bottle and contents were weighed accurately. Samples of the carbonyl compounds were withdrawn from their containers and transferred to the serum bottle by means of a hypodermic syringe. The resulting solution was weighed accurately and its concentration was computed. Samples of these stock solutions were withdrawn by means of the syringe and the syringe was used as a vessel for weighing individual samples. The samples were transferred to a volumetric flask for assay. The stock solutions were analysed within 30 min after preparation to avoid decomposition of the organic compound.

Aliquots of the standard solutions of the carbonyl compound were weighed into 100-ml volumetric flasks. To the sample was added 8.4 ml of 1.937 N sodium hydroxide followed by 5 ml of the 12-molybdosilicic acid solution. The contents of the flask were swirled for a few sec and made up to volume with water. The intensity of the color was measured with a Beckman Model DU or Model B spectrophotometer, at 675 mμ using distilled water as a blank.

In order to assure an excess of the color reagent, the concentration of the carbonyl compound in the final solution was limited to no more than one-tenth that of the heteropoly acid. Appropriate amounts of 0.1 M 12-molybdosilicic acid were used in all experiments designed to evaluate the method.

When the order of addition of reagents was reversed, that is the color reagent added before the base, the intensity of the color was diminished by nearly 100%. The color gradually deepened on standing when this technique was used.

Results and discussion

Experiments showed that the maximum intensity of color was attained immediately so it was not necessary to establish the optimum reaction time. However, the time variable was examined. The sodium hydroxide was allowed to stand in contact with the solution of the carbonyl compound for varying lengths of time prior to addition of 12-molybdosilicic acid. Little difference in intensity or stability of color was noted when this time was 0–30 min. However, slightly better results were obtained when the reagents were mixed rapidly.

The procedure given in the experimental section evolved from these early experiments. That is, approximately 80 molar equivalents of sodium hydroxide and 10 molar equivalents of 12-molybdosilicic acid were added to a solution of the carbonyl compound. The color was measured immediately after dilution of the mixture. The manipulations should be made as rapidly as possible and the color should be measured immediately after mixing in order to avoid errors due to fading. The color was stable for 5–10 min and then began to fade; 5–10% loss in color was observed after 30 min.

The above procedure was used to obtain data for Beer's law plots of the acetaldehyde, propionaldehyde, isobutyraldehyde, and cyclohexanone reactions. Beer's law held in all cases when distilled water was used as a blank. When the 12-molybdosilicic acid solution was used as a blank, the system did not conform to Beer's law but a plot of absorbance *vs.* concentration yielded a straight line. Analyses of the carbonyl compounds may be carried out in the following concentration ranges:

Acetaldehyde, 50–800 p.p.m.
Propionaldehyde, 60–400 p.p.m.
Isobutyraldehyde, 15–350 p.p.m.
Cyclohexanone, 70–800 p.p.m.

Parallel studies were conducted using 12-molybdophosphoric acid and sodium 12-molybdophosphate as color reagents. Beer's law did not hold for these reagents under any conditions investigated. Furthermore, it was not possible to reproduce data of replicate runs due to the rapid fading of the color. The disappearance of color is probably due to the degradation of the heteropoly anion by base[4]. Since it is much more severe in the case of the molybdophosphate, these materials must be less stable to alkali than the molybdosilicates.

The preparation of pure standard solutions of the carbonyl compounds was a source of some concern in the early part of this work. One approach to this problem was to use the solid sodium hydrogen sulfite addition products of the carbonyl compounds and allow these materials to decompose and liberate the free carbonyl in the basic solution. This approach met with little success since it was not possible to develop a reproducible color by this technique. Furthermore, separate experiments showed the 12-molybdosilicic acid was readily reduced by sodium hydrogen sulfite under the conditions of the color reaction. The intensity of the color produced by sodium hydrogen sulfite reduction was much more intense than that produced by reduction by an equivalent amount of a carbonyl compound. Therefore it would not be possible to determine carbonyl compounds in unknown mixtures using calibration curves obtained from sodium hydrogen sulfite addition compound standards. Since carbonyl compounds are rarely precipitated quantitatively as their sodium hydrogen sulfite products, this approach did not seem practical.

In general the presence of other organic compounds with different functional groups did not interfere with the determination. The few exceptions are listed in previous publications[1]. However, these interferences need not limit the utility of the method since all of the compounds except glyoxal, chloroactone, dihydroxyacetone, and pyruvaldehyde are soluble in acid or basic media. Therefore, these interfering substances may be extracted from their mixtures with carbonyl compounds by acid or base.

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Amperometric determination of palladium, silver and copper with 2-mercaptobenzoxazole

KURAŠ[1] introduced 2-mercaptobenzoxazole as a reagent for the detection of silver, mercury, lead, copper, cadmium, iron and cobalt. It has been utilised for the gravimetric determination of rhodium[2], for the spectrophotometric determination of palladium[3], and for the gravimetric determination of palladium, silver and copper[4] in acetate-buffered medium (pH 4–5). The object of the present investigation was to ascertain its potentiality for the amperometric titration of Pd, Ag and Cu.

Reagents and apparatus

The reagent was prepared by condensing *o*-aminophenol and carbon disulphide in presence of alcoholic caustic potash[5]. The reagent was soluble in alcohol and in dilute alkali solutions; the latter were used as titrants as they gave reproducible results. The titrants were about 20 times stronger than the metal ion solutions, so that no corrections for dilution were necessary. The alkaline solution of the reagent was stable for 48 h if kept in a dark bottle in a refrigerator.

Standard solutions of palladium and silver were prepared by proper dilution of standard palladium chloride and silver nitrate solutions. Standard solutions of copper nitrate were prepared by dissolving accurately weighed metallic copper in dilute nitric acid and removing the excess acid.

The characteristics of the capillary used were as follows: $m = 1.486$ mg/sec, $t = 6$ sec (open circuit in distilled water), $h = 41.7$ cm. The amperometric apparatus was as described by LINGANE[6]. The 50-ml titration cell was connected to the S.C.E. by means of an agar–potassium chloride bridge; an agar–potassium nitrate bridge was used in the silver titration.

Current–voltage studies

Aliquots of the metal solutions and the reagent solutions were separately placed in the titration cell, and 5 ml of 2 *M* sodium acetate–acetic acid buffer and 1 ml of gelatin solution (freshly prepared aqueous 0.2%, w/v) were added. The solution was diluted to 30 ml and deoxygenated by passing pure nitrogen gas for 10–15 min. After a few min, the steady current was noted; readings were made at potentials of 0.0–1.6 V *vs.* S.C.E.

The reagent yielded no diffusion current till a potential of −0.4 V *vs.* S.C.E. was reached; it then slowly diffused towards the cathode but failed to attain a constant diffusion rate anywhere in the voltage range up to −1.6 V. The diffusion currents for the metal ions were well defined. For palladium, silver and copper the diffusion currents remained constant over the potential ranges −0.3–0.7 V, −0.2– −0.6 V and −0.2– −0.5 V respectively. Accordingly, a potential of −0.3 V was selected for the titration.

Titration of palladium, silver and copper

An aliquot of the standard metal ion solution was placed in the cell, and 5 ml of the above acetate buffer and 1 ml of the gelatin solution were added; the mixture was diluted to 30 ml with water. Pure nitrogen was bubbled through the solution for 10 min. The titration was then carried out at an applied potential of −0.3 V *vs.* S.C.E. until either no current flowed or the value of the current remained constant for several readings. Typical titration curves are depicted in Fig. 1.

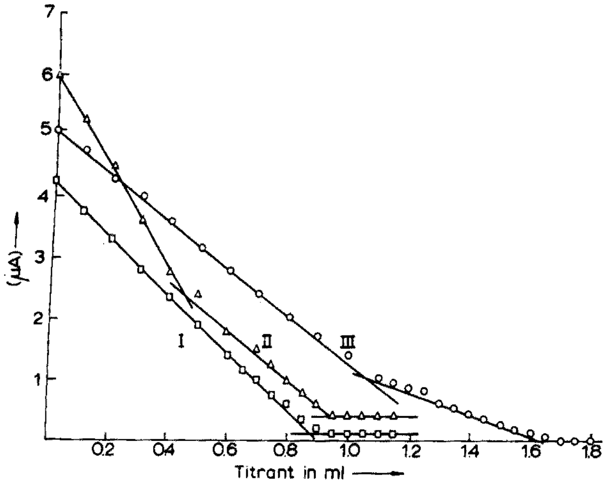

Fig. 1. Titration of palladium, I; copper, II, and silver, III.

It can be seen that the titration of palladium proceeded in a straightforward manner. For silver the current eventually decreased to zero but the titration curve showed 2 other linear portions, the extrapolation of which was taken as the equivalence point.

For copper, the current never decreased to zero, but stabilized at a very small value ($< 0.5\ \mu A$); the 3 linear portions of the curve resulted in 2 sharp intersections. The second intersection was taken as the equivalence point, corresponding to the metal–ligand ratio of 1:2. The first intersection corresponded approximately to a metal–ligand ratio of 1:1. When a $5\text{–}6 \cdot 10^{-2}\ M$ reagent solution was used for the titration of $1.5 \cdot 10^{-3}\ M$ copper concentrations this phenomenon was pronounced. Palladium and silver indicated the formation of 1:2 and 1:1 complex with the reagent. Probably the reaction between copper and the reagent was a stepwise complex formation as represented by the following equations:

$$Cu^{2+} + RSH \rightarrow [Cu(RS)]^{+} + H^{+}$$

$$[Cu(RS)]^{+} + RSH \rightarrow [Cu(RS)_2] + H^{+}$$

The ranges of metal ion concentration, over which the method gave reproducible results, were 1–5 mg for palladium, 0.5–4 mg for silver, and 1–4 mg for copper. The maximum relative error in these ranges was less than 1.5%. Above the specified ranges, the errors increased to about −3%.

The methods were found satisfactory in presence of 4–5-fold amounts of foreign ions such as Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}; mercury-(I and II) and platinum(IV) interfered seriously. Copper interfered with the determination of palladium and silver. Interference from silver was prevented by adding excess of potassium chloride solution before the addition of buffer solution, and then titrating the metal ion in the supernatant liquid. The tolerance for various ions is shown in Table I.

TABLE I

TOLERANCE LIMITS FOR DIVERSE IONS
(Pd taken= 1.540 mg, Cu taken=1.500 mg, Ag taken=1.500 mg)

Foreign ion added	*Amount added (mg)*	*Pd found (mg)*	*Cu found (mg)*	*Ag found (mg)*
Ag^+	7.5	1.540	1.503	—
	15	1.562	1.524	—
Pb^{2+}	7.5	1.553	1.518	1.512
	15	1.610	1.591	1.605
Co^{2+}	7.5	1.550	1.520	1.506
	15	1.580	1.578	1.576
Ni^{2+}	7.5	1.540	1.504	1.505
	15	1.590	1.568	1.591
Mn^{2+}	7.5	1.541	1.504	1.502
	15	1.574	1.562	1.509
Zn^{2+}	7.5	1.540	1.507	1.503
	15	1.583	1.535	1.540
Cd^{2+}	7.5	1.554	1.520	1.508
	15	1.602	1.582	1.578
Fe^{3+}	3	1.559	1.520	1.520
	6	1.602	1.604	1.580
As^{3+},Sb^{3+},Bi^{3+}	8 (each)	1.578	1.527	1.519

The authors express their thanks to the authorities of Jadavpur University, Calcutta, for providing laboratory facilities and to the Council of Scientific & Industrial Research (India), New Delhi, for awarding a research fellowship to B.C.B.

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Determination of silicon in minerals by microdiffusion technique

Recently we investigated the determination of silicon in talc-like materials, using the microdiffusion technique described by ALON *et al.*[1]. When the amount of sulfuric acid specified by the authors was used, little or no silicon was recovered. It was found that as the amount of sulfuric acid was increased, the recovery of silicon increased. When 2 ml of concentrated sulfuric acid was added to the reaction chamber, the recovery of silicon was at least 95%. A straight-line calibration curve was obtained by diffusion of samples containing 5–50 μg of silicon.

ALON *et al.*[1] used a sodium hydroxide fusion to solubilize the silicon in minerals but did not give any details of the fusion. We used the traditional sodium carbonate fusion and employed a 40:1 ratio of flux to sample. The diffusion was permitted to take place overnight, rather than during a 6-h period as described in the published procedure. A limited number of experiments indicated that any diffusion time over 6 h gave satisfactory recoveries.

By the modified procedure, recoveries of silicon from talc-like materials were 98–102% of the values obtained by the classical gravimetric procedure.

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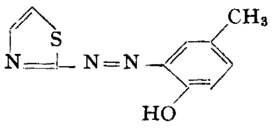
Anal. Chim. Acta, 33 (1965) 567

A new EDTA method for the determination of calcium in blood serum

It has been shown by FLASCHKA AND ABDINE[1] as well as by JENSEN[2] that under certain buffer conditions a copper–EDTA–indicator combination may be employed to determine many metals. CHENG AND BRAY[3] had previously pointed out the potential of utilizing an organic dye with a pyridine base, namely 1-(2-pyridylazo)-2-naphthol, as an indicator in compleximetric titrations for zinc, copper, cadmium and other metals, but this method was completely outside the scope of clinical chemistry value.

The new method for the determination of serum calcium which is described below is based on the principle that calcium chelates with ethylenediaminetetraacetate, with which it can be titrated when in a highly alkaline medium, and on the utilization of a new compleximetric metal indicator specific for calcium at pH 12.0–



(I)

12.5. Copper first chelates with EDTA, and is then displaced by calcium present in blood serum sample from its EDTA complex. The indicator employed in this procedure is 2-(2'-thiazolylazo)-*p*-cresol (I), an organic dye with a thiazole base, herein referred to as TAC.

Reagents

TAC indicator, 0.1%, was prepared in methanol. The 2-(2'-thiazolylazo)-*p*-cresol was prepared by JENSEN of the Danish Atomic Energy Commission by coupling of the diazotized 2-aminothiazole with *p*-cresol[2].

Stock standard solution, 100 mg Ca/100 ml, was prepared as follows: 2.50 g of Analar calcium carbonate, previously dried at 105° for 24 h, was transferred to a 1-l flask and 200 ml of distilled water and 50 ml of *N* hydrochloric acid were added. This preparation was allowed to stand overnight to dissolve completely and diluted to the mark with distilled water. The working standard solution, 10 mg Ca/100 ml, was prepared from the stock standard by diluting 10 ml to 100 ml with distilled water.

Procedure

Pipet 1.0 ml of 1.00 *M* potassium hydroxide solution (calcium-free reagent grade) into a 50-ml Erlenmeyer flask fitted with ground-glass stopper; add 0.04 ml of TAC indicator and briskly rotate the flask to mix. Next, add 0.02 ml of 0.1 *M* copper sulphate solution and mix well again. This mixture has a lilac color. Immediately, add 0.1 *M* EDTA (disodium salt) solution from a Rehberg buret[4] or automatic dispensing buret until the indicator just changes color to pale yellow, approximately 9–10 ml EDTA being required. From a buret, add 1.0 ml of the potassium hydroxide solution. At this point, add 0.2 ml of unhemolyzed and non-icteric blood serum from a freshly clotted blood specimen. (Appropriate standards were substituted for serum where necessary.) Then add 0.02 ml of the TAC indicator and rotate the flask briskly until a lilac color appears again. As quickly as possible continue the titration with EDTA to a yellow or pale amber color and record the value obtained. Blanks were tested in the same manner as outlined, except that 0.2 ml of distilled water was substituted for serum.

Results and discussion

The pH zone of 12.0 was employed in this method to eliminate interference by serum magnesium. By control experimentation it was found that magnesium could exceed calcium in serum by a factor of 10–20 without interference; the end-point remained definite up to this ratio. Without effect upon the end-point, interference by trace amounts of iron were obviated by the addition of 0.02 ml of 1.0% potassium cyanide solution just before the titration[4,5].

No attempt was made to determine the ionized calcium nor the ultrafiltrable calcium and the values reported herein are regarded as total serum calcium[6].

Small amounts of added phosphates, nitrates, chlorides, acetates, and sulphates did not interfere. Hemolyzed and moderately icteric blood samples invariably gave false values and poor reproducibility. Good end-points were only obtained when each analysis was completed within 10 min of making the first addition of potassium hydroxide. Temperature variations between 15 and 38° had no appreciable effect on the titration end-points. Recoveries of these blood serum samples when

TABLE I

COMPARISON OF THE PRESENT METHOD WITH CLARK AND COLLIP'S METHOD[7]

Serum no.	*Patient*	*EDTA method*[a] *(mg %)*	*Clark and Collip's method*[b] *(mg %)*
1	J.J.T.	9.0	8.9
2	K.H.	9.4	9.5
3	S.S.P.	9.8	9.2
4	O.R.W.	9.6	10.2
5	L.A.J.	9.5	9.6
6	A.J.	10.7	10.5
7	S.S.P.	9.9	10.0
8	J.L.H.	9.6	9.7
9	G.F.J.	9.8	9.9
10	E.M.S.	9.8	9.9
11	E.V.C.	9.9	10.3
12	E.S.	10.8	11.4
13	T.L.	10.1	10.2
14	K.J.	9.5	9.7
15	E.J.	10.5	10.6
16	Z.E.J.	10.3	10.4
17	H.B.W.	10.3	10.5
18	S.S.P.	9.8	9.9
19	K.B.H.	9.5	9.5
20	E.J.	9.9	10.1
21	G.E.W.	10.0	10.2
22	H.O.	9.2	9.1
23	A.L.	9.8	9.9
24	K.M.R.	8.9	8.9
25	R.M.J.	10.2	10.4
26	S.S.P.	9.8	9.9
27	Z.E.J.	10.2	10.4
28	E.C.S.	10.9	10.8
29	T.W.V.	10.8	11.1
30	T.K.L.	9.8	10.1
	Average:	9.9 mg %	10.0 mg %

[a] Mean of 3 determinations.
[b] Mean of 2 determinations.

quantities of standard calcium solution were added were 97–101%.

Findings were interpreted as normal when in agreement with established normal serum calcium concentration[6] at 9–11 mg % or 4.5–5.5 meq./l. The accuracy and precision of this EDTA method were studied by comparison with the CLARK AND COLLIP technique for blood serum calcium measurements[7] on the same samples. In general, values obtained by the EDTA method were slightly lower than those by the CLARK AND COLLIP method. Results are presented in Table I. The average mean difference was 0.1 mg % based on the 30 samples analyzed.

The author gratefully acknowledges the advice and suggestions of Prof. MOGENS FABER and Mr. BROR S. JENSEN.

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Determination of magnesium in needle-biopsy samples of muscle tissue by means of neutron activation analysis

The estimation of intracellular electrolytes in man is known to be of great importance in many diseased states, though in clinical practice they must for the most part be estimated indirectly from serum values. As regards magnesium, even serum values are difficult to obtain, owing to the lack of suitable analytical methods. In recent years, flame photometry has proved to be the most suitable method for the analysis of magnesium in research, though it has not yet been incorporated in clinical routine analysis. Magnesium has been estimated by a few researchers in surgical macrobiopsies performed in human material[1-3], and once in needle biopsies with flame photometry[4]. With the method of flame photometry, the sample is consumed for one magnesium determination.

However, the method of neutron activation analysis has the advantage of greater sensitivity, and it affords, moreover, the possibility of determining other elements of special clinical importance such as chlorine, potassium and sodium in the same sample. These elements have earlier been determined in the same needle-biopsy sample from human muscle[5].

Magnesium has previously been determined in biological material, *e.g.* blood and blood fractions, by neutron activation analysis[6,7]. However, little information is available concerning the precision of these determinations. Recently an activation analytical method for the determination of magnesium in biological material yielding a recovery of 75% has been reported[8].

In the present investigation the Szilard–Chalmers effect was applied in the separation of the induced ^{27}Mg activity from the organic matrix by extraction with concentrated hydrochloric acid[9]. In this way the common destruction process of the organic material, which might be a time-consuming procedure, is avoided. With the present technique parts of the organic material are also dissolved. However, this was found not to influence the analysis.

Experimental

Samples. Muscle-biopsy samples of 0.5–4 mg dry fat-free weight were irradiated in a thermal neutron flux of $2 \cdot 10^{13}$ n/cm^2/sec for periods of 10 min. After the irradiation the samples were crushed. The small biopsy samples had been weighed on a continuously recording electronic "Cahn" balance for 3 min and the wet weight was then extrapolated to the moment for the performance of the biopsy. The fat-free dry weight of the sample was determined on the same balance after drying at 100°.

Extraction and precipitation. After the irradiation the homogenized samples were extracted 3 times with concentrated hydrochloric acid in portions of 4 ml at a temperature of 100°. The concentrated hydrochloric acid solution contained *ca.* 1 mg magnesium as carrier.

The solution was passed through a G4 filter, and 10 mg of magnesium was then added before precipitation in strong alkaline solution ($\text{pH} > 12$). The solution was warmed to about 80° and allowed to stand for a few minutes to allow the hydroxide precipitate to settle. The solution was then passed through a Hyflogel filter of 5 mm height, which was washed with *ca.* 30 ml of sodium hydroxide solution of $\text{pH} > 12$. The filter had earlier been washed with the same solution.

Measurements. The γ-spectrometric measurements were performed with a 256-channel pulse-height analyser attached to a $3 \times 3''$ NaI (Tl) crystal. The quantitative determinations were made with the 1.02 MeV full energy peak. Residual disturbing activities of ^{24}Na and ^{38}Cl together with the ^{56}Mn activity that was also precipitated, could easily be stripped off.

Results

The ^{27}Mg activity was recovered in muscle tissue specimens to $97(\pm 2)\%$; this value is the mean yield of 5 determinations with the standard deviation of a single value.

The precipitation of magnesium as hydroxide including the filtration on a Hyflogel filter was found to give losses of less than 1%.

Triple magnesium determinations performed on muscle tissue from the same rat of 1–3 mg dry fat-free weight gave as result 1.24 ± 0.12 μg/mg sample. With flame photometry a mean value of 1.22 ± 0.08 μg/mg sample was obtained. In the latter case somewhat larger samples were analysed.

Magnesium in needle-biopsy specimens from living human quadriceps muscle with a dry weight of 0.5–3.5 mg were also determined by this activation method. In a series of 5 samples from different subjects a magnesium content of 1.16 ± 0.17 μg/mg sample was obtained. Values slightly less than 1 have previously been reported[2,4].

Discussion

In the present study magnesium was determined in biopsy samples as small as 0.5 mg dry weight. This may be advantageous in clinical studies, as such small needle biopsies can be taken from human quadriceps muscle without discomfort to the patient. At the same time as the magnesium is determined, chlorine, potassium and sodium can easily be determined in the same sample as previously described by BERGSTRÖM[5] using β- and γ-measurements or as follows, by means of an extraction procedure and γ-ray spectrometry.

(*1*) The ^{38}Cl activity is determined by performing measurements directly on the sample.

(*2*) The ^{27}Mg activity is then extracted from the sample, as described in the present paper.

(*3*) The ^{24}Na activity is determined by measuring the extract solution after the decay of ^{38}Cl. ^{42}K is simultaneously determined when stripping off the ^{24}Na contribution in the γ-spectrum. (The activities belonging to the alkali metals were earlier found to be nearly quantitatively extractable in concentrated hydrochloric acid[9].)

For the determination of phosphorus, which is also of special interest in this connection, longer irradiation periods must be used[5].

In the ^{27}Mg determination, the following 2 interfering reactions were considered:

^{27}Al (n, p) ^{27}Mg (cross-section for fission spectrum neutrons: 4.3 mb[10])

^{30}Si (n, α) ^{27}Mg (cross-section for fission spectrum neutrons: 1 mb[10])

Assuming the Al and Si contents in muscle tissue to be 1 p.p.m. and 20 p.p.m.[11,12], and the fast fission flux to be less than 1/10 of the thermal flux in the irradiation position used[13], the contribution of ^{27}Mg from these reactions is less than 0.1% and may therefore be neglected.

The sensitivity for magnesium with this method is estimated as 0.3 μg when irradiating biological samples at thermal neutron fluxes of $2 \cdot 10^{13}$ n cm^{-2} sec^{-1}.

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BOOK REVIEWS

SIR HARRY MELVILLE AND B. G. GOWENLOCK, *Experimental Methods in Gas Reactions*, 2nd Ed., Macmillan & Co. Ltd., London, 1964, vi + 464 pp., price 84/—.

The first edition of this book appeared in 1939, when it soon proved its worth as a source of information which hitherto had been widely scattered throughout the literature. This new edition has appeared at an appropriate time when interest in this field has expanded considerably. Although the new edition has been extended to include modern methods, a selected amount of the older material has been retained. This is particularly true of the section on gas analysis; the authors wisely remark that "... it seemed to us that these methods, which are rapidly becoming unfamiliar to the younger generation ..., might suggest analytical techniques in fields where gas chromatography is difficult to employ ...".

The first chapter surveys briefly the kinetic theory of gases. This is followed by chapters on the measurement of pressure and temperature. Methods for measuring pressure are described which range from the mercury manometer to the latest techniques for recording pressure automatically, whilst the measurement and control of temperature is dealt with from the temperature of liquid hydrogen to those of high temperature furnaces.

The next chapters describe the preparation and purification of gases and volatile compounds; some 50 compounds are considered. Generation, scrubbing, drying, fractionation and storage are dealt with and reference is made to gases which are commercially available. The fifth chapter surveys methods for the analysis of gases and is divided into non-chromatographic and chromatographic methods. The last section is somewhat brief, but nowadays this information is generally easier to find than that on the older techniques. The next chapter describes photochemical techniques and includes sources of radiation, control of radiation and measurement; methods used in flash photolysis are described. Finally (Chapter 7), problems of assembly of apparatus are considered, together with some of the techniques which have been developed for specific types of reaction.

This book should be of great value to newcomers to the techniques of high-vacuum and gas-manipulation, and it should be especially useful as a reference book for the research worker engaged on gas reactions.

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Anal. Chim. Acta, 33 (1965) 573

R. L. MITCHELL, *The Spectrochemical Analysis of Soils, Plants and Related Materials*, Technical Comm. No. 44A, Commonwealth Bureau of Soils, Harpenden, Reprinted with Addendum, Commonwealth Agricultural Bureau, Farnham Royal, Bucks, England, 1964, 225 pp., price 40 s or $6.00.

The Technical Communication *The Spectrographic Analysis of Soils, Plants and Related Materials* was published originally in 1948. This Communication has been reprinted in its entirety and a section added on the recent developments that have taken place at the Macaulay Institute for Soil Research. As indicated by the change in title, more emphasis is now placed on spectrochemical analysis. Attention is also paid to direct arc excitation, porous cup solution spark excitation, flame photometry and atomic absorption spectroscopy.

The value of this book is the wealth of information it contains on laboratory technique, sample handling and optimum arc and spark discharge conditions. This is particularly valuable to the practicing spectroscopist. The added addendum is written in the same style and has the same stamp of technical excellence as the old part of the book. The continued demand for this Communication over a number of years testifies to its enduring value to any spectrographic laboratory. The new edition maintains this high standard and is to be recommended to all spectrographic laboratories.

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Anal. Chim. Acta, 33 (1965) 573–574

CHR. KLIXBULL JØRGENSEN, *Inorganic Complexes*, Academic Press, London–New York, 1963, 220 pp., price 42 s.

Although this book is not of direct concern to analytical chemists, it does present a survey of recent progress in the understanding of chemical bonding and the preparation of unexpected and unusual inorganic compounds, which is of considerable general interest. The author is well-known for his work on the spectra of inorganic complexes and it is mainly from this personal aspect that the book has been written.

The chapters are arranged according to the type of ligand, *e.g.*, aquo, hydroxo, oxo, halogeno, nitrogen-containing, oxygen-containing, sulphur-containing, etc. An interesting feature of the book is the inclusion of an account of the chemistry of rare gas compounds, though the rapidly expanding nature of this branch of inorganic chemistry must make the present account rather incomplete.

There is much in this book to interest the analytical chemist who wishes to have a better understanding of the attitude and work of the modern inorganic chemist towards inorganic complexes. Many of the most useful organic reagents applied in inorganic analysis were studied initially by inorganic chemists, interested in the nature and behaviour of unusual compounds formed by metals. Who is to say that the present studies of the rare gas compounds may not also lead eventually to analytically useful reactions? For these reasons this book makes worthwhile reading, and the personal enthusiasm of its author has given it an unusual and refreshing style. Intending readers are warned, however, that the author's "Orbitals in Atoms and Molecules" is perhaps necessary additional reading.

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Anal. Chim. Acta, 33 (1965) 574

Treatise on Analytical Chemistry, Edité par I. M. KOLTHOFF ET P. J. ELVING avec l'assistance de E. B. SANDELL, Part I. *Theory and Practice.* Vol. 5, Section D-3, *Optical Methods of Analysis*, Interscience Publishers, New York, 1964, 2707–3346 pp., price 120 s.

Anal. Chim. Acta, 33 (1965) 574–575

E. J. MEEHAN introduit le sujet en quelques 44 pages et de façon remarquable. Après la classification des méthodes optiques l'auteur donne les caractéristiques de l'énergie radiante et les principaux mécanismes responsables de l'absorption et de l'émission.

Le second chapitre, du même auteur, s'intitule : bases fondamentales de spectrophotométrie; il comprend les lois et nomenclature, la sensibilité, les représentations graphiques, la précision et l'analyse des mélanges, c'est un modèle de clarté et concision.

Suivent deux chapitres qu'on ne rencontre pas dans les traités de chimie analytique ordinaires: la dispersion de la lumière et ses applications aux solutions colloïdales et aux polymères (F. W. BILLMEYER) et la spécification des couleurs (D. B. JUDD ET I. NIMENOFF). On y trouve une documentation intéressante et souvent inédite de sujets peu connus des chimistes analystes.

A. A. SCHILT ET B. JASELSKIS traitent de spectrophotométrie dans le visible et dans l'ultra-violet. Il nous semble qu'une meilleure entente entre les auteurs aurait permi d'éviter certaines redites (on trouve par exemple le même tableau à la page 2715 et à la page 2952). Les applications, tant à l'analyse qualitative que quantitative, terminent ce chapitre. Cette partie est fort bien faite; il est question du rôle du solvant, du choix de la longueur d'onde, des interférences et l'auteur donne une foule de renseignements pratiques et théoriques qui seront très précieux aux chimistes. La tâche difficile de B. JASELSKIS était de présenter l'appareillage: sources, monochromateurs, détecteurs, mode d'emploi. Un choix judicieux a été fait, l'auteur a su tirer l'essentiel d'un ensemble extrêmement complexe.

Nous avons été étonné qu'une place si petite ait été réservée à la fluorimétrie car cette méthode très sensible et souvent sélective est susceptible d'important développement, particulièrement en milieu non aqueux. Dans le court exposé de A. L. CONRAD, extrêmement bien fait, il n'est malheureusement question ni d'appareillage, ni des phénomènes secondaires de la fluorescence. En fin de chapitre l'auteur donne quelques exemples de dosage.

Le chapitre suivant s'intitule rayons X: absorption, diffraction et émission. Trois spécialistes en sont responsables: H. A. LIEBHAFSKY, H. G. PFEIFFER ET E. H. WINSLOW. Exposé concis, dépouillé de tout ce qui n'est pas l'essentiel.

L'analyse X par microsondes permet l'étude de très petites surfaces, l'appareillage est encore coûteux mais les possibilités d'un tel processus sont considérables.

Deux chapitres terminent ce livre: la spectrophotométrie par micro-ondes (J. H. GOLDSTEIN) et la néphélométrie et turbidimétrie (F. P. HOCHGESANG).

La lecture de cet ouvrage montre, s'il en était besoin, l'importance prise par les méthodes physiques et physico-chimiques dans l'analyse moderne. Bien documenté, peut-être pas toujours très bien dosé, c'est un livre remarquable, oeuvre de spécialistes de grande classe.

D. MONNIER (Genève)

Anal. Chim. Acta, 33 (1965) 574–575

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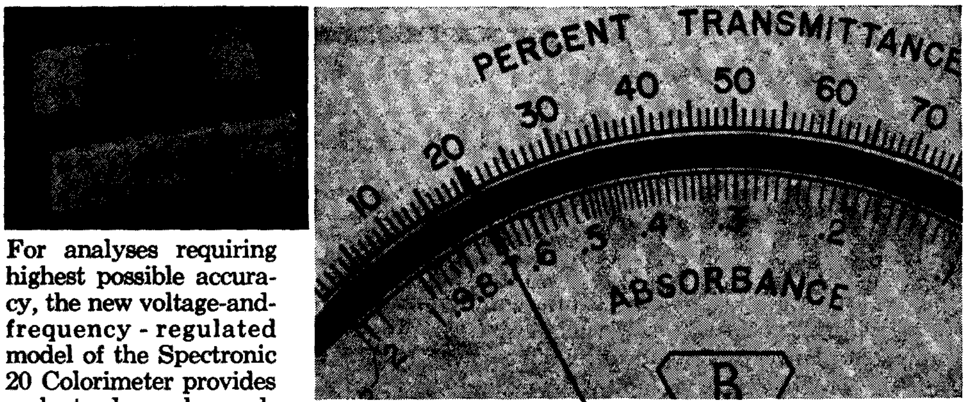
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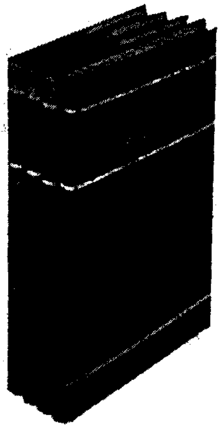

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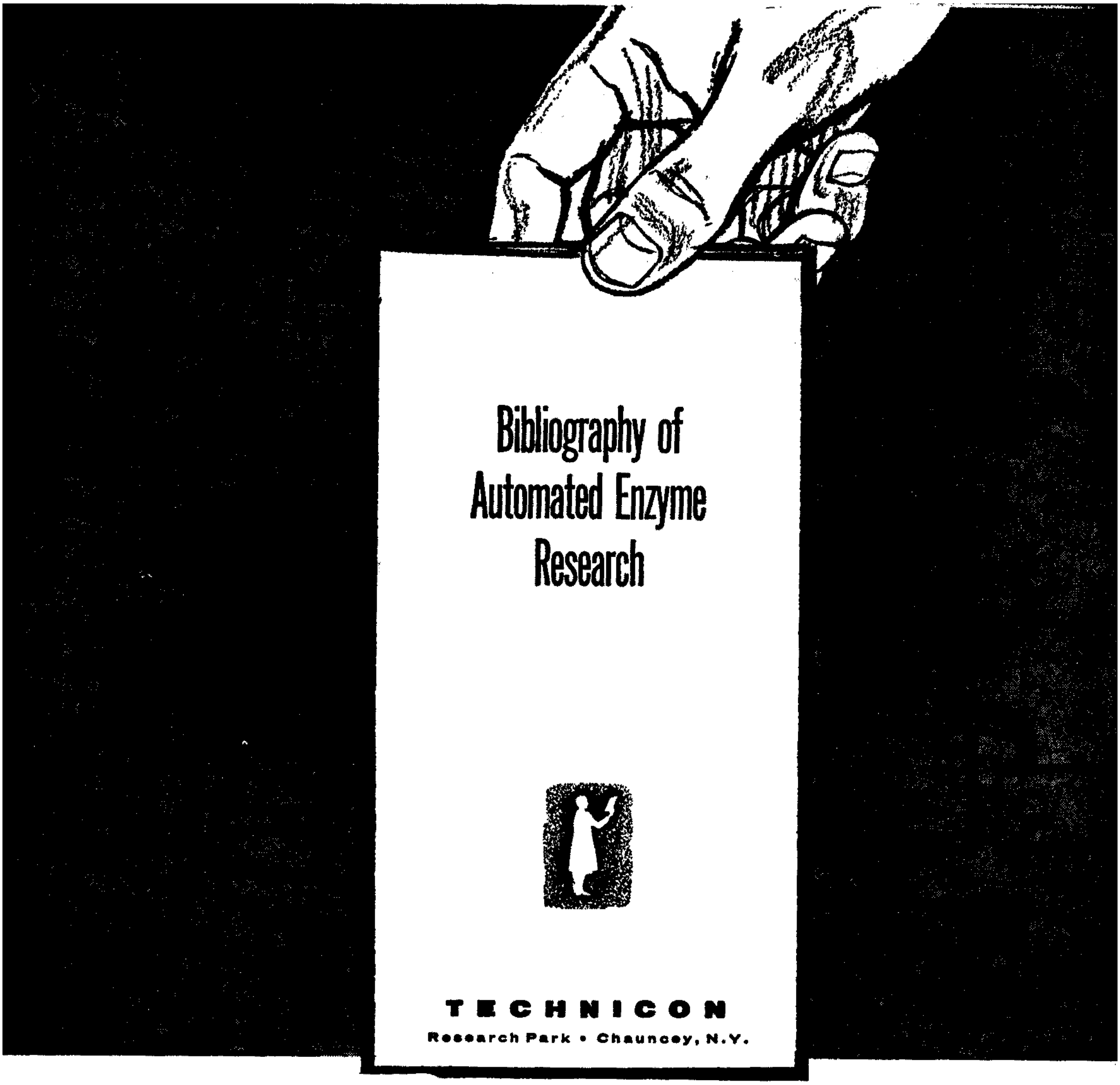

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