

# ANALYTICA CHIMICA ACTA

*International monthly devoted to all branches of analytical chemistry*  
*Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique*  
*Internationale Monatsschrift für alle Gebiete der analytischen Chemie*

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  2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.
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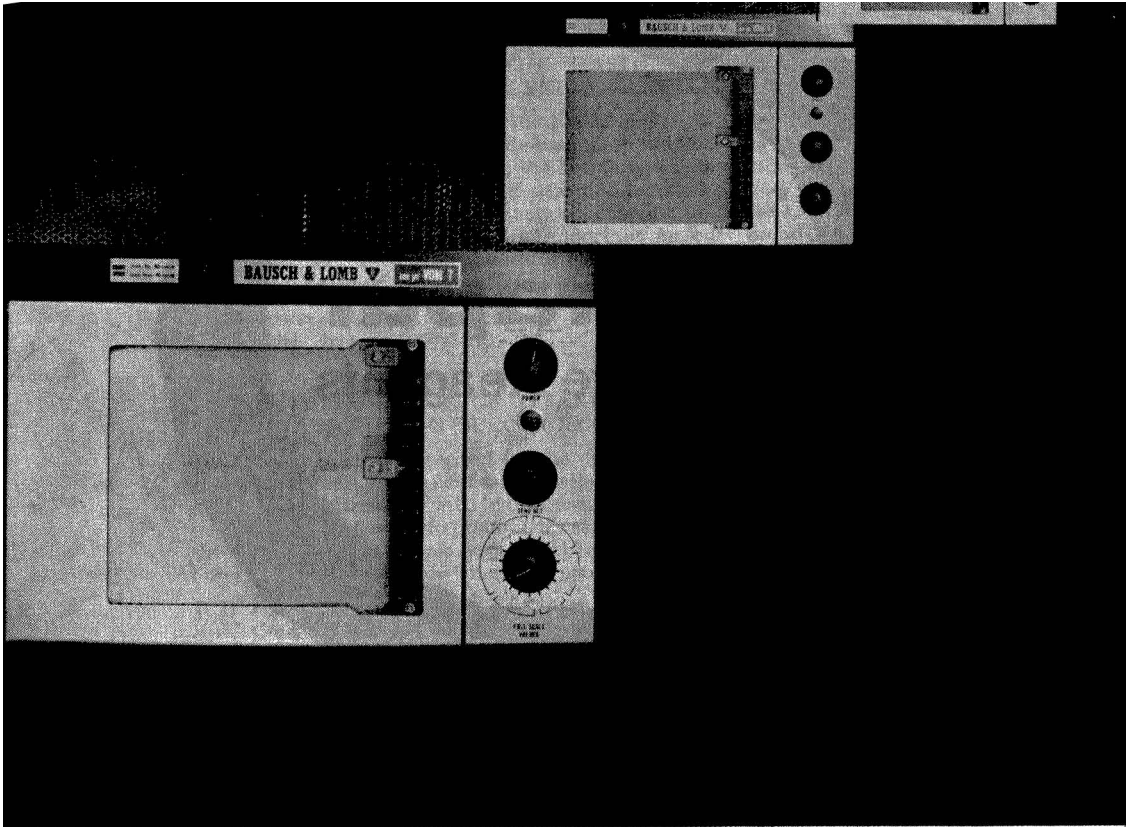
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## SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 37, No. 2, February 1967

### ANODIC REACTIONS OF THE HALIDES IN DIMETHYL SULFOXIDE AT THE PYROLYTIC GRAPHITE ELECTRODE

The anodic reactions of the halide ions in dimethyl sulfoxide at the pyrolytic graphite electrode have been studied. The iodide ion demonstrates a 3-step oxidation; the bromide, a 2-step oxidation and chloride, a 1-step oxidation. The electrode reaction ( $X^- \rightarrow \frac{1}{2} X_2 + e^-$ ) is complicated by a catalytic reaction occurring after the electrode reaction. The catalytic reaction is important for only bromide and chloride causing a considerable diffusion current enhancement. The  $\alpha_n$  value for all 3 primary reactions is of the order of 0.5.

H. E. ZITTEL AND F. J. MILLER,  
*Anal. Chim. Acta*, 37 (1967) 141-150

### THE DETERMINATION OF TITANIUM IN ALLOYS BY ATOMIC ABSORPTION SPECTROSCOPY

A method is described for the determination of 0.1-1.2% of titanium in steels, permanent magnet alloys and cast iron using atomic absorption spectroscopy with hydrofluoric acid solutions and a nitrous oxide-acetylene flame. No preliminary separations are required. When the correct conditions are employed there is no interference from the other elements commonly found in these alloys.

J. B. HEADRIDGE AND D. P. HUBBARD,  
*Anal. Chim. Acta*, 37 (1967) 151-155

### EFFECT OF MIXED ORGANIC SOLVENTS ON ATOMIC ABSORPTION SPECTROPHOTOMETRY OF REFRACTORY METALS

The effect of various mixed organic solvents on the absorption characteristics of vanadium was studied in fuel-rich oxy-acetylene and nitrous oxide-acetylene flames. The absorption of the 3183.9 Å line of vanadium was greatly enhanced by the use of various mixed organic solvents when fed to oxy-acetylene flames. In the case of the nitrous oxide-acetylene flame, the addition of diethylene glycol (about 8% in the final solution) and similar compounds to the aqueous solution of vanadium increased the absorption by about 50%. The observations and the possible role of the mixed organic solvents are discussed.

S. L. SACHDEV, J. W. ROBINSON AND P. W. WEST,  
*Anal. Chim. Acta*, 37 (1967) 156-163

### NEUTRON ACTIVATION ANALYSIS OF HIGH PURITY SELENIUM

#### PART I. DETERMINATION OF BROMINE

Neutron activation analysis for 2-0.8 p.p.m. bromine in selenium was performed by irradiating 1-g samples for 2 h at a neutron flux of  $4 \cdot 10^{11}$  n/cm<sup>2</sup>/sec. The bromine was separated by a double precipitation technique as silver bromide to obtain adequate decontamination and the isotope <sup>82</sup>Br ( $T_{\frac{1}{2}} = 35.87$  h) measured. Errors due to self-shielding in the standards and flux-depression in the selenium were calculated. Measurements on 2 different photopeaks were made to avoid errors from interfering isotopes.

C. BALLAUX, R. DAMS AND J. HOSTE,  
*Anal. Chim. Acta*, 37 (1967) 164-171

#### DETERMINATION OF COPPER, GALLIUM AND ZINC IN "STANDARD ROCKS" BY NEUTRON ACTIVATION

A neutron activation method for the simultaneous determination of copper, gallium and zinc in rocks is described. The method is based on anion-exchange separation steps and measurement of  $\gamma$ -activity. Chemical yields were determined by re-activation. Results for a series of igneous "standard rocks" are presented. The accuracy of the mean values is ca. 5% for concentrations exceeding 10 p.p.m.

A. O. BRUNFELT, O. JOHANSEN AND E. STEINNES,  
*Anal. Chim. Acta*, 37 (1967) 172-178

#### A SPECTROPHOTOMETRIC DETERMINATION OF THE STABILITY CONSTANTS OF THE COMPLEXES OF TITANIUM(III) WITH ACETYLACETONE

The stability constants of the consecutive complexes of titanium(III) with acetylacetonone were determined by means of spectrophotometric methods. The values are  $\log \beta_1 = 10.4$ ,  $\log \beta_2 = 18.8$ , and  $\log \beta_3 = 24.9$ . Because of the fact that  $K_1 K_2 = 10^{1.5}$  a high concentration of acetylacetonone results in a considerable formation of TiL even at pH 0.

W. E. VAN DER LINDEN AND G. DEN BOEF,  
*Anal. Chim. Acta*, 37 (1967) 179-186

#### TRACE METAL ANALYSIS BY COMBINED THIN-LAYER CHROMATOGRAPHY AND REFLECTANCE SPECTROSCOPY

Traces of nickel, cobalt and copper are separated on chromatoplates and, after reaction with rubeanic acid, are determined quantitatively by diffuse reflectance spectroscopy; 0.05  $\mu\text{g}$  of the elements can be determined with a probable percentage error of 2 to 5%. Temperature stability, aging, and pH dependence of the chelates and chelating agents in the adsorbed state were investigated. The method is simple and could find routine application in geochemistry, food analysis, etc.

R. W. FREI AND D. E. RYAN,  
*Anal. Chim. Acta*, 37 (1967) 187-199

#### APPLICABILITY OF THE DU PONT 900 DTA APPARATUS IN QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

Some problems of quantitative differential thermal analysis have been studied by means of a Du Pont 900 DTA instrument. Applying the equation of heat transfer the features of a thermogram (base line and peak surface) may be interpreted in terms of heat of transition, specific heat and thermal conductivity. Satisfactory results are obtained for substances with thermal conductivities lower than  $10^{-3}$  cal/sec deg.

P. PACOR,

*Anal. Chim. Acta*, 37 (1967) 200-208

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## THE DETERMINATION OF LANTHANUM, CERIUM AND THORIUM WITHOUT SEPARATIONS

### THE DETERMINATION OF LANTHANUM AND CERIUM IN THORIUM

A method is proposed for the spectrophotometric determination of small quantities of lanthanum, cerium and thorium in the presence of one another without separations. Cerium is estimated from its absorption peak in the ultraviolet region, thorium with thoria, and the 3 elements together with arsenazo. The lanthanum is calculated after subtraction of the combined absorbances of the arsenazo complexes of the thorium and cerium. The procedure can be readily applied to the determination of microgram amounts of the 2 rare earths in thorium. In this case the majority of the thorium is removed from the solution by solvent extraction with TTA before the estimation of the rare earths. The interference of iron is considered and proposals made for its removal.

K. HIRO, D. S. RUSSELL AND S. S. BERMAN,  
*Anal. Chim. Acta*, 37 (1967) 209-216

## SOLVENT EXTRACTION OF METAL IONS WITH MIXED LIGANDS

### PART VII. EXTRACTION AND SEPARATION OF CALCIUM AND STRONTIUM WITH TTA AND TBP IN CARBON TETRACHLORIDE

The solvent extraction of calcium(II) and strontium(II) by TTA has been studied using carbon tetrachloride containing trioctylphosphine oxide (TOPO), tributylphosphate (TBP), and methyl isobutyl ketone (hexone) as adduct-forming ligands. Stability constants for the systems are given. The separation of calcium and strontium can be effected by 0.1 M TTA + 0.01 M TBP in carbon tetrachloride.

T. SEKINE AND D. DYRSSEN,  
*Anal. Chim. Acta*, 37 (1967) 217-226

## OXALATES AS QUALITATIVE ORGANIC ANALYSIS DERIVATIVES OF ALL CLASSES OF AMINES

Methods of preparing either the acid or neutral ammonium oxalates of all classes of simple amines are presented. The usefulness of these compounds as qualitative organic analysis derivatives is pointed out. The method is applicable to semimicro analyses.

K. T. FINLEY, A. D. BAITSHOLTS, J. WILSON, JR. AND C. A. BISHOP,  
*Anal. Chim. Acta*, 37 (1967) 227-231

## A STUDY OF THE ACTION OF FLUORIDE ON THE THORIUM-SPADNS LAKE

(in French)

The reaction of fluoride with thorium-SPADNS lake was studied in detail with particular reference to the effects of pH and media. Two methods for the determination of microgram amounts of fluoride based on the reaction are described. The spectrophotometric method developed is more suitable for routine use, but the colorimetric titration method is less sensitive to the effect of large amounts of electrolyte.

S. FLEURY,  
*Anal. Chim. Acta*, 37 (1967) 232-239

## A STUDY OF GLUTAMINE INTERFERENCE IN THE ACIDIFIED NINHYDRIN REACTION FOR PROLINE

In the application of the acidified ninhydrin reaction to the estimation of free proline in plant extracts, glutamine was a major source of interference, all others being minor, absent or removable with Permutit. Some characteristics of glutamine interference in this reaction are described. A ratio of linear errors method for the correction of proline values to the glutamine free state is introduced. The glycine and proline concentration in the reaction mixtures are prime factors in obtaining a ratio of linear errors by spectrophotometric measurement at 2 wavelengths.

Y. KIMURA,  
*Anal. Chim. Acta*, 37 (1967) 240-245

## MICRODETERMINATION OF ZINC BY MEANS OF REAGENT CRAYONS AND THE RING-OVEN TECHNIQUE

A sensitive and highly selective method for the rapid micro-determination of zinc by the ring-oven technique is presented. Very few cations when present in 100-fold excess interfere while anions do not interfere. The optimal range is 0.1–1.0  $\mu\text{g}$  zinc, which suggests its special applicability in air pollution investigations.

P. W. WEST AND S. K. THABET,  
*Anal. Chim. Acta*, 37 (1967) 246–252

## POLAROGRAPHY OF URANYL-NITRILOTRIACETATE COMPLEX

Polarographic studies of solutions of uranium(VI) and nitrilotriacetic acid were carried out in perchlorate medium at ionic strength 0.25. Reversible and diffusion-controlled reduction waves were obtained in the pH range of 1.5–4.1. Above pH 4.1, the irreversible waves became reversible in the presence of acetate buffer. Four kinds of chelate species,  $\text{UO}_2\text{HX}$ ,  $\text{UO}_2\text{X}^-$ ,  $\text{UO}_2(\text{OH})\text{X}^{2-}$  and  $\text{UO}_2(\text{Ac})\text{X}^{2-}$ , were identified. The U(V)–NTA complex was unstable at high pH and completely dissociated at pH 6.30. The effects of pH and ligand concentration on the wave parameters are discussed in detail.

T.-T. LAI AND J.-Y. CHEN,  
*Anal. Chim. Acta*, 37 (1967) 253–259

## AMPEROMETRIC TITRATIONS OF ORGANOLEAD AND ORGANOTIN IONS

Mixtures of  $\text{R}_2\text{Sn}^{2+}$  and  $\text{R}_3\text{Sn}^+$  compounds can be analysed by titrating their total amount potentiometrically with alkali, and then determining  $\text{R}_2\text{Sn}^{2+}$  in another aliquot by amperometric titration with standard 8-hydroxyquinoline solution. In mixtures of  $\text{R}_2\text{Pb}^{2+}$  and  $\text{R}_3\text{Pb}^+$  compounds, dialkyllead ion can be titrated amperometrically with ferrocyanide solution and trialkyllead ions with tetraphenylboron solution. A potentiometric method is described for the determination of small amounts of lead chloride in the presence of any alkyllead chloride.

G. PLAZZOGNA AND G. PILLONI,  
*Anal. Chim. Acta*, 37 (1967) 260–266

## SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN STEEL

(Short Communication)

C. L. LUKE,  
*Anal. Chim. Acta*, 37 (1967) 267–269

## DETERMINATION OF RING PHOSPHATES IN SODIUM PHOSPHATE GLASS

(Short Communication)

H. N. BHARGAVA AND D. C. SRIVASTAVA,  
*Anal. Chim. Acta*, 37 (1967) 269–271

## THE RAPID DETERMINATION OF PHOSPHORUS IN PRESENCE OF ARSENIC, SILICON AND GERMANIUM

(Short Communication)

J. C. VAN SCHOUWENBURG AND I. WALINGA,  
*Anal. Chim. Acta*, 37 (1967) 271–274

## ANODIC REACTIONS OF THE HALIDES IN DIMETHYL SULFOXIDE AT THE PYROLYTIC GRAPHITE ELECTRODE\*

H. E. ZITTEL AND F. J. MILLER

*Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. (U.S.A.)*

(Received August 14th, 1966)

Halide reactions in non-aqueous media have become of particular interest as a further development of the numerous voltammetric studies with a variety of electrodes in aqueous halide systems<sup>1,2</sup>. The platinum electrode was used in almost all of the non-aqueous investigations. KOLTHOFF AND COETZEE<sup>3</sup> and POPOV AND GESKE<sup>4</sup> describe the electrode reactions of the halides in acetonitrile. IWAMOTO<sup>5</sup> reports a short chronopotentiometric study of the electro-oxidation of iodide in various media.

Polarography of various substances in non-aqueous media has been reviewed by GUTMANN AND SCHÖBER<sup>6</sup>, who have also discussed the polarographic reduction of various metallic ions in dimethyl sulfoxide (DMSO)<sup>7</sup>. SEARS, LESTER AND DAWSON<sup>8</sup> studied the dissociation of a number of univalent electrolytes in DMSO. Because of its unique solvent properties, DMSO is peculiarly suitable as a non-aqueous medium for the study of the anodic voltammetry of the halides.

In the present work we have studied the anodic reactions of iodide, bromide and chloride in DMSO and DMSO-water mixtures. Since in previous work in aqueous medium<sup>9</sup> iodide showed unusual behavior at the pyrolytic graphite electrode (PGE), this electrode was used exclusively. The anodic waves of all 3 ions are irreversible. The relationship between ion concentration,  $C$ , and peak current,  $i_p$ , is different for each of the 3 ions; especially the  $i_p/C$  ratio for chloride is anomalously large compared with that for iodide and bromide. The change in ion concentration is shown to affect the half-peak potential,  $E_{p/2}$ . The water content of the DMSO also affects the electrode reaction and consequently the values derived from it. The anodic halide reactions in DMSO at the PGE are postulated to be:



## EXPERIMENTAL

*Apparatus*

*Voltammeter.* ORNL Model Q-2792<sup>10</sup> controlled-potential D.C. polarographic-voltammeter. The 3-electrode function was used; consequently, the comparatively high resistances (up to 10,000 ohms) encountered in the cell have no significant effect on peak potentials ( $E_p$ ) or on peak currents ( $i_p$ ).

\* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

*X-Y recorder.* Moseley Model 2D-2A, F. L. Moseley Co., Pasadena, Calif.

*Cell.* The cell is described elsewhere<sup>9</sup>.

*Electrodes.* Reference, Beckman Model 39270 S.C.E.; indicator, PGE (0.24-cm<sup>2</sup> area)<sup>2</sup>; and counter, gauge platinum.

*Salt bridge.* The bridge consisted of a Vycor tube (0.328-in. dia., 5.5-in. length) with a porous tip, available from the Corning Glass Co., Corning, N. Y. The Vycor tube was inserted vertically through the Teflon cap of the cell and was filled with the supporting medium. The reference electrode was then inserted in the Vycor tube.

#### Reagents

Tetra-n-butylammonium perchlorate, (n-Bu)<sub>4</sub>NClO<sub>4</sub>; prepared as described by JASELSKIS AND DIEHL<sup>11</sup>.

Dimethyl sulfoxide (DMSO), 99.9% pure (Crown Zellerbach Corp.). The DMSO was purified further as recommended by KOLTHOFF AND REDDY<sup>12</sup>.

All other reagents were reagent grade. Solutions were prepared and standardized according to accepted procedures just before they were required for use; they were never stored.

#### Analysis of the wave

The same general procedure was used for the analysis of all voltammograms. The peak current,  $i_p$ , was measured at the peak value of current; the peak potential,  $E_p$ , referred to the S.C.E., was determined from the point on the potential axis at which the peak current occurred. The  $E_p$  values given in the discussion and in the Tables were measured directly from the voltammograms; no correction was made for the shifts caused by waves that preceded or followed the measured wave. Figure 1 shows typical voltammograms for the oxidation of iodide, bromide and chloride.

The  $i_p$  values were corrected by subtraction of the current produced by the supporting electrolyte and the current resulting from a preceding wave. The  $i_p$  value for  $E_p$ (I) was taken as the difference between the current obtained at the potential of  $E_p$ (I) for a solution containing only the supporting electrolyte and one containing both electrolyte and halide ion. The  $i_p$  value for  $E_p$ (II) (iodide and bromide) was obtained by measuring from an extrapolation of wave I. The extrapolation was carried out in two ways. In the first, the potential scan was stopped at  $E_p$ (I), and the current was allowed to decay at constant potential. The resulting  $i_p$ (I) vs. time plot provided a current value which at a fixed potential scan rate could be interpolated into a subsequent voltammogram to obtain the requisite correction at  $E_p$ (II) of the  $i_p$ (II). In the second method it was assumed that the electrode process was sufficiently diffusion-controlled that the relationship<sup>13</sup>

$$k = i t^{\frac{1}{2}} \quad (3)$$

was valid even at a constantly varying potential. In this expression  $k$  is a constant,  $i$  is the measured current in microamperes, and  $t$  is the time interval in sec at which  $i$  was measured. A value for  $k$  then was calculated by selecting a point on wave I at 0.01 V more positive than  $E_p$ (I) as the zero point and measuring the current at several points in the anodic direction on the potential axis just beyond the zero point. Since the potential scan was at a constant rate, the difference between potentials provided a known time increment. From the calculated  $k$ , the current attributed to

wave I at  $E_p(\text{II})$  was estimated. The corrected value for  $i_p(\text{II})$  was then obtained by subtracting the supporting electrolyte current and the estimated current due to wave I from the measured  $i_p(\text{II})$ . For the iodide oxidation, the results obtained by two methods agreed to within *ca.* 5%; for bromide, to within *ca.* 10%. All data given, however, are based on the first method because the latter method assumes the control of the electrode process by the diffusion process. Evidence indicates that the assumption is not valid.

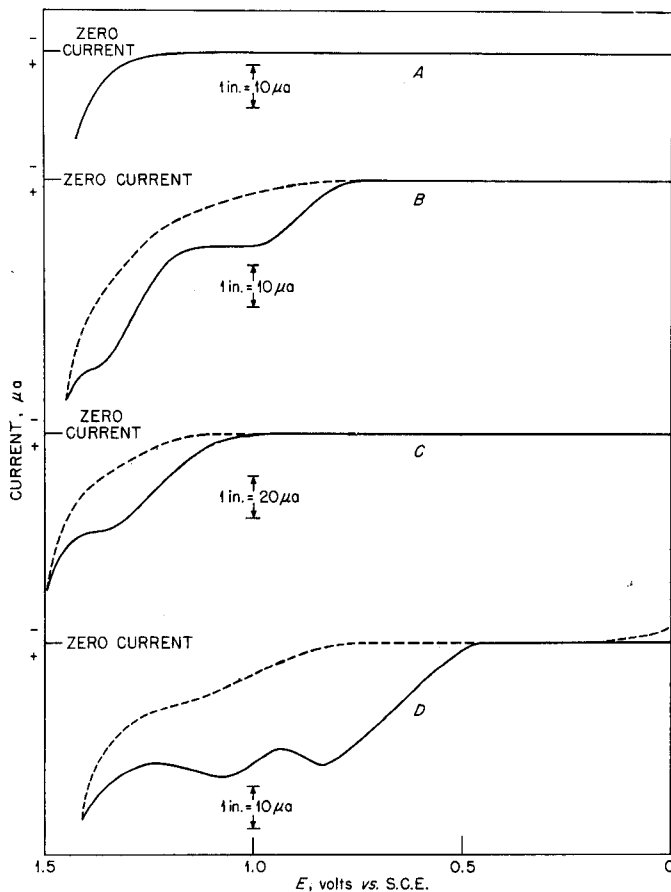


Fig. 1. Typical cyclic voltammograms. Test conditions: supporting medium, dimethyl sulfoxide; electrolyte,  $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ , 0.1 M. (A) Background, 1.0 V/min; (B)  $[\text{Br}^-]$ ,  $1.1 \cdot 10^{-3}$  M, 0.3 V/min; (C)  $[\text{Cl}^-]$ ,  $4.8 \cdot 10^{-4}$  M, 0.3 V/min; (D)  $[\text{I}^-]$ ,  $2.26 \cdot 10^{-3}$  M, 2.0 V/min; --- indicates reverse scan.

## RESULTS AND DISCUSSION

Comparison of the properties of DMSO and water (Table I) shows that DMSO has a relatively high dielectric constant and its autoprotolysis constant indicates that it is a stronger base than water. The difference in solvent characteristics should influence the oxidation of the halide ions. The object of the present study was to ascertain the differences.

Figure 1 shows representative cyclic voltammograms for the 3 halides. In no case was the electrode reaction found to be reversible since no cathodic wave was formed on reversal of the potential scan from +1.5 to 0.0 V. In the cyclic voltammogram for iodide, there is a slight indication of a cathodic reaction at 0.0 V. This cathodic reaction depends on the water content of the DMSO, and moves toward a more positive potential with increase in water content. A tendency toward reversibility of the reaction of  $E_p(I)$  for iodide with increase in water content is thus indicated.

TABLE I  
PHYSICAL PROPERTIES OF DIMETHYL SULFOXIDE AND OF WATER

Property	DMSO	H <sub>2</sub> O
Viscosity (25°) (poise)	0.196	0.00894
Dielectric constant	49.6	78.54
Specific conductance (ohm/cm)	$2 \cdot 10^{-8}$	$5.5 \cdot 10^{-8}$
Molecular weight	78.13	18.02
Autoprotolysis constant	$5 \cdot 10^{-18}$	$1 \cdot 10^{-14}$
Dipole moment (debyes)	3.9	1.84
Density (25°)	1.096	0.997

### Iodide

The  $i_p/AC$  value, in which  $A$  is the area of the stationary electrode and  $i_p$  and  $C$  are as previously defined, was determined over a concentration range as a measure of the effect of change in concentration of iodide on the characteristics of the voltammogram. Table II shows the obtained values.

The  $i_p/AC$  term is relatively constant for waves I and II. The fact that the ratio  $i_p(I)/i_p(II)$  approximates unity indicates that the electron change for both waves is the same. In accordance with the discussion given by POLCYN AND SHAIN<sup>14</sup> for irreversible charge transfers,  $E_p$  should shift  $30/\alpha n_a$  mV for each 10-fold increase in the rate of potential scan. In the term  $30/\alpha n_a$ ,  $\alpha$  is the charge transfer coefficient and  $n_a$  is the number of electrons involved in the rate-determining step of the electrode reaction. Since the cyclic voltammogram has shown the reaction to be essentially irreversible,  $\alpha n_a$  was thus determined to be ca. 0.5 for the reaction at  $E_p(I)$ .

The difference in the viscosity of the DMSO compared to water could reasonably be expected to change the  $i_p/AC(I)$  ratios. From the viscosities given in Table I,

TABLE II  
EFFECT OF IODIDE CONCENTRATION ON WAVE CHARACTERISTICS  
(Test conditions: [I<sup>-</sup>], as shown; [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub>], 0.1 M; potential scan rate, 1.0 V/min)

[I <sup>-</sup> ] (N · 10 <sup>4</sup> )	$i_p(I)/AC^a$ (A mole <sup>-1</sup> cm)	$i_p(II)/AC$ (A mole <sup>-1</sup> cm)	$E_{p/2}(I)$ (V vs. S.C.E.)	$E_p(I)$ (V vs. S.C.E.)	$E_p(II)$ (V vs. S.C.E.)
2.26	37.1	30.4	0.66	0.82	1.13
4.52	37.0	28.8	0.64	0.83	1.13
8.80	37.2	30.7	0.66	0.83	1.12
15.0	37.2	30.5	0.65	0.84	1.10
22.6	37.4	30.4	0.64	0.85	1.08

<sup>a</sup>  $i_p(I)/AC$  (in H<sub>2</sub>O-NaClO<sub>4</sub>) = 201.1 A mole<sup>-1</sup> cm.

the  $i_p(\text{I})/AC$  values for water and for DMSO should stand in the ratio of 4.7:1. The ratio actually found from previous work in aqueous medium<sup>2</sup> and the present study was 5.4:1. The agreement between the calculated ratio and the ratio actually found is sufficiently close to justify the assumption that the difference in viscosity of DMSO and water is the chief cause for the decrease in  $i_p$  in DMSO. It is also reasonable to assume that the same electrode reaction occurs at  $E_p(\text{I})$  in both water and DMSO.

To determine the effect of the water content of the iodide-DMSO solution on the characteristics of the iodide voltammogram, a series of test solutions that contained various amounts of water were scanned. Figure 2 shows the effect on the observed  $E_p(\text{I})$  and  $E_p(\text{II})$  values.

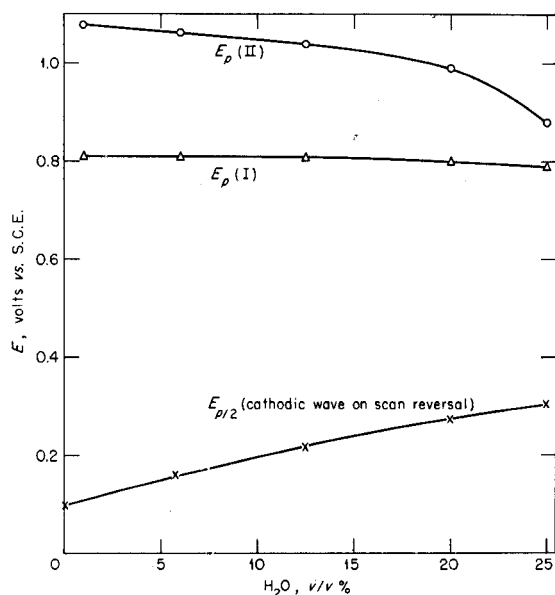


Fig. 2. Effect of water on iodide potentials. Test conditions:  $[\text{I}^-]$ ,  $2.26 \cdot 10^{-3} M$ ; supporting medium, dimethyl sulfoxide; supporting electrolyte,  $[(n\text{-C}_4\text{H}_9)_4\text{NClO}_4]$ ,  $0.1 M$ ; potential scan rate,  $0.5 \text{ V/min}$ .  $\circ = E_p(\text{II})$ , peak potential(II);  $\triangle = E_p(\text{I})$ , peak potential(I);  $\times = E_{p/2}$ , half-peak potential of cathodic wave or reverse scan.

$E_p(\text{I})$  is affected only slightly, but  $E_p(\text{II})$  shifts drastically to more negative potentials with increase in the water content of the solution. At approximately 30% (v/v) water, the 2 waves coalesce into one peak that does not decay significantly on scanning to more positive potentials. The results indicate that at  $E_p(\text{I})$  essentially the same reaction occurs in both water and in DMSO. The relatively large change in  $E_p(\text{II})$  with increase in water content indicates that the reaction and possibly the electrode mechanism is changing. This effect is also indicated by the fact that an  $\alpha n_a$  value for  $E_p(\text{II})$  changes from 0.5 for DMSO to ca. 0.3 for 20% (v/v) water solution.

The cathodic wave at 0.0 V, as previously mentioned, is also affected by the water content of the solution. The trend toward more positive potentials with increase in water content indicates an increase in degree of reversibility.

### Bromide

Figure 1 shows that bromide in DMSO also undergoes 2 irreversible anodic reactions. The effect of the bromide concentration on the various parameters of the waves is shown in Table III. The  $i_p/AC$  values are not constant for either of the 2 waves but do show a distinct interrelationship; as the bromide concentration increases,  $i_p(I)/AC$  decreases, whereas  $i_p(II)/AC$  increases. In both cases the lower

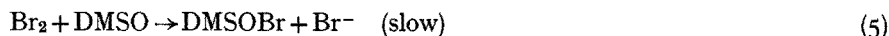
TABLE III

EFFECT OF BROMIDE CONCENTRATION ON WAVE CHARACTERISTICS

(Test conditions:  $[Br^-]$ , as shown;  $[(n-C_4H_9)_4NClO_4]$ , 0.1 M; potential scan speed, 1.0 V/min)

$[Br^-]$ ( $N \cdot 10^4$ )	$i_p(I)/AC$ ( $A \text{ mole}^{-1} \text{ cm}$ )	$i_p(II)/AC$ ( $A \text{ mole}^{-1} \text{ cm}$ )	$E_p(I)$ ( $V \text{ vs. S.C.E.}$ )	$E_p(II)$ ( $V \text{ vs. S.C.E.}$ )
2.26	356.0	27.9	1.07	1.31
4.52	186.0	91.0	1.05	1.33
11.3	87.9	135.2	1.03	1.39
22.6	58.1	150.2	1.03	1.44
45.2	50.2	—	0.98	1.46

values tend to approach the values obtained for iodide. Since the diffusion coefficients of iodide and bromide in DMSO should be about the same, some similarity is to be expected. The change in  $i_p(I)$  and  $i_p(II)$  with change in bromide concentration can be logically explained by postulating that as a result of the first oxidation of bromide,  $i_p(I)$ , a species is formed that reacts with the medium as shown:



On the basis of the postulated reactions, an increase of bromide would slow the second reaction, and consequently, the  $i_p(I)/AC$  ratio would decrease as a simple effect of the chemical equilibrium. As the potential becomes more positive, the electrode reaction becomes:



The second reaction (chemical) is then the rate-determining step. An increase in bromide will cause the chemical reaction to shift to the left and thus increase the amount of bromine available for the last reaction. An  $\alpha n_a$  value for the reaction at  $E_p(I)$  was found from variation of the scan rate to be *ca.* 0.5 as it was for iodide.

### Chloride

The data from the study of the effect of chloride concentration are shown in Table IV. The  $i_p/AC$  values for chloride are very high compared with those for iodide and even with the highest values found for bromide. Since only one wave appears before the rise in background current makes it impossible to achieve more anodic potentials, the electrode reaction is postulated to be



It is further postulated that the electrode reaction is immediately followed by the rapid chemical reaction





Since this is a fast reaction, the electrode reaction is the rate-determining step. The current,  $i_p$ , is about a factor of 10 higher than theory would predict if no catalytic effect were present. To check the postulate that the nascent halogen reacts with DMSO to regenerate the species electroactive at  $E_p$ , gaseous chlorine was bubbled briefly through a DMSO solution of supporting electrolyte. This solution was then scanned anodically. An anodic wave resulted that agreed exactly in position and shape with the wave formed when the initially present EAS is chloride. Therefore, it is almost certain that an irreversible electrode reaction is followed by a catalytic reaction that regenerates the original EAS. The  $\alpha n_a$  value for the chloride oxidation is 0.5, as was the  $\alpha n_a$  value of  $i_p(\text{I})$  for both iodide and bromide.

The effect of the water content of the test solution on the peak potential,  $E_p(\text{I})$ , of both bromide and chloride is shown in Fig. 3. The  $E_p(\text{I})$  for bromide and chloride

TABLE IV

## EFFECT OF CHLORIDE CONCENTRATION ON WAVE CHARACTERISTICS

(Test conditions:  $[\text{Cl}^-]$ , as shown;  $[(\text{n-Bu})_4\text{NClO}_4]$ , 0.1 M; potential scan speed, 1.0 V/min)

$[\text{Cl}^-]$ ( $N \cdot 10^4$ )	$i_p/A$ ( $\mu\text{A}/\text{cm}^2$ )	$i_p/AC$ ( $A \text{ mole}^{-1} \text{ cm}$ )	$E_p$ (V vs. S.C.E.)	$E_{p,2}$ (V vs. S.C.E.)
2.71	85.58	315.8	1.39	1.20
5.42	170.9	315.4	1.40	1.21
10.84	342.8	316.2	1.41	1.22
27.10	883.5	326.0	1.43	1.23
54.20	2,314.9	427.1	1.44	1.25

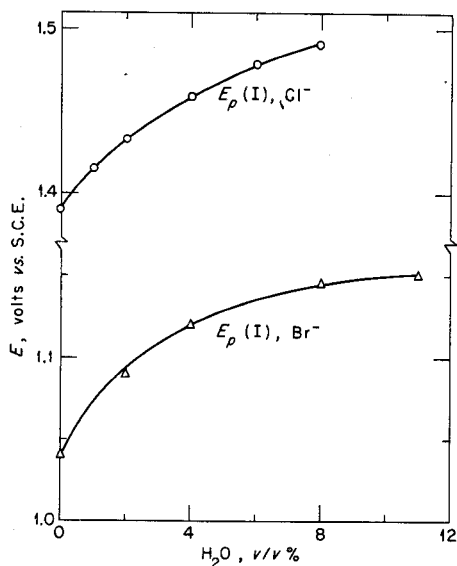


Fig. 3. Effect of water on  $E_p(\text{I})$  of bromide and chloride. Test conditions:  $[\text{Br}^-]$ ,  $2.26 \cdot 10^{-3} \text{ M}$ ;  $[\text{Cl}^-]$ ,  $2.71 \cdot 10^{-4} \text{ M}$ ; supporting medium, dimethyl sulfoxide; supporting electrolyte,  $[(\text{n-C}_4\text{H}_9)_4]$ , 0.1 M; potential scan rate, 1.0 V/min.  $\circ$  = Peak potential,  $E_p(\text{I}), \text{Cl}^-$ ;  $\triangle$  = Peak potential,  $E_p(\text{I}), \text{Br}^-$ .

shifts markedly positive with increase in water content in contrast to the slight negative shift of  $E_p(I)$  of iodide. The shift may be due either to a greater degree of solvation of these ions than for iodide when water is present or to the fact that the catalytic reaction of bromide and chloride takes place more rapidly with increase in the water content.

To distinguish between an electrode reaction in which only charge transfer is involved from one in which the charge transfer is coupled with a chemical reaction, the diagnostic criterion of POLCYN AND SHAIN<sup>15</sup> may be used. This criterion stipulates that if only charge transfer is involved in the electrode reaction, the ratio of peak current,  $i_p$ , to square root of the voltage scan rate,  $v^{\frac{1}{2}}$ , remains constant over a range of scan rates. Table V gives the data obtained when the peak current function,  $i_p/v^{\frac{1}{2}}$ , is plotted *vs.* the scan rate for mM concentrations of the 3 halides. For the iodide

TABLE V

VARIATION OF PEAK CURRENT FUNCTION WITH POTENTIAL SCAN RATE

(Test conditions:  $[Cl^-]$ ,  $1.08 \cdot 10^{-3} M$ ;  $[Br^-]$ ,  $2.24 \cdot 10^{-3} M$ ;  $[I^-]$ ,  $2.26 \cdot 10^{-3} M$ .  
All samples 0.1 M  $(n-C_4H_9)_4NClO_4$  in DMSO)

Potential scan rate (V) (V/min)	$i_p/v^{\frac{1}{2}}$ ( $\mu A \text{ min}^{\frac{1}{2}} V^{-\frac{1}{2}}$ )		
	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>
0.1	89.6	—	20.8
0.2	88.5	40.9	20.4
0.3	87.8	38.2	20.6
0.5	85.6	34.4	20.3
1.0	80.5	30.6	20.1
2.0	71.2	27.9	19.6
3.0	61.7	27.3	19.5

data, the  $i_p/v^{\frac{1}{2}}$  ratio is nearly independent of scan rate, indicating that there is no chemical reaction coupled to the charge transfer. The data for bromide show no such independence but do indicate that, as the higher scan rates are attained, the peak current function approaches constancy. The trend toward constancy indicates that the chemical reaction coupled with the charge transfer is sufficiently slow that at the higher scan rates it exerts less influence on the electrode reaction. The data for chloride clearly show a dependence on scan rate and thus indicate that the chemical reaction is so fast that its character is reflected in the peak current values obtained over the whole range of scan rates studied.

## CONCLUSIONS

The anodic halide reactions in DMSO at the PGE have been postulated to be



Similar reactions have been described by IWAMOTO<sup>5</sup> for the anodic reaction of iodide in pyridine at the platinum electrode. The nascent halogen formed in the first anodic reaction can react with DMSO to give an irreversible-catalytic-irreversible<sup>4</sup>, I-C-I, type of coupled reaction that leads to a multi-step charge transfer. From the voltage

scan *vs.* peak current function studies, it has been shown that the catalytic reaction is slow for iodide, intermediate for bromide, and fast for chloride. KHARASH<sup>16</sup> states that oxidative cleavage of dialkyl sulfoxides by chlorine may occur and thus give an alkyl chloride and an alkane sulfonyl chloride.  $\alpha$ -Chloro sulfides may also form. These reactions normally take place in the presence of water, but evidence from the present study indicates that they also occur in DMSO that contains very little water.

Comparison of previous work<sup>2,17</sup> on the anodic reaction of iodide in aqueous medium at the PGE with the DMSO study indicates that the first oxidation step is the same in both media, but that the second step differs. The second step in water results in an oxygenated species in water



and a simple  $\text{I}^+$  species in DMSO.

Because the postulated I-C-I type of reaction yields a current that is an order of magnitude higher than would be expected without the catalytic effect, the anodic oxidation of iodide, bromide and especially of chloride in DMSO can provide the basis for a sensitive voltammetric determination of these ions.

#### SUMMARY

The anodic reactions of the halide ions in dimethyl sulfoxide at the pyrolytic graphite electrode have been studied. The iodide ion demonstrates a 3-step oxidation; the bromide, a 2-step oxidation and chloride, a 1-step oxidation. The electrode reaction ( $\text{X}^- \rightarrow \frac{1}{2} \text{X}_2 + \text{e}^-$ ) is complicated by a catalytic reaction occurring after the electrode reaction. The catalytic reaction is important for only bromide and chloride causing a considerable diffusion current enhancement. The  $\alpha n_a$  value for all 3 primary reactions is of the order of 0.5.

#### RÉSUMÉ

Les auteurs ont examiné les réactions des halogénures, en milieu diméthylsulfoxyde, à l'électrode de graphite pyrolytique. On observe une oxydation en 3 stades pour les iodures, en 2 stades pour les bromures et en un stade pour les chlorures. La réaction d'électrode ( $\text{X}^- \rightarrow \frac{1}{2} \text{X}_2 + \text{e}^-$ ) est compliquée par une réaction catalytique se produisant après la réaction d'électrode. Cette réaction catalytique est importante pour les bromures et les chlorures, produisant une augmentation du courant de diffusion considérable. La valeur  $\alpha n_a$  pour ces 3 réactions est de l'ordre de 0.5.

#### ZUSAMMENFASSUNG

Es wurden die anodischen Reaktionen der Halogenidionen in Dimethylsulfoxid an der pyrolytischen Graphitelektrode untersucht. Die Jodidionen, zeigen eine Oxydation in 3 Schritten, die des Bromids in 2 und die des Chlorids in 1 Schritt. Bei der Elektrodenreaktion ( $\text{X}^- \rightarrow \frac{1}{2} \text{X}_2 + \text{e}^-$ ) tritt anschliessend eine katalytische Reaktion auf. Diese ist nur für das Bromid und Chlorid wichtig, die eine beträchtliche Erhöhung des Diffusionsstromes verursachen. Der  $\alpha n_a$ -Wert für alle 3 primären Reaktionen liegt in der Grössenordnung von 0.5.

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THE DETERMINATION OF TITANIUM IN ALLOYS BY  
ATOMIC ABSORPTION SPECTROSCOPY

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Although atomic absorption spectroscopy with an air-acetylene flame is a most versatile technique, it is not normally suitable for the determination of elements which form very stable oxide molecules in the flame, *e.g.* beryllium, aluminium, silicon, titanium, zirconium, vanadium, niobium, tantalum and tungsten. The stable oxide molecules can be dissociated by increasing the temperature of the flame and by arranging to have a fuel-rich flame in which reducing conditions are present. With this end in view, WILLIS AND AMOS<sup>1,2</sup> developed the nitrous oxide-acetylene flame for atomic absorption spectroscopy and obtained satisfactory sensitivities with this flame in the determination of beryllium, aluminium, silicon, titanium, vanadium and tungsten.

In the present paper, a method is described for the determination of titanium in steels, permanent magnet alloys and cast iron using the Hilger AA2 atomic absorption spectrophotometer and a nitrous oxide-acetylene flame. No preliminary separations are involved.

## EXPERIMENTAL

*Reagents*

Hydrochloric, hydrofluoric and nitric acids, ammonia solution, methanol, ethanol and isopropanol were of analytical reagent grade.

*Standard solutions of titanium, zirconium, niobium, tantalum and molybdenum.*

*Titanium (1000 p.p.m.).* 0.5 g of 'Specpure' titanium sponge was dissolved in hydrofluoric acid such that, on dilution to 500 ml, the concentration of acid was 1 *M*.

*Zirconium (500 p.p.m.).* 0.0676 g of 'Specpure' zirconium oxide was dissolved in concentrated hydrofluoric acid. The solution was evaporated just to dryness, the residue dissolved in 0.5 *M* hydrofluoric acid and the solution made up to 100 ml with this 0.5 *M* acid.

*Niobium (500 p.p.m.).* 0.0715 g of 'Specpure' niobium pentoxide was treated in the same way as for zirconium.

*Tantalum (500 p.p.m.).* 0.0611 g of 'Specpure' tantalum pentoxide was treated in the same way as for zirconium.

*Molybdenum (500 p.p.m.).* 0.0750 g of 'Specpure' molybdenum trioxide was dissolved in concentrated ammonia solution. The solution was evaporated to dryness, the residue dissolved in 0.5 *M* hydrofluoric acid, and the solution made up to 100 ml with this acid.

The standard solution of titanium was made up to exactly 500 ml in a graduated flask and immediately transferred to a dry polythene bottle. The other standard solutions were made up directly in polythene bottles.

### *Apparatus*

*Atomic absorption spectrophotometer.* The Hilger AA2 instrument was employed with the following modifications. The standard burner for compressed air-acetylene was replaced by the burner described below. The upper inlet tube to the atomizer chamber was closed off, so that all the nitrous oxide used in the flame passed through the atomizer. Both the flow rates for nitrous oxide and acetylene were measured using the 2 compressed air rotameters on the standard rotameter holder. (The third rotameter for low flow rates of acetylene was not employed.) The open arm on the glass U-tube containing the water seal, which is connected to the atomizer chamber, was lengthened to 14 cm because of the relatively high pressure of nitrous oxide employed.

*Hollow-cathode lamps.* Lamps for titanium, zirconium, niobium, tantalum and molybdenum were obtained from Hilger and Watts Ltd.

*Burner.* The standard jet at the base of the burner in the acetylene lead-in tube was replaced by a jet of diameter 0.020".

The burner head consisted of 2 bars of mild steel, each 6" long, 5/8" wide and 3/8" deep, fitted together and bolted on to a brass chamber. Between the 2 bars, pieces of steel shim were inserted at each end to provide a slot of dimensions 2" × 0.018". The brass chamber was designed so as to produce a smooth transition for the gases from the pipe, onto which this brass chamber was placed, to the slot from which the gases emerged. The burner could be operated with or without water-cooling, but it was found that the increase in temperature on removal of the water-cooling, caused the paint on the walls of the burner housing to blister. A burner with water-cooling was, therefore, preferred. Water-cooling was achieved by circulating cold water through a copper pipe, fixed around the brass chamber, immediately below the bars of mild steel.

The procedure for obtaining the correct type of flame is as follows.

Connect the nitrous oxide and compressed air supplies to one of the air rotameter tubes through a T-piece. Ignite an air-acetylene mixture at the burner with an air pressure of about 20 p.s.i. Open the valve on the nitrous oxide cylinder and increase the pressure of nitrous oxide to about 25 p.s.i. Turn off the air supply and adjust the pressure of nitrous oxide to 30 p.s.i. Increase the acetylene pressure until a rose-red cone, approximately 3/4" in height, is obtained.

The pressure and flow rates used were as follows: for nitrous oxide, pressure 30 p.s.i., flow rate 6.25 l/min; and for acetylene, pressure 12 p.s.i., flow rate 3.8 l/min.

## RESULTS AND DISCUSSION

### *Sensitivities for the determination of elements*

These were determined by spraying 0.1 M solutions of hydrofluoric acid containing 100 p.p.m. of the metal into the nitrous oxide-acetylene flame, and by assuming that flame absorbance is directly proportional to concentration, at least to a good approximation, over the concentration range of 0-100 p.p.m. The sensitivities are shown in Table I.

Hydrofluoric acid was chosen as solvent since it was desirable to develop a method suitable for many types of alloys. Niobium, tungsten, etc. are very conveniently held in solution in the presence of dilute solutions of this acid.

A considerable enhancement effect was found when aqueous alcoholic solutions of titanium were sprayed. The absorbances of aqueous ethanolic solutions were more than double those of the corresponding aqueous solutions; aqueous isopropanol solutions were less effective.

TABLE I

SENSITIVITIES FOR ELEMENTS WITH A NITROUS OXIDE-ACETYLENE FLAME

Element	Wavelength (Å)	Sensitivity (p.p.m. giving 1% absorption)	
		Aqueous solution	Aqueous-organic solution
Titanium	3643	6.5	2.0 <sup>a</sup> , 2.5 <sup>b</sup> , 3.5 <sup>c</sup>
Zirconium	3601	27	13 <sup>d</sup>
Niobium	3580	100	35 <sup>b</sup>
Tantalum	2715	45	17 <sup>b</sup>
Molybdenum	3133	1.5	0.7 <sup>b</sup>

<sup>a</sup> 1 M aq. hydrofluoric acid-ethanol (1:9, v/v).

<sup>b</sup> 0.5 M aq. hydrofluoric acid-ethanol (1:4, v/v).

<sup>c</sup> 0.2 M aq. hydrofluoric acid-ethanol (1:1, v/v).

<sup>d</sup> 0.5 M aq. hydrofluoric acid-methanol (1:4, v/v).

#### *Effect of other elements on the determination of titanium*

Since it was intended to determine titanium in iron-base alloys the effect of a large excess of iron on the titanium absorption was first studied. The absorption for 50 p.p.m. of titanium in aqueous ethanol (1:1, v/v), which was 0.1 M in hydrofluoric acid, was enhanced by 15% in the presence of 5,000 p.p.m. of iron. This enhancement effect has also been reported by AMOS AND WILLIS<sup>2</sup>. A calibration graph for 0-50 p.p.m. of titanium in the presence of 5,000 p.p.m. of iron in the same aqueous ethanolic solution was a straight line passing through the origin. The slight scatter of the points about this straight line was subjected to statistical analysis, and it was concluded that 50 p.p.m. of titanium could be determined with a standard deviation of 0.5 p.p.m. The limit of detection for titanium is, therefore, considered to be 1 p.p.m.

Any interfering effects from other elements were ascertained by determining absorbances for 50 p.p.m. of titanium in aqueous ethanol (1:1, v/v), 0.1 M in hydrofluoric acid, when part of the 5,000 p.p.m. of iron was replaced by another element.

The absorbance for 50 p.p.m. of titanium + 5,000 p.p.m. of iron in the aqueous ethanolic hydrofluoric acid solution was 0.075, and interference was considered to have occurred when this figure changed by 0.001 or more absorbance units, on replacing part of the iron with the other element. There was no interference from 1,000 p.p.m. Cr + 4,000 p.p.m. Fe, 1,000 p.p.m. Co + 4,000 p.p.m. Fe, 1,000 p.p.m. Ni + 4,000 p.p.m. Fe, 500 p.p.m. Mn + 4,500 p.p.m. Fe, 250 p.p.m. Cu + 4,750 p.p.m. Fe, 250 p.p.m. Nb + 4,750 p.p.m. Fe, 250 p.p.m. W + 4,750 p.p.m. Fe, 100 p.p.m. Mo + 4,900 p.p.m. Fe, 100 p.p.m. V + 4,900 p.p.m. Fe, 50 p.p.m. S + 4,950 p.p.m. Fe, and 50 p.p.m. Ta + 4,950 p.p.m. Fe.

However, the absorbance was increased to 0.079 in the presence of 500 p.p.m.

Al + 4,500 p.p.m. Fe. There is a straight line relationship between the aluminium interference and the amount of aluminium, and 125 p.p.m. or more of aluminium interfere in the determination of titanium in aqueous ethanolic solution.

*Analysis of steels, permanent magnet alloys and cast iron*

For convenience, 0.5 g of alloy should be present in 100 ml of the final solution; this corresponds to 5,000 p.p.m. of metal in the final solution and 1% of titanium in the alloy then corresponds to 50 p.p.m. of titanium in solution.

*Method.* Dissolve 0.5 g of alloy in a Teflon beaker with 10 ml of concentrated hydrofluoric acid and 3 ml of concentrated nitric acid (Note 1). Evaporate the solution just to dryness and take up the residue in 10 ml of 1 *M* hydrofluoric acid and 10 ml of water. Warm to effect solution. Transfer the solution to a 100-ml graduated flask and rinse the beaker twice with 10-ml portions of water. Add 50 ml of ethanol to the flask and make up to the mark with water (Note 2). Transfer the solution at once to a dry polythene bottle. Spray this solution and then a standard solution containing 50 p.p.m. of titanium and 5000 p.p.m. of iron into the flame in the usual way, and determine the absorbances. Calculate the concentration of titanium in the solution by comparing the readings.

*Note 1.* With cast irons, dissolve the alloy in aqua regia, evaporate the solution to about 5 ml, add about 25 ml of 4 *M* hydrochloric acid, and filter off any undissolved carbon. Evaporate the filtrate just to dryness and take up the residue in 10 ml of 1 *M* hydrofluoric acid and 10 ml of water.

*Note 2.* In the case of permanent magnet alloys omit the ethanol, otherwise precipitation may occur. The calibration graph of flame optical density *versus* concentration is also a straight line through the origin for 0–50 p.p.m. of titanium in the presence of 5000 p.p.m. of iron in an ethanol-free solution, which is 0.1 *M* in hydrofluoric acid. However, with this solution, the method is not so sensitive for titanium. A solution of 50 p.p.m. of titanium + 5000 p.p.m. of iron gave a flame optical density of 0.037 compared with 0.075 in aqueous ethanol (1:1, v/v). In the absence of ethanol, however, there was no interference from 500 p.p.m. of aluminium + 4500 p.p.m. of iron, in place of 5000 p.p.m. of iron.

Iron(III) fluoride is only moderately soluble in hydrofluoric acid solutions and an alloy concentration of 5,000 p.p.m. was chosen for the development of a satisfac-

TABLE II

RESULTS FOR THE DETERMINATION OF TITANIUM IN ALLOYS USING ATOMIC ABSORPTION SPECTROSCOPY

Alloy	Titanium content	
	Cert. value (%)	Found by A.A.S. (%)
BCS 235/2 Ti stabilized '18-9' stainless steel	0.32	0.31, 0.32
BCS 335 austenitic stainless steel	0.46	0.46, 0.46
BCS 233 permanent magnet alloy	0.79	0.78, 0.80
BCS 312 permanent magnet alloy	1.19	1.20, 1.22
BCS 206/1 high Si and P cast iron	0.18	0.17, 0.18



tory method. However it is possible to obtain clear solutions with more concentrated solutions of many alloys, particularly in the absence of ethanol.

Results for the determination of titanium in 5 standard alloys are shown in Table II.

These results are considered to be satisfactory. It seems very likely that this atomic absorption spectroscopic method could also be applied to the determination of titanium in many other alloys. At no time was there any evidence of attack by the dilute hydrofluoric acid solutions on the glass atomizer chamber or the burner.

The authors acknowledge with thanks the loan of an AA2 atomic absorption spectrophotometer from Hilger and Watts Ltd. and are indebted to that company, and particularly to Mr. R. LOCKYER, for laboratory facilities for one of us (D.P.H.) during part of this work. They also thank the British Iron and Steel Research Association for a maintenance grant (for D.P.H.)

#### SUMMARY

A method is described for the determination of 0.1–1.2% of titanium in steels, permanent magnet alloys and cast iron using atomic absorption spectroscopy with hydrofluoric acid solutions and a nitrous oxide–acetylene flame. No preliminary separations are required. When the correct conditions are employed there is no interference from the other elements commonly found in these alloys.

#### RÉSUMÉ

On décrit une méthode pour le dosage du titane (0.1–1.2%) dans les aciers, les alliages magnétiques et la fonte, par spectroscopie par absorption atomique. On utilise des solutions fluorhydriques et une flamme oxyde nitreux-acétylène. Il n'est pas nécessaire d'effectuer une séparation préliminaire. Lorsque les conditions sont correctes, les autres éléments généralement présents dans ces alliages ne gênent pas.

#### ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von 0.1–1.2% Titan in Legierungen mit der Flammenabsorptionsspektroskopie beschrieben unter Verwendung flusssaurer Lösungen und einer Stickstoffoxid–Acetylen-Flamme. Vorhergehende Trennungen sind nicht erforderlich. Wenn die genauen Bedingungen eingehalten werden, gibt es keine Störungen durch andere Elemente, die im allgemeinen in diesen Legierungen vorkommen.

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## EFFECT OF MIXED ORGANIC SOLVENTS ON ATOMIC ABSORPTION SPECTROPHOTOMETRY OF REFRACTORY METALS

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There is an increasing interest in the use of organic solvents in conjunction with atomic absorption spectrophotometry for the determination of various elements, especially those metals which form refractory oxides. Organic solvents can be used for separating and concentrating materials and for enhancing the sensitivity of tests.

Several studies<sup>1-11</sup> have appeared regarding the effect of various water-soluble as well as water-insoluble organic solvents on the absorption characteristics of a large number of metals in flames of different compositions. In general, these solvents, when added to aqueous solutions, or when metal ions are extracted into the organic phase, enhance the absorption. The enhancement of absorption signal depends upon many factors such as viscosity, surface tension, heat of evaporation, and heat of combustion of the solvent used as well as on the composition of the flame, portion of the flame observed and the type of atomizer burner, etc.

Refractory metals such as aluminum, beryllium, silicon, titanium, tungsten and vanadium, etc., which were originally listed<sup>12</sup> among the elements which could not be determined by atomic absorption spectrophotometry, can now be determined by this technique. This has been achieved by: (1) the use of organic solvents and fuel-rich oxy-acetylene flames fed through a total consumption burner<sup>6,10</sup> and (2) by the use of a fuel-rich nitrous oxide-acetylene flame from a premix-type atomizer burner<sup>13</sup>. Recently, such elements have also been determined by the use of induction coupled plasma<sup>14</sup>, in which case the atomization is achieved in an inert atmosphere in order to prevent the formation of refractory oxides. The sensitivities reported<sup>14</sup> by the use of induction coupled plasmas, however, are not as good as that from the simpler flame atomization methods.

Vanadium, a typical refractory metal, was chosen for the present investigation. The first atomic absorption measurement in the case of vanadium was made by ROBINSON<sup>15</sup> in 1961, who observed a very weak absorption signal (detection limit 300 mg/l) in the outer cone of an oxy-cyanogen flame. Intense UV radiation from the inner cone caused the detector to become unstable and no meaningful measurements could be obtained. Since then, certain improvements in the sensitivity limits of vanadium<sup>6,10,13</sup> have been made.

The present paper deals with the effect of various organic solvents on the absorption signal of vanadium in fuel-rich oxy-acetylene flames as well as in nitrous oxide-acetylene flames. Some interesting enhancements of the absorption have been observed that have resulted from the use of mixed organic solvents in the case of oxy-acetylene flames and upon the addition of ethylene glycol and similar compounds

to the aqueous solutions in the case of nitrous oxide-acetylene flames. The observations are discussed in detail.

#### EXPERIMENTAL

##### *Apparatus*

Spectrophotometer, Perkin-Elmer Model 303.  
Burner, Perkin-Elmer premix-type burner with a nitrous oxide burner head.  
Three large bore Beckman oxy-acetylene total consumption burners.

##### *Reagents*

*Stock solution of vanadium.* A stock solution containing 10.00 g/l of vanadium was prepared by dissolving 22.80 g of pure dry ammonium metavanadate in 100 ml of 9 M sulfuric acid and diluting to 1 l with double distilled water.

A standard solution of vanadium containing 100 mg/l vanadium was made up by diluting 10 ml of the stock solution to 1 l.

*Cupferron solution.* Six g of ammonium salt of N-nitrosophenylhydroxylamine in 100 ml of water (freshly made).

##### *Procedure for extraction*

Twenty-five ml of vanadium solution (100 mg/l) were mixed with 2.5 ml of concentrated sulfuric acid. This was cooled to 10° in ice, transferred to a separatory funnel, and 2.5 ml of cupferron solution were added followed by 25 ml of MIBK or MIBK and oleic acid. This was shaken for 1 min, allowed to separate, and the organic phase was then withdrawn.

##### *Setting of the instrument*

*Wavelength:* 3183.9 Å. *Lamp current:* 30 mA.

*Slit opening:* Reducing oxy-acetylene or nitrous oxide-acetylene flames emit a high background radiation, hence the slit opening was kept narrow to minimize the total intensity of background radiation falling on the photomultiplier tube and thus minimize detector noise level. A slit position at 3, which is equivalent to 0.3 mm slit opening, was used.

##### *Burner assembly*

A special rack was fitted for a total consumption Beckman burner in the place of Perkin-Elmer's premix-type burner. This permitted three-dimensional positioning of the flame. The beam of radiation from the hollow-cathode lamp passed through the upper part of the inner luminous cone in the case of oxy-acetylene flames and as near the base of the flame as possible in the case of nitrous oxide-acetylene flame.

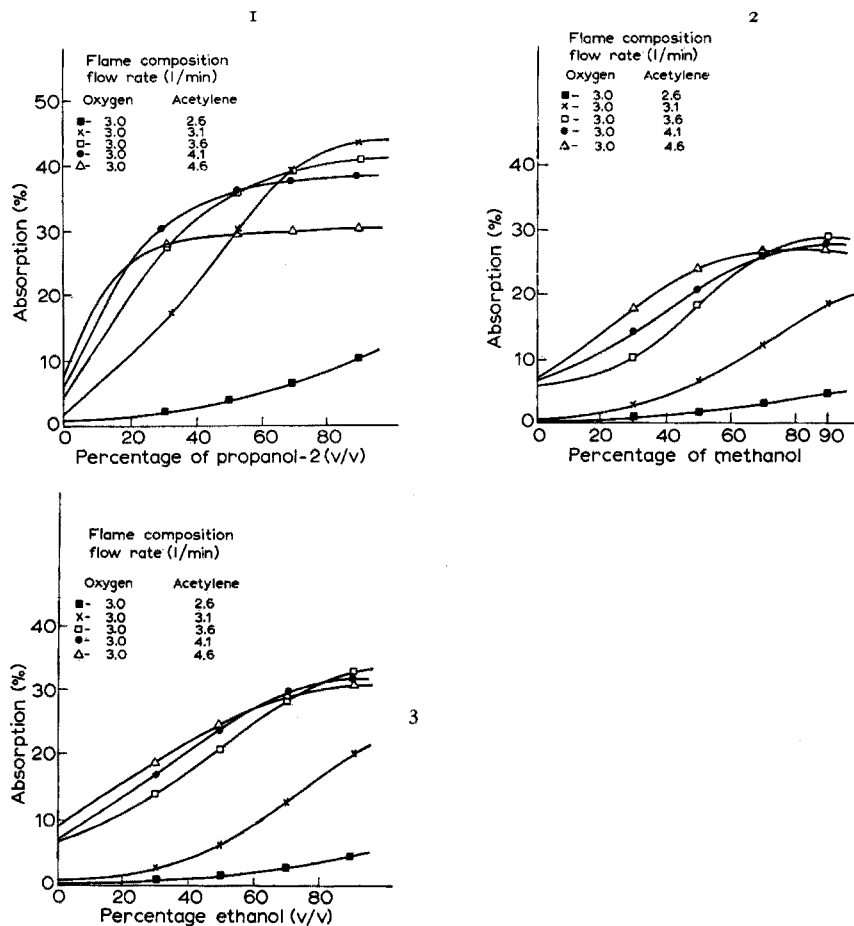
In all studies the pure solvent was used to set the instrument for zero absorption and the absorption reading for the blank was subtracted from that of the sample.

#### RESULTS AND DISCUSSION

##### *Oxy-acetylene flames*

Absorption by vanadium at 3183.9 Å was easily observed in a fuel-rich oxy-acet-

ylene flame. The absorption was found to be enhanced by the use of organic solvents. The effect of the addition to aqueous solutions of methanol, ethanol, and propanol-2 on the absorption signal was studied in flames of various compositions. These solvents, in general, enhance the absorption signal in the following order: propanol-2 > ethanol > methanol. The effect of concentration of these organic solvents on the absorption signal was also studied. Results are summarized in Figs. 1, 2, and 3, respectively.



Figs. 1-3. Effect on the absorption of 3183.9 Å line of vanadium in oxy-acetylene flames of various compositions of: (1) propanol-2; (2) methanol; (3) ethanol. Concentration of vanadium 1000 mg/l.

The results show that absorption was maximum in highly reducing flames and that the absorption increased as the concentration of organic solvent increased. Maximum absorption was observed when the solution contained more than 70% of the respective solvents.

A comparative study of the effect of some common organic solvents on the absorption signal for vanadium was made. Results are shown in Table I. In the case of methyl isobutyl ketone, vanadium was extracted as vanadium cupferrate. All other solutions were prepared by diluting concentrated stock solution with appropriate

TABLE I

EFFECT OF ORGANIC SOLVENTS ON ABSORPTION SIGNAL FOR VANADIUM  
(Concentration of vanadium: 1000 mg/l)

<i>Solvent used</i>	<i>B. p. (°)</i>	<i>Percentage absorption</i>
Water	100	6
Acetone (98%)	56.2	26
Methanol (98%)	64.7	29
Ethanol (98%)	78.4	33
Propanol-2 (98%)	82.4	43
Methyl isobutyl ketone	118.0	57

TABLE II

ABSORPTION OF 3183.9 Å LINE OF VANADIUM IN OXY-ACETYLENE FLAME

(Flow rates: 3.5 l O<sub>2</sub>/min; 3.1 l acetylene/min. Slit: mechanical 0.3 mm; spectral 2.0 Å. Lamp current: 30 mA)

<i>Solvent</i>	<i>Blank (flame absorption with solvent) (%)</i>	<i>Vanadium (400 mg/l)</i>	<i>Rate of aspiration (ml/min)</i>	<i>Net absorption (%)</i>
Ethanol	1.2	22.0	2.15	20.8
Ethanol + dioxane	3.0	22.0	2.22	19.0
Ethanol + 40% dioxane	3.8	23.0	2.30	19.2
Ethanol + 60% dioxane	4.2	25.0	2.22	19.8
Ethanol + 20% toluene	5.5	28.5	2.30	23.0
Ethanol + 40% toluene	10.5	34.5	2.72	24.0
Ethanol + 10% glycerine	7.0	21.0	1.76	14.0
Ethanol + 20% glycerine	8.3	19.5	0.90	11.0
Ethanol + 30% ethylene glycol	1.0	23.0	2.00	22.0
Ethanol + 20% oleic acid	1.9	36.0	1.67	34.0
Ethanol + 40% oleic acid	4.0	35.0	1.15	31.0
20% Acetic acid (aqueous)	0.5	7.5	3.75	7.0
20% Propionic acid	0.0	7.0	3.00	7.0
12% Valeric acid	1.0	6.0	1.14	5.0
20% Bis (2-ethoxy-ethyl) ether	0.0	6.0	2.15	6.0
20% Triethanolamine	0.0	1.5	3.53	1.5

amounts of the organic solvents. Further studies were made using mixtures of solvents. The results which are shown in Table II indicate that the addition of compounds with high boiling point and relatively long carbon chain enhanced the absorption. For example, the addition of oleic acid to ethanol (2:3) increased the absorption signal although the aspiration rate was reduced from 2.2 ml to 1.2 ml/min. The possible mechanism for this enhancement is discussed later. As shown in Table I, methyl isobutyl ketone was the best solvent studied for maximizing the absorption signal of vanadium. Methyl isobutyl ketone has also been widely used for extraction processes. Therefore, the addition of oleic acid, linoleic acid and linolenic acid to MIBK on the absorption signal for vanadium was studied. Results are shown in Table III. The addition of about 20–30% fatty acids to MIBK or other organic solvents, generally enhanced the absorption by vanadium. The increase of unsaturation in the fatty acid chain slightly decreases the absorption signal.

TABLE III

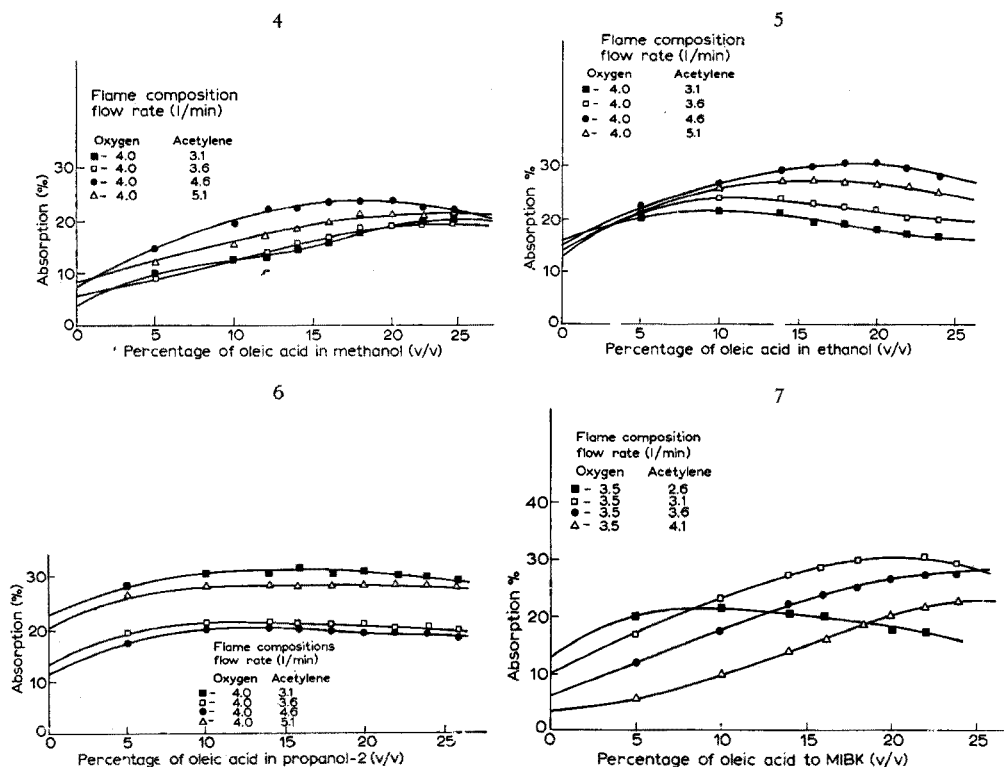
EFFECT OF FATTY ACID ADDITION

(Concentration of vanadium: 100 mg/l)

Solvent ratio, 4 : 1	Absorption (%)
MIBK : none	12.0
MIBK : oleic acid	32.0
MIBK : linoleic acid	27.4
MIBK : linolinic acid	24.5

The flame composition plays a very important role in the production of metal atoms. The effect of mixed organic solvents was therefore studied in flames of 4 different compositions. The results are shown in Figs. 4, 5, 6 and 7.

In general, there was enhancement in the absorption signal by the addition of increasing amounts of oleic acid to various organic solvents up to about 20–25% (v/v) of oleic acid. Further increases in the concentration of oleic acid decreased the absorption signal probably because the feed rate of the sample was progressively reduced.



Figs. 4–6. Effect of addition of oleic acid to the solution of vanadium in: (4) methanol; (5) ethanol; (6) propanol-2; on the absorption of 3183.9 Å line of vanadium in oxy-acetylene flames of various compositions. Concentration of vanadium 200 mg/l.

Fig. 7. Effect of addition of oleic acid to MIBK used for extracting vanadium cupferrate on the absorption of 3183.9 Å line of vanadium in oxy-acetylene flames of various compositions. Concentration of vanadium 100 mg/l.

*Role of organic solvents.* The enhancement of the absorption signal associated with the use of organic solvents indicates an increased population of ground state metal atoms in the flame. The mechanism for the production of metal atoms<sup>16</sup> and the possible role of organic solvents<sup>2,3,5,7,9,12,17</sup> have been discussed by various authors. The function of organic solvents such as propanol-2 or methyl isobutyl ketone, etc., appears to be (a) to increase the feed rate of the sample, (b) to decrease the droplet size by decreasing the surface tension of the solution, (c) to maintain the flame at a higher temperature than a similar flame in which aqueous solution is sprayed, (d) to increase the rate of evaporation of the solvent, and (e) to provide better reducing conditions in the flame.

As shown in Table II, the addition of oleic acid to ethanolic solution of vanadium decreased the feed rate to about half the feed rate of ethanolic solution, yet the absorption for vanadium was considerably higher. The data showed that the efficiency of metal atom production was increased about 3-fold by the addition of 20–40% (v/v) of oleic acid. This enhancement of the absorption signal or the increased efficiency of metal atom production may be due to a decrease in the droplet size of the spray.

After aspiration, the liquid sample becomes nebulized into droplets. Each droplet contains a mixture of high-molecular-weight solvent and low-molecular-weight solvent. The latter boils rapidly and deflagrates the droplet into several smaller droplets each containing the sample metal (vanadium) and the high-molecular-weight solvent. The latter may decompose and reduce the vanadium to the atomic state in the process, and thus increase the efficiency of the production of vanadium atoms. Other factors such as the heat of combustion of the solvent and better reducing conditions established in the flame by the use of certain organic solvents may also play a significant role in the production of metal atoms.

#### *Nitrous oxide-acetylene flame*

Similar studies were made using nitrous oxide-acetylene flames. The results are shown in Table IV.

The effect of addition of increasing amounts of diethylene glycol diethyl ether to vanadium solution on the absorption signal was studied. The results are shown in Fig. 8.

TABLE IV

EFFECT OF MIXED AQUEOUS-ORGANIC SOLVENTS ON ABSORPTION SIGNAL FOR VANADIUM

(Flame conditions: nitrous oxide (atomizer) 35 p.s.i.; nitrous oxide (auxiliary) 15 p.s.i.; acetylene 6.0 l/min. Concentration of vanadium 100 mg/l)

<i>Compound added (8%, v/v)</i>	<i>Percentage absorption</i>
1. Aqueous solution	33.8
2. Diethylene glycol	43.4
3. Ethylene glycol monomethyl ether	38.4
4. Ethylene glycol monoethyl ether	39.0
5. 1,2-Dimethoxy ether	36.0
6. Di-ethylene glycol monobutyl ether	44.7
7. 2-(2-Ethoxy ethoxy) ethanol	43.7
8. Diethylene glycol diethyl ether	48.0

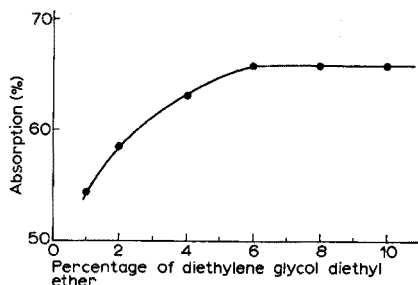


Fig. 8. Effect of addition of diethylene glycol diethyl ether to the aqueous solution of vanadium (100 mg/l).

The fact that larger concentrations of these compounds do not affect the absorption for vanadium shows that the enhancement of the absorption may be influenced by deflagration of the residues of the sample droplets formed after aspiration into the flame. Such deflagration would produce an increased surface area and therefore improved atomization of the vanadium. It would not be expected that enhancement would continue to increase with increasing concentrations of diethylene glycol-diethyl ether.

This investigation was supported by U.S. Public Health Service Grant Number AP 00128, Division of Air Pollution, Bureau of State Services.

#### SUMMARY

The effect of various organic solvents on the absorption characteristics of vanadium was studied in fuel-rich oxy-acetylene and nitrous oxide-acetylene flames. The absorption of the 3183.9 Å line of vanadium was greatly enhanced by the use of various mixed organic solvents when fed to oxy-acetylene flames. In the case of the nitrous oxide-acetylene flame, the addition of diethylene glycol (about 8% in the final solution) and similar compounds to the aqueous solution of vanadium increased the absorption by about 50%. The observations and the possible role of the mixed organic solvents are discussed.

#### RÉSUMÉ

On a examiné l'influence de divers mélanges de solvants organiques sur l'absorption du vanadium, dans des flammes oxy-acétylène et oxyde nitreux-acétylène. L'absorption de la raie 3183.9 Å du vanadium est grandement influencée par les solvants utilisés. Dans le cas d'une flamme oxyde nitreux-acétylène l'addition de diéthylèneglycol et de composés similaires produit une augmentation de l'absorption d'environ 50%.

#### ZUSAMMENFASSUNG

Der Einfluss zahlreicher organischer Lösungsmittelgemische auf die Absorptionscharakteristiken von Vanadin bei der Flammenabsorptionsspektralanalyse wurde



untersucht. Die Absorption der V-Linie bei 3183.9 Å wurde stark angeregt, wenn die organischen Lösungsmittelgemische in die Sauerstoff-Acetylen-Flamme gegeben werden. Bei der Stickstoffoxyd-Acetylen-Flamme steigerte die Zugabe von Diäthylenglykol und ähnlicher Verbindungen zur wässrigen Vanadinlösung die Absorption um etwa 50%. Die Beobachtungen und der mögliche Einfluss der organischen Lösungsmittel werden diskutiert.

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## NEUTRON ACTIVATION ANALYSIS OF HIGH PURITY SELENIUM

## PART I. DETERMINATION OF BROMINE

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Selenium is widely used as a semiconductor and rectifier. For these purposes a very high degree of purity is required, especially as far as the halogens are concerned. As the amounts to be determined are in the p.p.m. range, activation analysis has frequently been applied. Neutron activation analyses of antimony, arsenic, cadmium, calcium, chlorine, chromium, cobalt, copper, gallium, indium, iron, mercury, molybdenum, nickel, phosphorus, sodium, sulfur, tellurium, thallium, zinc and tungsten in selenium have already been described<sup>1-11</sup>.

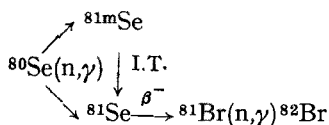
Several activation analyses for bromine in various materials have been published<sup>12,13</sup>, but no bromine determinations have been described in a selenium matrix.

*Nuclear data and interferences*

Neutron irradiation of bromine gives rise to a number of radioactive isotopes listed in Table I. The isotope <sup>82</sup>Br is formed in sufficiently large amounts to be used for activation purposes. After an irradiation of 2 h at a neutron flux of  $4 \cdot 10^{11}$  n/cm<sup>2</sup>/sec, amounts down to 0.1 p.p.m. can easily be determined by a measurement 3 days after the irradiation.

Possible interferences due to the fission of uranium (% yield of <sup>82</sup>Br:  $3.8 \cdot 10^{-5}$ %)<sup>19</sup> and the threshold reactions <sup>82</sup>Kr(n,p)<sup>82</sup>Br ( $\sigma = 23 \mu\text{b}$ )<sup>20</sup> and <sup>85</sup>Rb(n, $\alpha$ )<sup>82</sup>Br ( $\sigma = 9 \text{ mb}$ )<sup>20</sup> can be neglected as these elements are present in trace amounts only.

If quantities of bromine in the p.p.m. range have to be determined, the second order interference



can also be neglected. The amount of <sup>81</sup>Br, formed by this reaction, calculated as described by RICCI AND DYER<sup>21</sup>, does not exceed 1 p.p.b., after an irradiation of 2 h at  $4 \cdot 10^{11}$  n/cm<sup>2</sup>/sec.

The most important activities, due to the selenium matrix, are also listed in Table I. One day after the end of irradiation, the only remaining activity is due to the long-lived isotope <sup>75</sup>Se (ca. 16  $\mu\text{C/g}$ ), thus an efficient decontamination of the bromine from the selenium is required.

\* Research Fellow I.I.K.W.

TABLE I

RELEVANT NUCLEAR DATA<sup>14-18</sup>

Stable isotope	$\theta(\%)$	$\sigma(b)$	Isotope formed	$T_{1/2}$	Decay	Gamma energy (MeV)
<sup>79</sup> Br	50.52	2.9 8.5	<sup>80m</sup> Br	4.38 h	IT, $\gamma$	0.037, 0.048
			<sup>80</sup> Br	17.6 m	$\beta^-$ , $\beta^+$ ; EC, $\gamma$	0.511, 0.618, 0.665
<sup>81</sup> Br	49.48	3.1	<sup>82</sup> Br	35.87 h	$\beta^-$ , $\gamma$	0.554, 0.619, 0.70, 0.777, 0.827, 1.044, 1.317, 1.475
<sup>74</sup> Se	0.87	26	<sup>76</sup> Se	121 d	EC, $\gamma$	0.121, 0.136, 0.199, 0.265, 0.280, 0.402
<sup>76</sup> Se	9.02	7	<sup>77m</sup> Se	17.5 s	IT, $\gamma$	0.162
			<sup>77</sup> Se	st.	—	—
<sup>77</sup> Se	7.58		<sup>78</sup> Se	st.	—	—
<sup>78</sup> Se	23.52	0.4	<sup>79m</sup> Se	3.91 m	IT, $\gamma$	0.095
			<sup>79</sup> Se	$6.5 \cdot 10^4$ y	$\beta^-$	—
<sup>80</sup> Se	49.82	0.03	<sup>81m</sup> Se	56.8 m	IT, $\gamma$	0.103
		0.5	<sup>81</sup> Se	18.2 m	$\beta^-$	0.27
<sup>82</sup> Se	9.19	0.05	<sup>83m</sup> Se	70 s	IT, $\gamma$	0.350, 0.69, 1.01, 2.02
		0.004	<sup>83</sup> Se	25 m	$\beta^-$ , $\gamma$	0.58, 0.84
<sup>74</sup> Se	0.87	0.0162	<sup>74</sup> As	18 d	$\beta^+$ , $\beta^-$ , $\gamma$	0.596, 0.635
<sup>76</sup> Se	9.02	0.0016	<sup>76</sup> As	26.5 h	$\beta^-$ , $\gamma$	0.555, 0.648, 1.210, 1.765, 2.05
<sup>77</sup> Se	7.58	0.0038	<sup>77</sup> As	38.7 h	$\beta^-$ , $\gamma$	0.087, 0.160, 0.247, 0.270, 0.520
<sup>109</sup> Ag	48.65	3.2	<sup>110m</sup> Ag	270 d	$\beta^-$ , $\gamma$	0.447, 0.656, 0.759, 0.883, 0.945, 1.38

In addition, a significant part of the activity of the samples is due to the arsenic isotopes <sup>74</sup>As, <sup>76</sup>As and <sup>77</sup>As, which are produced by (n,p) reactions with the fast neutrons on the respective selenium isotopes, as is also shown in Table I. Consequently the separated bromine fraction must also be checked for a possible arsenic contamination.

#### Separation of bromine

Distillation of hydrogen bromide is inapplicable as a separation technique of bromine as up to 8% of the selenium can be distilled as tetrabromide.

Tracer experiments showed, however, that precipitation as silver bromide gave highly satisfactory results. When the selenium was dissolved in concentrated nitric acid in the presence of bromide carrier and silver nitrate, a recovery of 99.8% was achieved. Tracer experiments also showed that the silver bromide precipitate was contaminated with approximately 0.04% of the selenium. A double precipitation was therefore required by dissolving the silver bromide in ammonia and reprecipitating in the presence of selenium hold-back carrier. The yield of bromine was 99.6% and the contamination with selenium smaller than 0.001%. The arsenic contamination was completely negligible.

#### Counting

The radiochemical purity of the bromine separated from 1 g of irradiated selenium was checked by  $\gamma$ -spectrometry and decay curve analysis. Figure 1 shows the  $\gamma$ -spectra of the separated bromine (1.02 p.p.m.) and an irradiated ammonium bro-

mid standard. Figure 2 shows the decay curve of the separated bromine = 2.01 p.p.m. The half-life of 36 h agrees well with the value given in the literature (35.87 h).

From both figures it is obvious that the separated bromine is slightly contaminated by  $^{75}\text{Se}$ . This isotope emits no  $\gamma$ -rays with an energy higher than 0.402 MeV. Therefore small amounts of  $^{75}\text{Se}$  will not interfere with the measurement of the bromine photopeaks at 0.55 and 0.78 MeV. For quantitative measurements, these 2 photopeaks were selected and counted for 1 h starting 3 days after the end of irradiation. This separation technique does not provide for a decontamination of silver. As neutron irradiation gives rise to the long lived isotope  $^{110\text{m}}\text{Ag}$  (Table I), the separated bromine is contaminated by this isotope. The photopeak at 0.656 MeV interferes with the  $\gamma$ -spectrometric measurement of  $^{82}\text{Br}$ . From measurements 20

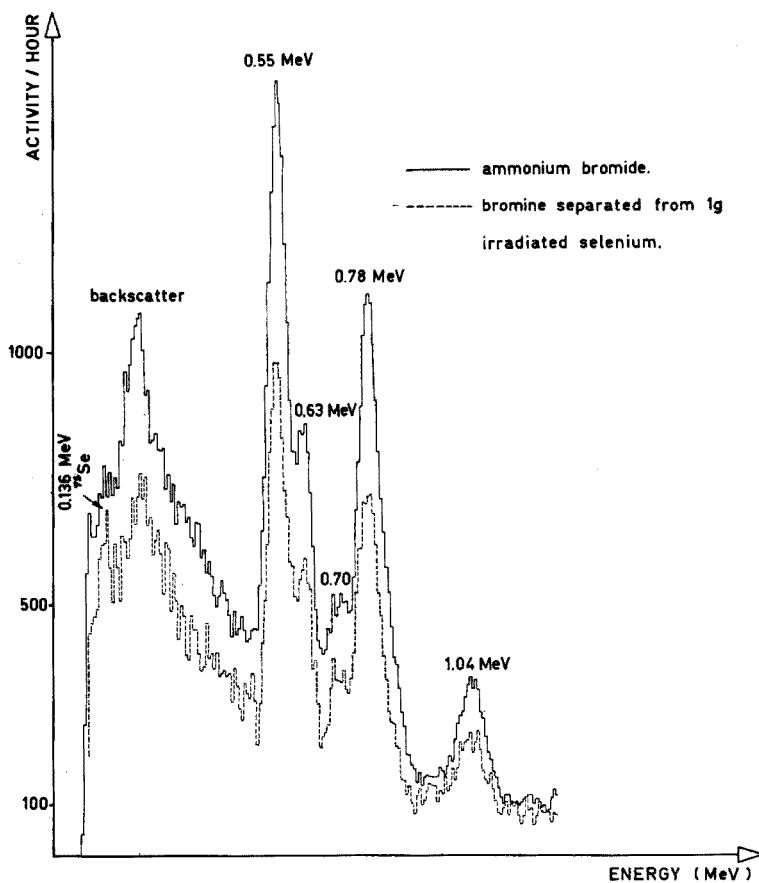


Fig. 1. Gamma spectra of  $^{82}\text{Br}$ .

days after the irradiation, when the  $^{82}\text{Br}$  activity had decayed, it became obvious that in the samples under investigation the silver content is less than 30 p.p.b. giving rise to an interference of less than 0.5% in the bromine determinations.

Counting at 0.55 and 0.78 MeV was applied as a purity check of the  $^{82}\text{Br}$  for a

possible arsenic contamination due to  $^{74}\text{As}$ ,  $^{76}\text{As}$  and  $^{77}\text{As}$ , formed from the respective selenium isotopes by (n,p) reactions. The peak at 0.55 MeV will indeed give rise to an interference due to the  $\gamma$ -emission at 0.595, 0.555 and 0.520 MeV of the respective isotopes  $^{74}\text{As}$ ,  $^{76}\text{As}$  and  $^{77}\text{As}$ . As these isotopes show no emission at 0.78 MeV, a constant value of the count rate ratio gives additional evidence of the satisfactory radiochemical decontamination.

#### Preparation of the standards

Usually activation analyses are performed by simultaneous irradiation of a standard. As the activation cross-section of  $^{82}\text{Br}$  is rather high (3.1 b), self-shielding could be expected in the standards. In order to investigate this possible effect, 100  $\mu\text{l}$  of aqueous solutions of potassium bromide were irradiated in quartz ampoules. The

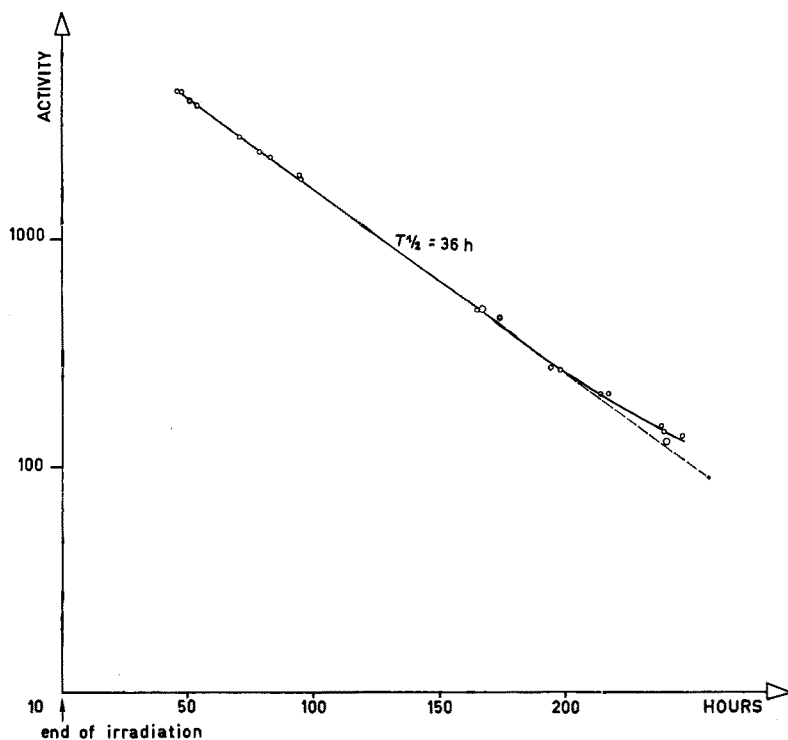


Fig. 2. Decay curve of the separated bromine.

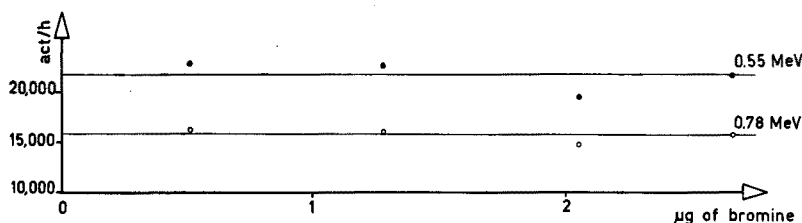


Fig. 3. Determination of the specific activity of standard bromide solutions.

induced activities were measured by summing the counts under the 0.55- and 0.78-MeV photopeaks. No self-shielding occurred for quantities up to  $4.5 \mu\text{g}$  of bromine/100  $\mu\text{l}$  (Fig. 3). For the considered concentration range, a specific activity of  $21,555 \pm 698$  (3.2%) and  $15,705 \pm 337$  (2.2%) counts/h/ $\mu\text{g}$  was found. A possible flux-depression in the sample itself, due to the important absorption cross-section of selenium ( $12.3 \text{ b}^{22}$ ), can also give rise to inaccurate results. Calculating the theoretical flux-depression in a selenium sphere of 1 g from the relations  $f_r = f_0 e^{-N\sigma R}$  and integrating over this

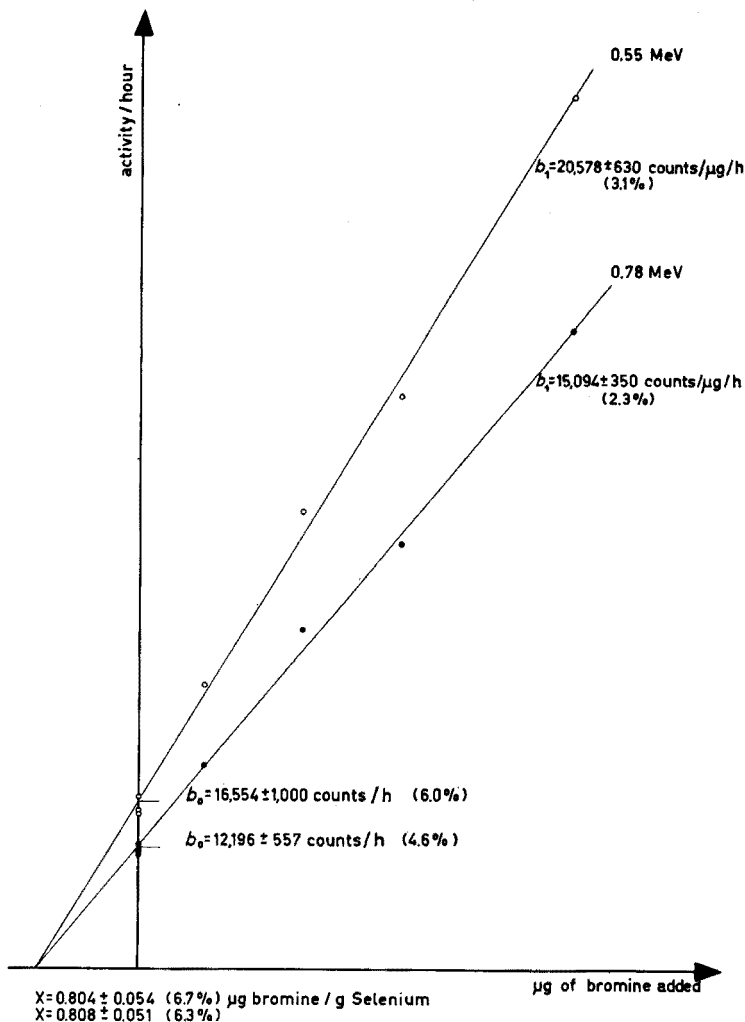


Fig. 4. Addition method of analysis.

sphere  $\int 4\pi R^2 e^{-\lambda R} dR$  ( $\lambda$  equals the flux-depression per unit of distance), a value of 4.3% was found. This result is also in good agreement with KENNA *et al.*<sup>22</sup> who found a value of 1.76 g for a flux-depression of 10%. Possible errors due to this effect were investigated by an addition method of analysis. Seven samples were prepared by placing 1 g of powdered selenium in a quartz ampoule. Four samples were spiked with

potassium bromide solution. The quartz ampoules were dried, sealed and their contents thoroughly mixed by shaking. After irradiation, the bromine was separated and measured as described above. The induced activities were plotted against the added amounts of bromine. The slope of the straight line ( $b_1$ ), its intercept with the ordinate ( $b_0$ ) and the standard deviations were calculated as described by GUEST<sup>23</sup>. It is obvious from Fig. 4 that no systematic error, due to unreproducible chemical separations, unstable measurements, local flux fluctuations and the above mentioned self-shielding, was perceptible up to 3.4  $\mu\text{g}$  of added bromine. In another experiment, up to 10.9  $\mu\text{g}$  of bromine was added and no systematic error was detected. The specific activity  $b_1$ ,  $20,578 \pm 630$  (3.1%) and  $15,094 \pm 350$  (2.3%) counts/h/ $\mu\text{g}$  was respectively 4.5 and 3.9% lower than the value obtained from the potassium bromide solutions. This experimental flux-depression caused by the selenium matrix thus agrees well with the calculated value.

#### EXPERIMENTAL

##### *Apparatus*

Integral gamma counting: 2"  $\times$  1.75" well-type NaI(Tl) detector.

Gamma spectrometer: 400-channel pulse-height analyser, with 3"  $\times$  3" NaI(Tl) detector (resolution 8%).

##### *Procedure*

Etch the irradiated selenium samples twice with 4 *N* nitric acid. Transfer the sample (1 g) to a flask with 2 necks, coupled to an efficient water-cooled condenser. Introduce 20 ml of 14 *N* nitric acid together with 1 ml of 0.17 *N* silver nitrate through a separatory funnel. Heat the flask until complete dissolution. Add 1 ml of carrier solution containing 1 mg of antimony, arsenic, chlorine, copper, phosphorus and sulfur and 1 ml of potassium bromide solution, containing 10 mg of bromide. Boil the solution for 5 min to insure isotopic exchange. Dilute the solution to about 6 *N* nitric acid. After one hour, the precipitate is settled. Filter through a fine porosity glass filter. Wash the precipitate subsequently with 2 *N* and 0.2 *N* nitric acid. Dissolve the precipitate in 30 ml of 14 *N* ammonia. Add 2 ml of selenium hold-back carrier (50 mg/ml) and repeat the precipitation by adding dropwise 14 *N* nitric acid. Boil the solution for a few minutes, allow to stand overnight in the dark and filter. Wash the precipitate with dilute nitric acid and redissolve in a saturated potassium cyanide solution. Dilute the solution to 50 ml in a calibrated flask and place on the detector.

TABLE II

DETERMINATION OF BROMINE IN BLOCK AND POWDERED SELENIUM (p.p.m.)

<i>Calculated from the 0.55-MeV peak</i>		<i>Calculated from the 0.78-MeV peak</i>	
<i>Block Se</i>	0.84 <sup>7</sup> 0.64 <sup>7</sup> 0.93 <sup>4</sup>		0.85 <sup>9</sup> 0.58 <sup>5</sup> 0.94 <sup>5</sup>
Mean value	0.80 <sup>9</sup> $\pm$ 0.08 <sup>5</sup> (10.5%)	Mean value	0.79 <sup>6</sup> $\pm$ 0.10 <sup>9</sup> (13.7%)
<i>Powdered Se</i>	0.76 <sup>8</sup> 0.83 <sup>8</sup> 0.75 <sup>0</sup>		0.77 <sup>7</sup> 0.81 <sup>8</sup> 0.75 <sup>7</sup>
Mean value	0.78 <sup>4</sup> $\pm$ 0.02 <sup>5</sup> (3.2%)	Mean value	0.78 <sup>4</sup> $\pm$ 0.01 <sup>8</sup> (2.3%)

## RESULTS

To investigate if bromine was introduced by powdering the samples, etched blocks of selenium were irradiated without previous treatment. The results of Table II show that the amounts of bromine found, agree well with the value 0.80<sup>6</sup> p.p.m. found from the addition method of analysis. Consequently no detectable contamination occurs by powdering. The low reproducibility of the determinations from unpowdered samples is probably due to the inhomogeneous distribution of the bromine, as the reproducibility of the determinations of powdered samples is much better.

TABLE III

DETERMINATION OF BROMINE IN THE SELENIUM SAMPLES (p.p.m.)

Sample no.	1st analysis	2nd analysis	3rd analysis	Mean value
1	1.07 <sup>1</sup>	0.89 <sup>2</sup>	1.10 <sup>7</sup>	1.02 <sup>3</sup> ± 0.06 <sup>7</sup> (6.5%)
2	1.63 <sup>6</sup>	1.59 <sup>3</sup>	1.70 <sup>9</sup>	1.64 <sup>6</sup> ± 0.03 <sup>4</sup> (2.1%)
3	1.73 <sup>1</sup>	1.77 <sup>2</sup>	1.85 <sup>8</sup>	1.78 <sup>7</sup> ± 0.03 <sup>7</sup> (2.1%)
4	1.98 <sup>4</sup>	1.98 <sup>9</sup>	1.85 <sup>3</sup>	1.94 <sup>2</sup> ± 0.04 <sup>4</sup> (2.3%)
5	1.98 <sup>9</sup>	2.03 <sup>7</sup>	2.02 <sup>0</sup>	2.01 <sup>5</sup> ± 0.01 <sup>4</sup> (0.7%)
6	2.19 <sup>9</sup>	1.95 <sup>2</sup>	2.05 <sup>2</sup>	2.06 <sup>8</sup> ± 0.07 <sup>2</sup> (3.5%)

In 6 different selenium samples of semiconductor quality, the amount of bromine present was determined. The samples were etched twice with 4 *N* nitric acid, washed with water and powdered. Amounts of 1 g were weighed and sealed in silica tubes. To avoid flux-depression and self-shielding effects, the standards were prepared by spiking 6.394 μg of bromide solution on 1 g of powdered selenium. Each sample was analysed in triplicate. The results are given in Table III.

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## SUMMARY

Neutron activation analysis for 2–0.8 p.p.m. bromine in selenium was performed by irradiating 1-g samples for 2 h at a neutron flux of  $4 \cdot 10^{11}$  n/cm<sup>2</sup>/sec. The bromine was separated by a double precipitation technique as silver bromide to obtain adequate decontamination and the isotope <sup>82</sup>Br ( $T_{1/2} = 35.87$  h) measured. Errors due to self-shielding in the standards and flux-depression in the selenium were calculated. Measurements on 2 different photopeaks were made to avoid errors from interfering isotopes.

## RÉSUMÉ

L'analyse par activation au moyen de neutrons est proposée pour le dosage du brome dans le sélénium de grande pureté. On peut doser 2 à 0.8 p.p.m. de brome par irradiation d'un échantillon d'un g pendant 2 heures avec un flux de neutrons de



$4 \cdot 10^{11}$  n/cm<sup>2</sup>/sec. Le brome est séparé par double précipitation sous forme de bromure d'argent; on mesure l'isotope <sup>82</sup>Br ( $T_{\frac{1}{2}} = 35.87$  h).

## ZUSAMMENFASSUNG

Mit der Neutronenaktivierungsanalyse wurden 2–0.8 p.p.m. Brom in hochreinem Selen bestimmt, indem 1-g-Proben zwei Stunden bei einem Neutronenfluss von  $4 \cdot 10^{11}$  n cm<sup>-2</sup> sec<sup>-1</sup> bestrahlt wurden. Um eine angemessene Dekontamination zu erhalten, wurde das Brom durch doppelte Fällung als Silberbromid abgetrennt und das Isotop <sup>82</sup>Br ( $T_{\frac{1}{2}} = 35.87$  h) gemessen. Fehler, die durch Abschirmung im Standard hervorgerufen werden und zur Fluss-Senkung im Selen führen, wurden berechnet. Die Messungen wurden bei 2 verschiedenen Photopeaks durchgeführt, um Fehler durch störende Isotopen zu vermeiden.

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## DETERMINATION OF COPPER, GALLIUM AND ZINC IN "STANDARD ROCKS" BY NEUTRON ACTIVATION

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As the sensitivity of neutron activation analysis is extremely high for most elements, it has become an important analytical method for establishing the concentrations of minor and trace elements in rocks and minerals. By this method the distribution of copper has been studied in samples from cosmic<sup>1-6</sup>, terrestrial<sup>1,7,8</sup> and oceanic sources<sup>1</sup>. Gallium has been determined by neutron activation in meteorites<sup>9-11</sup> and silicate rocks<sup>12</sup>, while the abundance of zinc has been investigated in meteorites<sup>6</sup>, igneous rocks<sup>13-15</sup>, ores<sup>14,16</sup>, refractories<sup>15</sup> and mill products<sup>16</sup>.

Radiochemical separations combined with  $\gamma$ -ray scintillation spectrometry can provide simple and selective procedures for many elements. Often more than one element can easily be determined in the same sample without any essential increase in work. In this report a method for the simultaneous determination of copper, gallium and zinc in silicate rocks by neutron activation analysis is presented.

The samples chosen for this work were a series of igneous "standard rocks" recently distributed by the U.S. Geological Survey. The series included granite G-2, nepheline syenite STM-1, granodiorite GSP-1, andesite AGV-1, basalt BCR-1, peridotite PCC-1 and dunite DTS-1. As a supplement a tonalite labelled T-1, issued from the Geological Survey of Tanganyika, was also analysed. In addition, to check the analytical method, the extensively analysed diabase W-1 was investigated.

The nuclear data for the relevant activation reactions for copper, gallium and zinc are given in Table I. Samples and standards were irradiated for 24 h in the

TABLE I  
NUCLEAR DATA

Element	Activation reaction	Abundance of stable nuclide (%)	Cross-section (barns)	Half-life of radio-nuclide (h)	$\gamma$ -energy used (MeV)
Cu	$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$	69.1	4.4	12.8	0.51 <sup>a</sup>
Ga	$^{71}\text{Ga}(n,\gamma)^{72}\text{Ga}$	39.8	4.6	14.3	0.84
Zn	$^{68}\text{Zn}(n,\gamma)^{69m}\text{Zn}$	18.6	0.10	13.8	0.43

<sup>a</sup> Positron annihilation.

JEEP I reactor (Kjeller, Norway) at a thermal neutron flux of about  $2 \cdot 10^{12}$  n/cm<sup>2</sup> sec. The irradiated rock specimens were decomposed by alkaline fusion. The cooled melt was dissolved in water and the chloride concentration was adjusted to 6 M with concentrated hydrochloric acid. Copper, gallium and zinc were adsorbed from this solution on a strongly basic anion-exchange resin<sup>17</sup>. Copper and gallium were eluted in one portion with 0.5 N hydrochloric acid, while zinc was subsequently eluted with 5% ammonia solution. The chemical yield was determined by a re-activation technique after the activities of interest had decayed away. Generally the chemical yield obtained was in the range 60–80% for each of the elements. The technique of re-activation is convenient to use in analyses of extensive series of geological samples. Besides its simplicity, the technique also often allows the simultaneous determination of more than one element in one fraction. This method could generally be used more extensively in chemical yield determinations.

The  $\gamma$ -spectrum of an eluate containing copper and gallium is shown in Fig. 1. The two smaller peaks at 1.10 MeV and 1.29 MeV are due to 45-d <sup>59</sup>Fe formed by neutron capture in iron present in the samples. However, in most cases these peaks did not disturb seriously the determination of copper and gallium by the 0.51 MeV

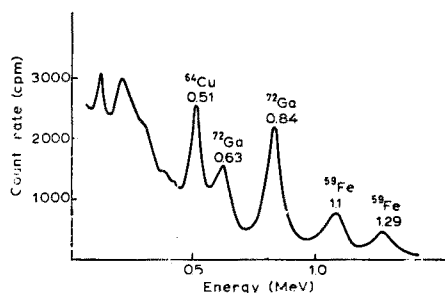


Fig. 1.  $\gamma$ -Spectrum of eluate containing copper and gallium.

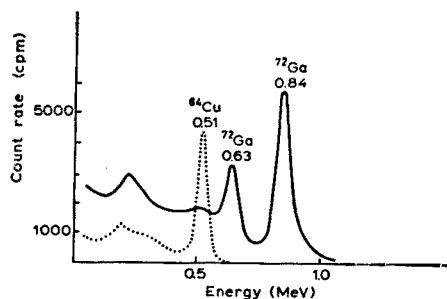


Fig. 2.  $\gamma$ -Spectra of copper and gallium standards.

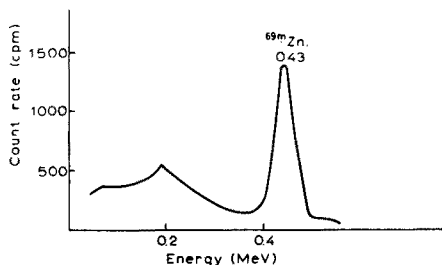


Fig. 3.  $\gamma$ -Spectrum of eluate containing zinc.

and 0.84 MeV peaks respectively. In Fig. 2  $\gamma$ -spectra of copper and gallium standards are shown. A  $\gamma$ -spectrum of an eluted zinc fraction is shown in Fig. 3. Spectra of zinc standards and zinc eluates were quite identical in shape. The peak areas were evaluated by the method of COVELL<sup>18</sup>.

## EXPERIMENTAL

*Apparatus*

The  $\gamma$ -activities were measured with an "Intertechnique" 400-channel analyser SA-40 with a well-type  $3 \times 3''$  NaI(Tl) crystal.

*Anion-exchange columns*

Fill a column of internal diameter 9 mm with Dowex 2-X8 (100–200 mesh, chloride form) to 8 cm height of resin bed. Preequilibrate with 9 *N* hydrochloric acid.

*Chemicals*

*Carrier solutions.* Dissolve in water amounts of copper chloride, gallium chloride and zinc chloride corresponding to *ca.* 5 mg Cu/ml, 2 mg Ga/ml and 5 mg Zn/ml.

*Standard solutions.* Dissolve accurately weighed amounts of copper metal in nitric acid, gallium oxide in sulphuric acid and zinc metal in hydrochloric acid. Dilute with water to suitable concentrations. The following concentrations are recommended: Cu, 5 p.p.m.; Ga, 2 p.p.m.; Zn, 50 p.p.m.

*Treatment of samples and standards for irradiation*

Weigh *ca.* 100 mg of the rock powder accurately into polyethylene vials of small diameter and length. Close with a stopper. Seal about 1.2 ml of the standard solutions of copper, gallium and zinc separately into quartz ampoules. Place the samples and standards as close to each other as possible in an aluminium container and irradiate at a thermal neutron flux of about  $2 \cdot 10^{12}$  n/cm<sup>2</sup>sec for 24 h.

*Radiochemical separation steps*

Allow the irradiated sample to cool for 24 h for the decay of short-lived activities, mainly 2.56-h <sup>56</sup>Mn. Pipette exactly 1.00 ml of each carrier solution of copper, gallium and zinc into a nickel crucible and evaporate carefully to dryness under a heating lamp. Pour the sample into the crucible, and add 2 g of sodium hydroxide pellets. Heat the crucible over a Meker burner for 5 min. Cool. Dissolve the fusion cake in 10 ml of water and transfer to a 250-ml beaker. Add carefully 10 ml of concentrated hydrochloric acid. Cool. Filter the solution through a funnel placed on the top of the prepared ion-exchange column. After the solution has passed through the resin, remove the funnel and discard the precipitate.

Wash the resin twice with 5 ml of 9 *N* hydrochloric acid. Discard the effluent. Elute copper and gallium with 10 ml of 0.5 *N* hydrochloric acid and collect the eluate in a 50-ml polyethylene screwcap bottle. Wash twice with 10 ml of 0.5 *N* hydrochloric acid. Discard the effluent. Finally elute the zinc with 10 ml of a 5% ammonia solution and again collect the eluate in a 50-ml polyethylene screwcap bottle.

*Treatment of the standards*

Pipette 1.00 ml of each standard solution from the quartz ampoules and transfer to separate 50-ml polyethylene screwcap bottles. Dilute to 10 ml with water to obtain the same counting geometry as for the eluted fractions.

*Activity measurements*

Record the  $\gamma$ -spectra for the samples and standards with a multichannel analyser. Evaluate the area under the peaks of interest corresponding to the  $\gamma$ -energies listed in Table I. Repeat the recording of the spectra after 5–15 h to check the disintegration rates.

*Determination of chemical yield*

Allow the activities of  $^{64}\text{Cu}$ ,  $^{72}\text{Ga}$  and  $^{69\text{m}}\text{Zn}$  to decay for one week. Dilute the fraction containing copper and gallium to 250 ml with distilled water. Similarly dilute the zinc eluate to 50 ml. Seal about 1.2 ml of each solution separately into polyethylene tubes and activate for 1 h together with aliquots of the carrier solutions diluted in the same manner, at a thermal neutron flux of about  $2 \cdot 10^{12}$  n/cm<sup>2</sup>/sec.

After the irradiation, allow the solutions to "cool" for 3–4 h. Pipette 1.00 ml of each solution into separate polyethylene vials and measure the activity as described above.

## RESULTS AND DISCUSSION

The results obtained for copper, gallium and zinc in the geochemical rock standards analysed in this work are presented in Table II, together with the mean value for each element. In Table III the mean values obtained for the copper, gallium and zinc content in standard diabase W-1 are compared with the recommended values quoted in the recent compilation of data on W-1 given by FLEISCHER<sup>19</sup>, and also with available values of other workers using neutron activation analysis. The results of the present work are in good agreement with previously reported activation results. However, the data obtained by neutron activation are slightly higher than the recommended values.

G-2 is intended to be a replacement of the now nearly exhausted G-1. The

TABLE II  
RESULTS FOR COPPER, GALLIUM AND ZINC (IN p.p.m.)

	<i>Granite G-2</i>	<i>Tonalite T-1</i>	<i>Diabase W-1</i>	<i>Nepheline- syenite STM-1</i>	<i>Grano- diorite GSP-1</i>	<i>Andesite AGV-1</i>	<i>Basalt BCR-1</i>	<i>Perido- tite PCC-1</i>	<i>Dunite DTS-1</i>
Cu	6.1	41	123	2.0	31	48	12	7.4	6.6
	5.8	41	111	1.9	35	54	13	8.3	5.4
	8.2	39	113	2.1	32	53	14	11.4	6.2
Av.	6.7	40	116	2.0	33	52	13	9.0	6.1
Ga	22	19	19	36	25	20	23	1.2	1.0
	27	19	21	39	24	21	26	1.3	1.2
	24	20	19	38	23	22	23	1.4	1.6
Av.	24	19	20	38	24	21	24	1.3	1.3
Zn	71	175	87	204	102	84	115	41	64
	76	160	83	206	105	85	116	42	56
	85	173	80	218	117	92	114	43	62
Av.	77	169	83	209	108	87	115	42	61

results obtained for G-2 show fairly good agreement with the recommended values<sup>19</sup> for G-1 on copper and gallium (respectively 13 p.p.m. and 18 p.p.m.). However, the recommended value of zinc in G-1, 45 p.p.m., is considerably lower than the present result for G-2. A significant difference between other trace element contents of G-1 and the replacement G-2 has also been established previously<sup>25,26</sup>.

TABLE III

COMPARISON OF PRESENT RESULTS FOR W-1 WITH RECOMMENDED VALUES<sup>19</sup> AND PREVIOUS NEUTRON ACTIVATION RESULTS

<i>Element</i>	<i>Present work (mean p.p.m.)</i>	<i>Recommended values<sup>19</sup> (p.p.m.)</i>	<i>Previously published neutron activation data (p.p.m.)</i>
Cu	116	110	112 <sup>1</sup> , 120 <sup>20</sup> , 110 <sup>7</sup> , 116 <sup>21</sup>
Ga	20	16	18 <sup>12</sup> , 18.3 <sup>19</sup> , 16.5 <sup>19</sup>
Zn	83	82	85 <sup>13</sup> , 82.8 <sup>14</sup>

TABLE IV

PRESENT RESULTS FOR TONALITE T-1 COMPARED WITH PREVIOUS PUBLISHED DATA (p.p.m.)

<i>Reference</i>	<i>Method</i>	<i>Cu</i>	<i>Ga</i>	<i>Zn</i>
INGAMELLS AND SUHR <sup>22</sup>	Spectrochemical	62		160
THOMAS <sup>23</sup>	Chemical and spectrographic	40-55 <sup>a</sup>	17-25 <sup>a</sup>	160-220 <sup>a</sup>
KAYE <sup>24</sup>	X-ray fluorescence	45		198
This work	Neutron activation	40	19	169

<sup>a</sup> Range of values reported by several workers.

As can be seen from Table IV, the agreement between the present results of tonalite T-1 and previous published data for copper, gallium and zinc in this standard rock is satisfactory.

#### *Precision and accuracy*

From Table II it can be seen that the average precision for the determination of copper, gallium and zinc by the present method is about  $\pm 5\%$  for concentrations exceeding 10 p.p.m. The results were obtained by repeated runs on duplicate samples of each rock. No systematic errors due to flux inhomogeneity within the irradiation unit are therefore likely to influence the mean values. On the other hand, the accuracy may be considerably affected by shielding effects in samples or standards either in the primary activation or in the chemical yield determination. However, as none of the major constituents of the rock samples are strong neutron absorbers, and as dilute solutions of the elements were used as standards, such effects can be neglected.

Serious systematic errors may occur due to interfering nuclear reactions induced by fast neutrons. In the present work  $^{64}\text{Zn}(n,p)^{64}\text{Cu}$  is the only fast neutron reaction which can result in significant interference. In the case of nepheline syenite STM-1 where the ratio Zn:Cu is about 200, the correction due to the contribution from the (n,p)-reaction amounts to approximately 5%. For the other standards the

interference is negligible. Interference from fission of  $^{235}\text{U}$  is also negligible, as the fission yields of the elements analysed are known to be extremely small.

On the basis of the discussion above and of the good agreement between the present results and recommended values for W-1, it seems reasonable that the mean values reported in this work are accurate to about  $\pm 5\%$  when the concentration of the actual elements exceeds 10 p.p.m.

#### *Sensitivity*

The sensitivity of the present method for the determination of copper and gallium depends on the respective amounts of gallium and iron present (*cf.* Fig. 1). Usually the limit of sensitivity is of the order of 0.5 p.p.m. for both elements. If required, far better sensitivity can be achieved by introducing additional separation steps. The sensitivity of the zinc determination depends on the weight of sample and the neutron flux employed. With 100-mg samples and a neutron flux of  $2 \cdot 10^{12}$  n/cm<sup>2</sup>sec the limit of sensitivity is about 0.4 p.p.m.

The method described is simple and sufficiently sensitive for the general determination of copper, gallium and zinc in igneous rocks. The method should be attractive for studies of fractionation processes of these elements within igneous rock systems.

This work was carried out while one of the authors (A.O.B.) held a research fellowship granted by the Norwegian Research Council for Science and the Humanities.

#### SUMMARY

A neutron activation method for the simultaneous determination of copper, gallium and zinc in rocks is described. The method is based on anion-exchange separation steps and measurement of  $\gamma$ -activity. Chemical yields were determined by re-activation. Results for a series of igneous "standard rocks" are presented. The accuracy of the mean values is *ca.* 5% for concentrations exceeding 10 p.p.m.

#### RÉSUMÉ

On décrit une méthode par activation au moyen de neutrons pour le dosage simultané du cuivre, du gallium et du zinc dans des roches. Elle est basée sur des séparations à l'aide d'échangeur d'anions et mesure de l'activité  $\gamma$ . Des résultats sont donnés pour des échantillons standards. La précision des valeurs moyennes est d'environ de 5% pour des concentrations dépassant 10 p.p.m.

#### ZUSAMMENFASSUNG

Es wird die gleichzeitige Bestimmung von Kupfer, Gallium und Zink in Gesteinen mit der Neutronenaktivierungsanalyse beschrieben. Das Verfahren verwendet zur Trennung Anionenaustauscher und die Messung der  $\gamma$ -Aktivität. Die chemischen Ausbeuten wurden durch Reaktivierung bestimmt. Es werden Ergebnisse einer Reihe von Beispielen angegeben. Die Genauigkeit der Mittelwerte beträgt etwa 5% bei Konzentrationen von mehr als 10 p.p.m.

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## A SPECTROPHOTOMETRIC DETERMINATION OF THE STABILITY CONSTANTS OF THE COMPLEXES OF TITANIUM(III) WITH ACETYLACETONE

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In a search for suitable chelating agents for a spectrophotometric determination of titanium it was found that there is considerable complex formation between acetylacetonone and titanium(III) even in solutions with a pH of about 0. In such acidic solutions, which are required to avoid hydrolysis of titanium(III), the color of the complex is intensely red. On increasing the pH the color becomes bluish-red and finally blue at a pH greater than 3-4. These observations are in agreement with those of FUJIWARA *et al.*<sup>1</sup>. Since no data were available on the composition and the stability constants of the complexes, an investigation of these properties was carried out.

There is little information on the interaction of titanium(III) with acetylacetonone (in the subsequent discussion, HL indicates acetylacetonone and L the acetylacetonate ion). In organic media complexes of titanium(III) chloride with some ketones and dioxane are known<sup>2</sup>; in aqueous solutions of pH *ca.* 0 the titanium(III) ion is predominantly<sup>3</sup> present as  $Ti(H_2O)_6^{3+}$ , so that the existence of  $TiCl_3(HL)_n$  is not to be expected. BARNUM<sup>4</sup> gives the absorption curve of  $TiL_3$  in ethanol in a paper dealing with the chemical bonding of some trisacetylacetonato complexes.

The composition and stability constants of many metal-acetylacetonate complexes are described in the literature<sup>5</sup>. Generally, there is a tendency to form neutral molecules which implies that in the case of titanium, the highest complex to be expected is  $TiL_3$ . In all cases the successive stability constants decrease by a factor of 10 to 100. At the start of this work, there was no reason to expect an anomalous behaviour from titanium(III).

### EXPERIMENTAL

#### *Materials*

The titanium(III) solution was prepared by boiling 10 ml of a 15% titanium(III) chloride solution with 100 ml of concentrated hydrochloric acid and diluting to about 1 l in a nitrogen atmosphere. The solution was passed through a zinc reductor, to make sure that all titanium was present in the tervalent state, and then collected in a vessel under nitrogen. Standardization was accomplished by adding a certain volume of the solution to an excess of iron(III) and titrating the iron(II), formed by the reaction with titanium(III), potentiometrically with cerium(IV).

As a gas-chromatographic analysis of the acetylacetonone used showed a

sufficient purity, no purification was carried out. The solutions were obtained by dissolving weighed amounts of the reagent.

The different pH values were established by addition of sodium hydroxide or hydrochloric acid. Values for temperature and ionic strengths are mentioned in the Tables.

### Apparatus

The spectrophotometer used was a Zeiss PMQ II with titrating equipment and 20-mm glass cells. The pH values of all solutions were measured with a Radiometer pHM 4c pH-meter using a combined glass-calomel electrode (Radiometer GK 2024c) that could stand in the cell during the recording of the pH vs. absorbance curves. The electrodes were standardised with a potassium hydrogen phthalate buffer (pH = 4).

### RESULTS AND DISCUSSION

The complex composition in the case of successive complex formation depends on the free ligand concentration. As acetylacetonone is a weak acid ( $pK_a = 8.9$ ), the free ligand concentration,  $[L]$ , varies with the pH if the total amount of acetylacetonone is constant and there will also be a dependence of complex composition on the pH. Such a change in the complex composition is mostly accompanied by a change in the absorption curve. Figure 1 shows a number of absorption curves of solutions containing titanium(III) and acetylacetonone at different pH values. A shift of the maxima is observed on increasing the pH from 1.7 to 4 (Table I).

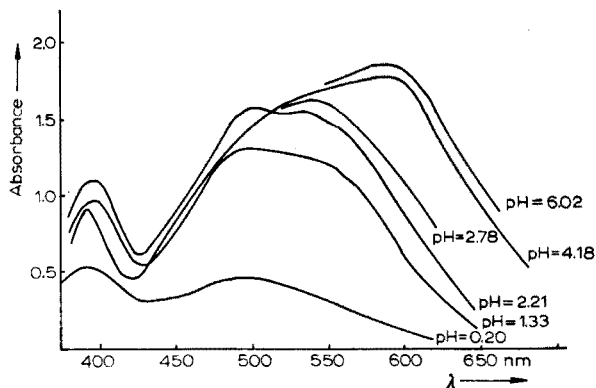


Fig. 1. Absorption curves of solutions containing titanium(III) and acetylacetonone at different pH values.  $C_{Ti} = 7.5 \cdot 10^{-4} M$ ;  $C_L = 0.75 M$ .

It was supposed that with the given concentration of acetylacetonone, the neutral 1:3 complex would be formed at pH values above 4 whereas the 1:1 complex would predominate at very low pH values. In the intermediate pH regions there should be first a region of equilibrium between the 1:1 and 1:2 complexes, and then a region where the 3 complexes coexist followed by a region where only the equilibrium between the 1:2 and 1:3 complexes is important.

Since it did not seem possible to measure both the concentration of the various

complexes (by means of the absorbance) and the concentration of free metal ion or free ligand, the problem was approached by calculating the stability constants from absorbance readings either in relation to the total amount of chelating agent added or in relation to the pH of the solutions.

TABLE I  
VARIATION OF ABSORPTION MAXIMA WITH pH

pH	Maximum in 395 nm region (nm)	Maximum in 500-600 nm region (nm)
0.5 < pH < 1.7	397.5	495.0
1.7 < pH < 4.0	shift to 393.0	shift to 585.0
pH > 4.0	393.0	585.0

*Dependence of the absorbance on the total ligand concentration*

The absorbance of a solution containing successive complexes with acetylacetone is given by

$$A b^{-1} = a_{\text{Ti}}[\text{Ti}] + a_{\text{TiL}}[\text{TiL}] + \dots + a_{\text{TiL}_n}[\text{TiL}_n] + a_{\text{L}}[\text{L}] + a_{\text{HL}}[\text{HL}] \quad (1)$$

where  $A$  = absorbance;  $b$  = pathlength;  $a_{\text{X}}$  = molar absorptivity of the compound X. At low pH values and at moderate concentration of acetylacetone one would expect the formation of TiL only; but a plot of the absorbance vs. the ratio of total ligand to total metal concentration indicated that at pH ca. 0 even the formation of the 1:1 complex is very incomplete. In that case we may put

$$C_{\text{L}} = [\text{HL}] + [\text{L}] + [\text{TiL}] \approx [\text{HL}]$$

Moreover  $a_{\text{L}}$  and  $a_{\text{HL}}$  are negligible at the wavelengths used (490 and 505 nm) so that eqn. (1) can be simplified to

$$A b^{-1} = a_{\text{Ti}}[\text{Ti}] + a_{\text{TiL}}[\text{TiL}] \quad (2)$$

Substitution of the stability constant  $K_1$  ( $K_n = [\text{ML}_n][\text{ML}_{n-1}]^{-1}[\text{L}]^{-1}$ ) and the dissociation constant of acetylacetone  $K_{\text{a}} = [\text{H}][\text{L}][\text{HL}]^{-1}$  gives, after dividing by  $C_{\text{Ti}}$

$$A b^{-1} C_{\text{Ti}}^{-1} = \frac{a_{\text{Ti}} + a_{\text{TiL}} K_1 K_{\text{a}} [\text{H}]^{-1} C_{\text{L}}}{1 + K_1 K_{\text{a}} [\text{H}]^{-1} C_{\text{L}}} \quad (3)$$

or

$$(A b^{-1} C_{\text{Ti}}^{-1} - a_{\text{Ti}}) C_{\text{L}}^{-1} = a_{\text{TiL}} K_1 K_{\text{a}} [\text{H}]^{-1} - K_1 K_{\text{a}} [\text{H}]^{-1} A b^{-1} C_{\text{Ti}}^{-1} \quad (4)$$

A plot of  $(A b^{-1} C_{\text{Ti}}^{-1} - a_{\text{Ti}}) C_{\text{L}}^{-1}$  against  $A b^{-1} C_{\text{Ti}}^{-1}$  must yield a straight line provided that the pH is constant and only the 1:1 complex is formed as was postulated. The slope gives the value  $K_1 K_{\text{a}} [\text{H}]^{-1}$  and the intercept a value for  $a_{\text{TiL}}$ .

As titanium(III) is easily oxidized, titanium(III) solutions cannot be handled without precautions in volumetric flasks. Accordingly, a known amount of titanium(III) was placed in the cell under a nitrogen atmosphere and "titrated" with a concentrated deaerated solution of acetylacetone. The absorbance readings were corrected for dilution. As the total dilution was less than 10% the error introduced on changing

the ionic strength could be neglected. After the titration the solutions were diluted 100 times with distilled water and the pH was measured. The pH values obtained in this way were used to calculate the original acidity. The error introduced in this procedure—since the difference in ionic strength between diluted and original solution was not taken into account—means that the value of  $\log K_1$  is not valid to more than one decimal place.

Figure 2 shows some of the plots obtained. As can be seen straight lines are

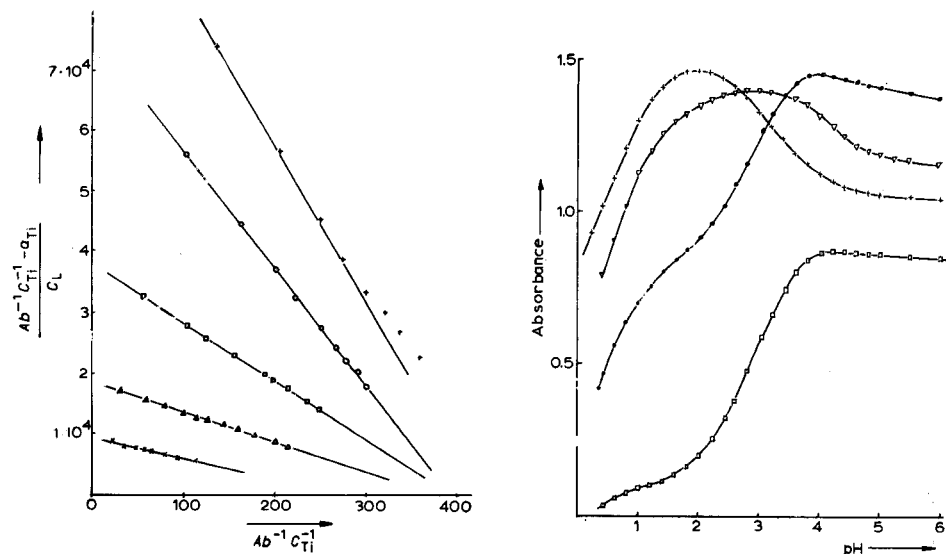


Fig. 2. Plot of  $(Ab^{-1}C_{Ti}^{-1} - a_{Ti})C_L^{-1}$  vs.  $Ab^{-1}C_{Ti}^{-1}$  for different pH values. pH = -0.08(x); 0.19(Δ); 0.43(□); 0.74(○); 0.91(+).

Fig. 3. Absorbance in dependence of the pH for different wavelengths.  $C_{Ti} = 8.5 \cdot 10^{-4} M$ ;  $C_L = 0.67 M$ .  $\lambda = 590$  nm(●); 540 nm(∇); 495 nm(+); 650 nm(□).

TABLE II  
VALUES FOR  $\log \beta_1$  AND  $a_{TiL}$

$C_{Ti}$ ( $\cdot 10^{-4} M$ )	pH	Temp. (°)	Ionic strength	$\lambda$ (nm)	$a_{TiL}$	$\log \beta_1$
3.55	0.14	23-25	I	490	368	10.42
3.55	0.14	23-25	I	490	—	10.41
7.10	0.12	23-25	I	490	380	10.44
7.10	0.12	23-25	I	490	409	10.40
10.65	0.08	23-25	I	490	382	10.42
10.65	0.08	23-25	I	490	384	10.44
14.20	0.065	23-25	I	490	376	10.47
14.20	0.065	23-25	I	490	386	10.43
21.30	0.05	23-25	I	490	386	10.41
21.30	0.05	23-25	I	490	403	10.44
14.20	-0.08	26-28	Decreasing	505	—	10.43
14.20	0.19	26-28	from	505	370	10.44
14.20	0.43	26-28	I	505	392	10.45
14.20	0.74	26-28	to	505	392	10.44
			0.1			

Mean values:  $\overline{a_{TiL}^{490}} = 383$   $\overline{a_{TiL}^{505}} = 385$   $\overline{\log \beta_1} = 10.43$

obtained, indicating that the assumption that only TiL is formed, was correct. Table II gives a summary of the results.

#### *Dependence of the absorbance on the pH*

To change the acetylacetonato-ion concentration in a wider range the pH of the solutions was varied. The absorbance *vs.* pH curves were obtained by titrating solutions containing a known amount of titanium(III) and a large excess of acetylacetonate with sodium hydroxide under nitrogen, recording both absorbance (corrected for dilution) and the pH. In Fig. 3 some of these curves at different wavelengths are shown.

Using the values for  $K_1$  and  $K_a$ , it can be calculated that at pH *ca.* 0.3 and a concentration of acetylacetonate of 0.67 *M* the ratio TiL:Ti is about 40:1. The curve for  $\lambda = 495$  nm shows an increase of the absorbance in the pH-region 0.3–1.9. This increase can probably be attributed to the conversion of the 1:1 to the 1:2 complex. The decrease of the absorbance at pH > 2 would then be the result of the conversion of the 1:2 into the 1:3 complex.

If the successive stability constants decrease with a factor 10 to 100 as in the case with most other metal ions, no values for pH and  $C_L$  can be found where only TiL or TiL<sub>2</sub> is present. The maximum at pH = 2 for  $\lambda = 495$  nm does not mean that all titanium is converted to TiL<sub>2</sub>, but corresponds to the point where the maximum amount of TiL<sub>2</sub> is formed. It is reasonable to assume that with  $C_L = 0.67$  *M* at pH values below 1.5, the amount of TiL<sub>3</sub> will be negligible and that above pH 2.5 the amount of TiL can be neglected.

In the pH region 0–1.5 we can write for the absorbance

$$Ab^{-1}C_{Ti}^{-1} = \frac{a_{Ti} + a_{TiL}K_1K_aC_L[H]^{-1} + a_{TiL_2}K_1K_2K_a^2C_L^2[H]^{-2}}{1 + K_1K_aC_L[H]^{-1} + K_1K_2K_a^2C_L^2[H]^{-2}} \quad (8)$$

This can be converted to

$$\begin{aligned} (Ab^{-1}C_{Ti}^{-1} - a_{Ti})[H]^2 + (Ab^{-1}C_{Ti}^{-1} - a_{TiL})K_1K_aC_L[H] &= \\ &= (a_{TiL_2} - Ab^{-1}C_{Ti}^{-1})K_1K_2K_a^2C_L^2 \quad (9) \end{aligned}$$

A plot of the left-hand side of eqn. (9) against  $Ab^{-1}C_{Ti}^{-1}$  for different pH values will yield a straight line. The intercept provides  $a_{TiL_2}$ . In Fig. 4 the plots are shown for 4 different wavelengths. It will be clear that only wavelengths can be used for which  $a_{TiL}$  and  $a_{TiL_2}$  are sufficiently different. In Table III the results are summarized.

In the pH region 2.5–4.0 an equilibrium between TiL<sub>2</sub> and TiL<sub>3</sub> only can be expected; by means of the known value of  $\log K_2$  the ratio TiL<sub>2</sub>:TiL at pH 2.5 was found to be 67:1, so that TiL could in fact be neglected.

$$Ab^{-1} = a_{TiL_2}[TiL_2] + a_{TiL_3}[TiL_3]$$

After substitution of  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_a$ , and dividing by  $C_{Ti}$  this can be transformed to

$$Ab^{-1}C_{Ti}^{-1} = \frac{a_{TiL_2} + a_{TiL_3}K_3K_aC_L[H]^{-1}}{1 + K_3K_aC_L[H]^{-1}} \quad (10)$$

Rearrangement provides

$$\frac{Ab^{-1}C_{Ti}^{-1} - a_{TiL_2}}{a_{TiL_3} - Ab^{-1}C_{Ti}^{-1}} = K_3K_aC_L[H]^{-1} \quad (11)$$

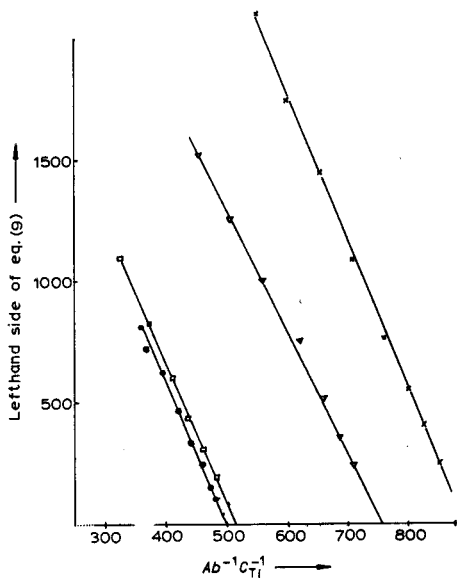


Fig. 4. Left-hand term of eqn. (9) vs.  $Ab^{-1}C_{Ti}^{-1}$  for different wavelengths.  $\lambda = 590$  nm ( $\square$ ); 450 nm ( $\bullet$ ); 540 nm ( $\nabla$ ); 495 nm ( $\times$ ).

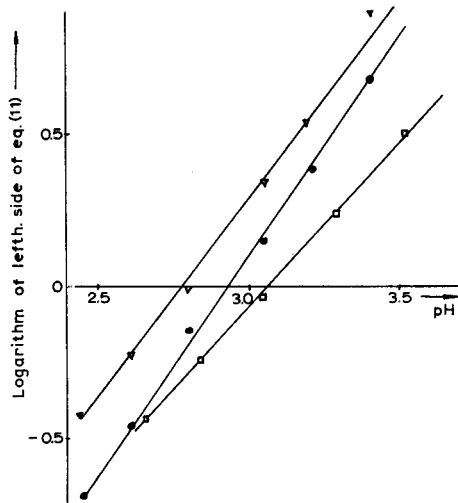


Fig. 5. Left-hand term of eqn. (11) vs. pH for different wavelengths.  $\lambda = 590$  nm ( $\nabla$ ); 650 nm ( $\bullet$ ); 495 nm ( $\square$ ).

TABLE III

VALUES FOR  $\log \beta_2$  AND  $a_{TiL_2}$   
(at 25° and ionic strength 1)

$\lambda$ (nm)	$\log \beta_2$	$a_{TiL_2}$	
450	18.82	502	$C_{Ti} = 8.5 \cdot 10^{-4} M$
595	18.86	888	$C_L = 0.67 M$
540	18.79	758	
590	18.82	510	Mean value $\log \beta_2 = 18.82$

TABLE IV

VALUES FOR  $\log K_3$

(at 25° and ionic strength 1)

$\lambda$ (nm)	$\log K_3$	
495	6.02	$C_{Ti} = 8.5 \cdot 10^{-4} M$
590	6.29	$C_L = 0.67 M$
650	6.11	Mean value $\log K_3 = 6.1$

$a_{TiL_2}$  is known from the preceding part;  $a_{TiL_3}$  can be calculated from the absorbance of the solution at pH greater than 4. A plot of the logarithm of the left-hand side of eqn. (11) vs. pH gives a straight line. The intercept supplies a value for  $K_3 K_a C_L$  from which  $K_3$  can be calculated. OKÁČ AND SOMMER<sup>6</sup> used the same equation for the determination of some titanium(IV) complexes. Figure 5 shows some plots and Table IV gives the results. The calculated values of  $\log K_3$  show a rather large variation; this is partly due to the fact that in the value of  $a_{TiL_2}$  all deviations in  $a_{TiL}$  and  $K_1$  are accumulated, while  $a_{TiL_3}$  also shows some error. Because at 650 nm,

$a_{TiL_2} \ll a_{TiL_3}$ , a relatively large error in  $a_{TiL_2}$  has only a small influence on the result. The value of  $\log K_3$  at this wavelength is the most reliable.

To check the results, the complex composition as a function of the pH was calculated with the aid of the found stability constants for a concentration of acetylacetonate of 0.67 M. Also the absorbance *vs.* pH curves for  $\lambda = 495$  nm and  $\lambda = 590$  nm were calculated. Figure 6 illustrates the agreement between the calculated and experimental curves.

The application of these results to the spectrophotometric determination of titanium is being investigated.

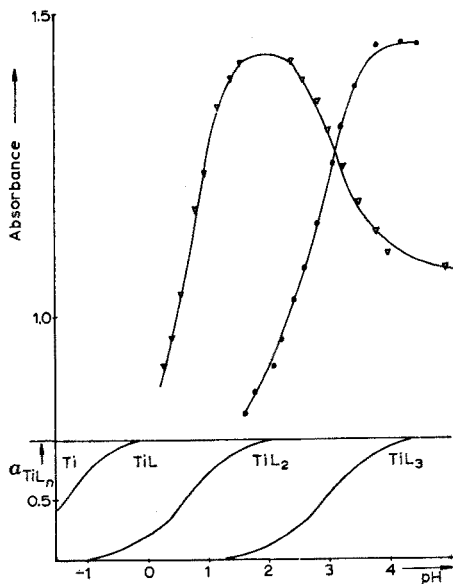


Fig. 6. Calculated complex composition for the system titanium(III)-acetylacetonate in dependence of the pH; as well as the calculated absorbance-pH curves for  $\lambda = 495$  nm and  $\lambda = 590$  nm.  $\nabla$ ,  $\bullet$  = experimental; — = calculated.

#### SUMMARY

The stability constants of the consecutive complexes of titanium(III) with acetylacetonate were determined by means of spectrophotometric methods. The values are  $\log \beta_1 = 10.4$ ,  $\log \beta_2 = 18.8$ , and  $\log \beta_3 = 24.9$ . Because of the fact that  $K_1 K_a = 10^{1.5}$  a high concentration of acetylacetonate results in a considerable formation of TiL even at pH 0.

#### RÉSUMÉ

On a déterminé les constantes de stabilité des complexes du titane(III) avec l'acétylacétone à l'aide de méthodes spectrophotométriques. Ces valeurs sont:  $\log \beta_1 = 10.4$ ,  $\log \beta_2 = 18.8$  et  $\log \beta_3 = 24.9$ .

## ZUSAMMENFASSUNG

Mit Hilfe von spektralphotometrischen Methoden wurden die Stabilitätskonstanten der Komplexe des Titan(III) mit Acetylaceton bestimmt. Die Werte betragen  $\log \beta_1 = 10.4$ ,  $\log \beta_2 = 18.8$ ,  $\log \beta_3 = 24.9$ . Da  $K_1 K_a = 10^{1.5}$  ist, ergibt eine hohe Konzentration von Acetylaceton eine beträchtliche Bildung von TiL sogar beim  $\text{pH} = 0$ .

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## TRACE METAL ANALYSIS BY COMBINED THIN-LAYER CHROMATOGRAPHY AND REFLECTANCE SPECTROSCOPY\*

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Thin-layer chromatography for the separation and determination of trace metals requires shorter development times than paper chromatography and gives sharper delineation of the spots. Despite these advantages and even though little or no alteration of paper-chromatography procedures is required on cellulose layers, very little work has been done in inorganic thin-layer chromatography<sup>1</sup>. The separation of various cation groups, on silica gel layers, has been reported by SEILER *et al.*<sup>2-5</sup>; little information exists at the moment for separation of cations on alumina layers.

The application of diffuse reflectance spectroscopy to the evaluation of chromatoplates in connection with organic systems<sup>6-9</sup> has been extended, in this paper, to the inorganic field and to trace metals in particular. Rubenic acid, a widely used chelating agent for nickel, cobalt, and copper trace analysis in solution as well as on column or paper chromatograms<sup>10-13</sup>, was used as developing reagent; the behaviour of such complexes adsorbed on media commonly used in chromatography, under varying temperature, pH, and humidity conditions, was also investigated.

## EXPERIMENTAL

*Reagents*

Solvents, rubenic acid (0.1% in ethanol) and metal chloride stock solutions (1 g of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> per litre) were reagent grade; doubly distilled water was used throughout. Thin-layer chromatography grade Alumina G and Silicagel G from "Merck" Darmstadt with particle size 10-40  $\mu$  and 15% plaster of paris binder were used. The cellulose layers were prepared from MN cellulose 300 (Macherey, Nagel & Co., Dueren, Germany) without binder and of 10  $\mu$  maximum particle size.

*Apparatus*

The diffuse reflectance and transmission spectra were measured with a Bausch and Lomb Spectronic 505 recording spectrophotometer equipped with the standard reflectance attachment for the ultraviolet and visible region; barium sulphate plates made with a powder press were used as reference standards. A Beckman DU spectrophotometer with reflectance attachment was used for photometric measurements at wavelength settings determined from the recorded spectra. Measure-

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ments of pH were made with a Beckman Model G pH-meter. The chromatoplates were coated with a "Desaga" thin-layer chromatography applicator; the layer thickness was adjusted to 0.25 mm.

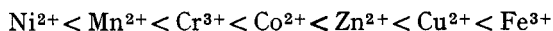
### Procedure

The 20 × 5-cm plates, after coating, were heated at 110° (1 h for silica gel and alumina, 15 min for cellulose) and were then stored in a dry cabinet over silica gel adsorbent. The spots were applied with a 10- $\mu$ l Hamilton microsyringe. The samples were then dried for 5 min at 110°, were cooled to room temperature and then chromatographed in a preconditioned (12 h) chromatography chamber; the solvent systems used for the chromatographic separations are described in the specific sections. The plates were dried in air for 15 min after separation or were heated at 110° for 5 min and treated as described in the following sections. The cells and the technique used in preparing the separated material for examination have been described previously<sup>14</sup>; although the prepared barium sulphate plates were occasionally used, the plate adsorbent usually served as the reference standard. The 20–30 mg samples removed from the plates for analysis of the spots were weighed to  $\pm 0.1$  mg and were ground in a small agate mortar for two periods of 1 min each to insure homogeneity and a more uniform particle size. Samples that were not analyzed immediately were stored in a desiccator over silica gel.

## RESULTS AND DISCUSSION

### Separation on silica gel layers

The procedure recommended by SEILER *et al.*<sup>2,3</sup> was intended for the separation of cations of the ammonium sulphide group. Since copper was added to the mixture in the present study, a slightly modified solvent, 0.5% concentrated hydrochloric acid in acetone, was used. The addition of 1% acetylacetone, as a complexing agent to prevent tailing, was unnecessary if only nickel, cobalt and copper were present; it was not necessary to purify the commercial silica gel from iron impurities in this instance since the iron was chromatographed almost even with the solvent front. The order of separation for the investigated cations was



When iron was present in the sample, iron was first removed from the commercial silica gel by chromatographing the silica gel plates with the solvent mixture;

TABLE I

THE REPRODUCIBILITY OF  $R_F$ -VALUES FOR NICKEL, COBALT AND COPPER SEPARATED ON SILICA GEL PLATES

	$R_F$ -values for 7 trials	Average	Standard deviation	% standard deviation
Cu	0.89–0.96	0.93	$\pm 0.027$	2.9
Co	0.75–0.86	0.81	$\pm 0.048$	5.3
Ni	0.030–0.040	0.034	$\pm 0.0045$	13

iron impurities moving with the solvent front were then cut off and the plate used for the analysis. The separation time was 20–30 min. The reproducibility of  $R_F$ -values for nickel, cobalt and copper are presented in Table I; with such a fast separation time they are, as would be expected, of rather poor reproducibility.

#### *Separation on cellulose layers*

On cellulose plates, for the separation of the same cations, a solvent (15 methyl ethyl ketone : 3 concentrated hydrochloric acid : 2 water) recommended by various authors for paper chromatograms<sup>10–13</sup> was used. The mixture had to be freshly prepared; after 1–2 days the solvent became yellow in colour and increased tailing and changed  $R_F$ -values resulted. Good separation was achieved and the separation time, over a distance of 15 cm, was 40–60 min.

The reproducibility of  $R_F$ -values ( $\text{Ni}^{2+}$ , 0.09;  $\text{Co}^{2+}$ , 0.80;  $\text{Cu}^{2+}$ , 0.87) was similar to that obtained on silica gel plates. The poor reproducibility was again not critical if only nickel, cobalt and copper were present since a complete separation was always achieved for these metals and their rubeanic acid chelates have distinctly different colours.

#### *Separation on alumina layers*

The solvent mixture of 25% 12 N hydrochloric acid in *n*-butanol, recommended by ZAYE *et al.*<sup>15</sup> for the separation of cations of the ammonium sulfide group, was

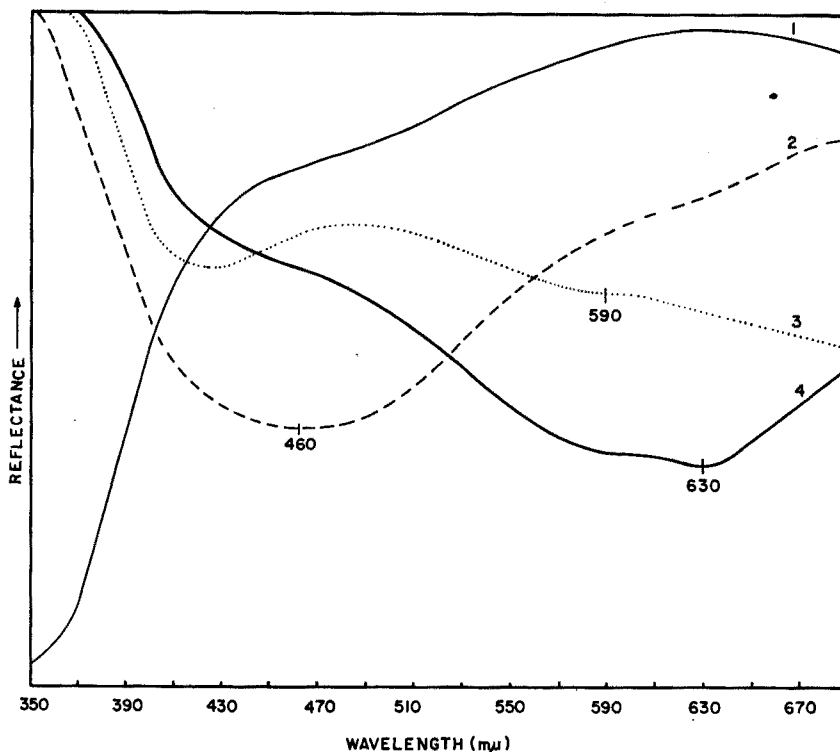


Fig. 1. Reflectance spectra of (1) rubeanic acid and the complexes of (2) cobalt, (3) copper, and (4) nickel adsorbed on Silicagel G.

used. The approximate  $R_F$ -values were:  $\text{Ni}^{2+}$ , 0.15;  $\text{Mn}^{2+}$ , 0.18;  $\text{Cr}^{3+}$ , 0.21;  $\text{Co}^{2+}$ , 0.60;  $\text{Zn}^{2+}$ , 0.73;  $\text{Cu}^{2+}$ , 0.90;  $\text{Fe}^{3+}$  *ca.* 1.00 (following the solvent front).

The separation time, to chromatograph the mixture over 15 cm, was 6–8 h. This reduces the expediency of alumina plates considerably over silica gel (20–30 min) and cellulose (40–60 min); however, the  $R_F$ -values are of better reproducibility (standard deviation  $\pm 2.0\%$ ). Iron impurities can be removed from alumina by treatment with methanolic hydrochloric acid (9:1)<sup>16</sup>; the plates are chromatographed over a distance of 18 cm and the iron front removed.

#### *Spectra of nickel, cobalt and copper chelates*

The reflectance spectra of the rubeanic acid chelates adsorbed on Silicagel G are shown in Fig. 1; to the eye they appear blue-purple for nickel, orange-yellow for cobalt, and olive-green for copper. The reflectance spectra have absorption peaks somewhat broader than the corresponding transmission spectra in aqueous solution and show a shift in absorption maxima to higher wavelengths (Fig. 2, Table II); these results are consistent with earlier literature reports. ZEITLIN AND NIIMOTO<sup>17</sup> found that the absorption peaks become broader with increasing particle size of the adsorbent and attributed this to scattering effects. The bathochromic shift for reflectance

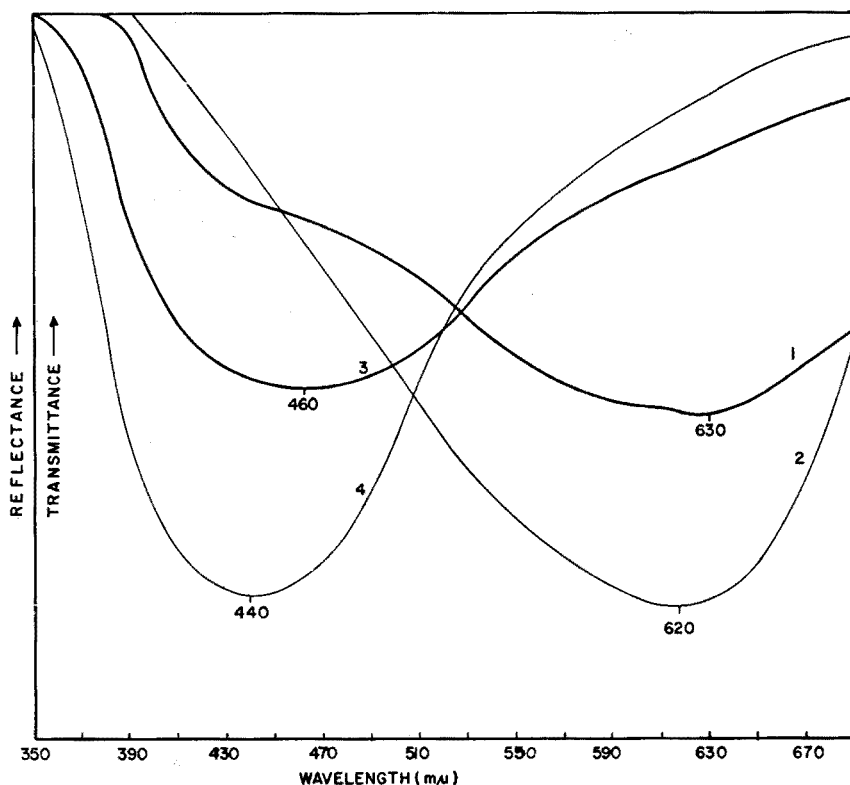


Fig. 2. Reflectance spectra of the rubeanic acid complexes of (1) nickel and (3) cobalt adsorbed on Silicagel G. Transmission spectra of the rubeanic acid complexes of (2) nickel and (4) cobalt in aqueous solution.

tance spectra (compared to transmission spectra) was reported fifteen years ago<sup>18</sup>. The shift increases in the order cellulose < silica gel < alumina (Table II).

#### *Influence of pH on chelates*

For this study the plates were sprayed with ethanolic 0.05–0.5 M solutions of hydrochloric acid or sodium hydroxide and dried before complexation. The pH values of aqueous slurries of the adsorbents were measured with a Beckman Model G pH-meter.

Below pH 7, slow or no complex formation occurred on the adsorbents. In

TABLE II

ABSORPTION MAXIMA OF THE RUBEANIC ACID CHELATES OF NICKEL, COBALT AND COPPER IN AQUEOUS SOLUTION AND ADSORBED ON VARIOUS ADSORBENTS

(wavelength in nm  $\pm$  5 nm)

Chelates of	Water	Cellulose	Silica gel	Alumina
Ni	620	620	630	630
Co	440	455	465	475
Cu	580	580	580	600

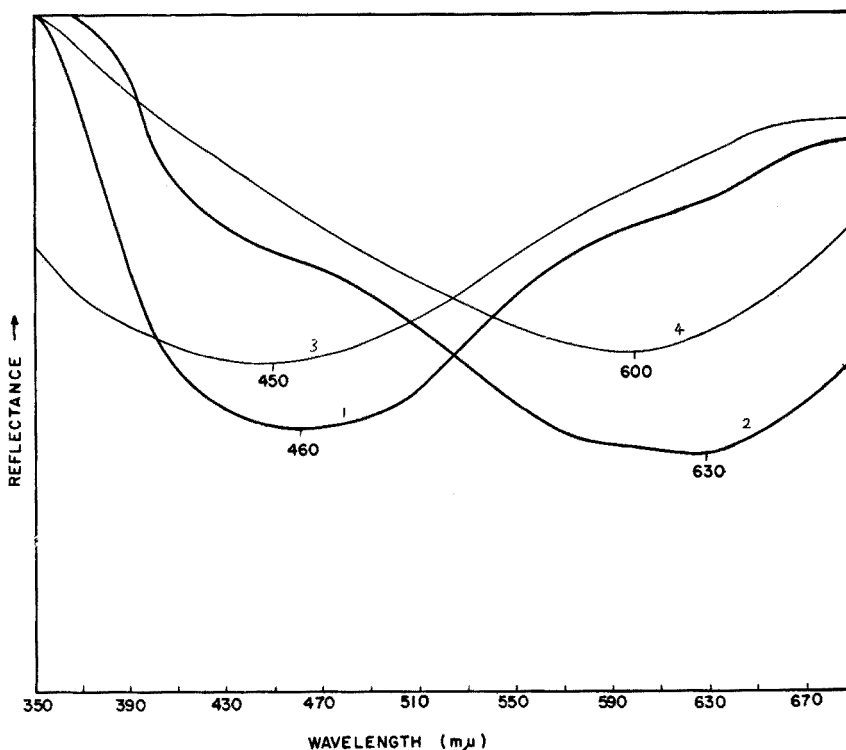


Fig. 3. Reflectance spectra of the rubeanic acid complexes of (1) cobalt, (2) nickel adsorbed on neutral Silicagel G (pH 7–8) and (3) cobalt, (4) nickel adsorbed on basic Silicagel G (pH 10–11).

basic media (pH 10–11) the absorption maximum was shifted to shorter wavelengths (hypsochromic shift) in comparison to the spectra obtained on neutral adsorbents (Fig. 3); a considerable decrease of the absorption peak height was also observed in basic media. All adsorbents behaved similarly.

These data suggest that, for quantitative work, best results would be obtained at pH 7–8; this was achieved by subjecting the plates to ammonia vapor for 10 min before the complexation step to neutralize the small amount of hydrochloric acid present from the separation of the metals. Better results were obtained for cellulose layers by first spraying or dipping the plates, after separation, in ethanolic rubeanic acid solution, drying at 110° for 5 min, and then dipping in a 5% ammonia solution and redrying at 110° for 5–10 min.

#### *Influence of temperature on chelates*

To determine the best treatment for the chromatoplates after applying the complexing agent, the plates were heated, for different periods, at temperatures commonly used in chromatographic work; results are shown in Table III and Fig. 4.

TABLE III

A STUDY OF TEMPERATURE AND TIME EFFECT ON THE REFLECTANCE MAXIMA OF RUBEANIC ACID COMPLEXES ADSORBED ON VARIOUS ADSORBENTS

Adsorbent	Complex of	% R <i>Air dry</i>	60°		110°		
			5 min	30 min	5 min	30 min	2 h
			Cellulose	Co	86.7	86.4	85.7
	Ni	84.8	84.9	84.2	84.2	83.6	—
	Cu	87.0	87.0	86.7	86.5	86.2	—
Alumina	Co	89.8	88.6	84.5	84.2	83.2	82.5
	Ni	83.0	82.9	80.2	80.0	79.6	79.1
	Cu	87.8	87.6	86.8	87.0	86.6	86.9
Silica gel	Co	87.4	86.4	83.7	83.9	83.1	82.3
	Ni	83.8	82.9	81.6	81.2	80.4	79.9
	Cu	85.2	84.9	84.0	83.8	83.4	83.7

The cobalt, nickel, and copper complexes were very stable; the rubeanic acid background, however, disappeared, almost completely, after heating for 5 min at 110°.

On all adsorbents the intensity of the complex was enhanced by heating. This was greater for alumina and silica gel than for cellulose; the increase was also greater for cobalt and nickel chelates. It is probable that the surface water of the adsorbent is removed on heating leaving adsorption sites free for the metal complex and resulting in stronger complex-adsorbent interaction. The initial increase in intensity after heating for 30 min at 60° or 5 min at 110° suggests that most of the water has been removed; a further but small increase in intensity occurs after heating at 100° for 30 min and 2 h but further heating produces little change. The process is reversible; a decrease in the intensity of heated samples was observed after storage of the samples in an aqueous atmosphere. Cellulose, a less effective adsorbent than alumina or

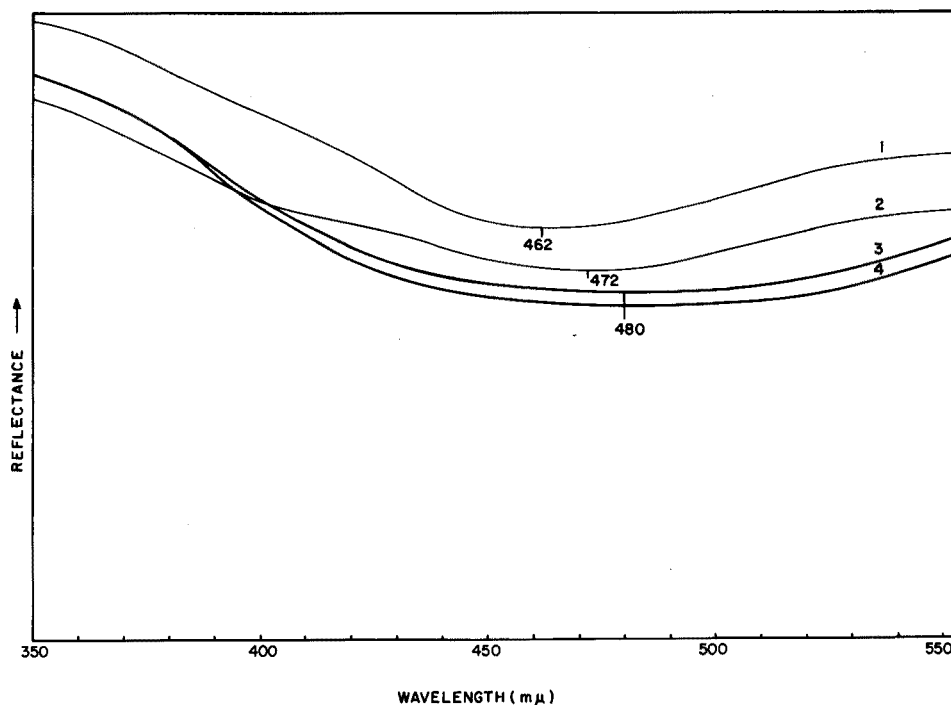


Fig. 4. Reflectance spectra of the cobalt-rubeanic acid complex adsorbed on Silicagel G and heated at  $110^{\circ}$ . (2) for 5 min; (3) for 30 min; (4) for 2 h; (1) stored at air-dry condition for 1 h.

silica gel, showed an increase in intensity of the cobalt-chelate peak of only 1–2% R-units compared to 7–8% R-units on alumina.

Increasing dehydration of the adsorbent resulted also, particularly for the cobalt chelate, in a shift of absorption maxima to higher wavelength and a broadening of the absorption peak (Fig. 4); these results are similar to those obtained previously for dyes on thin-layer chromatography grade adsorbents<sup>19</sup>. Prolonged heating of cellulose at  $110^{\circ}$  produced a dark background.

The experiments show that heating of the chromatoplates at  $110^{\circ}$  for 5 min is satisfactory; analysis time and adsorption intensity are most favorable and the reagent background is sufficiently reduced to avoid any interference. Samples were stored in a desiccator over silica gel to avoid fluctuations; reflectance readings of individual samples kept in a desiccator varied by only 1–2% R-units over several weeks.

#### *Concentration-reflectance relationships*

The sensitivity with the spectrophotometer using 20-mg samples from the chromatoplates was  $0.05 \mu\text{g}$  for nickel and copper and  $0.1 \mu\text{g}$  for cobalt. The visual sensitivity was  $0.03 \mu\text{g}$  per spot for nickel and copper and  $0.05 \mu\text{g}$  for cobalt if the initial spot size was small (0.5 cm diameter) and no excessive tailing occurred. The cobalt chelate absorbs strongly in a region of severe background interference from the reagent (Fig. 1) resulting in poorer sensitivity for cobalt; even when samples are

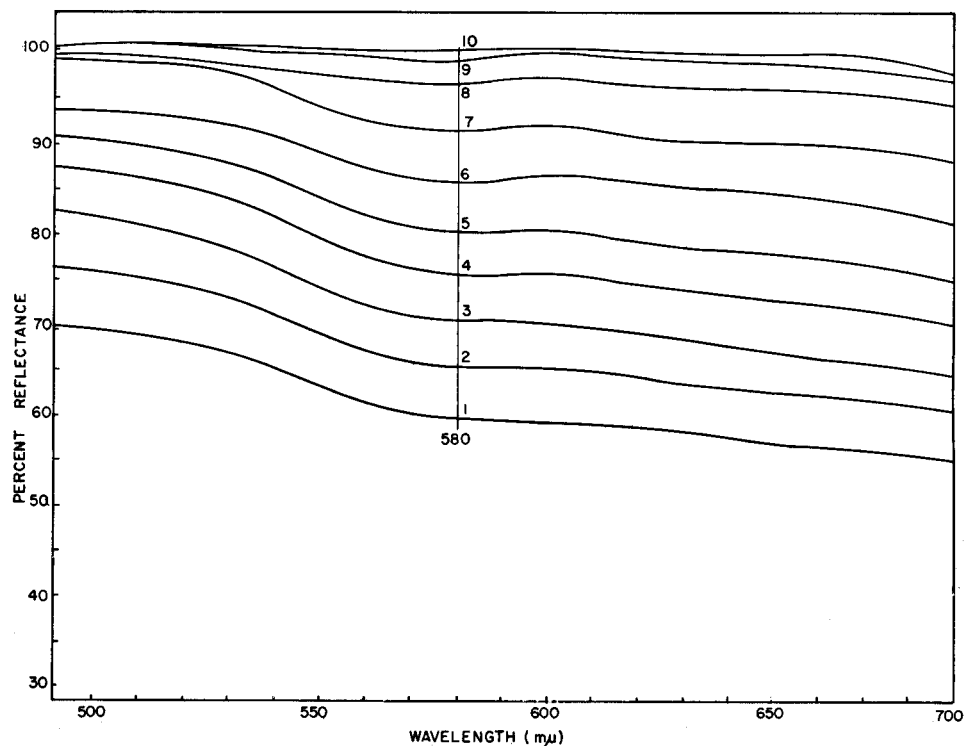


Fig. 5. Reflectance spectra of (1) 20  $\mu\text{g}$ ; (2) 15  $\mu\text{g}$ ; (3) 10  $\mu\text{g}$ ; (4) 6  $\mu\text{g}$ ; (5) 4  $\mu\text{g}$ ; (6) 2  $\mu\text{g}$ ; (7) 1  $\mu\text{g}$ ; (8) 0.2  $\mu\text{g}$ ; (9) 0.05  $\mu\text{g}$ ; (10) 0  $\mu\text{g}$  (base line) copper per sample of rubeanic acid complex adsorbed on Silicagel G.

measured against reagent blank from the same plate, the sensitivity was still limited.

Dilution series of the 3 metals were prepared to determine the optimum working wavelength for a larger concentration range and to study sensitivity, shift of absorption maxima with concentration and concentration-reflectance relationships. Figure 5 shows such a typical series for the copper-rubeanic acid complex. The optimum wavelength is 580 nm; the copper spectra show no distinct absorption peak, particularly at high concentrations, but the low concentration spectra show the suitability of this wavelength. The optimum wavelengths for nickel and copper were 630 nm and 460 nm respectively.

Reflectance-concentration plots gave relatively smooth curves (Fig. 6) over the concentration range 0.05–20  $\mu\text{g}$  per spot but at higher concentrations the curves flattened to such a degree that very poor accuracy was obtained. The useful concentration range could be extended by dilution of the 20-mg samples with neutral adsorbent.

To study the adherence of the systems to the Kubelka-Munk law<sup>20</sup>, the Kubelka-Munk functions  $(1-R)^2/2R$  were plotted against concentration. A linear curve was obtained for up to 10  $\mu\text{g}$  for cobalt and nickel and over the entire concentration range for copper (Fig. 7). Factors causing deviation from Kubelka-Munk's law have been discussed in several papers<sup>14,20-23</sup>.



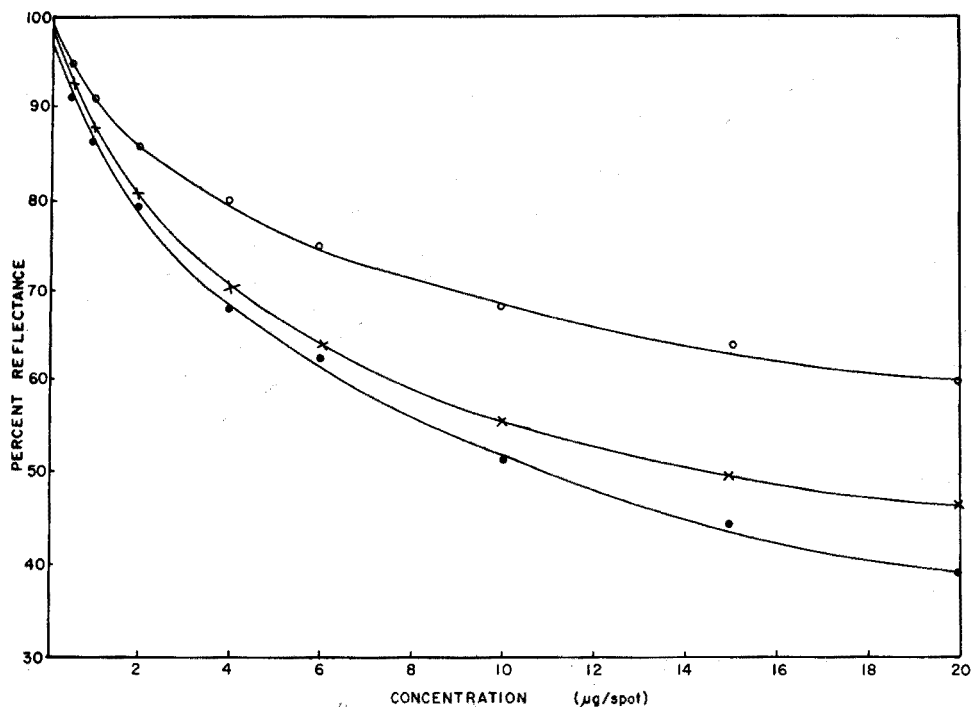


Fig. 6. Calibration plots. Percent reflectance vs. concentration for ●—● nickel, ×—× cobalt, ○—○ copper.

#### *Reproducibility and accuracy*

For quantitative analysis, reproducibility of the reflectance measurements must be determined. Samples were therefore prepared as described earlier in the paper and packed into a semimicro cell<sup>14</sup>. The ideal sample size for greatest sensitivity was determined experimentally to be 20 mg for silica gel and cellulose and 30 mg for alumina; the improvement in sensitivity over the 40-mg sample size used in earlier work<sup>6,7</sup>, for 1 µg of nickel, was nearly 10% R-units. The impinging beam from the light source should fall entirely on the sample; for the Beckman DU the beam was adjusted by focussing the tungsten lamp and checking with a piece of white paper mounted on the reflectance attachment. No adjustment was necessary for the Spectronic 505.

The reproducibility of sample placement was studied by repeatedly mounting the same sample in the reflectance attachment. The standard deviation, for a series of 8 such measurements, was 0.1% R; 40-mg rather than 20-mg samples gave similar results. The instrument error for the Beckman DU has been reported previously<sup>7</sup> to be negligibly small (0.05% R standard deviation at the usual slit widths).

The reproducibility of the method was investigated by chromatographing 12 1.6-µg samples of each metal over a distance of 15 cm; after complexation the spots were removed and prepared for analysis as described above. Standard deviations on silica gel layers, shown in Table IV, are considerably higher than for sample placement and instrument error. As concluded earlier for amino acids and dyes<sup>6-8</sup>, the color development procedure as well as sample homogeneity limits the reproducibility (and

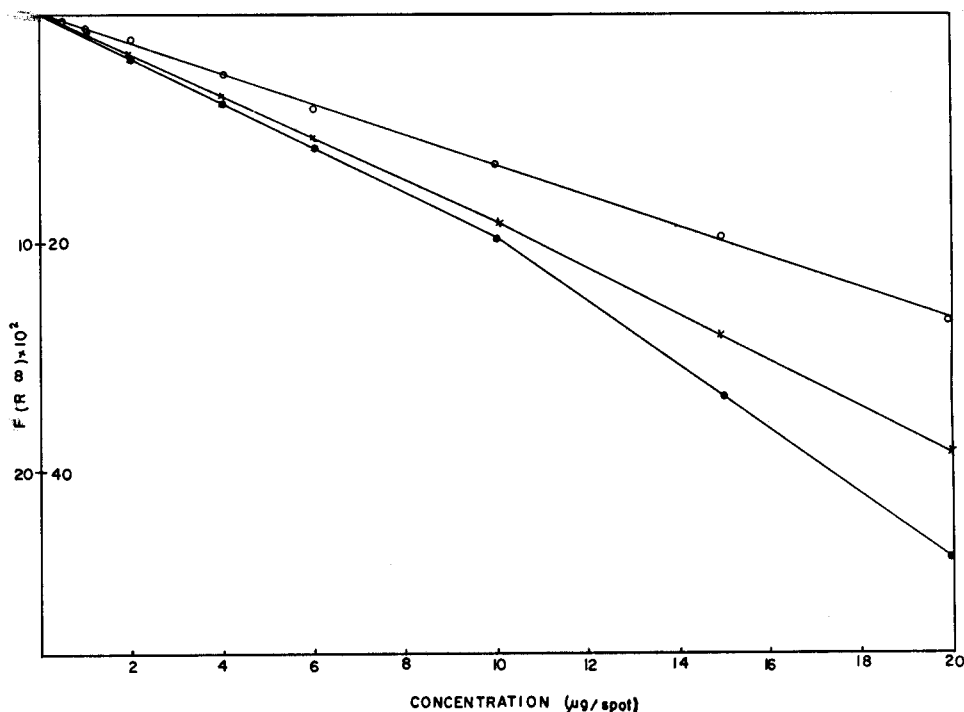


Fig. 7. Kubelka-Munk plots for ●—● nickel, ×—× cobalt, ○—○ copper.

TABLE IV

PROBABLE RELATIVE ERROR IN THE MEASUREMENT OF THE CONCENTRATION OF NICKEL, COBALT AND COPPER SEPARATED ON SILICAGEL G AND DEVELOPED BY THE SPRAYING TECHNIQUE

	<i>Nickel</i>	<i>Cobalt</i>	<i>Copper</i>
Range (% R) <sup>a</sup>	80.0–81.2	78.9–81.5	84.6–85.9
Mean (% R)	80.5	79.4	85.3
Standard deviation (% R)	0.55	0.77	0.65
Equivalent change (μg) in measured concentration	0.07	0.10	0.13
Probable % relative error	4.4	6.2	8.1

<sup>a</sup> For 12 replicate samples of 1.6 μg cation per spot.

therefore the accuracy) of the method. Reagent background interference can account for the poorer reproducibility for cobalt. Weighing and volumetric errors are again considered to be insignificant.

Since the chelates are stable for several weeks, the reproducibility of results obtained by chromatographing and analyzing the cations on different days was studied; the same reagent, chromatoplates, and chromatographic solvent were used for every experiment. Standard deviations were 0.74% R for nickel, 1.37% R for cobalt, and 0.75% R for copper; the reproducibility for nickel and copper is only slightly poorer than for a single trial (Table IV) and can be attributed to atmospheric

and temperature fluctuations, tailing, and other factors difficult to control in chromatographic techniques. The larger drop in reproducibility for cobalt can be attributed to variation in background interference of reagent and to the greater temperature sensitivity of the cobalt chelate (Table III and Fig. 4). Reproducibility on alumina layers was similar to that on silica gel.

It was reported in an earlier paper<sup>6</sup> that the limiting factor for reproducibility was the chromogenic step primarily because of the difficulty in controlling the spraying technique; the method was improved considerably by using a non-spray technique. In the present study, the background is hard to control and, even though it fades considerably on brief heating at 110°, some technique other than spraying would be desirable. For cellulose layers, which are mechanically very stable, dipping rather than spraying gave better control and was more convenient. The plates were dipped into a 0.1% rubeanic solution in ethanol; a 20 × 25 cm photographic tray contained the solution.

Reproducibility data for nickel, cobalt, and copper, chromatographed on cellulose and developed by the dipping technique, are shown in Table V. The improve-

TABLE V

PROBABLE RELATIVE ERROR IN THE MEASUREMENT OF THE CONCENTRATION OF NICKEL, COBALT AND COPPER SEPARATED ON CELLULOSE AND DEVELOPED BY THE DIPPING TECHNIQUE

	<i>Nickel</i>	<i>Cobalt</i>	<i>Copper</i>
Range (% R)*	78.0-79.0	80.1-81.0	84.8-85.6
Mean (% R)	78.4	85.1	85.1
Standard deviation (% R)	0.44	0.43	0.39
Equivalent change in measured concentration ( $\mu\text{g}$ )	0.06	0.06	0.07
Probable % relative error	3.7	3.7	4.4

\* For 12 replicate samples of 1.6  $\mu\text{g}$  cation per spot.

ment in reproducibility is particularly significant for cobalt; data for cellulose layers obtained by the spraying technique were similar to silica gel and alumina results. The reproducibility for cobalt separated on cellulose on different days and treated by the dipping technique (4 trials) was  $\pm 0.70\%$  R average standard deviation; this is a decided improvement on similar trials using the spraying technique (standard deviation 1.37% R). Although the best reproducibility and accuracy are achieved by processing standards and samples simultaneously, a single calibration curve can be used with satisfactory results; this is particularly true for cellulose layers using the dipping technique.

The probable relative error in the measurement of the concentration of nickel, cobalt, and copper was determined from the data reported in Tables IV and V and the calibration curves of Fig. 6. The accuracies for cobalt and copper are lower than for nickel; this was attributed to background interference for cobalt but, for copper, it is because the calibration curve flattens off faster than for cobalt and nickel. Accuracies are largely improved by the dipping technique (Table V), partic-

ularly for cobalt and copper, but the data apply only to a concentration of 1.6  $\mu\text{g}$  per spot; it is to be expected that the accuracy would vary with concentration despite the good reproducibility of reflectance readings. For nickel (Table VI), the accuracy decreases at low concentrations to 20% relative error for 0.1  $\mu\text{g}$  per spot; below 0.5  $\mu\text{g}$  the sensitivity limit is approached (0.05  $\mu\text{g}$  per spot with probable 50% relative error). The best accuracy was observed for 10  $\mu\text{g}$  per spot; the accuracy decreases with a further increase in concentration since the calibration curve flattens off strongly at concentrations greater than 20  $\mu\text{g}$ .

TABLE VI

PROBABLE RELATIVE ERROR IN THE MEASUREMENT OF THE CONCENTRATION OF NICKEL AS A FUNCTION OF CONCENTRATION

	Concentration of Ni ( $\mu\text{g}$ per spot)							
	0.1	0.5	1.0	2.0	4.0	6.0	10	20
Standard deviation	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Equivalent change in measured concentration of nickel ( $\mu\text{g}$ per spot)	0.02	0.04	0.05	0.07	0.10	0.14	0.22	1.0
Probable % error	20	8.0	5.0	3.5	2.5	2.3	2.2	5.0

## CONCLUSIONS

Thin-layer chromatography can be substituted for other chromatographic separation procedures for trace metal analysis and reflectance spectroscopy applied for quantitative analysis of the chromatoplates. Since the rubeanic acid complexes have unique and reproducible spectra, the poor reproducibility of  $R_F$ -values can be offset by visual and reflectance spectroscopic evaluation of the plates; similar results were reported earlier for amino acid mixtures<sup>24</sup>.

Sensitivity, stability, and background interference can be considerably improved by a suitable choice in temperature and pH. The pH and temperature stability data of the rubeanic acid complexes should also prove useful in column and paper chromatography and electrophoresis.

Quantitative evaluation of nickel, cobalt, and copper by reflectance spectroscopy was most successful because the rubeanic acid complexes were stable and the complexation reaction fast and reproducible. The method is suitable for time-saving routine analysis since results are reproducible over a period of several days on the same sample and a calibration curve can be used. The method could undoubtedly be applied to other inorganic systems and chelating agents; it should find wide application for trace metal analysis in geochemistry, food chemistry, oceanography and other fields.

This work was supported by grants from the Defence Research Board and the National Research Council. R.W.F. gratefully acknowledges support provided by Dalhousie University through a Dalhousie Postdoctoral Fellowship.

## SUMMARY

Traces of nickel, cobalt and copper are separated on chromatoplates and, after reaction with rubeanic acid, are determined quantitatively by diffuse reflectance spectroscopy; 0.05  $\mu\text{g}$  of the elements can be determined with a probable percentage error of 2 to 5%. Temperature stability, aging, and pH dependence of the chelates and chelating agents in the adsorbed state were investigated. The method is simple and could find routine application in geochemistry, food analysis, etc.

## RÉSUMÉ

Des traces de nickel, de cobalt et de cuivre ont pu être séparées par chromatographie sur couches minces, à l'aide d'acide rubéanique et dosées quantitativement par spectroscopie par réflexion. On peut doser ainsi 0.05  $\mu\text{g}$  de chacun de ces éléments avec un pourcentage d'erreur de 2 à 5. On examine divers facteurs (température, pH, etc). La méthode est simple et pourrait être utile pour des analyses de routine en géochimie, analyse de denrées alimentaires, etc.

## ZUSAMMENFASSUNG

Spuren Nickel, Kobalt und Kupfer werden auf Chromatographierplatten getrennt und nach Reaktion mit Rubeansäure quantitativ durch diffuse Reflektionspektroskopie bestimmt. 0.05  $\mu\text{g}$  dieser Elemente können mit einem prozentualen Fehler von 2–5% bestimmt werden. Die Temperaturstabilität und die pH-Abhängigkeit der Chelate und chelatbildenden Reagenzien im adsorbierten Zustand wurden untersucht. Die Methode ist einfach und kann für Routineanalysen in der Geochemie, für Nahrungsmittelanalysen usw. angewendet werden.

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## APPLICABILITY OF THE DU PONT 900 DTA APPARATUS IN QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

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Differential thermal analysis (DTA) is a method of obtaining<sup>1,2</sup> information about the transitions and reactions that a substance undergoes on being heated (melting and transition points, phase diagrams, kinetics of reaction, etc.). The substance and an inert material are heated at a constant rate, and the difference in temperature ( $\Delta T$ ) between active and inert material is recorded against the time or against the temperature of the sample or the reference.  $\Delta T$  is constant until the sample undergoes a transition or a chemical reaction, in which case a larger difference in temperature is observed between sample and reference which disappears when the reaction ends (peak) (Fig. 2 shows a typical thermogram). It is evident that the base line and the peak are related to the thermochemical constants of the sample and the reference. If this relationship is known, a method will be available for determining the enthalpy of transition (or reaction), the specific heat and the thermal conductivity of the sample.

Since 1940 several papers have appeared on this subject, but apparently it has not been possible to find a solution which is generally valid. The geometry and the experimental conditions in the different DTA instruments were different. Therefore we applied the equations of the heat transfer to the system heating block-sample-reference of the Du Pont 900 DTA apparatus. Under certain assumptions the solutions obtained give an interpretation of the base line and the peak in terms of the thermochemical constants of the sample and the reference. If these solutions are applied to the thermograms of substances with low thermal conductivity (*e.g.* organic compounds), satisfactory results may be obtained. A possible way to extend the method to substances with high thermal conductivities is proposed.

In view of the application of the method to oils, fats and soap, most of the measurements have been carried out at temperatures between 0° and 120°. Chemical reactions have not been studied.

## THEORY

The assumption that the temperature of the heating block of the DTA apparatus is raised at a constant rate, and is the same in every point of the system heating block-capillary, defines, together with the geometry of the system, the problem.

A simplified diagram of the cell of the Du Pont DTA instrument, is given in Fig. 1\*. The heating block (a) accommodates 2 wells containing the glass capillaries

\* For a detailed description, see ref. 3.

(b) with  $R=0.15$  cm for 'macro' or  $R=0.065$  cm for 'micro' tubes. One of them contains the substances under examination (s), the other one the reference (r). The thermocouples (c) are placed in the centre of the capillaries.

To find a solution, it is necessary to calculate how the temperature,  $T$ , varies with the time,  $t$ , and the coordinate in the 2 capillaries, the most interesting point

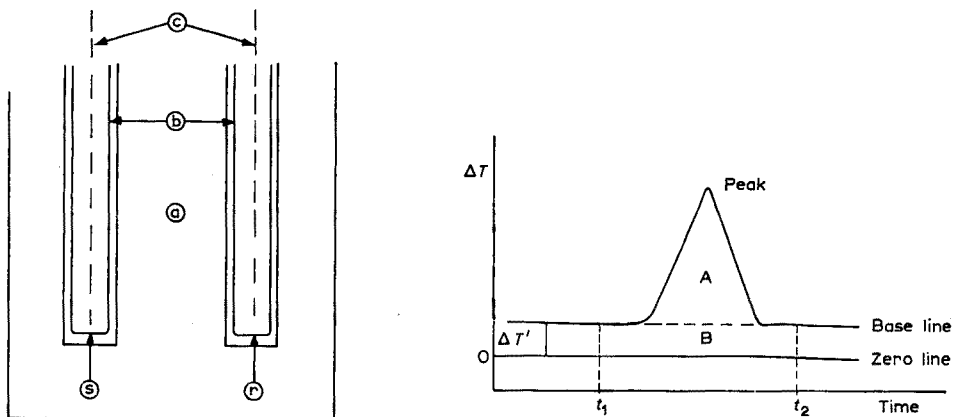


Fig. 1. Diagram of the cell of the Du Pont 900 DTA apparatus; (a) heating block; (b) glass capillaries; (c) thermocouples; (s) sample; (r) reference.

Fig. 2. Thermogram: (A) area used for quantitative DTA, eqn. (10); (A + B) area given in eqn. (8).

being at the thermocouples ( $r=0$ ). Analysis of the base line and the peak of the thermograms (that of Fig. 2, for instance) implies the solution of the differential equation of the heat conduction which, in cylindrical coordinates, for an infinitely long\* cylinder, reads\*\*:

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{1}{\lambda} \dot{Q}(r, t) = \frac{\rho c_p}{\lambda} \frac{\partial T}{\partial t} \quad (1)$$

*Analysis of the base line*  $\dot{Q}(r, t) = 0$

A solution can be found by means of a Laplace Transformation<sup>4</sup>. Such a solution consists of a time-dependent and a coordinate-dependent part. It will be shown that the latter is the most important. Using the boundary conditions:

$$T = T_0 + \alpha t \quad \text{for } t > 0 \text{ and } r = R \quad (2)$$

we obtain

$$T = T_0 + \alpha \left( t - \frac{R^2 - r^2}{4a} \right) + \frac{2\alpha}{Ra} \sum_{n=1}^{\infty} \exp[-\beta_n^2 at] \frac{J_0(\beta_n, r)}{\beta_n^3 J_1(\beta_n, R)} \quad (3)$$

where  $J_0$  and  $J_1$  are Bessel functions and  $\pm \beta_{n=1,2,\dots}$  are the roots of  $J_0(\beta_n, R) = 0$ .

\* The assumption that in a Du Pont instrument the capillaries may be considered infinitely long ( $r \ll z$ ) is discussed at the end of the following section.

\*\* List of symbols, see Table I.

Equation (3) is valid for both the sample and the reference provided that for  $a$  the constant characteristic of the material is introduced.

The temperature difference,  $\Delta T$ , measured at the centre of the cylinders ( $r=0$ ), having equal radii ( $R_{\text{ref}}=R_s=R$ ), is

$$\Delta T = \frac{\alpha R^2}{4} \left( \frac{1}{a_{\text{ref}}} - \frac{1}{a_s} \right) + \frac{\alpha R^2}{3.7} \left[ \frac{1}{a_s} \exp\left(-5.8 \frac{a_s t}{R^2}\right) - \frac{1}{a_{\text{ref}}} \exp\left(-5.8 \frac{a_{\text{ref}} t}{R^2}\right) \right] \quad (4)$$

From eqn. (4) it is seen that for  $t=0$ ,  $\Delta T=0$  and for  $t \rightarrow \infty$ , approximately:

$$\Delta T = \frac{\alpha R^2}{4} \left( \frac{1}{a_{\text{ref}}} - \frac{1}{a_s} \right)^* \quad (5)$$

We must now discuss (i) the relative importance of the transient part of eqn. (4) and (ii) the validity of the condition  $r \ll z$  for the system under consideration.

TABLE I  
LIST OF SYMBOLS

Symbol	Meaning	Dimension
Suffix ref	Reference	—
Suffix s	Sample	—
$T$	Temperature	deg
$T_0$	Ambient temperature	deg
$\Delta T = T_s - T_r$	Temperature difference	deg
$t$	Time	sec
$\alpha = dT/dt$	Heating rate	deg/sec
$R$	Radius of the holder	cm
$r$	Radial coordinate	cm
$z$	Vertical coordinate	cm
$Q$	Transition heat/unit of volume	cal/cm <sup>3</sup>
$Q_w$	Transition heat/unit of weight	cal/g
$c_p$	Specific heat	cal/g deg
$\lambda$	Thermal conductivity	cal/sec cm deg
$\rho$	Density	g/cm <sup>3</sup>
$a = \lambda/\rho c_p$	Thermal diffusivity	cm <sup>2</sup> /sec
$S$	Surface of the peak	deg <sup>2</sup>
$\epsilon$	Porosity	dimensionless

(i) From eqn. (3) it can be seen that if  $t > R^2/a$  an error  $< 1\%$  is made by neglecting the transient part. Thus also in eqn. (4) an error  $< 1\%$  is made by neglecting the transient part if  $t > R^2/a^*$  where  $a^*$  is the lower of the two  $a$  values. Thus for hydrocarbons which are among the substances with a low  $a$  value, we obtain, for macro tubes:  $R^2/a = 2.25 \cdot 10^{-2}/5 \cdot 10^{-4} = 45$  sec. Equation (5) can be used after 45 sec.

(ii) A discussion on this point has been given by ERIKSSON<sup>6</sup>. It appears that a cylinder can be considered to be of infinite length if  $r < 2z$ . In the system considered this condition is always satisfied in the micro tubes. When macro tubes are used, care should be taken to fill the tube to the proper height.

#### Analysis of the peak

A complete solution of the problem can be given if  $Q(r,t)$  is known. This gives

\* This equation can be obtained directly from eqn. (1) when the rate of heating  $\partial T/\partial t$  is taken as a constant. This equation has already been derived by ARENS<sup>5</sup>.



rise to mathematical difficulties, therefore it has been assumed that  $Q$  is only a function of the time<sup>6,7</sup>. This implies that the rate of heat production is the same throughout the sample. Under this restrictive condition  $Q(t)$  may be expanded into series and introduced into eqn. (1).

A better approach consists in deriving a relationship between the area of the peak and the total amount of heat produced (or absorbed), avoiding the introduction of  $Q(r, t)$ . Such a solution is valid under much less restricted conditions<sup>8-11</sup>. For the reference, which is not subject to chemical reaction we write:

$$\frac{1}{a_{\text{ref}}} \frac{\partial T_{\text{ref}}}{\partial t} = \nabla^2 T_{\text{ref}} \quad (6)$$

and for the sample, in which chemical reaction (or transition) occurs:

$$\frac{1}{a_s} \frac{\partial T_s}{\partial t} = \nabla^2 T_s + \frac{1}{\lambda} \dot{Q} \quad (7)$$

Introducing the differential temperature,  $\Delta T$ , and multiplying both sides by  $dt$  and integrating over a time interval large enough to make all the transient terms negligible, we get:

$$\int_{t_1}^{t_2} \left( \frac{1}{a_s} \frac{\partial T_s}{\partial t} - \frac{1}{a_{\text{ref}}} \frac{\partial T_{\text{ref}}}{\partial t} \right) dt = \nabla^2 \int_{t_1}^{t_2} \Delta T dt + \frac{Q}{\lambda} \quad (8)$$

In general, the peak surface measured in quantitative DTA is the area enclosed by the peak line and the base line (see Fig. 2), while the integral of eqn. (8) represents the area enclosed by the peak line and the zero line (defined as the line for which  $\Delta T = 0$ ). Thus from this area the area between the zero line and the base line must be subtracted. The latter is obtained from eqn. (4):

$$\int_{t_1}^{t_2} \Delta T^1 dt = \int_{t_1}^{t_2} \left( \frac{1}{a_s} \frac{\partial T_s}{\partial t} - \frac{1}{a_{\text{ref}}} \frac{\partial T_{\text{ref}}}{\partial t} \right) dt \quad (9)$$

Subtracting eqn. (9) from eqn. (8) and recalling that  $dT_{\text{ref}}/dt = \alpha$  we obtain:

$$\nabla^2 \int_{t_1}^{t_2} (\Delta T - \Delta T^1) dt = \frac{Q}{\lambda} = \nabla^2 \frac{S}{\alpha} \quad (10)$$

where  $S$  is the surface of the peak, expressed in  $\text{deg}^2$ .

In the case of a cylinder of infinite length, with the boundary condition  $\nabla^2 T = 0$  for  $r = R$  (thus  $S = 0$ ), the solution with the thermocouple in the centre is:

$$S = \frac{\alpha R^2}{4} \frac{Q}{\lambda} = \frac{\alpha R^2}{4} \frac{Q_w \rho}{\lambda} \quad (11)$$

Equation (11) may be combined with eqn. (5):

$$S = \left( \frac{\alpha R^2}{4 a_{\text{ref}}} - \Delta T \right) \frac{Q_w}{c_{p(s)}} \quad (12)$$

In eqn. (12) it is of interest that  $\lambda_s$  is absent, so the relation can be used also when  $\lambda_s$  is not known. The radius of the sample holder,  $R$ , and the heating rate,  $\alpha$ , are represented by only one term, so that errors which can be introduced by those

parameters are reduced. Equation (12) may be used to calculate either  $Q_w$  or  $c_p$  if one of them is known.

#### EXPERIMENTAL

The DTA apparatus was used following the instruction manual with one exception: in deriving the eqns. (4) and (11) the rate of heating,  $\alpha$ , was taken to be constant. This is always valid for the references but for the sample only when no transition occurs. Therefore the thermocouples have to be connected with the detector in such a way that  $\Delta T$  is recorded against  $T_{ref}$  and not  $T_s$ . Because  $\alpha$  is not rigorously constant over the whole temperature range, an error is introduced in quantitative DTA (< 2 or 3% at  $\alpha = 0.167$  ( $10^\circ/\text{min}$ )).

If eqn. (4) or eqn. (12) is applied, the curve resulting from a run where sample and reference are equal (glass powder) must be taken as the zero line. The run is made before measurement of the sample. In that way small differences in thermocouples, tube size, and so on, are overcome.

The peak surfaces were measured with a planimeter.  $a_{ref}$  was determined by measuring  $\Delta T$  using solids with high thermal conductivities as sample. In this case  $\Delta T \sim \alpha R^2/4a_{ref}$ , from which  $a_{ref}$  can be calculated. Experiments carried out with lead and ice in macro tubes at  $\alpha = 0.167$  ( $10^\circ/\text{min}$ ) yielded:  $\Delta T = 0.7^\circ$ , corresponding to  $a_{ref} = 1.34 \cdot 10^{-3}$ . In all experiments, therefore, this value was used in eqn. (4).  $\Delta T$  can be measured before or after melting of the sample (provided that the proper values for  $c_p$  are used), but the best results are obtained when  $\Delta T$  is measured *after* the peak, especially in the case of powders. Therefore this method was applied in all experiments.

#### RESULTS

##### Application of eqn. (11)

*Organic substances.* In order to investigate whether eqn. (11) can be applied it

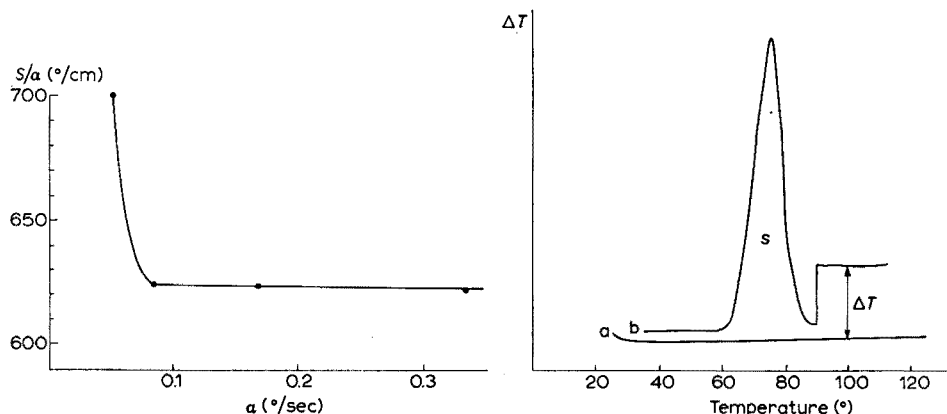


Fig. 3. Peak surface as a function of the heating rate for palmitic acid.

Fig. 4. DTA curves of: (a) glass (sensitivity  $0.5^\circ/\text{inch}$ ); (b) palmitic acid:  $S = 103 \text{ deg}^2$  (sensitivity  $2^\circ/\text{inch}$ ),  $\Delta T = -0.57$  (sensitivity  $0.5^\circ/\text{inch}$ ).

is necessary to determine (i) in what range of heating rates  $S$  and  $\alpha$  are proportional, (ii) the reproducibility of the measurements with different  $R$  values and the influence of the form of the sample (powder or preheated to form a non-porous solid), (iii) the accuracy of the measured heat of transition,  $Q_w$ .

(i) At the heating rates  $\alpha = 0.050, 0.083, 0.167$  and  $0.333$ ,  $S$  was measured for palmitic acid using macro tubes ( $R = 0.15$  cm). The results are shown in Fig. 3. As predicted by eqn. (11),  $S$  and  $\alpha$  are proportional to each other except at  $\alpha = 0.050$ , where  $S$  is larger than expected.  $\alpha = 0.167$  ( $10^\circ/\text{min}$ ) was chosen for all experiments involving quantitative DTA.

(ii) Reproducibility measurements were carried out on the melting of palmitic acid and 1-naphthol. The influence of the size of the capillaries and of the form of the substance (premelted around the thermocouple or powder) was investigated. The reproducibility lies within 10%. When the experiments are carried out under the same conditions (macro capillaries and premelted sample) a coefficient of variation of 5% may be obtained. Somewhat unexpected is the fact that the powdered and the melted substance have the same peak surfaces. A powder has a different thermal conductivity,  $\lambda$ , which should be reflected in  $S$ . An explanation could be that also the density,  $\rho$ , of the substance is changed, and that the decrease of the 2 quantities is roughly proportional in most cases, so that the ratio is not changed. It has been proposed<sup>12</sup> that  $\lambda_{\text{powder}} = (1 - \epsilon)\lambda_{\text{solid}} + \epsilon\lambda_{\text{air}}$ . The density of a powder is  $(1 - \epsilon)\rho_{\text{solid}}$ . Thus the ratio  $\rho_{\text{powder}}/\lambda_{\text{powder}} = (1 - \epsilon)\rho_{\text{solid}}/[(1 - \epsilon)\lambda_{\text{solid}} + \epsilon\lambda_{\text{air}}] \approx \rho_{\text{solid}}/\lambda_{\text{solid}}$  if  $\epsilon\lambda_{\text{air}}$  is low in comparison with  $(1 - \epsilon)\lambda_{\text{solid}}$ .

(iii) For the calculation of the transition heat,  $Q_w$ , eqn. (11) was tested on 5 substances of known characteristics. The data are collected in Table II; each value is the mean of several measurements. The results are satisfactory in 4 out of 5 measurements. The difference between  $Q_{w \text{ calc.}}$  and  $Q_{w \text{ lit.}}$  is within the experimental error and it may be said that  $Q_w$  can be calculated from a DTA measurement if  $\lambda$  is known. The  $Q_w$ -value obtained is, in general, correct to within 6%.

*Inorganic substances.* In several cases the value  $\lambda$  for inorganic substances is higher than that for organic ones. The validity of eqn. (11) was investigated in a range of  $\lambda$  varying from  $4 \cdot 10^{-4}$  (sulfur) to  $8 \cdot 10^{-2}$  (lead). With the technique described previously, at low  $\lambda$  values, as in the case of sulfur, satisfactory results were obtained

TABLE II

MELTING AND TRANSITION HEAT FOR SEVERAL ORGANIC COMPOUNDS CALCULATED FROM THE PEAK SURFACE USING EQN. (11)

Substance	Transition	$T$ ( $^\circ$ )	$4S/\alpha R^2 (\cdot 10^4)$ (deg sec/cm <sup>2</sup> )	$\rho^a$ (g/cm <sup>3</sup> )	$\lambda (\cdot 10^{-4})^a$ (cal/sec cm deg)	$Q_w \text{ calc.}$ (cal/g)	$Q_w \text{ lit.}^a$ (cal/g)	Error (%)
Palmitic acid	Melting	63	10.6	0.85	4.1	51.2	51	0
1-Naphthol	Melting	96	7.9	1.15	5.6	38.5	38.9	- 1
Benzoic acid	Melting	122	9.3	1.2	4.1	31.8	33.9	- 6
Benzene	Melting	5.5	5.95	0.89	4.1	27.4	30.3	- 10
Nitrobenzene	Melting	5.7	6.1	1.19	4.1	21.0	22.5	- 6
Sulfur	Rhombic $\rightarrow$ monoclinic	112	2	2	3.9	3.9	3.3	+ 18
Sulfur	Melting	119	5.8	1.9	3.9	11.9	13.2	- 10

<sup>a</sup> Values from ref. 13-16.

(Table II). As the  $\lambda$  values for the substances increase, the results become more inaccurate. This phenomenon is not unexpected because samples of high  $\lambda$  are enclosed in sample holders of relatively low  $\lambda^{9-11}$ . Under these conditions the boundary condition used to solve eqn. (10) is no longer valid: strictly speaking it could be applied only when using sample holders of infinitely high  $\lambda$ , although it appears from the measurements on organic substances and sulfur that if  $\lambda$  of the sample is lower than  $\lambda$  of the sample holder\*, good results are obtained. In a further investigation of the applicability of eqn. (11), some tentative experiments done without a sample holder gave results which were in good agreement with theory (Table III).

*Conclusion.* The theory cannot be applied to solids with  $\lambda > 10^{-3}$  cal/sec cm deg using the Du Pont 900 DTA apparatus without modification. In principle the experimental difficulties could be solved by using holders with very high thermal conductivity (metal).

TABLE III

MELTING AND TRANSITION HEAT FOR SOME INORGANIC SUBSTANCES AS CALCULATED FROM THE PEAK SURFACE USING EQN. (11)

Substance	Transition	T (°)	$\rho^*$ (g/cm <sup>3</sup> )	$\lambda(\cdot 10^{-4})^a$ (cal/sec cm deg)	$Q_w$ calc. (cal/g)		$Q_w$ lit. <sup>b</sup> (cal/g)	Error (%)	
					With sample holder	Without sample holder		With sample holder	Without sample holder
CaSO <sub>4</sub> ·2 H <sub>2</sub> O	Dehydration	156	2.13	17	224	23	23	+ 875	0
Ice	Melting	0	0.9	23 <sup>b</sup>	750	84	80	+ 940	+ 5
Lead	Melting	327	11.3	800	293	5.05	5.47	+5250	-8

\* Values from ref. 13-16.

<sup>b</sup>  $\lambda$  of melting ice from ref. 14.

TABLE IV

SPECIFIC HEAT OF MOLTEN SUBSTANCES AS CALCULATED FROM THE BASE LINE AND THE PEAK SURFACE USING EQN. (12) ( $\alpha R^2/4 a_{ref} = 0.7$ )

Substance	S (deg <sup>2</sup> )	$Q_w$ lit. <sup>b</sup> (cal/g)	$\Delta T$ (°)	$\Delta T$ measured at T (°)	$c_p$ calc. (cal/g deg)	$c_p$ lit. <sup>b</sup> (cal/g deg)	Error (%)
Palmitic acid	103	51	-0.57	100	0.63	0.65	-3
1-Naphthol	78	38.9	-0.22	120	0.47	0.48	-2
Benzoic acid	82	33.9	-0.54	140	0.51	0.53	-3.5
Benzene	58.5	30.3	-0.08	25	0.40	0.41	-2.5
Nitrobenzene	57	22.5	-0.16	30	0.34	0.34	0
Sulfur	57	13.2	-0.48	145	0.27	0.25	+7.5

\* Values from ref. 13-16.

#### Application of eqn. (12)

The most interesting application of eqn. (12) may be the calculation of  $Q_w$  if  $c_p$  is known or of  $c_p$  if  $Q_w$  is known. In Fig. 4 an example is given for palmitic acid. The zero line (a) has been recorded using glass both as sample and reference at a sensitivity

\* Depending on the chemical composition  $\lambda_{glass} = 1-2.5 \cdot 10^{-3}$  cal/sec cm deg.

of  $0.5^\circ/\text{inch}$ . In the same tube palmitic acid was melted and cooled after which line b was obtained using a sensitivity of  $2^\circ/\text{inch}$  to keep the peak on the paper. After melting,  $\Delta T$  was measured, again at a sensitivity of  $0.5^\circ/\text{inch}$ . For  $Q_w = 51 \text{ cal/g}$  we found  $c_p = 51(0.7 + 0.57)/103 = 0.63$  (lit.<sup>13-16</sup>  $0.65 \text{ cal/g deg}$ ). The results for the other substances given in Table IV also show good agreement with the literature values.

#### CONCLUSIONS

On applying quantitative DTA to substances with not too high a thermal conductivity (*e.g.* organic substances) enthalpies may be obtained with an accuracy of 5–10%. Another method in which the knowledge of the thermal conductivity is not required seems to be of wider application than the preceding one. However, this method also is limited to solids with a low thermal conductivity. At high thermal conductivities the enthalpies obtained are too high due to disturbance by the sample holder. However, a minor modification of the instrument used could possibly solve this difficulty.

Even when the DTA apparatus is used *only* for qualitative DTA (to measure transition and melting points, etc.) such an analysis seems to be of interest for a better understanding of the features of the thermograms obtained.

The author is indebted to Miss M. P. C. HAANAPPEL who carried out all the measurements.

#### SUMMARY

Some problems of quantitative differential thermal analysis have been studied by means of a Du Pont 900 DTA instrument. Applying the equation of heat transfer the features of a thermogram (base line and peak surface) may be interpreted in terms of heat of transition, specific heat and thermal conductivity. Satisfactory results are obtained for substances with thermal conductivities lower than  $10^{-3} \text{ cal/sec deg}$ .

#### RÉSUMÉ

L'auteur a examiné quelques problèmes d'analyse thermique différentielle à l'aide d'un appareil Du Pont 900 DTA. Le thermogramme peut être interprété en chaleur de transition, chaleur spécifique et conductivité thermique. On a obtenu des résultats satisfaisants pour des substances ayant une conductivité thermique inférieure à  $10^{-3} \text{ cal/sec deg}$ .

#### ZUSAMMENFASSUNG

Mit der Apparatur 900 DTA von Du Pont wurden einige Probleme der quantitativen Differentialthermoanalyse untersucht. Unter Anwendung der Gleichung für den Wärmeübergang konnten die Formen der Thermogramme in Abhängigkeit vom Wärmeübergang, der spezifischen Wärme und der thermischen Leitfähigkeit interpretiert werden. Befriedigende Ergebnisse wurden für Substanzen mit thermischen Leitfähigkeiten  $< 10^{-3} \text{ cal sec}^{-1} \text{ gr}^{-1}$  erhalten.

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## THE DETERMINATION OF LANTHANUM, CERIUM AND THORIUM WITHOUT SEPARATIONS

## THE DETERMINATION OF LANTHANUM AND CERIUM IN THORIUM

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The determination of microgram quantities of lanthanum and cerium in thorium where the sample available usually does not exceed 25 mg has been a problem in this laboratory. A common approach to this analysis is to employ emission spectroscopy<sup>1-4</sup>. These methods are sensitive and good but even here the problem of the analysis of standards to be used in the calibration of the spectrographic methods remains. A chemical method would be of value.

The absorption peak at 253 nm of cerium(III) is well known. STEWART AND KATO<sup>5</sup> have reported a molar extinction coefficient of  $7.55 \cdot 10^2$  for this species in 0.1 M hydrochloric acid solution. Because thorium and lanthanum show little or no absorbance in this region the determination of microgram quantities of cerium in the presence of these elements should be feasible.

Thorin [disodium salt of 2-(2-hydroxy-3,6-disulpho-1-naphthylazo)benzenearsonic acid] is probably the most widely used reagent for the spectrophotometric determination of thorium. Most applications involve some modification of the procedure recommended by THOMASON *et al.*<sup>6</sup>. It has been demonstrated that several hundred micrograms of lanthanum and cerium do not interfere with the determination of microgram quantities of thorium<sup>7</sup>.

Arsenazo [2-(1,8-dihydroxy-3,6-disulpho-2-naphthylazo)benzenearsonic acid] has been used as a group reagent for rare earths<sup>8,9</sup> as well as for thorium<sup>10,11</sup>. A mixture of the arsenazo complexes of lanthanum, cerium and thorium should produce an absorbance which is the sum of the absorbances of the individual complexes. If the amounts of cerium and thorium have been determined beforehand it should be possible to estimate the quantity of lanthanum if proper calibration curves for all 3 elements with arsenazo are available.

## EXPERIMENTAL

*Apparatus and reagents*

Photometric measurements were made with a Beckman Model DU spectrophotometer using optically matched 1.00-cm Corex cells in the visible region and 5.00-cm quartz cells for the determination of cerium in the ultraviolet region. Extrac-

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tions were made with the aid of a shaking apparatus (Virtis Co.) in glass extraction tubes, 44 cm long and 2.7 cm in diameter.

Solutions of cerium(III) and lanthanum(III) in 0.1 *M* hydrochloric acid solution were prepared from the pure rare earth oxides (Lindsay Chemical Co.). A similar solution of thorium was prepared from pure thorium nitrate (Baker Analyzed) by precipitation of thorium hydroxide with ammonium hydroxide solution and the subsequent dissolution of the hydroxide in hydrochloric acid solution.

Triethanolamine buffer solutions were prepared from 10 parts of aqueous 15% triethanolamine solution and 7 parts of 1 *M* nitric acid solution, adjusted to pH 7.2 with nitric acid or ammonium hydroxide.

#### *Examination of the arsenazo method for the rare earths and thorium*

Preliminary experiments revealed that although each of the elements gave a stable colour with arsenazo as well as straight-line calibration curves, the total measured absorbance of a mixture of the 3 elements was always somewhat less than that calculated from the sum of the individual absorbances of the components. The discrepancy could be minimized by increasing the quantity of arsenazo (Table I) and it was found that 6.0 ml of a 0.1% solution of the reagent yielded satisfactory results.

TABLE I  
THE EFFECT OF ARSENAZO CONCENTRATION  
(40  $\mu\text{g}$  La, 47  $\mu\text{g}$  Ce, 45  $\mu\text{g}$  Th)

0.1% arsenazo added (ml)	Absorbance					$\frac{A_{\text{La,Ce,Th}}}{A_{\text{La}} + A_{\text{Ce}} + A_{\text{Th}}}$
	$A_{\text{La}}$	$A_{\text{Ce}}$	$A_{\text{Th}}$	$A_{\text{La,Ce,Th}}$	$A_{\text{La}} + A_{\text{Ce}} + A_{\text{Th}}$	
2.0	0.304	0.251	0.281	0.799	0.836	0.956
3.0	0.307	0.254	0.290	0.821	0.851	0.965
5.0	0.318	0.255	0.300	0.854	0.873	0.978
6.0	0.305	0.260	0.290	0.841	0.855	0.984
7.0	0.310	0.271	0.290	0.849	0.871	0.975

For convenience in future measurements this was changed to 5.0 ml of a 0.12% solution.

The pH of the final solution was 7.2 and photometric measurements were made at 570 nm against reagent blanks.

#### *The determination of lanthanum, cerium and thorium without separations*

A series of solutions containing various quantities of lanthanum, cerium and thorium was examined according to the following procedure. The solution was made up to volume in a 25-ml volumetric flask with 0.1 *M* hydrochloric acid solution. A portion of this solution was then transferred to a 5.00-cm quartz cell and the absorbance of the cerium(III) was measured against a 0.1 *M* hydrochloric acid solution blank at 253 nm. The solution was returned to the volumetric flask (without rinsing) and an appropriate aliquot transferred to a second 25-ml volumetric flask. To this solution were added 1.5 ml of 6 *M* hydrochloric acid solution and 2.0 ml of 0.1% thorian solution. The solution was diluted to volume and the absorbance of the



thorium-thorin complex measured in 1.00-cm cells against a reagent blank at 545 nm. Another aliquot was transferred to a 50-ml beaker to which were also added 5.0 ml of 0.12% arsenazo solution and 5 ml of triethanolamine buffer solution and the pH adjusted to 7.2. The solution was transferred to a 25-ml volumetric flask and diluted to volume with water. The absorbance of the arsenazo complexes was measured at 570 nm in 1.00-cm cells against a reagent blank.

The concentrations of cerium and thorium were calculated directly from their respective calibration curves. It should be noted that milligram amounts of thorium do produce an absorbance at 253 nm. For example  $A_{253\text{ nm}}^{\text{Th}} = 0.012$  for 14.9 mg of thorium and the absorbance is linear with the concentration of thorium. Thus a correction must be made to the cerium value when more than 0.5 mg of thorium is present in the solution. The concentration of the lanthanum was calculated from the absorbance of the arsenazo solution after correction for the absorbances due to the concentration of cerium and thorium determined earlier. The results are shown in Table II.

TABLE II

DETERMINATION OF LANTHANUM, CERIUM AND THORIUM WITHOUT SEPARATIONS

(Amounts in  $\mu\text{g}$ )

<i>La</i>		<i>Ce</i>		<i>Th</i>	
<i>Taken</i>	<i>Found</i>	<i>Taken</i>	<i>Found</i>	<i>Taken</i>	<i>Found</i>
0	8	125	125	2250	2260
25	25	40	40	25	25
25	36	200	192	25	23
25	21	200	194	25	24
40	43	40	40	300	287
50	50	50	48	275	274
50	52	150	147	150	123
50	52	250	240	50	51
125	155	0	5	2250	2270
125	55	0	2	2250	2250
125	133	125	124	125	126
125	128	125	132	2250	2260
125	190	2250	2220	125	123
125	175	2250	2220	125	119
150	151	50	48	150	150
150	150	150	146	50	53
275	278	50	51	50	53
300	303	40	40	39	39
2250	2300	125	125	125	119
2250	2260	125	145	125	104

It is apparent from Table II that the method yields satisfactory results except when milligram quantities of one of the elements are present. As might be expected the most serious errors are in the determination of lanthanum. This number, being dependent upon both the thorium and cerium values, is prone to the cumulative errors of all 3 determinations.

*The determination of lanthanum and cerium in thorium*

It was obvious from the above results that in order to determine microgram

quantities of cerium and lanthanum in a 10–25 mg sample of thorium, a separation of the rare earths from the thorium is mandatory. The separation of thorium from rare earth by extraction with thenoyltrifluoroacetone (TTA)<sup>2,12–15</sup> is in wide use and was felt to be the best approach to this problem. Although the literature cited above pertains only to the extraction of microgram quantities of thorium it was found that milligram amounts are also readily extracted. For example, the percent extractions of thorium from a 12-mg sample in 20 ml of solution with 40 ml of TTA solution were 98.9% and 99.9% at pH 1.0 and pH 2.0 respectively.

Also, the quantitative separation of the thorium from the rare earths is not necessary as the traces of thorium left in the solution after the extraction must be determined. For, even at 99.9% efficiency, 12  $\mu\text{g}$  of thorium would be left from a 12-mg sample, which would, of course, be measured as lanthanum unless compensation were made.

A series of solutions containing 10–25 mg of thorium along with microgram amounts of the 2 rare earths was examined by a procedure identical to that described above except that after the measurement of the absorbance of the solution at 253 nm in order to determine the cerium content, 20.0 ml of the solution (pH = 1) were transferred to an extraction tube. Aqueous 1% hydrazine dihydrochloride solution (1 ml) was added to ensure the presence of cerium(III), and then 40 ml of TTA solution in xylene. The mixture was shaken for 15 min and the aqueous solution transferred to a 50-ml beaker. The solution was evaporated just to dryness, 1 ml of 70% perchloric acid and 1 ml of concentrated nitric acid were added dropwise and the solution was evaporated again to dryness in order to destroy any organic residues. The sides of the beaker were washed with a minimum of water and the evaporation repeated. The evaporations were carried out at a relatively low temperature (120°) and care was taken not to bake the residue lest erratic results be obtained.

The residue was dissolved in hydrochloric acid solution and the thorium and

TABLE III  
DETERMINATION OF LANTHANUM AND CERIUM IN THORIUM

<i>Th</i>		<i>La</i>		<i>Ce</i>	
<i>Taken</i> (mg)	<i>Found</i> <sup>a</sup> ( $\mu\text{g}$ )	<i>Taken</i> ( $\mu\text{g}$ )	<i>Found</i> ( $\mu\text{g}$ )	<i>Taken</i> ( $\mu\text{g}$ )	<i>Found</i> ( $\mu\text{g}$ )
9.9	224	30	30	30	30
9.9	91	30	29	30	30
9.9	96	30	31	60	60
9.9	105	30	32	90	90
9.9	86	60	60	30	30
9.9	126	60	60	60	60
9.9	89	90	87	30	30
11.9	143	40	42	40	40
11.9	106	40	41	150	148
11.9	74	100	101	100	98
11.9	81	150	150	40	40
24.8	243	40	46	80	78
24.8	213	60	66	60	62
24.8	244	80	80	40	39

<sup>a</sup> Found in aqueous solution after one extraction with TTA at pH 1.0.

lanthanum contents determined as described earlier. The results are shown in Table III and appear to be satisfactory although there is an indication of high lanthanum values when a 25-mg sample of thorium was used.

*The interference of iron and its elimination*

As the majority of samples to be analysed were contaminated with microgram quantities of iron, a procedure was necessary to eliminate the interferences caused by this element. The interferences are two-fold. Iron(III) has an absorption spectrum in the ultraviolet region which hinders the cerium determination and iron reacts with arsenazo disturbing the estimation of lanthanum.

The former interference can be eliminated simply by reducing the iron to iron(II). Two reducing agents, hydrazine hydrochloride and hydroxylamine hydrochloride, were tried but only the latter proved to be successful for the purpose. Table IV shows the results of experiments where solutions containing cerium and iron in 0.02 *M* hydrochloric acid were boiled for 30 min with various amounts of the reductants before the determination of the cerium.

TABLE IV

THE EFFECT OF HYDRAZINE AND HYDROXYLAMINE AS REDUCING AGENTS FOR IRON(III)

Reducing agent (ml)		Taken				Found Ce(μg)
		Fe(μg)	Th(mg)	La(μg)	Ce(μg)	
Hydrazine (5%)	0.2	50			40	1400
	0.5	50			40	1390
	1.0	50			40	1390
	2.0	50			40	1380
Hydroxylamine (10%)	0.5	50			40	65
	1.0	50			40	57
	2.0	20	9.9	90	90	93
	2.0	25	9.9	50	125	124
	2.0	25	9.9	125	50	51
	2.0	200	14.9	60	190	192
	2.0	200	14.9	130	120	121
	2.0	200	14.9	190	60	60

The interference with the arsenazo complexes, however, necessitates the removal of iron from the system. Following the TTA extraction data given by STEVENSON AND NERVIK<sup>16</sup>, an attempt was made to extract the iron along with the thorium at pH 2.0 after ensuring the oxidation of the iron to iron(III) with bromine water. This was not successful.

An extraction procedure for iron with bathophenanthroline based on the method of SMITH *et al.*<sup>17</sup> was evolved. After extraction of the thorium and destruction of organic material with nitric and perchloric acids, the residue was dissolved in 40 ml of 0.1 *M* hydrochloric acid solution and the iron reduced by boiling the solution with 2 ml of 10% hydroxylamine solution. Aqueous 10% sodium acetate solution (4 ml) was added and the pH adjusted to 4.0. The solution was transferred to a separatory funnel and the iron extracted with isoamyl alcohol after addition of bathophenanthroline in 95% ethanol. The aqueous phase was transferred to a beaker, the organic phase

washed with a few ml of water and the combined aqueous solutions extracted once more.

The efficacy of the extraction procedure is shown in Table V.

Iron extractions were also made using the procedure of ONISHI AND BANKS<sup>18</sup> where 8-quinolinol in chloroform is the extractant. The results (Table VI) are comparable to those obtained above. A double extraction is required here also.

TABLE V

DETERMINATION OF LANTHANUM AND CERIUM IN THORIUM AFTER THE DOUBLE EXTRACTION OF IRON WITH BATHOPHENANTHROLINE

(200  $\mu\text{g}$  Fe)

<i>Th</i>		<i>La</i>		<i>Ce</i>	
<i>Taken</i> (mg)	<i>Found</i> <sup>a</sup> ( $\mu\text{g}$ )	<i>Taken</i> ( $\mu\text{g}$ )	<i>Found</i> ( $\mu\text{g}$ )	<i>Taken</i> ( $\mu\text{g}$ )	<i>Found</i> ( $\mu\text{g}$ )
9.9	9	60	63	190	189
9.9	12	130	129	120	121
9.9	8	190	200	60	60
14.9	11	50	51	50	54
14.9	11	50	51	50	53
14.9	2	50	52	200	200
14.9	7	50	51	200	195
14.9	11	70	71	190	187
14.9	8	200	208	50	55
14.9	2	200	186	50	52
14.9	8	200	199	70	75

<sup>a</sup> Found in aqueous solution after one extraction with TTA at pH 2.0.

TABLE VI

DETERMINATION OF LANTHANUM AND CERIUM IN THORIUM AFTER THE DOUBLE EXTRACTION OF IRON WITH 8-QUINOLINOL

(200  $\mu\text{g}$  Fe, 14.9 mg Th)

<i>La</i>		<i>Ce</i>	
<i>Taken</i> ( $\mu\text{g}$ )	<i>Found</i> ( $\mu\text{g}$ )	<i>Taken</i> ( $\mu\text{g}$ )	<i>Found</i> ( $\mu\text{g}$ )
50	51	200	193
60	51	190	188
120	119	110	113
130	132	120	119
130	123	120	121
190	194	60	58
200	202	50	50

#### *Recommended procedure*

*Determination of cerium.* To a 0.02 *M* hydrochloric acid solution of the sample containing up to 15 mg of thorium and several hundred  $\mu\text{g}$  of lanthanum, cerium and iron add 2 ml of 10% hydroxylamine hydrochloride solution and boil for about 30 min. After cooling, transfer to a 25-ml volumetric flask and dilute to volume with water. Measure the absorbance of the solution at 253 nm in 5.00-cm quartz cells against a

reagent blank. If more than 0.5 mg thorium is present in the sample correct for the small absorbance due to the thorium. Calculate the cerium from a previously prepared calibration curve.

*Thorium extraction.* Return the sample from the absorbance cell to the volumetric flask without rinsing and transfer a 20-ml aliquot of the solution to a 50-ml beaker. Adjust the pH to 2.0 with ammonium hydroxide solution and transfer to an extraction tube, washing the beaker with a minimum of 0.01 *M* hydrochloric acid solution. Add 40 ml of 0.5 *M* TTA solution in xylene and extract for 15 min. Drain the aqueous phase into the original beaker and evaporate just to dryness. Add 1 ml of 70% perchloric acid solution and 1 ml of concentrated nitric acid solution dropwise. Evaporate carefully to dryness. Wash the beaker walls with a minimum of water and evaporate again. During the evaporations care must be taken not to bake the residue.

*Iron extraction.* Dissolve the residue in several drops of 6 *M* hydrochloric acid solution and dilute to about 40 ml with water. Add 2 ml of 10% hydroxylamine solution and boil the solution for about 30 min. After cooling, add 4 ml of 10% sodium acetate solution and adjust the pH to 4.0. Transfer the solution to a separatory funnel. Add 4.0 ml of  $2 \cdot 10^{-3}$  *M* bathophenanthroline in 95% ethanol, plus 10 ml of isoamyl alcohol and extract for 1 min. After the layers separate, drain the aqueous solution into the original beaker and wash the organic solution with a few ml of water. Repeat the complete extraction procedure on the combined aqueous solutions.

Evaporate the iron-free solution to dryness. Add 1 ml of concentrated hydrochloric acid solution and 1 ml of concentrated nitric acid solution and evaporate again. Wash the beaker walls with water and take to dryness a third time. Dissolve the residue in 2 ml of 0.1 *M* nitric acid solution. Transfer the solution to a 25-ml volumetric flask and dilute to volume with water.

*Determination of thorium.* Transfer a 10-ml aliquot of the solution to a 25-ml volumetric flask. Add 1.5 ml of 6 *M* hydrochloric acid solution plus 2.0 ml of aqueous 0.1% thorian reagent and dilute to volume. Measure the absorbance of the solution at 545 nm in a 1.00-cm cell against a reagent blank. Calculate the thorium content from a previously prepared calibration curve.

*Determination of lanthanum.* Transfer a second 10-ml aliquot of the solution to a 50-ml beaker. Add 5.0 ml of aqueous 0.12% arsenazo reagent followed by 5 ml of triethanolamine buffer solution and 1 ml of 0.5% ascorbic acid solution. Adjust the pH to 7.2. Transfer the solution to a 25-ml volumetric flask and dilute to volume with water. Measure the absorbance at 570 nm in a 1.00-cm cell against a reagent blank.

From previously prepared calibration curves for cerium and thorium with arsenazo, and the above-determined values for these metals, calculate the absorbance due to the combined cerium and thorium arsenazo complexes. Subtract their value from the measured absorbance to obtain the absorbance of the lanthanum complex. Estimate the quantity of lanthanum from a lanthanum-arsenazo calibration curve.

#### SUMMARY

A method is proposed for the spectrophotometric determination of small quantities of lanthanum, cerium and thorium in the presence of one another without separations. Cerium is estimated from its absorption peak in the ultraviolet region, thorium with thorian, and the 3 elements together with arsenazo. The lanthanum is

calculated after subtraction of the combined absorbances of the arsenazo complexes of the thorium and cerium. The procedure can be readily applied to the determination of microgram amounts of the 2 rare earths in thorium. In this case the majority of the thorium is removed from the solution by solvent extraction with TTA before the estimation of the rare earths. The interference of iron is considered and proposals made for its removal.

#### RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique de faibles quantités de lanthane, cérium et thorium, en présence l'un de l'autre, sans séparation. On dose le cérium dans l'ultra-violet en mesurant son pic d'absorption, le thorium à l'aide de thorian et les trois éléments ensemble au moyen d'arsénazo. Le lanthane est calculé après soustraction des absorptions combinées des complexes arsénazo du thorium et du cérium. On examine également l'influence du fer.

#### ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, mit der nebeneinander ohne Trennungen spektralphotometrisch kleine Mengen von Lanthan, Cer und Thorium bestimmt werden können. Cer wird mit Hilfe seines Absorptionmaximums im Ultravioletten bestimmt, Thorium mit Thorian und alle drei Elemente zusammen mit Arsenazo. Lanthan wird nach Subtraktion der zusammengefassten Absorptionen der Arsenazo-Komplexe von Thorium und Cer berechnet. Das Verfahren eignet sich zur schnellen Bestimmung von Mikrogrammen der 2 Seltenen Erden in Thorium. In diesem Falle wird der Hauptanteil des Thoriums vor der Bestimmung der Seltenen Erden durch Extraktion mit TTA entfernt. Die Störung durch das Eisen wird berücksichtigt und Vorschläge zu seiner Beseitigung gemacht.

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## SOLVENT EXTRACTION OF METAL IONS WITH MIXED LIGANDS

## PART VII. EXTRACTION AND SEPARATION OF CALCIUM AND STRONTIUM WITH TTA AND TBP IN CARBON TETRACHLORIDE

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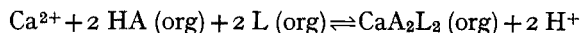
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The analytical chemist who wishes to choose a suitable system for the solvent extraction of calcium and strontium is usually referred to the 8-hydroxyquinoline method<sup>1,2</sup>. This tradition seems to originate from a study by DYRSSEN<sup>3</sup> of the solvent extraction of strontium oxinate with chloroform, followed by a study by UMLAND AND MECKENSTOCK<sup>4</sup> of the extraction of calcium oxinate with butylamine in chloroform.

In the present paper, a study of the extraction of the thenoyltrifluoroacetone (TTA=HA) chelates of calcium and strontium is described, in the hope that a better understanding of these systems will lead to a wider use of this reagent in the extraction and separation of calcium and strontium. As carbon tetrachloride generally gives both rapid and satisfactory phase separation, this solvent was chosen for the investigation. Trioctylphosphine oxide (TOPO), tributylphosphate (TBP), and methyl isobutyl ketone (hexone) were chosen as adduct-forming ligands (L).

Previous investigations<sup>5-10</sup> of the extraction of calcium and strontium with TTA have overlooked the formation of A<sup>-</sup> in the aqueous phase at pH > 6.5, and the possibility of adding effective donors to enhance the distribution. It has been shown by HEALY<sup>11</sup> that the addition of trioctylphosphine oxide (TOPO) and tributylphosphate (TBP) enhances considerably the extraction of calcium(II) with TTA. HEALY, however, only studied the following equilibrium:



It will be shown below that this equilibrium applies only to a limited concentration range of L and A<sup>-</sup> (or  $[\text{HA}]_{\text{org}}[\text{H}^+]^{-1}$ ). It is also shown that those solvents with CO groups which have been suggested<sup>6-8</sup> as being suitable for the extraction of calcium and strontium TTA chelates are rather weak donors.

*Definition of symbols and equilibrium constants*

HA = TTA.

L = TOPO, TBP or hexone (neutral adduct-forming ligand).

org = carbon tetrachloride.

 $C_L$  = initial concentration of TOPO, TBP, or hexone in the organic phase. $C_{\text{org}}$  = initial concentration of HA in the organic phase ( $C_{\text{org}} = 0.1 \text{ M}$ ). $C_{\text{OH}}$  = initial concentration of OH<sup>-</sup> in the aqueous phase.

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$$\begin{aligned}
[\text{H}^+] &= \text{concentration of H}^+ \text{ in } 0.1 M (\text{H, Na})\text{ClO}_4. \\
D &= \text{net distribution ratio of } \text{M}^{2+} \text{ (org/aq).} \\
K_d &= [\text{HA}]_{\text{org}}[\text{HA}]^{-1}. \\
K_a &= [\text{H}^+][\text{A}^-][\text{HA}]^{-1}. \\
K_a K_d^{-1} &= [\text{H}^+][\text{A}^-][\text{HA}]_{\text{org}}^{-1}. \\
\alpha_n &= [\text{MA}_n][\text{M}^{2+}]^{-1}[\text{A}^-]^{-n}. \\
K_{\text{ex}} &= [\text{MA}_2]_{\text{org}}[\text{H}^+]^2[\text{M}^{2+}]^{-1}[\text{HA}]_{\text{org}}^{-2}. \\
K &= [\text{MA}_2]_{\text{org}}[\text{M}^{2+}]^{-1}[\text{A}^-]^{-2} = K_{\text{ex}}K_d^2K_a^{-2}. \\
\beta_n &= [\text{MA}_2\text{L}_n]_{\text{org}}[\text{MA}_2]_{\text{org}}^{-1}[\text{L}]_{\text{org}}^{-n}.
\end{aligned}$$

## EQUATIONS FOR THE DISTRIBUTION RATIO

In order to simplify the expressions for  $D$ , some assumptions, which are partly based on our previous experience with TTA, are introduced. The tendency for HA to form adducts with  $\text{MA}_2$  is low at  $C_{\text{org}} \leq 0.1 M$  (this is not the case with oxine<sup>3</sup> or  $\beta$ -isopropyltropolone<sup>12,13</sup>), and no more than 2 L can be added to  $\text{MA}_2$ . From comparison with ligands such as acetylacetone<sup>14</sup>, kojic acid<sup>14</sup>, oxine<sup>14</sup> and  $\beta$ -isopropyltropolone<sup>15</sup>, it seems likely that  $\alpha_1 \approx 100$  and  $\alpha_2 \approx 1000$  for the complex formation between calcium(II) or strontium(II) and  $\text{A}^-$ . Thus the formation of  $\text{MA}^+$  and  $\text{MA}_2$  in the aqueous phase cannot be neglected when  $[\text{A}^-]$  exceeds  $10^{-3}$ . The expression for  $D$  is then

$$D = \frac{[\text{MA}_2]_{\text{org}} + [\text{MA}_2\text{L}]_{\text{org}} + [\text{MA}_2\text{L}_2]_{\text{org}}}{[\text{M}^{2+}] + [\text{MA}^+] + [\text{MA}_2]} \quad (1)$$

or

$$D = \frac{K[\text{A}^-]^2 (1 + \beta_1[\text{L}]_{\text{org}} + \beta_2[\text{L}]_{\text{org}})}{1 + \alpha_1[\text{A}^-] + \alpha_2[\text{A}^-]^2} \quad (2)$$

If  $[\text{L}]_{\text{org}} = 0$ , then

$$D_0 = \frac{K[\text{A}^-]^2}{1 + \alpha_1[\text{A}^-] + \alpha_2[\text{A}^-]^2} \quad (3)$$

and at low  $[\text{A}^-]$

$$D = K[\text{A}^-]^2 (1 + \beta_1[\text{L}]_{\text{org}} + \beta_2[\text{L}]_{\text{org}}^2) \quad (4)$$

and

$$D_0 = K[\text{A}^-]^2 \quad (5)$$

At constant  $[\text{A}^-]$ , *i.e.* constant  $[\text{HA}]_{\text{org}}[\text{H}^+]^{-1}$ ,

$$DD_0^{-1} = 1 + \beta_1[\text{L}]_{\text{org}} + \beta_2[\text{L}]_{\text{org}}^2 \quad (6)$$

If the distribution data are plotted as  $\log DD_0^{-1}$  against  $\log [\text{L}]_{\text{org}}$  then  $\beta_1$  and  $\beta_2$  can be determined by curve-fitting<sup>12,13</sup> with the normalized curves  $Y = \log (1 + pv + v^2)$ ;  $X = \log v$ . The value of the parameter  $p$  gives  $p = \beta_1/\beta_2$ , and the intersection of the asymptotes,  $\log DD_0^{-1} = 0$  and  $\log DD_0^{-1} = \log \beta_2[\text{L}]_{\text{org}}^2$ , gives  $\log \beta_2$ . Since the distribution constants for TOPO, TBP, and hexone between carbon tetrachloride and water are large,  $[\text{L}]_{\text{org}}$  can be put equal to  $C_L$ .

In order to calculate  $[\text{A}^-]$  the following expressions may be used (equal phase volume,  $C_{\text{org}} = 0.1 M$ ):

$$[\text{A}^-] = K_a K_d^{-1} [\text{HA}]_{\text{org}} [\text{H}^+]^{-1} \quad (7)$$



$$C_{\text{org}} - [A^-] = [\text{HA}]_{\text{org}} + [\text{HA}] = [\text{HA}]_{\text{org}}(1 + 1/K_a) \quad (8)$$

$$[A^-] = C_{\text{OH}}(-[\text{OH}^-]) \quad (9)$$

At  $-\log[\text{H}^+] < 11$ ,  $[\text{OH}^-]$  can be neglected for  $C_{\text{org}} = 0.1 \text{ M}$  TTA. Otherwise,  $[\text{OH}^-]$  may be calculated from  $[\text{H}^+]$  by  $[\text{OH}^-] = 10^{-13.81} [\text{H}^+]^{-1}$ . The  $C_{\text{OH}}$  and  $-\log[\text{H}^+]$  data for  $0.095 \text{ M} \geq C_{\text{OH}} \geq 0.005 \text{ M}$  and  $C_{\text{org}} = 0.1 \text{ M}$  can be used to calculate  $K_a$   $(1 + K_a)^{-1}$  from

$$K_a(1 + K_a)^{-1} = [\text{H}^+]C_{\text{OH}}(0.1 - C_{\text{OH}})^{-1} \quad (10)$$

If  $K_a \gg 1$ , the two-phase system has a buffer maximum at  $[\text{H}^+] = K_a K_d^{-1}$ . After separation of the phases the aqueous phase will of course have a buffer maximum at  $[\text{H}^+] = K_a$ .

## EXPERIMENTAL

### Tracers

The tracers were obtained from the Radiochemical Centre, Amersham, England. The tracer for calcium(II) was <sup>45</sup>Ca and was supplied as an aqueous solution of calcium chloride, which contained 1 mC per 0.2 mg of calcium (code CES. 2). The tracer for strontium(II) was <sup>85</sup>Sr and was supplied as an aqueous solution of strontium chloride, which contained 0.5 mC per 0.14 mg of strontium (code SOS. 1). The tracers were diluted in 0.1 M sodium perchlorate, the resulting solutions being used for stock solutions.

### Reagents

All the reagents used were of analytical grade. TTA (Fluka AG Chemische Fabrik), hexone and TBP (KEBO AB) and TOPO (Eastman Kodak Co.) were used. The solutions of TBP and hexone in carbon tetrachloride were washed first with 0.1 M perchloric acid and 0.1 M sodium hydroxide and then 2-3 times with water. The sodium perchlorate was recrystallized twice from water. The sodium hydroxide solution was prepared by dilution of standard commercial solution (Chemtam AB, Sweden). The other reagents were used without further purification.

### Procedures

All experiments were carried out in a thermostatted room at  $25 \pm 1^\circ$ . The organic solution of TTA, a neutral ligand, and the aqueous solution of the tracer, sodium perchlorate, sodium hydroxide or perchloric acid and, in some cases, a buffer, were placed in stoppered 50-ml glass tubes. The initial volume of both phases was in all cases 10.0 ml and the initial concentration of the tracer was less than  $10^{-7} \text{ M}$ . The aqueous phase was adjusted to ionic strength 0.1. The organic solution was allowed to stand overnight after preparation, in order to obtain equilibrium between the components.

The 2 phases in the tubes were agitated by a mechanical shaker for 1 h and then centrifuged. Preliminary experiments showed that agitation for 15 min by this shaker was sufficient to attain the distribution equilibrium; agitation for 2 h did not alter  $D$  and  $[\text{H}^+]$  appreciably. After agitation and centrifugation, a small portion of the aqueous solution was transferred to a small glass beaker and  $[\text{H}^+]$  was measured

potentiometrically with a glass electrode using 0.0100 *M* HClO<sub>4</sub>+0.09 *M* NaClO<sub>4</sub> as standard ( $-\log [H^+] = 2.000$ ).

The concentration of the metal ions in the 2 phases was measured radio-metrically as follows. For <sup>85</sup>Sr, 4-ml aliquots were pipetted from both phases and transferred to small polyethylene test tubes and the  $\gamma$ -radioactivity was counted with a well-type scintillation counter. For <sup>45</sup>Ca, 0.5 ml of the organic phase was placed in small nickel discs (diameter 2 cm) and evaporated slowly under an infrared lamp; 4 ml of the aqueous phase was back-extracted at pH 8 with 4 ml of a 1 : 1 mixture of carbon tetrachloride and hexone containing 0.1 *M* TTA. Samples of 0.5 ml were then removed and evaporated as before. In the experiments with TBP or TOPO an identical amount of these reagents as was present in the organic phase was added to the aqueous samples to make the  $\beta$ -ray absorption comparable to the samples from the organic phase. The 2 samples thus prepared were heated to about 250° to decompose TOPO and TBP and then measured with a GM-counter.

The distribution ratio was calculated from the following equation:

$$D = \frac{\text{count rate per ml of the organic phase}}{\text{count rate per ml of the aqueous phase}}$$

## RESULTS

### *The dependence of D on [H<sup>+</sup>]*

Figures 1 and 2 show the plot of  $\log D$  vs.  $-\log [H^+]$  at an initial concentration of TTA ( $C_{\text{org}}$ ) of 0.1 *M* in the organic phase. They show that the extraction of both calcium(II) and strontium(II) with 0.1 *M* TTA into carbon tetrachloride is very low even at the highest  $-\log [H^+]$  (8.9), where 95% of the TTA is present in the aqueous phase as A<sup>-</sup>. The slope  $d \log D / d \log [H^+]^{-1}$  gradually decreases as  $-\log [H^+]$  is increased.

Figure 3 shows the same data plotted as  $\log D$  vs.  $\log [A^-]$ . [A<sup>-</sup>] was calculated from [H<sup>+</sup>] and  $C_{\text{OH}}$  using eqns. (7)–(9). The data, which are given in Tables I and

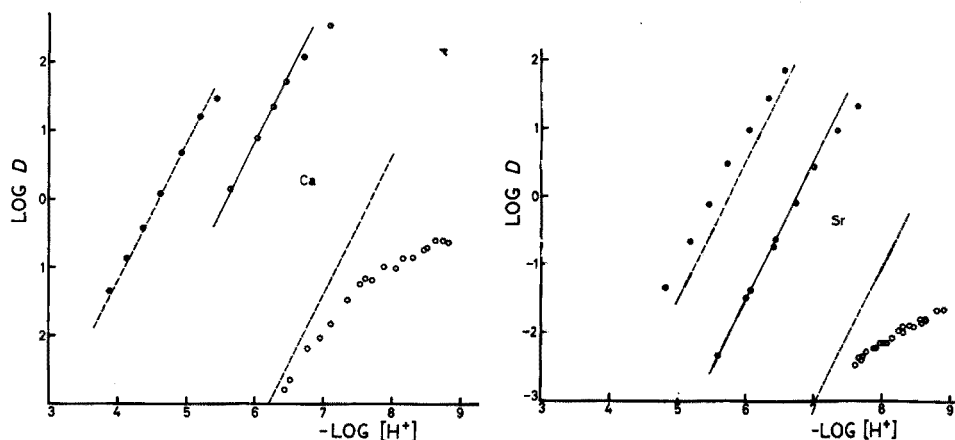


Fig. 1 (to the left) and Fig. 2 (to the right). The distribution of <sup>45</sup>Ca (Fig. 1) and <sup>85</sup>Sr (Fig. 2) as a function of  $-\log [H^+]$  for 0.1 *M* TTA in carbon tetrachloride containing no TBP (○), 0.01 *M* TBP (◐) or 0.1 *M* TBP (●). The straight lines (see text) are drawn with slope 2.

II, also allowed the calculation of  $\log K_a (1 + K_d)^{-1}$  for the TTA-CCl<sub>4</sub> system. A mean value of  $7.68 \pm 0.01$  was obtained. Using  $\log K_d = 1.57$ , as determined previously<sup>12</sup>, a value for  $\log K_a$  of  $6.10 \pm 0.02$  was found, which agrees very well with previous determinations<sup>1,2,9,14</sup>, considering that the pH-scales were then related to standard buffers.

Figures 1 and 2 also show the dependence of  $D$  on  $[H^+]$  when the carbon tetra-

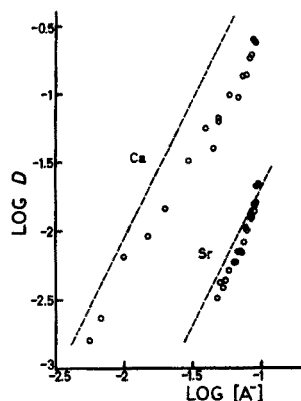


Fig. 3. The distribution of <sup>46</sup>Ca and <sup>88</sup>Sr between carbon tetrachloride containing TTA ( $C_{org} = 0.1 M$ ) and  $0.1 M Na(ClO_4, A)$  as a function of  $\log [A^-]$ . The same data are shown in Figs. 1 and 2 ( $\circ$ ) as a function of  $-\log [H^+]$ . The straight lines are drawn with slope 2 assuming that no complexes between  $M^{2+}$  and  $A^-$  are formed in the aqueous phase (see text).

TABLE I

DISTRIBUTION DATA FOR CALCIUM(II) BETWEEN CARBON TETRACHLORIDE WITH AN INITIAL CONCENTRATION OF TTA ( $C_{org}$ ) OF  $0.1 M$  AND  $0.1 M Na(ClO_4, OH)$

(Equal phase volumes)

$C_{OH}$	$-\log[H^+]$	$\log D$	$\log[A^-]$	$\log([HA]_{org} + [HA])$	$\log \frac{[H^+][A^-]}{[HA]_{org} + [HA]}$
0.095	8.827	-0.629	-1.022	-2.301	(-7.548)
0.093	8.746	-0.616	-1.032	-2.155	-7.623
0.090	8.641	-0.602	-1.046	-2.000	-7.687
0.088	8.516	-0.719	-1.056	-1.959	-7.613
0.085	8.477	-0.740	-1.071	-1.824	-7.724
0.080	8.306	-0.863	-1.097	-1.699	-7.704
0.075	8.172	-0.873	-1.125	-1.602	-7.695
0.070	8.066	-1.022	-1.155	-1.523	-7.698
0.060	7.890	-1.008	-1.222	-1.398	-7.714
0.050	7.716	-1.199	-1.301	-1.301	-7.716
0.050	7.616	-1.174	-1.301	-1.301	-7.616 <
0.045	7.625	-1.392	-1.347	-1.260	-7.712
0.040	7.547	-1.249	-1.398	-1.222	-7.723
0.030	7.359	-1.488	-1.523	-1.155	-7.727 >
0.020	7.124	-1.839	-1.699	-1.097	-7.726
0.015	6.962	-2.037	-1.824	-1.071	-7.715
0.010	6.676	-2.188	-2.000	-1.046	-7.630
Mean value:					-7.689

TABLE II

DISTRIBUTION DATA FOR STRONTIUM(II) BETWEEN CARBON TETRACHLORIDE WITH AN INITIAL CONCENTRATION OF TTA ( $C_{\text{org}}$ ) OF 0.1 M AND 0.1 M Na(ClO<sub>4</sub>,OH)

(Equal phase volumes)

$C_{\text{OH}}$	$-\log[H^+]$	$\log D$	$\log[A^-]$	$\log([HA]_{\text{org}}+[HA])$	$\log \frac{[H^+][A^-]}{[HA]_{\text{org}}+[HA]}$
0.095	8.926	-1.656	-1.022	-2.301	-7.647
0.093	8.825	-1.663	-1.032	-2.155	-7.702
0.091	8.663	-1.793	-1.041	-2.046	-7.658
0.090	8.654	-1.815	-1.046	-2.000	-7.700
0.090	8.590	-1.851	-1.046	-2.000	-7.636
0.088	8.585	-1.796	-1.056	-1.959	-7.682
0.086	8.424	-1.886	-1.066	-1.854	-7.636
0.084	8.320	-1.093	-1.076	-1.796	-7.600<
0.083	8.402	-1.900	-1.081	-1.769	-7.714
0.080	8.320	-1.996	-1.097	-1.699	-7.718>
0.078	8.264	-1.971	-1.108	-1.658	-7.714
0.075	8.161	-2.081	-1.125	-1.602	-7.684
0.073	8.091	-2.155	-1.137	-1.569	-7.659
0.070	8.049	-2.144	-1.155	-1.523	-7.681
0.068	7.985	-2.143	-1.168	-1.495	-7.658
0.065	7.927	-2.228	-1.187	-1.456	-7.658
0.063	7.888	-2.225	-1.201	-1.432	-7.657
0.058	7.789	-2.285	-1.237	-1.377	-7.649
0.055	7.723	-2.356	-1.260	-1.347	-7.636
0.053	7.704	-2.417	-1.276	-1.328	-7.652
0.050	7.675	-2.372	-1.301	-1.301	-7.675
0.048	7.625	-2.489	-1.319	-1.284	-7.660
Mean value					-7.667

chloride layer contains 0.01 and 0.1 M TBP. Straight lines with slope 2 obviously fit the data except at the highest  $-\log[H^+]$ , where  $[HA]_{\text{org}}$  is again decreased due to the formation of  $A^-$ . The straight lines with slope 2 demonstrate that aqueous complexes of calcium(II) and strontium(II) with  $A^-$  are not appreciably formed below  $-\log[H^+] = 6$  ( $[A^-] < 10^{-2.7}M$ ). The equation for the straight lines may thus be obtained from eqns. (4) and (7).

$$D = K K_a^2 K_d^{-2} [HA]_{\text{org}}^2 [H^+]^{-2} (1 + \beta_1 [L]_{\text{org}} + \beta_2 [L]_{\text{org}}^2) \quad (11a)$$

or

$$D = K_{\text{ex}} [HA]_{\text{org}}^2 [H^+]^{-2} (1 + \beta_1 [L]_{\text{org}} + \beta_2 [L]_{\text{org}}^2) \quad (11b)$$

For  $-\log[H^+] < 6$ ,  $[HA]_{\text{org}} \approx C_{\text{org}}(1 + 1/K_d)^{-1}$  and  $[L]_{\text{org}} = 0.01 M$ ,  $K$  or  $K_{\text{ex}} = K K_a^2 K_d^{-2}$  can be calculated from the straight lines by the following equation:

$$D = K_{\text{ex}} 10^{-2.02} [H^+]^{-2} (1 + \beta_1 10^{-2} + \beta_2 10^{-4}) \quad (12)$$

$$\text{For calcium: } K_{\text{ex}} = 10^{-9.18} (1 + \beta_1 10^{-2} + \beta_2 10^{-4})^{-1} \quad (13)$$

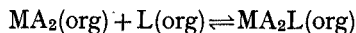
$$\text{For strontium: } K_{\text{ex}} = 10^{-11.50} (1 + \beta_1 10^{-2} + \beta_2 10^{-4})^{-1} \quad (14)$$

It is obvious that values for  $\beta_1$  and  $\beta_2$  are necessary in order to determine  $K_{\text{ex}}$  (or  $K$ ).

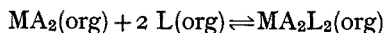
#### The dependence of $D$ on $[L]_{\text{org}}$

Figures 4 and 5 show the increase of  $D$  on the addition of TOPO, TBP or

hexone to carbon tetrachloride. The curves represent the "best-fit" with the family of normalized curves and their asymptotes (the abscissa and the dashed lines of slope 2). The data  $\log DD_0^{-1}$  vs.  $\log [L]_{\text{org}}$  fit the normalized curves well except in the highest concentration region of hexone. This confirms eqn. (6) which is based on the formation of 2 adducts  $MA_2L$  and  $MA_2L_2$  according to the following equilibria:



and



The formation constants  $\beta_1$  and  $\beta_2$  obtained by curve-fitting are listed in Table III.

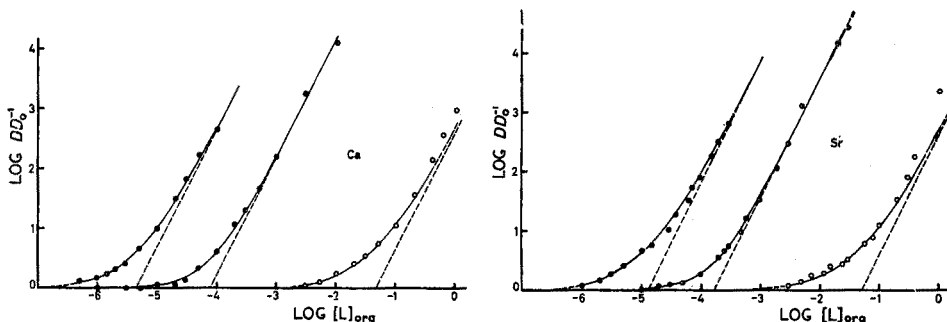


Fig. 4 (to the left) and Fig. 5 (to the right). The increase in the distribution as a function of  $[L]_{\text{org}}$  on the addition of different adduct-forming ligands to 0.1 M TTA in carbon tetrachloride. L = TOPO (●), L = TBP (○), and L = hexone (○). The normalized curves  $Y = \log(1 + pv + v^2)$ ;  $X = \log v$  are fitted to the data. The values of  $p$ ,  $\beta_1$  and  $\beta_2$  thus determined (see text) are given in Table III.

TABLE III

FORMATION CONSTANTS OF THE BIS-TTA COMPLEXES OF CALCIUM(II) AND STRONTIUM(II) WITH TRIOCTYLPHOSPHINE OXIDE, TRIBUTYLPHOSPHATE, AND METHYL ISOBUTYL KETONE IN CARBON TETRACHLORIDE AT 25°

(The constants are defined in the text)

Ligand	Constant	Ca <sup>2+</sup>	Sr <sup>2+</sup>
no L	$\log K_{\text{ex}}$		
L = Hexone	$\log \beta_1$	1.83	1.80
	$\log \beta_2$	2.66	2.60
	$\log p$	0.50	0.50
L = TBP	$\log \beta_1$	4.11	3.76
	$\log \beta_2$	8.22	7.52
	$\log p$	0	0
L = TOPO	$\log \beta_1$	5.64	5.39
	$\log \beta_2$	10.68	9.78
	$\log p$	0.30	0.50

*Note.* Some turbidity was observed in the aqueous phase and a decrease in  $DD_0^{-1}$  in solutions with more than  $2 \cdot 10^{-4}M$  TOPO at  $-\log [H^+] \approx 7.6$ . This might be due to a micelle formation between TOPO and  $A^-$  in the aqueous layer, and consequently in practical analytical work it is probably safer to use TBP instead of TOPO for the extraction of calcium(II) and strontium(II).

## DISCUSSION

The values of  $\beta_1$  and  $\beta_2$  may be used to calculate  $K_{\text{ex}}$  from eqns. (13) and (14), thus for  $\text{Ca}^{2+}$ :  $K_{\text{ex}} = 10^{-13.40}$ , and for  $\text{Sr}^{2+}$ :  $K_{\text{ex}} = 10^{-15.03}$ .

Since  $K_a K_d^{-1} = 10^{7.67}$ ,  $K$  can also be calculated: for  $\text{Ca}^{2+}$ :  $K = 10^{1.94}$ , and for  $\text{Sr}^{2+}$ :  $K = 10^{0.31}$ .

Using eqns. (11b) and (4) and the values for  $K_{\text{ex}}$  and  $K$  it is possible to see how the data fit for  $[\text{L}]_{\text{org}} = 0$  and 0.1 M TBP, if the  $\text{MA}^+$  and  $\text{MA}_2$  complexes in the aqueous phase are neglected. The data for  $[\text{L}]_{\text{org}} = 0$  in Figs. 1 and 2 (open circles) do not fit the dashed straight lines according to eqn. (11b). This is partly due to the fact that  $[\text{HA}]_{\text{org}}$  is not constant. From Fig. 3, however, it is obvious that the deviation from eqn. (4) may be due to the formation of TTA complexes in the aqueous layer. A deviation from the dashed straight lines might be expected for reasonable values of the formation constants for  $\text{MA}^+$  and  $\text{MA}_2$ , but the form of the experimental distribution curve differs from the theoretical (*cf.* DYRSSEN<sup>15</sup> Fig. 3a). This might be due to the extraction of mixed salts such as  $\text{Na}_2\text{SrA}_4$ , which would explain the increase between 0.05 and 0.1 M  $\text{A}^-$  in the case of strontium(II). Such co-extractions have been found previously in the zinc-IPT system<sup>15</sup> and with the oxinates of calcium and strontium<sup>16,17</sup>. Accordingly, the data in Fig. 5 were not used to calculate the stability constants for the TTA complexes in the aqueous phase. For  $[\text{L}]_{\text{org}} = 0.1$  M TBP, it can be seen from Fig. 1 (full circles) that the data for calcium(II) fit excellently. In the case of strontium(II) (Fig. 2, full circles), however, the distribution data lie somewhat above the dashed line, which indicates a slight tendency for  $\text{SrA}_2$  to add 3 TBP.

The values of  $\log \beta_1$  and  $\log \beta_2$  in Table III show that  $\text{CaA}_2$  is a slightly better acceptor for the donors TOPO and TBP than  $\text{SrA}_2$ ; the difference in  $\beta_1$  and  $\beta_2$  for hexone is, however, small. The order of  $\beta_2$  for different types of L reflects the donor tendency of  $\text{R}_3\text{PO}$ ,  $(\text{RO})_3\text{PO}$  and  $\text{R}_1\text{R}_2\text{CO}$  found previously in other TTA complexes<sup>13</sup>. The values of  $\log p$  ( $p^2 = K_1/K_2$  if  $\beta_1 = K_1$  and  $\beta_2 = K_1K_2$ ) in Table III indicate that the addition of one TBP does not appreciably hinder the addition of a second TBP. The values of  $\log K_{\text{ex}}$  are quite different considering that the formation constants for complexes of calcium(II) and strontium(II) with similar ligands do not differ appreciably. The difference may therefore reflect a greater tendency for  $\text{SrA}_2$  to be hydrated, leading to a lower value of the distribution constant,  $[\text{MA}_2(\text{H}_2\text{O})_x]/[\text{MA}_2(\text{H}_2\text{O})_y]$  ( $x$  and  $y$  unknown). Such a hydration might lower the acceptor tendency of  $\text{SrA}_2$  for L, and explain why the smaller calcium ion in  $\text{MA}_2$  gives larger values of  $\beta_2$ .

*Separation of calcium and strontium ions*

Percentage extraction curves for different  $[\text{L}]_{\text{org}}$  may be calculated from the data obtained above, and the curves for 0.01 M TBP are shown in Fig. 6. An extraction at pH 4 with carbon tetrachloride containing 0.1 M TTA + 0.01 M TBP removes most other metal ions (*cf.* ref. 9,13), but leaves calcium(II) and strontium(II) (probably also group IA metals and  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Ra}^{2+}$ ) in the aqueous layer. The pH is then raised to 6.6 in order to extract 99% of the calcium(II). To remove most of the 30% of strontium(II) which is extracted simultaneously, the organic layer is washed 3 times at pH 6.6 with water buffered with *p*-nitrophenol or veronal. The maximum solubilities of  $\text{CaA}_2$  and  $\text{SrA}_2$  in 0.01 and 0.1 M TBP were determined by Ing. KERSTIN ÅRÉN to

be  $5.3 \cdot 10^{-3} M$  (Ca),  $6.4 \cdot 10^{-3} M$  (Sr) and  $2.1 \cdot 10^{-2} M$  (Ca),  $2.2 \cdot 10^{-2} M$  (Sr) respectively, and those values indicate the upper concentration limits that can be extracted with the TTA-TBP-CCl<sub>4</sub> system.

Curves similar to Fig. 6 have been plotted for the C<sub>7</sub>F<sub>15</sub>COONa-TBP-CCl<sub>4</sub> system (ref.<sup>18</sup> Fig. 5). Soap-like ligands such as C<sub>7</sub>F<sub>15</sub>COO<sup>-</sup> should, however, be avoided in the solvent extraction of metal ions since they lead to the formation of more or less stable emulsions.

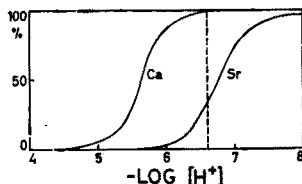


Fig. 6. The percentage extraction of Ca<sup>2+</sup> and Sr<sup>2+</sup> into 0.1 M TTA + 0.01 M TBP in carbon tetrachloride as a function of  $-\log [H^+]$ . The dashed line shows the suggested optimum pH for separation.

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#### SUMMARY

The solvent extraction of calcium(II) and strontium(II) by TTA has been studied using carbon tetrachloride containing trioctylphosphine oxide (TOPO), tributylphosphate (TBP), and methyl isobutyl ketone (hexone) as adduct-forming ligands. Stability constants for the systems are given. The separation of calcium and strontium can be effected by 0.1 M TTA + 0.01 M TBP in carbon tetrachloride.

#### RÉSUMÉ

Les auteurs ont examiné l'extraction dans un solvant du calcium et du strontium au moyen de TTA. On a utilisé le tétrachlorure de carbone, en présence de trioctylphosphine oxyde (TOPO), de tributylphosphate (TBP) et de méthylisobutylcétone (hexone). Les constantes de stabilité de ces systèmes sont données. La séparation du calcium et du strontium peut être effectuée au moyen de TTA 0.1 M + TBP 0.01 M dans le tétrachlorure de carbone.

#### ZUSAMMENFASSUNG

Die Flüssigextraktion von Calcium und Strontium wurde untersucht unter Verwendung von Tetrachlorkohlenstoff, das folgende sich anlagernde Liganden enthielt: Trioctylphosphinoxid (TOPO), Tributylphosphat (TBP) und Methylisobutylketon (Hexon). Die Stabilitätskonstanten dieser Systeme werden angegeben. Eine Trennung des Calciums und des Strontiums wird durch 0.1 M TTA + 0.01 M TBP in Tetrachlorkohlenstoff erreicht.

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OXALATES AS QUALITATIVE ORGANIC ANALYSIS DERIVATIVES  
OF ALL CLASSES OF AMINES\*

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A recent investigation of sulfone adducts as derivatives of aliphatic amines indicated that the application of this reaction to secondary amines was successful in only a limited number of cases and that tertiary amines did not yield useful products<sup>1</sup>. A number of years ago some work was done in these laboratories under the National Cooperative Undergraduate Chemical Research Program on the use of oxalic acid salts as amine derivatives<sup>2</sup>. Those experiments were sufficiently promising to warrant a further study to include the acid salts of secondary and tertiary amines as well as the neutral salts of primary amines. This paper reports findings for a selected number of commercially available amines.

The critical step of derivative preparation in qualitative organic analysis requires a high yield of easily purified product obtained in as brief a time as possible. These considerations have made salts of organic acids and bases very attractive as derivatives<sup>3-7</sup>. From an analytical viewpoint, the most important requirement is that the melting points observed for the derivatives show sufficient variation to allow differentiation among similar compounds. Most of the salts previously reported have shown numerous decomposition points as well as an inadequate range of melting points<sup>3,5</sup>. This has prevented the wide application of salts as analytical derivatives in spite of their other desirable characteristics.

In this rather dark picture there are some bright spots. Reference to a standard table of derivative melting points shows that a large number of picrates have been prepared and that they possess satisfactory melting points<sup>8</sup>. It is also well known that oxalates are frequently used in the alkaloid field<sup>9</sup>. There has been no systematic study of oxalates as derivatives of simple aliphatic amines, but there is an example of such a derivative of amides<sup>10</sup>. A search of Beilstein revealed that several of the compounds selected for the present study had been reported. As will be pointed out in the discussion, only a few of these reports are of much use to the analytical chemist.

## EXPERIMENTAL

*Reagents*

All of the amines studied were Eastman "White Label" grade or the practical

\* Taken from the senior research theses of C.A.B., 1956 and A.D.B., 1966.

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grade which was carefully distilled prior to use. The solvents and oxalic acid were Baker "reagent" grade and were used without further purification.

### Procedures

Three separate procedures were employed at different stages of this work. These differed in the ratio of amine to oxalic acid or in the choice of solvent. Still a fourth technique was used in order to demonstrate the use of this derivative with semimicro quantities of amines.

(A) A saturated solution (20 ml) of oxalic acid in 95% ethanol was placed in an Erlenmeyer flask and cooled in an ice bath. A primary amine (10 ml) was added with constant swirling. The oxalate precipitated immediately.

(B) A secondary amine (2 ml) was dissolved in 2 ml of absolute ethanol and 20 ml of ethanol saturated with oxalic acid was added with brisk stirring. The solution and the oxalate precipitate were cooled in an ice bath.

(C) A tertiary amine (1 ml) was added with constant swirling to 20 ml of a saturated ether solution of oxalic acid. In nearly every case the precipitate formed immediately. All mixtures were cooled in an ice bath to complete precipitation prior to filtration.

The products of all reactions were filtered and washed with the solvent in which they had been prepared. Primary diammonium oxalates (procedure A) and secondary ammonium hydrogen oxalates (procedure B) were easily recrystallized from either methanol or ethanol. Tertiary ammonium hydrogen oxalates (procedure C) were recrystallized from acetone. In all cases several recrystallizations produced no change in melting points. Drying overnight at 110° or under vacuum were both used successfully. Melting points were taken on a variety of different types of apparatus with no observable difficulty in reproducing the reported values. Mixed melting points of selected compounds as indicated in the Tables showed the expected depression (50–50 by weight). All melting points are corrected.

Semimicro scale preparations of all 3 of the above procedures were carried out. The only modification was the use of 0.1 ml of the amine and 2 ml of the appropriate solvent saturated with oxalic acid. In every case an ample amount (*ca.* 50 mg) of the oxalate was obtained for the required recrystallization and melting point determination.

### RESULTS AND DISCUSSION

When the first work with the primary amines was carried out using Procedure A, the results presented in Table I indicate that only the neutral oxalates were obtained. While the range of melting points is not great, there are several instances of closely related amines whose salts differ significantly.

In an effort to improve the situation, an investigation of the acid salts was undertaken. Preliminary experiments working at about a 1:1 molar ratio of amine to oxalic acid produced only mixtures of acid and neutral salts which could not be separated. An exception was found in the case of one secondary amine which analyzed correctly for the hydrogen oxalate<sup>11</sup>.

The large excess of oxalic acid used in Procedure B gave the excellent agreement with acid salts as shown in Table II. With tertiary amines, the use of ethanol

TABLE I

PROPERTIES OF NEUTRAL PRIMARY AMMONIUM OXALATES (PROC. A)

Amine	Formula	M.p. (°) <sup>a</sup>	Analysis		
			Calculated % N		Found % N
			Acid	Neutral	
Ethyl	C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	187-188.5	10.4	15.6	15.3
<i>n</i> -Propyl	C <sub>8</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>	182-184	9.4	13.4	13.4
Isopropyl	C <sub>8</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>	206.5-207.5 <sup>b</sup>	9.4	13.4	13.4
<i>n</i> -Butyl	C <sub>10</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub>	185-186	8.6	11.9	11.8
Isobutyl	C <sub>10</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub>	184-185.5	8.6	11.9	11.7
<i>sec</i> -Butyl	C <sub>10</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub>	204.5-206.5	8.6	11.9	11.8
<i>t</i> -Butyl	C <sub>10</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub>	263-264(d)	8.6	11.9	12.2
<i>n</i> -Pentyl	C <sub>12</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub>	185-187	7.9	10.6	10.6
Isopentyl	C <sub>12</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub>	168-170	7.9	10.6	10.8
<i>n</i> -Hexyl	C <sub>14</sub> H <sub>32</sub> N <sub>2</sub> O <sub>4</sub>	191-193	7.3	9.6	9.8
Aniline	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	154-156 <sup>b</sup>	7.7	10.1	10.4
Benzyl	C <sub>16</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>	189-190 <sup>b</sup>	7.1	9.2	9.5

<sup>a</sup> Corrected.<sup>b</sup> Melting points (Beilstein): isopropyl = 160-160.5; aniline = 150-164; benzyl = 195-202.

TABLE II

PROPERTIES OF SECONDARY AMMONIUM HYDROGEN OXALATES (PROC. B)

Amine	Formula	M.p. (°) <sup>a</sup>	Analysis					
			Calculated %			Found %		
			C	H	N	C	H	N
Dimethyl	C <sub>4</sub> H <sub>8</sub> NO <sub>4</sub>	148-149	35.6	6.7	10.3	35.7	6.9	10.2
Diethyl	C <sub>8</sub> H <sub>16</sub> NO <sub>4</sub>	215-216 <sup>b,d</sup>	44.2	7.8	8.3	44.3	8.0	8.6
Di- <i>n</i> -propyl	C <sub>8</sub> H <sub>17</sub> NO <sub>4</sub>	233.5-234.5 <sup>d</sup>	50.3	9.0	7.3	50.8	9.4	7.3
Diisopropyl	C <sub>8</sub> H <sub>17</sub> NO <sub>4</sub>	168.5-169.5	50.3	9.0	7.3	50.4	9.2	7.4
Di- <i>n</i> -butyl	C <sub>10</sub> H <sub>21</sub> NO <sub>4</sub>	227.5-228.5 <sup>c</sup>	54.8	9.6	6.4	54.9	9.8	6.2
Diisobutyl	C <sub>10</sub> H <sub>21</sub> NO <sub>4</sub>	253.5-254.5 <sup>d</sup>	54.8	9.6	6.4	54.4	9.8	6.3
Di- <i>n</i> -pentyl	C <sub>12</sub> H <sub>25</sub> NO <sub>4</sub>	225.5-226.5 <sup>c,d</sup>	58.3	10.1	5.7	58.6	10.2	5.8
Diisopentyl	C <sub>12</sub> H <sub>25</sub> NO <sub>4</sub>	264.5-265.5	58.3	10.1	5.7	57.9	10.3	5.7
Di- <i>n</i> -heptyl	C <sub>16</sub> H <sub>33</sub> NO <sub>4</sub>	223-224	63.3	11.0	4.6	63.6	11.4	4.5
Di- <i>n</i> -octyl	C <sub>18</sub> H <sub>37</sub> NO <sub>4</sub>	219-220	65.2	11.3	4.2	65.1	10.9	4.2
Di- <i>n</i> -decyl	C <sub>22</sub> H <sub>45</sub> NO <sub>4</sub>	214-215 <sup>b</sup>	68.2	11.7	3.6	67.7	12.0	3.6
Morpholine	C <sub>6</sub> H <sub>11</sub> NO <sub>5</sub>	198.5-199.5	40.7	6.3	7.9	40.6	6.3	8.0

<sup>a</sup> Corrected.<sup>b</sup> Mixed m.p. = 200.5-202.5°.<sup>c</sup> Mixed m.p. = 201-204°.<sup>d</sup> Melting points (Beilstein): diethyl = 220; di-*n*-propyl = 225; diisobutyl = 245-248; di-*n*-pentyl = 210-213.

did not provide the desired salts apparently because of their high solubility. The substitution of ethyl ether, Procedure C, overcame this difficulty. High yields of pure hydrogen oxalates were obtained as indicated in Table III.

In all cases Procedure A yielded only the neutral salt, while Procedures B and C produced only the acid salt. Their preparation is virtually instantaneous and in

TABLE III

PROPERTIES OF TERTIARY AMMONIUM HYDROGEN OXALATES (PROC. C)

Amine	Formula	M.p. (°) <sup>a</sup>	Analysis					
			Calculated %			Found %		
			C	H	N	C	H	N
N-Methyldiethyl	C <sub>7</sub> H <sub>15</sub> NO <sub>4</sub>	119-119.5	47.5	8.5	7.9	47.3	8.3	7.9
Triethyl	C <sub>8</sub> H <sub>17</sub> NO <sub>4</sub>	140-142	50.3	8.9	7.3	50.0	8.7	7.1
Tri- <i>n</i> -propyl	C <sub>11</sub> H <sub>23</sub> NO <sub>4</sub>	106-107	56.6	9.9	6.0	56.4	9.6	6.1
Tri- <i>n</i> -butyl	C <sub>14</sub> H <sub>29</sub> NO <sub>4</sub>	125-126.5 <sup>b</sup>	61.1	10.6	5.1	60.9	10.3	5.2
N,N-Dimethyl- <i>t</i> -butyl	C <sub>8</sub> H <sub>17</sub> NO <sub>4</sub>	156-157	50.3	8.9	7.3	50.0	8.8	7.2
Tri- <i>n</i> -pentyl	C <sub>17</sub> H <sub>35</sub> NO <sub>4</sub>	136-137.5	64.3	11.0	4.4	63.8	10.9	4.6
Triisopentyl	C <sub>17</sub> H <sub>35</sub> NO <sub>4</sub>	156-157.5	64.3	11.0	4.4	63.8	11.1	4.5
Tri- <i>n</i> -heptyl	C <sub>23</sub> H <sub>47</sub> NO <sub>4</sub>	111-112	68.8	11.7	3.5	68.6	11.7	3.7
N-Methyldi- <i>n</i> -octyl	C <sub>19</sub> H <sub>39</sub> NO <sub>4</sub>	127.5-128.5 <sup>b</sup>	66.0	11.3	4.1	65.9	11.2	4.2

<sup>a</sup> Corrected.<sup>b</sup> Mixed m.p. = 109-111.5°.

very high (80-90%) yield. The salts are easily recrystallized and, most important, their melting points are in the very convenient 100-250° range with only one decomposition point observed. It was found that each of the procedures described above could be carried out on a much smaller amount of sample. If 0.1 ml of an amine was employed, the oxalate could be easily obtained in sufficient quantity for subsequent identification tests.

The fact that several of these oxalates were found in Beilstein would seem to make the present paper unnecessary. However, a close examination of these entries indicates that of the 33 compounds included only 7 can be compared. The agreement in cases where comparison is possible, is good with the exception of the neutral oxalate of isopropyl amine and the acid oxalate of *n*-pentyl amine. In view of the facts: (1) starting material of known purity, (2) melting points checked by more than one operator, and (3) the complete analytical data which are missing from the other references, we are satisfied with the values reported here.

Seven other amines included in this study are listed as their oxalate in Beilstein, but either no melting point is given or the nature of the salt (acid or neutral) is not indicated. Some of these physical constants agree with the present values and others do not. All of this work is found in older and scarcer journals making it very difficult to check for the missing data.

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## SUMMARY

Methods of preparing either the acid or neutral ammonium oxalates of all

classes of simple amines are presented. The usefulness of these compounds as qualitative organic analysis derivatives is pointed out. The method is applicable to semimicro analyses.

#### RÉSUMÉ

On propose des méthodes de préparation d'oxalates de toutes les classes d'amines simples, en vue de leur utilisation pour l'analyse qualitative organique. Ce procédé est applicable à des semimicroanalyses.

#### ZUSAMMENFASSUNG

Es werden Methoden zur Herstellung entweder der sauren oder der neutralen Ammoniumoxalate aller Klassen einfacher Amine angegeben. Die Brauchbarkeit dieser Verbindungen als qualitative organische Analysenderivate wird dargestellt. Die Methode ist für Halbmikroanalysen anwendbar.

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## ETUDE DE L'ACTION DE L'ION FLUOR SUR LA LAQUE THORIUM-SPADNS

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A la suite de difficultés rencontrées dans l'application du dosage titrimétrique de l'ion fluor par le thorium en présence du sel trisodique de l'acide *p*-sulfophénylazochromotropique (ou SPADNS\*) selon BANERJEE<sup>1</sup>, nous avons fait dans un précédent travail<sup>2,3</sup> une étude approfondie du comportement de la laque Th-SP dans différents milieux, en particulier en milieu exclusivement chlorhydrique<sup>2</sup> et en présence du "réactif salin" à l'acétate de sodium-acide chlorhydrique utilisé par BANERJEE<sup>3</sup>. Nous avons pu alors entreprendre en connaissance de cause l'étude de l'action de l'ion fluor sur cette laque, étude qui fait l'objet de ce présent mémoire. Cette action est basée sur les propriétés classiques de l'ion fluor: mis en présence d'un excès de laque, cet ion complexe le métal et détruit donc une partie de la laque, libérant ainsi du colorant en quantité proportionnelle à celle du fluor.

L'étude spectrophotométrique de l'action de l'ion fluor sur la laque Th-SP, faite sur une solution aqueuse de NaF, parallèlement en milieu exclusivement chlorhydrique et en présence du réactif salin à l'acétate de sodium-acide chlorhydrique de BANERJEE<sup>3</sup>, a été menée par 2 voies différentes et nous a conduite à la mise au point de 2 techniques instrumentales de dosage de l'ion fluor: une technique spectrophotométrique et une technique par titrimétrie colorimétrique.

## MODES OPÉRATOIRES PROPOSÉS

*Matières premières*

Les principales matières premières utilisées pour ce travail\*\* ont été, comme précédemment:  $\text{Th}(\text{NO}_3)_4 \cdot 6 \text{H}_2\text{O}$ , SPADNS = sel trisodique de l'acide *p*-sulfophénylazochromotropique, acétate de sodium, acide chlorhydrique officinal, et, en outre, NaF (teneur en F: 45.2%).

*Technique de dosage spectrophotométrique*

Ce dosage s'effectue à l'aide d'une laque chlorhydrique Th-SP extemporanée\*\*\*.

\* Pour simplifier, nous désignerons le SPADNS par le sigle SP.

\*\* Pour plus de précision sur ces matières premières et les réactifs qu'elles servent à préparer, se reporter à <sup>2</sup> et <sup>3</sup>.

\*\*\* Il est très possible d'opérer avec une laque préparée à l'avance car celle-ci se conserve de façon remarquable (plusieurs années). Mais dans ce cas, il faut s'attendre à voir augmenter le nombre de points "aberrants" qui peuvent se rencontrer au cours d'un dosage. Malgré nos recherches, nous n'avons pu déterminer la raison de cette augmentation.

*Préparation de la laque:*

	Laque "a" (ml)	Laque "b" (ml)
SP 0.004 M	2	4
Th 0.004 M	1	2
HCl officinal dilué au dixième (v/v)	0.2	0.2
Eau distillée	Q.S.P. 100	100

*Etablissement de la courbe d'étalonnage.* Selon la concentration éventuelle en fluor et le volume de solution à doser dont on dispose, préparer l'une des 3 gammes ci-dessous.

Dans une série de 6 tubes de Nessler (20 cm ; 2.2 cm environ), particulièrement favorables à un mélange rapide, mesurer exactement:

(a) pour une gamme de 0 à 5  $\mu\text{g}$  de F (volume total: 10 ml): 5 ml de laque "a" et 5 ml de solutions de NaF de concentrations croissantes (contenant de 0 à 5  $\mu\text{g}$  de F dans 5 ml).

(b) pour une gamme de 0 à 10  $\mu\text{g}$  de F (volume total: 10 ml): 5 ml de laque "b" et 5 ml de solutions de NaF de concentrations croissantes (contenant de 0 à 10  $\mu\text{g}$  de F dans 5 ml).

(c) pour une gamme de 0 à 50  $\mu\text{g}$  de F (volume total: 50 ml): 25 ml de laque "b" et 25 ml de solutions de NaF de concentrations croissantes (contenant de 0 à 50  $\mu\text{g}$  de F dans 25 ml).

Dans les trois cas, agiter chaque tube au fur et à mesure de sa préparation. Lire en cuves de 20 mm pour la gamme (a) et en cuves de 10 mm pour les deux autres gammes, à 580 nm en prenant comme référence le tube contenant la plus forte dose de F ou à 600 nm en prenant l'eau distillée comme milieu de référence.

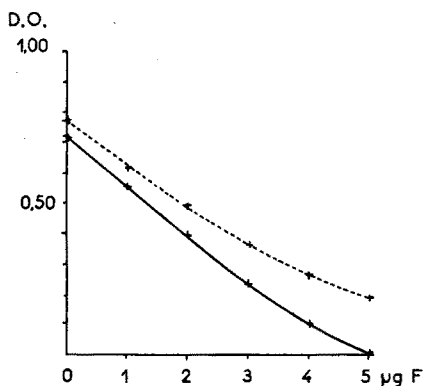


Fig. 1. Courbe d'étalonnage de la solution de F<sup>-</sup> par la laque Th/SP.  
 ----- lecture à 600 nm, milieu de référence: eau distillée;  
 ——— lecture à 580 nm, milieu de référence: laque Th/SP + 5  $\mu\text{g}$  de F<sup>-</sup>.

Nous donnons comme exemple en Fig. 1 une courbe d'étalonnage entre 0 et 5  $\mu\text{g}$  de F pour un volume total de 10 ml (pH voisin de 3.0).

Le dosage s'effectue de la même façon sur des prises d'essai inférieures ou égales à 5 ml pour les 2 premiers cas et inférieures ou égales à 25 ml pour le troisième (compléter éventuellement au volume par de l'eau distillée).

### Technique de dosage par titrimétrie colorimétrique

Ce dosage titrimétrique s'effectue, en milieu chlorhydrique, par une solution de Th 0.001 M en présence de SP. La densité optique est suivie au spectrophotomètre tout au long du titrage et le point d'équivalence est déterminé graphiquement à partir du tracé de la courbe obtenue.

*Étalonnage de la solution de Th.* Dans une cuve carrée à faces parallèles de 36 mm, mesurer exactement: 1 ml SP 0.004 M, 0.2 ml HCl officinal dilué au centième (v/v), un volume  $v$  ml de la solution étalon de NaF contenant au plus 10 ou 20  $\mu\text{g}$  de F, et de l'eau distillée Q.S.P. environ 40 ml (un repère sur la cuve suffit à la mesure approximative de ce volume).

Titre au spectrophotomètre à 580 nm à l'aide d'une microburette de 2 ml au 0.01 ml, par la solution de Th 0.001 M, et tracer sur papier millimétré la courbe d'évolution de la densité optique en fonction du volume de Th ajouté. Déterminer le point d'équivalence en prenant le point de rencontre des 2 tangentes à la courbe. Nous donnons comme exemple en Fig. 2 une courbe de titrage obtenue à partir de 5  $\mu\text{g}$  de F (pH voisin de 3.3).

Recommencer l'expérience avec d'autres doses de F et tracer ensuite sur papier millimétré la courbe d'étalonnage de la solution de Th pour des doses de F allant de 0 à 10 ou au plus 20  $\mu\text{g}$ . Nous donnons en Fig. 3 la courbe obtenue.

Le dosage s'effectue dans les mêmes conditions, sur une prise d'essai contenant au plus 10 ou 20  $\mu\text{g}$  de F.

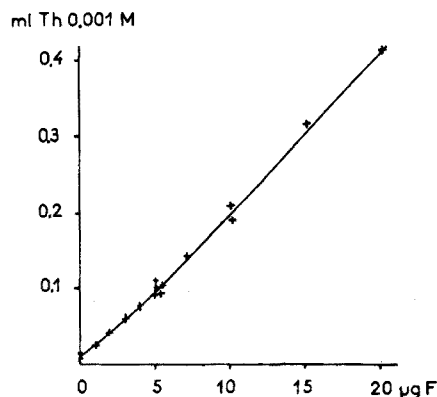
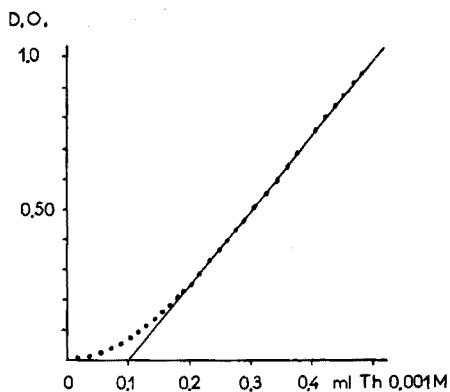


Fig. 2. Courbe de titrage de 5  $\mu\text{g}$  de  $\text{F}^-$  à 580 nm.

Fig. 3. Courbe d'étalonnage de la solution de Th 0.001 M.

### JUSTIFICATION DES CONDITIONS OPÉRATOIRES

#### Choix du milieu

Notre étude détaillée de la laque Th-SP<sup>2,3</sup> montre nettement que le milieu le plus favorable à sa formation est sans conteste le milieu exclusivement chlorhydrique, la présence de divers sels (chlorure de sodium, acétate de sodium) ou d'un acide tel que l'acide acétique, amenant toujours une dissociation supplémentaire plus ou moins marquée de la laque (même lorsque ces corps ne donnent avec le Th, du moins en principe, ni complexe ni précipité).



Cette laque servant d'indicateur pour le dosage des ions fluor, il était à prévoir que, là encore, le milieu exclusivement chlorhydrique serait le plus favorable. Aussi bien dans l'étude spectrophotométrique que dans l'étude par titrimétrie colorimétrique, les essais effectués en présence d'ions fluor, parallèlement en milieu "salin" et en milieu exclusivement chlorhydrique, ont confirmé le fait.

Pour le dosage spectrophotométrique, la dissociation supplémentaire apportée par le fait d'un milieu salin se traduit par une "pente" moins forte, donc moins favorable, des courbes obtenues. Dans ces conditions, la présence d'électrolytes en quantité notable dans la solution à doser, même s'il s'agit comme ici d'électrolytes qui ne peuvent agir que par la seule force ionique, peut "simuler" la présence de fluor et obliger à effectuer la courbe d'étalonnage dans un milieu de même composition ionique. Mais notons que pour observer un même résultat quantitatif (libération d'une même dose de SP), l'expérience montre<sup>3</sup> qu'il faut atteindre pour les électrolytes une concentration molaire  $10^4$  à  $10^6$  fois plus élevée que celle de l'ion fluor. Cette différence d'"activité" considérable conserve malgré tout à la méthode spectrophotométrique une certaine sélectivité. Il n'est évidemment pas question non plus ici, pour ce qui concerne le milieu dit "salin", de substances susceptibles de réagir avec le fluor et dont l'influence perturbatrice (qui a déjà fait l'objet de nombreuses études) se ferait sentir inéluctablement sur le dosage de cet ion par la laque Th-SP, quelle que soit la technique employée.

Pour le dosage par titrimétrie colorimétrique une dissociation supplémentaire de la laque indicatrice (en milieu dit "salin") entraîne une plus grande ouverture de l'angle formé par les 2 tangentes servant à la détermination graphique du point d'équivalence. Mais si la présence en quantité notable de ces mêmes électrolytes aggrave ainsi l'imprécision des résultats, elle n'a pas ici le grave inconvénient de les perturber. En aucun cas, par cette technique, les électrolytes précisés plus haut ne peuvent "simuler" la présence de fluor puisqu'ils interviennent seulement sur la dissociation de la laque, traduite par l'inclinaison plus ou moins forte de la tangente, mais pratiquement pas sur la consommation même de Th qui, seule, en définitive, détermine le point d'équivalence. Cette distinction fondamentale assure ici une spécificité plus étroite de la réaction de dosage.

Aux doses où nous opérons (dans les deux cas), la libération de H<sup>+</sup> au cours de la réaction est négligeable<sup>4</sup>. L'addition d'un tampon se révèle donc, dans les conditions opératoires, non seulement inutile mais défavorable. Et nous sommes donc amenée à préférer, toutes les fois que cela est possible, et contrairement à BANERJEE, le milieu exclusivement chlorhydrique.

#### Choix du pH

L'étude spectrophotométrique du comportement de la laque Th-SP à différents pH a montré une zone optimale en palier pour sa formation. En milieu chlorhydrique<sup>2</sup>, ce palier s'étend approximativement de pH 3.2 à pH 3.8. De chaque côté de cette zone, l'abaissement ou l'élévation du pH accentue plus ou moins la dissociation de la laque.

Il apparaîtrait donc au premier abord que les milieux les plus favorables au dosage de l'ion fluor par cette laque seraient assujettis à rester à l'intérieur de cette zone optimale. Mais, en réalité, l'étude, par titrimétrie colorimétrique, de l'action de l'ion fluor sur la laque Th-SP, nous a montré que la "consommation" de Th par F,

consommation qui règle aussi les conditions optimales de dosage, augmentait très nettement et très progressivement lorsque le pH s'abaissait. Nous avons constaté qu'entre pH 3.4 et pH 1.9, le rapport Th/F double pratiquement et que le pH correspondant à la formation stoechiométrique de  $\text{ThF}_4$  est voisin de 3.9. Peut-être la continuité dans le déplacement du point d'équivalence (ou, si l'on préfère, l'absence de palier) provient-elle simplement de la molarisation progressive de l'acide fluorhydrique au fur et à mesure que l'acidité du milieu augmente (à moins encore qu'il ne se forme en réalité, non pas un seul composé fluoré mais un mélange de deux ou plusieurs composés, mélange dont l'équilibre serait réglé par le pH).

Remarquons que c'est cette variation du rapport Th/F en fonction du pH, lié au fait que la réaction conduit à la libération de  $\text{H}^+$ , qui oblige à opérer en milieu tamponné dès que les doses de fluor qui interviennent sont suffisamment élevées (supérieures à  $70 \mu\text{g}$ ), ce qui n'est pas le cas dans nos conditions opératoires.

Pour le choix du pH lui-même, un juste équilibre peut donc être trouvé, se situant à la limite inférieure du palier optimal de formation de la laque réactif.

Cette limite donne en effet, en titrimétrie colorimétrique, des conditions opératoires correctes et nous avons donc adopté pour cette méthode un pH voisin de 3.3. Les expériences faites à des pH un peu inférieurs n'ont montré aucun avantage ou désavantage final, les deux phénomènes qui interviennent variant en sens inverse en s'équilibrant. On peut d'ailleurs se permettre d'opérer à un pH très légèrement différent, mais la condition essentielle est de respecter strictement le même pH pour les expériences d'étalonnage et pour les courbes de titrage.

Par contre, dans les conditions opératoires de la spectrophotométrie, l'expérience a montré que le phénomène "consommation" de Th l'emporte sur le phénomène "dissociation" de la laque et qu'il est préférable d'opérer légèrement en-dessous du palier optimal de pH de sa formation. Pour cette dernière, nous avons donc adopté finalement un pH voisin de 3.0. Mais là encore, la condition primordiale est que le pH soit strictement identique dans les tubes de dosage et dans ceux de la gamme étalon.

#### *Choix de la concentration en Th et de la dose de SP*

C'est l'expérience qui nous a dicté le choix de l'excès de Th nécessaire dans la technique spectrophotométrique, comme celui de la concentration de la solution titrante  $0.001 M$  de Th pour le dosage par titrimétrie colorimétrique.

Dans les deux techniques, on pourrait penser au premier abord que l'on a tout intérêt à choisir la dose de SP la plus élevée possible afin d'aboutir à une dissociation minimale de la laque formée, et que, seule, l'intensité de la coloration du SP imposerait une limite supérieure. Mais, en réalité, une série de courbes de titrage effectuées par titrimétrie colorimétrique sur une dose toujours identique de fluor ( $5 \mu\text{g}$ ) mais en faisant varier chaque fois la dose de SP, a montré que le point d'équivalence semblait aussi sous la dépendance de la concentration en SP\*. Apparemment, le SP, à partir d'une certaine concentration, entre en concurrence avec le fluor pour capter le Th (ce

\* Nous avons été conduite à approfondir davantage l'influence de la dose de SP à la suite de 2 mémoires. D'une part, GUNTZ ET ARENE<sup>5</sup> constatent simplement que "si à un pH déterminé paraît exister un rapport F/Th donné, cette proportionnalité n'est valable que dans des limites assez étroites de concentration des réactifs". D'autre part, nous avons été frappée, dans un travail de HOLLINGWORTH<sup>6</sup> par la faiblesse de la dose de SP utilisée (20 fois plus faible environ que la nôtre) pour doser du fluor dans les roches.

phénomène expliquerait l'étalement visible du virage que traduit l'"arrondi" de l'angle de la courbe titrimétrique). Pour obtenir le rapport Th/F le plus avantageux possible, on a donc avantage à opérer, *contrairement aux conclusions précédentes*, en présence d'une dose de SP aussi faible que possible. Dans ces conditions, il faut alors se maintenir dans un juste milieu, et c'est encore l'expérience qui a déterminé notre choix dans l'une et l'autre technique.

#### *Choix du mode de lecture*

C'est l'examen des spectres respectifs de la laque et du SP (voir la Fig. 1 du premier mémoire<sup>2</sup>) qui nous a dicté les longueurs d'onde à choisir pour les deux techniques. Pour le dosage spectrophotométrique, l'expérience a montré qu'il n'y a pas lieu de s'attendre à une coïncidence absolument parfaite entre les résultats donnés par les deux modes de lecture retenus, les causes d'erreur inhérentes à chacun d'eux n'étant pas toujours identiques.

#### CONCLUSIONS

Ces considérations nous paraissent apporter aux deux techniques que nous proposons une justification suffisante des conditions opératoires choisies.

Quand au choix entre les deux techniques elles-mêmes, il peut être dicté par des considérations d'ordre pratique et de teneur en électrolytes de la solution à doser, car il ne faut pas perdre de vue la différence essentielle entre les deux procédés, à savoir que les deux phénomènes "consommation de Th par le F" et "dissociation de la laque-réactif sous l'influence de la composition ionique du milieu" se manifestent tous les deux de la même façon dans la méthode spectrophotométrique mais non forcément dans celle par titrimétrie colorimétrique.

#### INTÉRÊT ET RÉSULTATS OBTENUS

Le réactif Th/SP est d'une très grande sensibilité\*, ce qui permet d'obtenir des écarts importants de densité optique pour des doses très faibles de fluor. De plus, il présente un avantage qui ne semble pas partagé par de nombreuses laques: celui d'une remarquable stabilité (pouvant atteindre et même dépasser un an). Les deux techniques instrumentales que nous proposons présentent par rapport à la technique primitive de BANERJEE une très nette amélioration de la sensibilité et de la précision. Il est d'ailleurs possible, si l'on veut réserver un volume plus grand à la prise d'essai, de préparer un réactif 5 fois plus concentré (dans ce cas, sa conservation atteint 3 ou 4 ans, même dans de très mauvaises conditions). La laque Th/SP, contrairement à certaines autres, peut d'ailleurs tout aussi bien être utilisée immédiatement, sans qu'il soit nécessaire de la laisser mûrir. Nous avons également constaté que la lecture des gammes colorées et des tubes de dosage pouvait être faite indifféremment soit dès leur préparation soit après attente, même longue.

Par la méthode spectrophotométrique, appliquée à des solutions de NaF pures, l'écart absolu observé entre le résultat expérimental et la théorie varie en

\* C'est cette sensibilité particulièrement avantageuse qui avait déjà fait choisir entre de nombreux autres ce réactif à MATTHEY et ses collaborateurs<sup>7</sup> qui appliquaient sous sa forme primitive de technique volumétrique, la méthode de BANERJEE.

général entre 0 et  $\pm 0.2 \mu\text{g F}$  (il atteint rarement  $0.5 \mu\text{g}$  et ne les dépasse qu'exceptionnellement). L'erreur relative varie donc avec l'importance de la dose de fluor, et il semble que les résultats obtenus soient très acceptables en considérant la faiblesse des doses mises en oeuvre. La méthode par titrimétrie colorimétrique, un peu moins pratique, donne des résultats sensiblement analogues, mais demande peut-être un expérimentateur plus entraîné, et surtout un contrôle très strict du pH si l'étalonnage et le dosage ne sont pas effectués en même temps et donc pas forcément avec les mêmes réactifs. La spectrophotométrie ne présente pas au même degré cet inconvénient puisque la préparation des gammes et celle des tubes de dosage sont en général simultanées. Mais, par contre, la titrimétrie colorimétrique peut permettre de déceler la présence d'un élément perturbateur inattendu qui, dans certains cas, pourrait passer inaperçu dans la technique des gammes.

Nous avons appliqué ces deux techniques au dosage du fluor, après minéralisation par la méthode de SCHÖNIGER, dans quelques produits organiques fluorés dont certains contenaient également de l'azote, du soufre et du chlore. Sur des séries de dosages effectués sur un même minéralisat par spectrophotométrie, nous retrouvons en général des écarts absolus du même ordre mais pouvant parfois être un peu plus élevés (environ  $1 \mu\text{g}$ ). La titrimétrie colorimétrique donne des résultats d'une exactitude comparable, mais qui, dans le cas des minéralisats, sont parfois plus difficiles à déterminer avec précision. De toute façon, il est possible d'améliorer cette dernière en effectuant la moyenne de plusieurs déterminations, de préférence du reste sur des minéralisats différents.

#### RÉSUMÉ

On a étudié en détail la réaction fluorure-laque thorium/SPADNS, en examinant en particulier l'influence du pH et du milieu. On décrit deux méthodes de microdosage des fluorures, basées sur cette réaction. Le dosage spectrophotométrique convient mieux pour les analyses de routine; cependant la titrimétrie colorimétrique est moins sensible à l'influence de fortes teneurs en électrolyte.

#### SUMMARY

The reaction of fluoride with thorium-SPADNS lake was studied in detail with particular reference to the effects of pH and media. Two methods for the determination of microgram amounts of fluoride based on the reaction are described. The spectrophotometric method developed is more suitable for routine use, but the colorimetric titration method is less sensitive to the effect of large amounts of electrolyte.

#### ZUSAMMENFASSUNG

Die Reaktion von Fluorid mit Thorium-SPADNS-Lack wurde im einzelnen untersucht unter besonderer Berücksichtigung der Einflüsse des pH-Wertes und des Mediums. Zwei Methoden zur Bestimmung von Mikromengen Fluorid, die auf dieser Reaktion beruhen, werden beschrieben. Die spektralphotometrische Methode ist für Routineanalysen geeigneter. Die kolorimetrische Titrationsmethode reagiert weniger empfindlich auf den Einfluss grosser Elektrolytmengen.

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## A STUDY OF GLUTAMINE INTERFERENCE IN THE ACIDIFIED NINHYDRIN REACTION FOR PROLINE\*

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The colorimetric procedure for proline based on the formation of a red-orange reaction product with acidified ninhydrin<sup>1,2</sup> is subject to a variety of interferences. These include color formation by other imino and amino acids<sup>1-5</sup>, inhibition of color formation by cystine<sup>5</sup>, and color intensification by glycine and other noncolor-forming amino acids<sup>3</sup>. However, it appears that a limited amount of interferences can be tolerated and that color intensification can be used to advantage. Glutamine interference is normally not encountered when this procedure is used for protein hydrolysates. However, during the application of this procedure to the analysis of free proline, a high concentration of glutamine in plant extracts was a source of major error. The use of a ratio of linear errors (RLE) method for the correction of error due to the presence of a high concentration of glutamine without prior quantitative assay of glutamine or further processing of the sample, the conditions for obtaining the RLE, and some characteristics of glutamine interference are described in this paper. The RLE method is based on the delineation of the upper and lower limits of proline content of a ninhydrin-reacted sample containing glutamine by spectrophotometric measurement at 517 and 495 mm and subsequent division of the spread in the same ratio as the RLE.

### EXPERIMENTAL

#### *Proline analysis*

The procedure for proline determination was essentially that of TROLL AND LINDSLEY<sup>2</sup>. Five ml of plant extract in 70% ethanol or an aliquot of standard diluted to 5 ml with 70% ethanol was measured into a test tube. To this was added 5 ml of water containing glycine and/or glutamine (double the desired amount per reaction mixture) and one g of Permutit unless otherwise indicated. The mixture was shaken for 15 min and then centrifuged. Five ml of the supernatant liquid was measured into a screw-capped 20 × 150-mm borosilicate test tube. To this was added 5 ml each of acetic acid and ninhydrin reagent. This is referred to as the reaction mixture. After capping and thorough mixing, the tube was placed in a 95° steam bath for 30

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min, and, after the addition of 5 ml of benzene, shaken vigorously for 2 min. The benzene-ethanol phase was siphoned into a 10-ml volumetric flask using 70:30 benzene-ethanol mixture for rinsing. The color was measured spectrophotometrically at 517 (absorption maximum) and 495 nm (minimum shoulder).

## RESULTS

Interference of glutamine in the Troll and Lindsley modification of the Chinard procedure became apparent when values could not be confirmed by the chromatographic method of PASIEKA AND MORGAN<sup>6</sup>. Subsequent two-dimensional chromatograms of the plant extracts showed a high concentration of glutamine and little or no proline in certain portions of the plant. Spectral characteristics of the glutamine-ninhydrin product were identical with that of the interfering compound (Fig. 1). Glutamine was only partially removed by treatment with Permutit. The residue formed an orange color<sup>1,3</sup> with acidified ninhydrin very similar to the red-

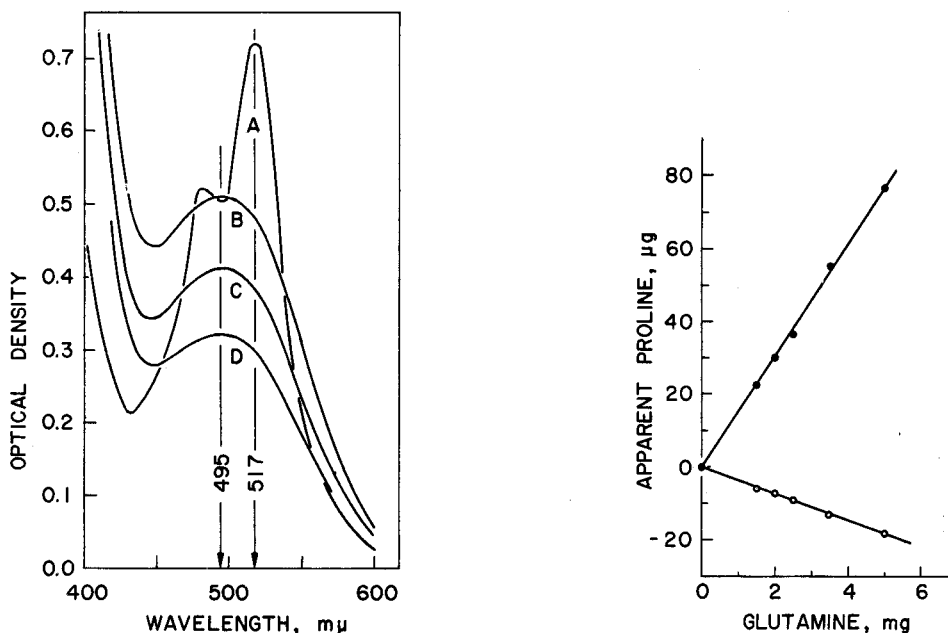


Fig. 1. Spectral characteristics of the proline- and glutamine-ninhydrin reaction products. (A) 35  $\mu$ g of proline. (B) 2.5 ml of diluted ( $3\times$ ) iris root extract. (C) 1.0 mg of glutamine without Permutit. (D) 1.0 mg of glutamine treated with 1 g of Permutit.

Fig. 2. Apparent proline-glutamine relationship. No proline was added; 4 mg of glycine per reaction mixture was added. Upper line is based on  $OD_{517}$  and the lower line on  $OD_{517} - OD_{495}$ . Unit weights are per reaction mixture.

orange of proline; 70  $\mu$ g of glutamine produced a color equivalent to roughly 1  $\mu$ g of proline measured at 517 nm.

Measurement of developed proline solutions at the usual 517 nm absorption peak ( $OD_{517}$ ) was compared to the measurement of 517 nm absorption peak minus the 495 nm shoulder ( $OD_{\Delta}$ ) since proline changed greatly in this region while glutamine

changed little. The interference encountered at  $OD_{517}$ , the principal absorption peak of the proline-ninhydrin compound, could be partially overcome by using  $OD_{\Delta}$ . However, a relatively small negative error resulted in this case in contrast to the positive error using  $OD_{517}$ . The true value for proline was situated between the value based on  $OD_{517}$  and the value based on  $OD_{\Delta}$ . Thus, the upper and lower limits of proline content in a sample containing glutamine could be described by photometric measurements at 517 and 495 nm. The errors of the two methods of measurement were linear functions of glutamine concentration (in the presence of adequate glycine) so that dividing the error ( $\mu\text{g}$ ) obtained from the  $OD_{517}$  measurement by the error obtained from the  $OD_{\Delta}$  measurement gave a RLE independent of glutamine concentration.

In photometrically measuring developed solutions containing glutamine but no proline (Fig. 2), the  $OD_{517}$  measurement resulted in an apparent proline error 4 times greater than that of the  $OD_{\Delta}$  measurements. Both errors were linear with respect to glutamine concentration. With the introduction of proline into the system, the ratio of the error of the proline value based on  $OD_{517}$  to the error of the value based on  $OD_{\Delta}$  decreased. Thus, increasing the proline level has a tendency to change the propor-

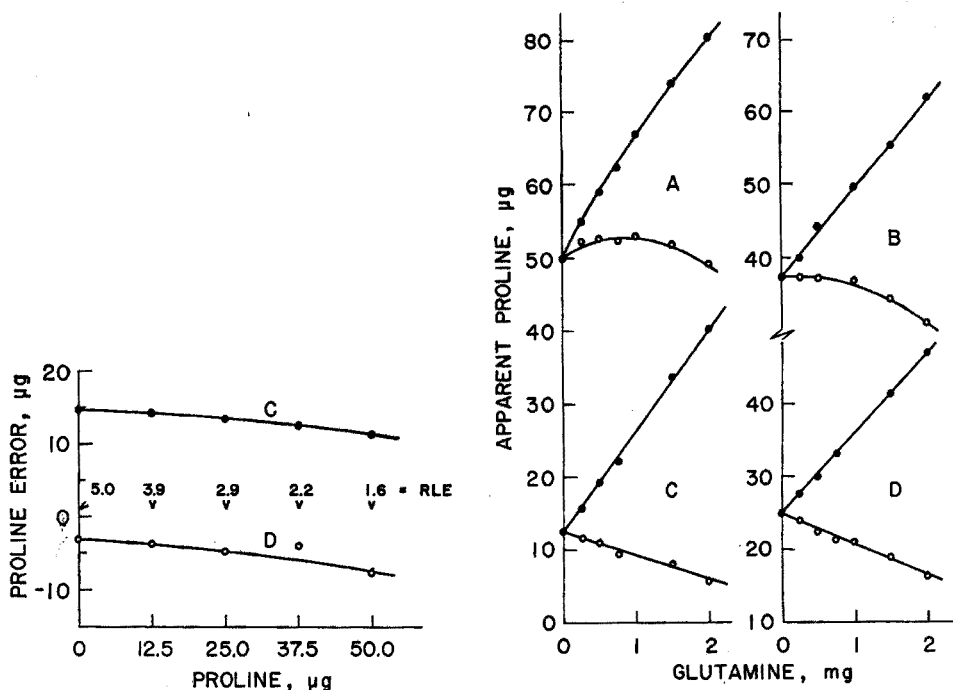


Fig. 3. Relationship of error to concentration of proline per reaction mixture in the presence of 1 mg of glutamine. Curve C is based on  $OD_{517}$ ; curve D is based on  $OD_{517}-OD_{495}$ . No Permutit was used. Each point was calculated on the basis of a glutamine-free standard run at the given proline level with 2.5 mg of glycine.

Fig. 4. Linear and non-linear glutamine errors. (A) 50  $\mu\text{g}$  of proline, 0.65 mg of glycine per reaction mixture. (B) 37.5  $\mu\text{g}$  of proline, 1.0 mg of glycine. (C) 12.5  $\mu\text{g}$  of proline, 0.5 mg of glycine. (D) 25  $\mu\text{g}$  of proline, 2.0 mg of glycine. The upper lines of A, B, C, and D represent measurements based on  $OD_{517}$ . The lower represent those based on  $OD_{517}-OD_{495}$ . All apparent values were calculated on the basis of standards equivalent in proline and glycine concentration to a glutamine-free mixture.



tionality of the errors in favor of a decrease in the numerical value of the RLE. This is more clearly illustrated in Fig. 3 which shows that with increasing proline the positive error decreases and the negative error increases resulting in an exponential decrease of the RLE.

In the absence of, or in the presence of insufficient glycine or glycine effect during color development, apparent proline–glutamine relationships of types A and B shown in Fig. 4 were obtained, where the errors are not linear with glutamine concentration. At a suitable glycine concentration, proline–glutamine relationships of types C and D (Fig. 4) were obtained where the errors are linear. Linearity of the errors with glutamine was maintained if the minimum glycine concentration for a given proline level was present. The lower limits of the glycine concentrations were about 1.5 mg for the 25- $\mu$ g and 37.5- $\mu$ g proline level and 0.5 mg for the 12.5- $\mu$ g level.

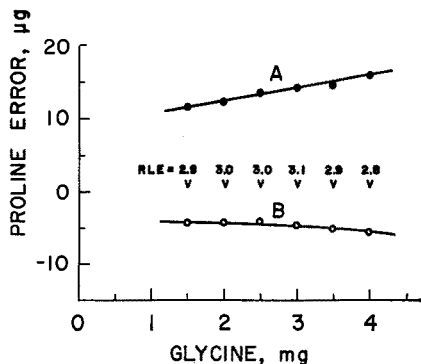


Fig. 5. Relationship of error to the concentration of glycine per reaction mixture in the presence of 1 mg of glutamine. Proline present was 25  $\mu$ g. No Permutit was used. Curve A is based on  $OD_{517}$ ; Curve B is based on  $OD_{517}-OD_{495}$ . Each point was calculated on the basis of a glutamine-free standard at the given glycine level.

Figure 5 shows changes in errors resulting from the measurement of 25  $\mu$ g of proline in the presence of 1 mg of glutamine based on  $OD_{517}$  (A) and  $OD_{\Delta}$  (B). The positive error increased almost proportionally to the negative error with the increase in glycine resulting in a nearly constant RLE of about 3.0. Thus, the RLE at the 25- $\mu$ g level is relatively unaffected by the glycine concentration in the range of 1.5 to 4 mg per reaction mixture although the optimum developed density is lowered if the glycine concentration is excessive or insufficient. At 12.5  $\mu$ g of proline similar errors were obtained with the RLE centering on 3.8.

The optimum glycine concentration for color development in the 12.5–37.5  $\mu$ g proline range (using Permutit) was 2.5 mg per reaction mixture for a development time of 30 min at 95° (Fig. 6). The presence of glycine in lesser or greater amounts resulted in the loss of the final optical density. With the introduction of one mg of glutamine the optimum glycine level remained essentially the same. If Permutit was not used an unexplained increase in the density took place and the optimum glycine concentration shifted from 2.5 mg to 1.0 mg per reaction mixture. The cause appears to be an adsorption of proline in the presence of an insufficient concentration of glycine. However, this effect disappeared at 4.0 mg of glycine.

The optimum development time (using Permutit) at 95° was 35–40 min with 1–2 mg of glycine per reaction mixture; 30–35 min with 2–4 mg of glycine; and about

30 min with 5 mg of glycine. The relative optimum density at 3, 4 and 5 mg of glycine were 97, 89 and 83 %, respectively, when compared with the density obtained with 2.5 mg of glycine. With 9 mg the optimum time was reduced to 18 min but with 40% loss of density. As noted by MESSER<sup>3</sup>, faster development of color with glycine was accompanied by a more rapid fading.

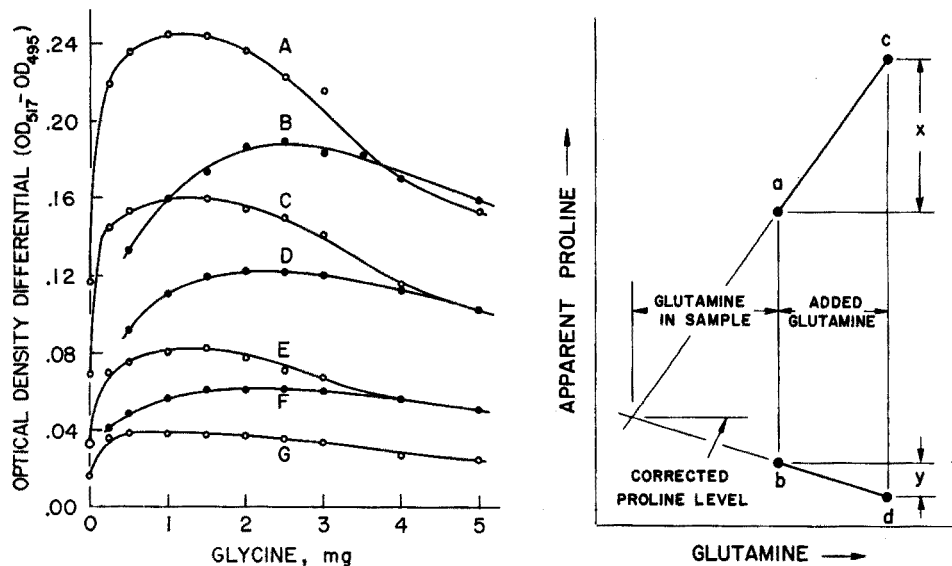


Fig. 6. Relationship of optical density differential ( $OD_{517}-OD_{495}$ ) to glycine concentration per reaction mixture. Proline concentration was (A and B)  $37.5 \mu\text{g}$ , (C and D)  $25.0 \mu\text{g}$ , (E and F)  $12.5 \mu\text{g}$ , (G)  $6.25 \mu\text{g}$ . In A, C, E, and G no Permutit was used.

Fig. 7. Diagram illustrating the ratio of linear errors method for converting proline values to the glutamine-free state. Points a and b represent apparent proline values of the sample in  $\mu\text{g}$  based on  $OD_{517}$  and  $OD_{517}-OD_{495}$ , respectively. Points c and d represent proline values of an identical sample run after addition of glutamine. The intercept of the lines extended through points a, c and b, d indicates the corrected proline value.

## DISCUSSION

In practice, proline concentration can be regulated by dilution. However, the additive intensification effect<sup>3</sup> of the several amino acids is more difficult to control. The answer here is to run the unknown sample with Permutit at several dilutions (or with added glycine) to determine the point where the unit proline value falls to three-fourths of the optimum value. If the assumption is made that at this point the intensification effect present in the sample is equivalent to 0.5 mg of glycine per reaction mixture (Fig. 6), then 2.0 or 3.5 mg of additional glycine can be added so that it will be comparable with a standard containing 2.5 or 4.0 mg of glycine per reaction mixture. Linear errors being assured at these glycine concentrations, the numerical value of the RLE,  $x/y$  (Fig. 7), can be obtained by adding glutamine and rerunning the sample along with a comparable sample containing no added glutamine to obtain points a, b, c, d, where a and c represent proline values ( $\mu\text{g}$ ) based on  $OD_{517}$  without and with added glutamine, respectively. Points b and d represent proline values based on  $OD_{\Delta}$  with-

out and with added glutamine, respectively. The change in the respective readings caused by the added glutamine ( $x$  and  $y$ ) will give the RLE applicable in this case. The corrected proline value ( $\mu\text{g}$ ) then equals

$$\left[ b + \left( \frac{1}{x/y + 1} \right) (a - b) \right]$$

The standard deviation of a corrected proline value based on added glutamine at any given level in the range 250–2000  $\mu\text{g}$  was  $\pm 0.4 \mu\text{g}$  at the 25- $\mu\text{g}$  proline level.

The valuable technical assistance of Mrs. Clara BEDNORZ is gratefully acknowledged.

#### SUMMARY

In the application of the acidified ninhydrin reaction to the estimation of free proline in plant extracts, glutamine was a major source of interference, all others being minor, absent or removable with Permutit. Some characteristics of glutamine interference in this reaction are described. A ratio of linear errors method for the correction of proline values to the glutamine free state is introduced. The glycine and proline concentration in the reaction mixtures are prime factors in obtaining a ratio of linear errors by spectrophotometric measurement at 2 wavelengths.

#### RÉSUMÉ

La réaction de la ninhydrine acidifiée pour le dosage de la proline libre dans des extraits de plantes, est perturbée par la glutamine. On propose une méthode pour la correction des teneurs en proline par rapport à la glutamine à l'état libre.

#### ZUSAMMENFASSUNG

Bei der Anwendung der sauren Ninhydrinreaktion für die Abschätzung von freiem Prolin in Pflanzenextrakten stört Glutamin am meisten, während andere Störungen gering oder mit Permutit zu beseitigen sind. Einige Charakteristiken der Störung durch Glutamin bei dieser Reaktion werden beschrieben. Es wird eine Methode zur Korrektur der Pyrolinwerte eingeführt. Dabei werden die Glycin- und Prolin-konzentrationen, die durch spektralphotometrische Messungen bei 2 Wellenlängen erhalten werden, berücksichtigt.

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## MICRODETERMINATION OF ZINC BY MEANS OF REAGENT CRAYONS AND THE RING-OVEN TECHNIQUE

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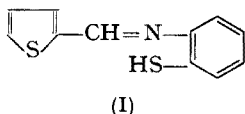
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Although zinc is not a highly toxic element, its wide occurrence and use warrants the development of a rapid and simple method for its microdetermination. Such a method could find application in the study of the pathological effects of zinc fumes and dust in air on the human system<sup>1</sup>.

Conventional methods for the determination of zinc in air are described by JACOBS<sup>2</sup>. Both the ferrocyanide and the dithizone methods are long and tedious and require special steps for removing interferences. KAWASE<sup>3</sup> has recently developed a spectrophotometric method for the determination of trace amounts of zinc down to 0.1  $\mu\text{g}$  using 1-(2-thiazolylazo)-2-naphthol. Mercury(II), bismuth(III), manganese(II), cadmium and uranium(VI) interfere. TRENHOLM AND RYAN<sup>4</sup> report that dibenzothiazolylmethane produces a specific fluorescence with zinc in ethanol-water solution; they determined zinc quantitatively in solutions containing 0.05–50 mg of zinc per liter.

THABET AND TABIBIAN<sup>5</sup> have shown that *o*-mercaptothelalaniline is a selective and sensitive reagent for zinc producing intensely red chelates which are extractable into chloroform. The ring-oven which has proved to be a simple and efficient tool for air pollution investigations<sup>6–11</sup> seems to be particularly suited for the microdetermination of zinc provided the reagent is selective. In the method which is proposed, *o*-mercaptothelalaniline (I) is used as a reagent for zinc with necessary modifications introduced to make the procedure adaptable to the ring-oven. The reagent can be applied in conventional solution form or it may be applied in the form of a convenient reagent crayon.



The effect of interfering or colored ions is overcome by addition of potassium cyanide which complexes many ions or provides a sufficiently alkaline medium to precipitate possible interfering species. Zinc must be demasked before it can be determined but this is selectively accomplished by the addition of chloral hydrate. Gratifying specificity is obtained. The concentration effect obtained by the ring-oven technique permits the detection of as little as 0.04  $\mu\text{g}$  of zinc. The method is particularly suited for the rapid microdetermination of zinc in the range 0.1 to 1.0  $\mu\text{g}$ .

## EXPERIMENTAL

*Reagents and standard solutions*

*o*-Mercaptothenalaniline is prepared by adding 1.12 g of thiophene-2-aldehyde to 1.25 g of *o*-aminobenzenethiol in a 15-ml centrifuge tube. The mixture is well shaken, 4 ml of distilled water are added and the test tube is placed in a bath of boiling water for 30 min after which it is centrifuged for 3 min and allowed to stand overnight. The clear supernatant liquid is decanted and the condensed product, spread on a watch glass, dries to a yellow solid upon exposure to the atmosphere. The solid is repeatedly recrystallized from low-boiling petroleum ether, the dark oily residue being discarded. Bright yellow crystals are obtained (m.p. 96–97°). Reagent solutions are prepared by dissolving 0.1 g of reagent in 10 ml of chloroform and should be kept in a dark bottle and stored in the refrigerator when not in use. In this form the reagent is stable for at least one month. The reagent in crayon form is prepared by melting 3.5 g of monoglyceryl stearate and 1.5 g of paraffin wax in a test tube maintained in a hot water bath, adding 0.1 g of reagent, stirring well and then drawing the melt into a waxed paper straw. Upon cooling the crayon may be exposed as needed by peeling off the protective paper and is used by rubbing its tip so as to contact the reagent with the deposit in the ring.

*Standard stock zinc solution.* A solution containing 1.00  $\mu\text{g}$  zinc per  $\mu\text{l}$  was prepared by dissolving 100 mg of pure zinc metal in a few drops of concentrated nitric acid, boiling gently to expel brown fumes and making up to 100 ml with distilled water. The standard stock solution was diluted as necessary for preparing standard working solutions.

*Apparatus*

Weisz ring-oven with accessories, National Appliance Co., Portland, Oregon.  
Powerstat, Superior Electric Co., Bristol, Connecticut, Type 116.

Pandux surface temperature thermometer, range +20° to 180°, Pacific Transducer Corp., Los Angeles 64, California.

Munktells No. 00 filter paper, 55 mm diameter, or Whatman No. 41 either in the form of filter paper (55 mm diameter) or as sequential dust sampler tapes.

*Elimination of interferences*

A limited number of ions react with the reagent giving colored products.

Extraction techniques whereby the reaction was carried out in the center of the filter paper and the zinc chelate washed out with chloroform were investigated in attempts to attain test specificity. Results were not, however, encouraging and because such a technique would also eliminate the possibility of using the reagent in crayon form, this approach was abandoned. Precipitation of the interfering ions with rubenic acid or with sulfide did not give satisfactory results.

An interesting and promising technique consisted in precipitating most of the cations with sodium hydroxide and washing the zinc to the ring zone in the form of zincate. This gave excellent results for zinc alone, but when other ions and particularly iron(III) were present, the sodium hydroxide was no longer able to wash the zinc through the precipitate to the ring zone. If ammonium hydroxide was used to wash the zinc, certain of the ammine-forming cations would interfere.

Before adopting the final procedure, various masking agents were investigated. Ligands tested for possible masking ability included acetate, oxalate, tartrate, citrate, malonate, thiosulfate, thiourea, phosphate, pyrophosphate, triphosphate, thioglycolic acid, EDTA and triethanolamine. None of the ligands studied could be used because they each either reduced the sensitivity of the zinc reactions or prevented it completely.

The most effective masking agent proved to be the cyanide ion. With it, zinc, cadmium, cobalt(II), nickel, copper(II), mercury(I,II), gold(III) and the platinum metals are converted into stable complexes. Addition of chloral hydrate selectively liberates zinc and cadmium from mixtures of the various cyanide complexes and the demasked zinc can be determined directly.

#### *Recommended procedure*

Make a tiny pencil mark on the center of the filter paper and then place on a ring-oven at 90–95°. Add 10  $\mu$ l of 2% potassium cyanide solution from a calibrated  $\mu$ l pipet followed by an appropriate volume of zinc solution. Add another 10  $\mu$ l of potassium cyanide, followed by 5  $\mu$ l of 10% chloral hydrate solution, and wash the mixture to the ring zone using 5 10- $\mu$ l portions of 6 *M* ammonium hydroxide. Leave the filter paper on the ring-oven until the outer part is dry, then remove and allow to dry completely at room temperature. Add the reagent either by spotting the ring with reagent solution or by rubbing the test area with the reagent crayon. If the reagent has been added in the crayon form, expose the filter paper to a current of hot air from a hair drier until the wax melts and makes intimate contact with the deposited zinc. Regardless of the manner in which the reagent has been added, dip the filter paper finally in a 0.2% sodium hydroxide bath and allow to dry at room temperature. Orange rings, the intensities of which depend on the concentration of zinc, will appear against a very pale yellow background.

A simplified approach suitable for many air pollution studies is to collect samples with a sequential tape sampler and determine the zinc directly on the tape. The sampler orifice preferably should be less than 22 mm so that the total sample can be centered on the ring oven without the spot extending to the ring area. The sample spot is first positioned on the ring-oven moistened with hydrochloric acid (1 *M*) and the dissolved salts washed to the ring zone using a 10- $\mu$ l portion of distilled water followed by 2 10- $\mu$ l portions of potassium cyanide solution. Chloral hydrate (5  $\mu$ l) is then added followed by the ammonium hydroxide washes, reagent treatment and following operations as described above. Results will be only semi-quantitative because only a single ring of sample is compared with the standards.

## RESULTS AND DISCUSSION

#### *Choice of filter paper*

An investigation of the characteristics of a number of filter papers showed that the best results are obtained with Munktells No. 00. This paper which is available already washed with hydrochloric and hydrofluoric acids produces no blank and has uniform concentric diffusion, its strength while wet is good and the speed of diffusion is satisfactory. Munktells No. 00R proved to be equally satisfactory although it exhibits a lower strength when wet. Whatman No. 41 leaves no blank and has good

speed and strength. Whatman filter paper No. 41 which is also available in the form of tapes for use on sequential dust samplers can be used for collecting airborne particulates.

#### *Precautions and observations*

The usual recommendations in ring-oven techniques must be followed. Care must be taken to have all pipets well centered on the pencil mark. The order of addition of reagents is important; cyanide should be added both before and after the sample so that irrespective of diffusion rates, the sample will be properly mixed with the masking agent.

For rings containing  $0.3 \mu\text{g}$  of zinc or more, the orange rings appear immediately after treatment with the reagent and without dipping in sodium hydroxide. For lower concentrations of zinc the rings develop completely in 20 min. In all cases, however, it was found that dipping in sodium hydroxide increased the intensity of the ring color. For quantitative estimations the color intensity of the ring should be compared at least 20 min after the sodium hydroxide bath. The rings obtained tend to fade slowly with time. Therefore the standard scale should be prepared on the day the quantitative determination is carried out.

Unsuccessful attempts were made to wash out the very pale yellow background left by excess reagent without affecting the intensity of the rings. However, the background color does not prevent the observation and evaluation of rings and the problem must be considered as an aesthetic rather than practical one.

#### *Analysis of an unknown*

The preparation of rings for the standard scale and for an unknown follows the above procedure. A standard scale can be conveniently prepared by making rings with 0, 1, 3, 5, 7, 9 portions of  $10 \mu\text{l}$  of a solution of zinc containing  $0.01 \mu\text{g}$  per  $\mu\text{l}$ . Three rings made from different numbers of microliters of solution are sufficient for each unknown. The color of each of the 3 rings is matched with the standard scale and it is decided whether it matches one of the rings or it falls between 2 rings. The quotient obtained from dividing the total number of microliters of the 3 unknown rings, by the total microliters of the matching standard ring, where multiplied by the concentration of the standard solution gives the concentration of the unknown<sup>12</sup>.

#### *Interferences and foreign ions*

The effect of foreign ions was investigated by developing 2 rings for each species using the above procedure. The first ring contained  $10 \mu\text{g}$  of the foreign ion while in the second ring  $10 \mu\text{g}$  of the foreign ion and  $0.1 \mu\text{g}$  of zinc were present. Non-interference was recorded for all cases when the first ring gave no blank or gave a ring less intense than  $0.05 \mu\text{g}$  zinc and the second matched a ring containing  $0.1 \mu\text{g}$  zinc when judged visually. The following ions did not interfere:

Group I.  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Au}^{3+}$ .

Group II.  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ .

Group III.  $\text{BO}_2^-$ ,  $\text{Al}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ .

Group IV.  $\text{CO}_3^{2-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{Ti}^{4+}$ ,  $\text{GeO}_3^{2-}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Th}^{4+}$ , acetate, oxalate, citrate, tartrate, malonate, phthalate and succinate.

Group V.  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{VO}_3^-$ ,  $\text{AsO}_3^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sb}^{5+}$  and  $\text{Bi}^{3+}$ .

Group VI.  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{TeO}_3^{2-}$ ,  $\text{TeO}_4^{2-}$ ,  $\text{Cr}^{3+}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{ReO}_4^-$  and  $\text{UO}_2^{2+}$ .

Group VII.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_3^-$ ,  $\text{Mn}^{2+}$ ,  $\text{MnO}_4^-$ ,  $\text{Br}^-$ ,  $\text{BrO}_3^-$ ,  $\text{I}^-$ ,  $\text{IO}_3^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ .

Group VIII.  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Rh}^{4+}$ ,  $\text{Ru}^{3+}$  and  $\text{Pt}^{4+}$ .

The following ions were found to interfere: silver(I), thallium(I), mercury(I and II) and gallium(III). Mercury(I and II), silver(I), thallium(I) or cadmium when present in concentrations of 10  $\mu\text{g}$  give intense yellow rings which mask zinc. Gallium(III) gives an orange ring which can be mistaken for zinc. When mercury(I and II) and silver(I) are decreased to 1  $\mu\text{g}$  they no longer interfere while cadmium at concentrations of 1  $\mu\text{g}$  masks the zinc test. The interfering effect of cadmium can be overcome by changing the procedure when the latter is present. First 10  $\mu\text{l}$  of 1% sodium hydroxide solution is added followed by the sample containing cadmium; 10 10- $\mu\text{l}$  portions of sodium hydroxide are then added and the filter paper is dried and dipped in a 0.2% sodium hydroxide solution. No ring is obtained with 10  $\mu\text{g}$  of cadmium and 1  $\mu\text{g}$  of cadmium does not prevent the formation of a ring with 0.1  $\mu\text{g}$  zinc.

While the interfering effect of cadmium is expected since the overall  $\text{p}K$  values of the cyanide complexes of cadmium and zinc are 18.9 and 16.7 respectively, the interfering effect of mercury is surprising since mercury forms stable cyanide complexes with overall  $\text{p}K$  values of the order of 41.5<sup>13</sup>. Silver cyanide with a  $\text{p}K$  value of 20.7 is expected to interfere. No further investigations were carried out on the interfering effects of gallium and thallium since these would be of little concern in air pollution.

When manganese is present, care must be taken to avoid washing the hydrated manganese oxide to the ring zone. This can be achieved by allowing the filter paper to dry between addition of reagents and adding ammonium hydroxide very slowly.

When copper is present, a black to grey stain appears around the ring zone on standing, probably due to the slow release of copper by chloral hydrate. This however, takes place about 60 min after the ring has been developed and does not therefore interfere with the zinc ring at the time of comparison. With nickel a violet stain appears towards the center of the filter paper about 24 h after the ring has been developed.

The non-interference of anions illustrates the effectiveness of cyanide and ammonia masking.

#### *Accuracy and reproducibility of quantitative estimation*

The accuracy and reproducibility of this method for the microdetermination of zinc were ascertained by the method of WEISZ<sup>12</sup>. Standard scales covering the range 0.05–1.0  $\mu\text{g}$  zinc were prepared by the described procedure. Rings obtained from 10, 30, 50 and 70  $\mu\text{l}$  of an unknown were also developed and matched with standard rings. The ratio of the number of microliters of unknown to the number of microliters of standard is the concentration of the unknown solution referred to the standard solution. When this ratio is multiplied by the concentration of the standard (0.01  $\mu\text{g}$  zinc per  $\mu\text{l}$ ) the concentration of the unknown sample is obtained.

Results of analyses of 2 unknowns are given in Table I.



Although the method presented permits the detection of 0.04  $\mu\text{g}$  of zinc, the recommended range covers 0.1–1.0  $\mu\text{g}$  of zinc. For air pollution investigations a greater sensitivity would not be required particularly in view of the fact that the MAC value for zinc is 15 mg/m<sup>3</sup>. Concentrations above 1.0  $\mu\text{g}$  of zinc give rings of such intensity that visual comparison becomes difficult.

TABLE I  
DETERMINATION OF ZINC

Taken ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ ) <sup>a</sup>
0.3	0.297 $\pm$ 0.013 <sup>b</sup>
0.5	0.497 $\pm$ 0.033 <sup>b</sup>

<sup>a</sup> Based on averaging 5 values calculated from 3 rings each.

<sup>b</sup> Calculated at 90% confidence limit.

This investigation was supported in whole by Public Health Service Research Grant AP 00117 from the Division of Air Pollution, Bureau of State Services.

#### SUMMARY

A sensitive and highly selective method for the rapid microdetermination of zinc by the ring-oven technique is presented. Very few cations when present in 100-fold excess interfere while anions do not interfere. The optimal range is 0.1–1.0  $\mu\text{g}$  zinc, which suggests its special applicability in air pollution investigations.

#### RÉSUMÉ

On propose une méthode sensible et très sélective pour le microdosage rapide du zinc, à l'aide de la technique du four circulaire. Très peu de cations, en concentration 100 fois supérieure gênent; aucun anion ne gêne. Il est possible de doser 0.1 à 1  $\mu\text{g}$  de zinc, ce qui est intéressant dans le cas de recherches sur la pollution de l'air.

#### ZUSAMMENFASSUNG

Es wird eine empfindliche und hochselektive Methode zur schnellen Mikrobestimmung von Zink mit der Ringofentechnik beschrieben. Sehr wenige Kationen stören, wenn sie im hundertfachen Überschuss anwesend sind; Anionen stören nicht. Der optimale Bereich liegt bei 0.1–1.0  $\mu\text{g}$  Zink, was darauf schliessen lässt, dass diese Bestimmung sich besonders zur Untersuchung von Luftverunreinigungen eignet.

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## POLAROGRAPHY OF URANYL-NITRILOTRIACETATE COMPLEX

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The rate of dissociation of complexes of some metals such as cadmium, lead and zinc with nitrilotriacetic acid has been investigated polarographically<sup>1,2</sup>. The polarographic behaviour of the complexes of thallium and iron with nitrilotriacetic acid has been studied by several authors and the kinetics of the electrode processes and complex species at various pH values has been reported<sup>3-6</sup>.

The uranyl-nitrilotriacetic acid system has not been studied previously. In the present work this system was studied at 30° by the polarographic method.

## EXPERIMENTAL

*Apparatus*

The current-potential curves were obtained manually using a Sargent Model XII Polarograph, with a Leeds and Northrup Student's Potentiometer. The dropping mercury electrode used had an *m* value of 5.03 mg/sec and a drop time of 3.42 sec, being measured in an air-free 0.2 *M* sodium perchlorate solution at an applied potential of -0.200 V vs. S.C.E. and at 70 cm mercury height. All experiments were carried out at 30° ± 0.01°.

The pH values of the polarographic solutions were adjusted with perchloric acid or sodium hydroxide and determined by a Toa Denpa Model HM-5A glass electrode pH meter.

*Chemicals*

The preparation and standardization of the uranyl perchlorate solution used were the same as given in a previous paper<sup>7</sup>.

A 0.500 *M* nitrilotriacetic acid (NTA) solution was prepared by dissolving 9.558 g of N(CH<sub>2</sub>COOH)<sub>3</sub> (Dotite reagent grade) in concentrated sodium hydroxide solution and diluting to 100 ml with distilled water.

In all this work unless otherwise noted, the ionic strength was adjusted to 0.25 with 2 *M* sodium perchlorate solution. Triton X-100 (0.002% solution) was used as a maximum suppressor.

## RESULTS AND DISCUSSION

Because of the strong buffer action of nitrilotriacetic acid itself at pH < 4.0 and pH > 8.0, well defined and reversible reduction waves were obtained in the

absence of buffer when the ligand concentration was 0.025 *M*–0.500 *M* and the pH 1.5–4.1. However, above pH 4.1, the reversible waves became irreversible due to the lack of buffer action of the system and the acetate buffer was indispensable to the reversible electrode reduction. This was demonstrated by the slopes of the traditional plots of  $\log i/(i_a - i)$  vs.  $E_{a.e.}$ . As shown in Table I, at pH 1.50–4.10 in unbuffered solutions and at pH 3.00–6.50 in 0.020 *M* acetate buffer, the slopes were 0.055–0.064 indicating that the electrode reactions were one-electron reversible processes. The reversibility of the electrode process was further proved by the temperature coefficient of the half-wave potential, which was found to be  $-0.4 \text{ mV}/^\circ$  over the temperature range  $20^\circ$ – $40^\circ$  (Fig. 1).

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF URANYL-NITRILOTRIACETATE COMPLEX

(1.0 mM  $\text{UO}_2(\text{ClO}_4)_2$ , 0.025 *M* NTA, 0.002% Triton X-100 at  $\mu$  0.25)

Unbuffered solution				0.020 <i>M</i> acetate buffer			
pH	$-E_{\frac{1}{2}}$	$i_a$ ( $\mu\text{A}$ )	$\frac{E_{a.e.}}{\log i/(i_a - i)}$	pH	$-E_{\frac{1}{2}}$	$i_a$ ( $\mu\text{A}$ )	$\frac{E_{a.e.}}{\log i/(i_a - i)}$
1.50	0.192	5.70	0.055	3.00	0.246	5.75	0.058
2.50	0.231	5.75	0.056	4.00	0.297	4.82	0.056
3.70	0.284	4.03	0.059	5.00	0.344	4.10	0.059
3.90	0.295	3.45	0.057	6.00	0.368	2.75	0.059
4.00	0.300	3.17	0.061	6.30	0.380	2.40	0.060
4.10	0.305	2.90	0.064	6.40	0.384	2.35	0.062
4.20	0.314	2.67	0.068	6.50	0.389	2.30	0.064
5.00	0.362	2.50	0.071	6.60	0.397	2.10	0.068
6.00	0.427	2.30	0.073	6.70	0.402	2.00	0.071

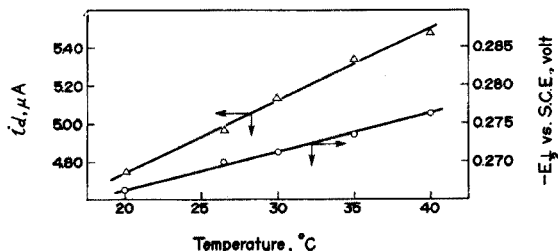


Fig. 1. Half-wave potential and diffusion current as a function of temperature.

The variation of the limiting current with the height of mercury column was measured by polarographing a solution of  $1.0 \cdot 10^{-3} \text{ M}$  uranyl perchlorate, 0.05 *M* nitrilotriacetic acid, 0.002% Triton X-100 and 0.2 *M* sodium perchlorate at pH 3.23. The current varied with the height of mercury; the value,  $i_d/h$ , where  $h$  is the height of column after correction for the back pressure, was  $0.491 \pm 0.007 \mu\text{A}/\text{cm}^{\frac{1}{2}}$  for  $h$  values of 50.2–85.3 cm, indicating that the electrode reactions are essentially diffusion-controlled.

The temperature coefficient of the diffusion current, 0.85% per degree, as shown in Fig. 1, also demonstrated that the reduction is a diffusion-controlled

process. This process is distinctly different from the iron(III)-nitrilotriacetic acid system, which is kinetic in nature<sup>5</sup>.

From the pronounced asymmetry of the polarograms in the solutions of pH 1.5-3.3, it was evident that the polynuclear complexes were formed<sup>8</sup>. However, above pH 3.3, the U(VI)-U(V) waves became symmetrical showing that no dimeric forms were present in detectable amount<sup>8</sup>.

#### *Effects of pH and ligand concentration on half-wave potential*

The effects of pH and ligand concentration on the half-wave potential were studied in the pH range 1.50-6.00 in unbuffered solutions and in the pH range 3.00-6.70 in 0.050 M acetate buffer solutions.

Figure 2 shows the half-wave potential as a function of pH value. In the pH range of 1.5-2.1, the half-wave potentials remain constant at -0.200 V, which is slightly more negative than that of the simple uranyl ion, -0.180 V vs. S.C.E.

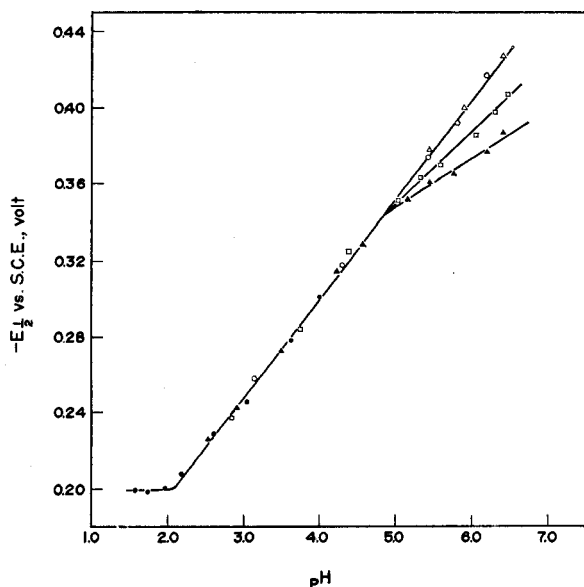


Fig. 2. Plot of  $E_{1/2}$  as a function of pH (1.0 mM  $\text{UO}_2(\text{ClO}_4)_2$  and 0.002% Triton X-100).

	Acetate (M)	NTA (M)	$\mu$
●	0	0.050	0.25
▲	0.050	0.050	0.25
□	0.050	0.100	0.25
○	0.050	0.250	0.50
△	0.050	0.500	1.00

Therefore, it was inferred that a weakly bound mono-protonated complex,  $\text{UO}_2\text{HX}$ , is present and undergoes electrode reduction without the participation of the hydrogen ion. In the pH range 2.1-4.8,  $-\Delta E_{1/2}/\Delta\text{pH}$  is 0.053, indicating that one hydrogen ion or hydroxyl ion was involved in the electrode reduction. Above pH 4.8, the line splits into 3 straight lines corresponding to the 3 concentrations of nitrilotriacetic

acid used. The slopes increase with increasing concentration of nitrilotriacetic acid until when  $[NTA] = 0.250 M$  (i.e. 5 times that of acetate buffer), the line just coincides with the original line.

From the  $pK_a$  (4.8) of acetic acid, it is evident that below pH 4.8 no appreciable amount of acetate ion is available to compete with the nitrilotriacetate ion for coordination with the uranyl ion. Even at  $pH > 4.8$ , when  $[NTA]:[Ac] > 5:1$ , the nitrilotriacetate ion still predominates and no acetate participates in the coordination. This was verified by the coincidence among the slopes of the plots of  $[NTA] = 0.250 M$ ,  $[NTA] = 0.500 M$  and that of  $[Ac] = 0$  and  $[NTA] = 0.050 M$  in Fig. 2. Thus, at  $pH > 4.8$  and when  $[NTA]:[Ac] > 5:1$ , the U(VI) and U(V) have the same ligand number and one hydrogen ion is consumed or one hydroxyl ion is released in the cathodic reduction.

However, at  $pH > 4.8$  and when  $[NTA]:[Ac] < 5:1$ , there will be enough acetate ion to compete with the nitrilotriacetate ion and to form a mixed ligand complex,  $UO_2(Ac)X^{2-}$ . The lower the ratio of  $[NTA]:[Ac]$ , the less steep the line, indicating that fewer hydrogen ions are involved in the reduction of the mixed ligand complex.

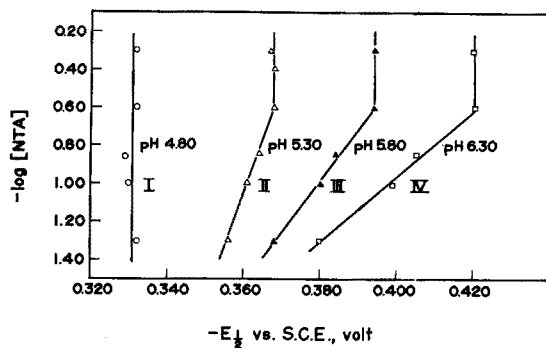
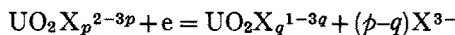


Fig. 3. Effect of  $\log [NTA]$  on  $E_{1/2}$  (1.0 mM  $UO_2(ClO_4)_2$ , 0.002% Triton X-100 and 0.050 M acetate).

Figure 3 illustrates the influence of the ligand concentration on the half-wave potentials. It is obvious from Figs. 2 and 3 that the half-wave potential is practically unaffected by variation in the ligand concentration in the pH range of 1.5–4.8. This shows that no nitrilotriacetate ion was involved in the electrode reduction of



wherein  $p - q = 0$  in the pH range of 1.5–4.8.

Beyond pH 4.8 and when  $[NTA] < 0.250 M$ , as shown in Fig. 3, the half-wave potentials depend on the ligand concentration; the reciprocal slopes increase with increasing pH value and reach 0.059 at pH 6.30, corresponding to  $p - q = 1$  (curve IV, Fig. 3). Since  $p = 1$  (as will be shown below) then  $q = 0$ . Therefore, it was concluded that the uranium(V)–nitrilotriacetate complex is unstable at high pH value and dissociates completely at pH 6.30. At  $pH > 4.8$  and  $[NTA] > 0.250 M$ , the half-wave potentials became independent of the ligand concentration, giving  $p - q = 0$ .

#### Effects of pH and ligand concentration on diffusion current

The effect of pH on diffusion current is shown in Fig. 4. As can be observed,

the diffusion current is independent of the hydrogen ion concentration up to pH 3.1 and pH 3.5 for unbuffered solution and acetate buffer solution, respectively, showing that a complex species with constant composition exists in this pH region. From the  $pK$  value of nitrilotriacetic acid ( $pK_1=1.9$  and  $pK_2=2.49$ )<sup>9</sup>, the ligand species is  $N(CH_2COO)_3^{3-}$  ion at  $pH > 2.49$ <sup>10</sup>, and the complex species is  $UO_2X^-$ . As the pH increases, the diffusion current decreases rapidly and attains a constant value at pH 4.2 and pH 6.4 for unbuffered and buffered solutions respectively. These results reflect the competition between hydroxyl ion, acetate ion and nitrilotriacetate ion for the electron pair donor group. In unbuffered solutions, from pH 3.1 to pH 4.2, the

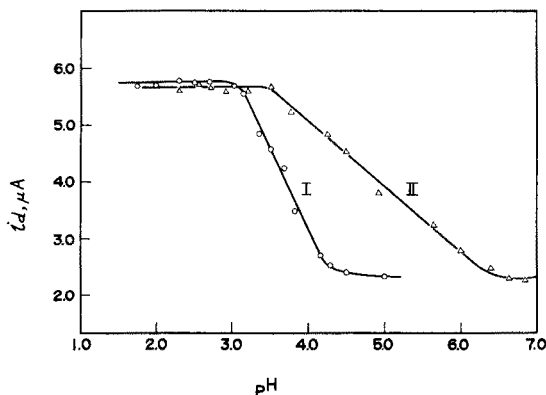


Fig. 4. Variation of diffusion current with pH (1.0 mM  $UO_2(ClO_4)_2$  and 0.002% Triton X-100).

	Acetate (M)	NTA (M)
(I)	0	0.050
(II)	0.050	0.050

TABLE II

EFFECT OF LIGAND CONCENTRATION ON DIFFUSION CURRENT

(1.0 mM  $UO_2(ClO_4)_2$  and 0.002% Triton X-100)

NTA (M)	$\mu$	$i_d (\mu A)$ [Ac]=0		$i_d (\mu A)$ [Ac]=0.050 M		
		pH 2.50	pH 3.50	pH 2.70	pH 4.50	pH 6.00
0.025	0.25	5.70	4.53	5.65	4.60	2.76
0.050	0.25	5.78	4.60	5.68	4.56	2.80
0.100	0.25	5.68	4.69	5.67	4.52	2.74
0.250	0.50	5.83	4.63	5.72	4.70	2.85
0.500	1.00	5.86	4.70	5.77	4.67	2.90

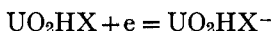
hydroxyl ion incorporates into the uranyl-nitrilotriacetate complex, forming  $UO_2(OH)X^{2-}$  chelate species. On the other hand, in acetate buffer solution, from pH 3.5 to 6.4, hydroxyl and then acetate substitute in the uranyl-nitrilotriacetate complex.

Table II illustrates the influence of ligand concentration on the diffusion current. Since uranyl ion is characteristically 4-coordinate and nitrilotriacetic acid behaves as tridentate or tetradentate, it seems reasonable to assign only one kind

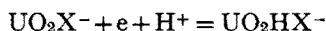
of 1:1 chelate for uranyl-nitrilotriacetate complex, although copper-nitrilotriacetate has been reported to form 1:1 and 1:2 chelates<sup>11</sup>. This deduction was supported by Table II, in which the constancy of the diffusion current with increasing ligand concentration, reflected the formation of a complex having only one kind of ligand number.

Based on the foregoing data and discussion the chelate species and electrode reactions may be summarized as follows:

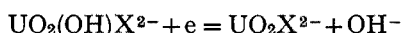
1.5 < pH < 2.1:



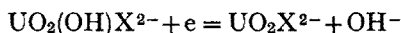
2.1 < pH < 3.1 (unbuffered); 2.1 < pH < 3.5 (acetate buffer):



3.1 < pH < 4.2 (unbuffered); 3.5 < pH < 4.8 (acetate buffer):



4.8 < pH < 6.5 (acetate buffer), [NTA]/[Ac] > 5:



The authors thank the National Council of Science Development which supported the work described.

#### SUMMARY

Polarographic studies of solutions of uranium(VI) and nitrilotriacetic acid were carried out in perchlorate medium at ionic strength 0.25. Reversible and diffusion-controlled reduction waves were obtained in the pH range of 1.5–4.1. Above pH 4.1, the irreversible waves became reversible in the presence of acetate buffer. Four kinds of chelate species,  $\text{UO}_2\text{HX}$ ,  $\text{UO}_2\text{X}^-$ ,  $\text{UO}_2(\text{OH})\text{X}^{2-}$  and  $\text{UO}_2(\text{Ac})\text{X}^{2-}$ , were identified. The U(V)–NTA complex was unstable at high pH and completely dissociated at pH 6.30. The effects of pH and ligand concentration on the wave parameters are discussed in detail.

#### RÉSUMÉ

Des études polarographiques ont été effectuées sur des solutions uranium(VI)–acide nitrilotriacétique, en milieu perchlorate, avec force ionique de 0.25. Echelle de pH: 1.5–4.1; au-dessus de 4.1, les vagues deviennent réversibles en présence d'un tampon acétate. On a identifié 4 composés:  $\text{UO}_2\text{HX}$ ,  $\text{UO}_2\text{X}^-$ ,  $\text{UO}_2(\text{OH})\text{X}^{2-}$  et  $\text{UO}_2(\text{Ac})\text{X}^{2-}$ . Le complexe U(V)–NTA est instable à pH élevé et complètement dissocié à pH 6.30.

#### ZUSAMMENFASSUNG

Es wurden polarographische Untersuchungen mit Uran(VI)-Lösungen und Nitrilotriessigsäure (NTE) im Perchloratmedium bei einer Ionenstärke von 0.25



durchgeführt. Reversible und diffusionskontrollierte Reduktionsstufen wurden im pH-Bereich von 1.5-4.1 erhalten. Oberhalb vom pH 4.1 wurden die irreversiblen Stufen in Gegenwart eines Acetatpuffers reversible. Vier Chelate wurden identifiziert:  $\text{UO}_2\text{HX}$ ,  $\text{UO}_2\text{X}^-$ ,  $\text{UO}_2(\text{OH})\text{X}^{2-}$  und  $\text{UO}_2(\text{Ac})\text{X}^{2-}$ . Der U(V)-NTE-Komplex war bei höherem pH instabil und beim pH 6.30 völlig dissoziiert. Die Einflüsse des pH-Werts und der Ligandenkonzentration auf die Stufenparameter werden im einzelnen diskutiert.

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*Anal. Chim. Acta*, 37 (1967) 253-259

## AMPEROMETRIC TITRATIONS OF ORGANOLEAD AND ORGANOTIN IONS

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In recent years, coordination compounds of lead and tin have been subjected to much study. It has been shown that dialkyltin and dialkyllead ions form stable coordination compounds with dithizone<sup>1,2</sup>, acetylacetone<sup>3</sup>, phenanthroline<sup>3</sup>, picoline<sup>3</sup>, 8-hydroxyquinoline<sup>4</sup>, 2,2'-dipyridyl<sup>4</sup>, alizarin S<sup>5</sup> and 4-(2-pyridylazo)-2-resorcinol<sup>6</sup>. Although some of these complexes may be utilized for spectrophotometric determinations of lead and tin ions, no rapid and selective procedure for the titration of mixtures of  $R_3M^+$  and  $R_2M^{2+}$  ( $M = Pb$  and  $Sn$ ) ions is available. Only the reaction with dithizone, after laborious separations and solvent extractions<sup>2</sup>, or by means of differential analysis<sup>1</sup>, provides a solution to this problem.

In an analytical research program on organometallic compounds in this Institute, some electrochemical methods have been developed for the analysis of mixtures containing organometallic ions of the  $R_3M^+$  and  $R_2M^{2+}$  type. It has been found that potassium ferrocyanide and sodium tetraphenylborate (TPB) yield precipitates with  $R_2M^{2+}$  and  $R_3M^+$  compounds, respectively. It is known that 8-hydroxyquinoline forms isolatable complexes with dialkyltin ions<sup>4</sup>. Reagents which yield precipitates with organometallic ions are obviously useful for the amperometric titration of the latter, using a conventional dropping mercury as indicator electrode; accordingly, suitable procedures based on these reactions have been developed. The sensitivity, selectivity and simple equipment necessary for polarometric titrations make the methods highly suitable for routine use.

## EXPERIMENTAL

*Reagents*

*Test solutions.*  $(CH_3)_2PbCl_2$  and  $(C_2H_5)_2PbCl_2$  were prepared by the method of HEAP *et al.*<sup>7</sup>.  $(CH_3)_3PbCl$  and  $(C_2H_5)_3PbCl$  were prepared by the method of HEAP AND SAUNDERS<sup>8</sup>.  $(CH_3)_2SnCl_2$  and  $(C_2H_5)_2SnCl_2$  were prepared by the method of KOZESCHKOW<sup>9</sup>. Solutions ( $1 \cdot 10^{-2} M$ ) of these materials were prepared by dissolving weighed amounts of the compounds in water. All the solutions were standardized by potentiometric titration with silver nitrate solution.

*Potassium ferrocyanide.* An approximately  $5 \cdot 10^{-3} M$  solution in water was amperometrically standardized with zinc sulphate<sup>10</sup>.

*8-Hydroxyquinoline.* An approximately  $2 \cdot 10^{-3} M$  solution in ammoniacal

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buffer was prepared and amperometrically standardized with potassium bromate (dead-stop).

*Sodium tetraphenylboron.* A  $1 \cdot 10^{-2}$  M solution was prepared by dissolving 0.34224 g of compound in 100 ml of water. The purity of the TPB sample was checked by amperometric titration with thallium(I) nitrate<sup>11</sup>.

All other chemicals employed were reagent grade and were used without further purification.

#### *Amperometric titration procedure*

Titration were performed in a 100-ml cell. A dropping mercury electrode was used as the cathode and a saturated calomel electrode as the anode. Before the titration the solution was deoxygenated by passing nitrogen. The titrant was added from a 5–10-ml burette in steps of 0.2–0.5 ml. Nitrogen was passed through the solution to mix the content of the cell.

#### *Potentiometric titration procedure*

Titration curves were recorded with a Sargent recorder model MR and a Vibron M33b vibrating reed electrometer, using a combined glass electrode. Standard sodium hydroxide solution was added from a syringe driven by a synchronized motor.

## RESULTS

### *Amperometric titrations of $R_2PbCl_2$ compounds ( $R=CH_3, C_2H_5$ ) with ferrocyanide*

As above reported dialkyllead ions yield precipitates with potassium ferrocyanide; amperometric titration of these compounds with ferrocyanide as reagent could be carried out with accuracy and precision even at high dilutions.

The optimum conditions for rapid quantitative precipitation occurred in 1:1 alcohol–water (v/v). Consequently, a brief study of the polarographic behavior of dimethyl and diethyllead in 50% aqueous methanol, with 0.5 M lithium nitrate as background electrolyte, was made. At  $-0.550$  V vs. S.C.E., the diffusion current was found to be proportional to the concentration in the range  $5 \cdot 10^{-5}$ – $2 \cdot 10^{-3}$  M. Excellent titration curves were obtained after correction for dilution effects. Typical

TABLE I

AMPEROMETRIC TITRATION OF  $R_2PbCl_2$  COMPOUNDS WITH FERROCYANIDE

( $5.375 \cdot 10^{-3}$  M titrant. Ratio  $R_2Pb^{2+}/Fe(CN)_6^{4-} = 2$ . Each sample contained 1–5 ml of  $1.0 \cdot 10^{-2}$  M  $R_2PbCl_2$  in 50 ml of solution. Background electrolyte: 0.5 M  $LiNO_3$  in 1:1 water–methanol + 0.002% gelatin. Applied potential:  $-0.550$  V vs. S.C.E.)

<i>Species</i>	<i><math>R_2PbCl_2</math> taken (mmole)</i>	<i>Obs. end-point (ml)</i>	<i>Calc. end-point (ml)</i>
$(C_2H_5)_2Pb^{2+}$	0.050	$4.65 \pm 0.04$	4.65
$(C_2H_5)_2Pb^{2+}$	0.030	2.81	2.79
$(C_2H_5)_2Pb^{2+}$	0.020	1.83	1.86
$(C_2H_5)_2Pb^{2+}$	0.010	0.91	0.93
$(CH_3)_2Pb^{2+}$	0.020	1.84	1.86
$(CH_3)_2Pb^{2+}$	0.020	1.84	1.86

results are shown in Table I; the end-points in these titrations corresponded to the composition  $(R_2Pb)_2[Fe(CN)_6]$ . The same results were obtained when an excess of ferrocyanide was added and back-titrated with zinc solution, and also when dialkyllead dihalide solution was added to ferrocyanide.

There was no interference from  $R_3PbCl$  compounds provided that the concentration was  $1 \cdot 10^{-3} M$  or less. Thus the dialkyllead ions could be titrated in the presence of amounts of  $R_3Pb^+ \leq 10^{-3} M$ .

The described method gave good results in the titration of diorganolead ions in the concentration range  $2 \cdot 10^{-3} - 2 \cdot 10^{-4} M$ .

Dialkyltin compounds also gave precipitates with ferrocyanide and amperometric titrations could be carried out. In the case of  $(CH_3)_2Sn^{2+}$ , the titration curves showed that a considerable excess of reagent had to be present to initiate precipitation; direct titration was not possible. However, back-titration of excess of reagent with zinc(II) solution allowed titrations of dimethyltin dichloride in the concentration range  $2 \cdot 10^{-3} - 2 \cdot 10^{-4} M$ , with an accuracy and precision of the order of 2%.

Diethyltin ions could be titrated directly in a 50% aqueous methanolic medium containing 0.2 M hydrochloric acid at an applied potential of  $-0.950 V$  vs. S.C.E., in the concentration range  $2 \cdot 10^{-3} - 2 \cdot 10^{-4} M$ .

Unfortunately, the reagent is not specific for  $R_2Sn^{2+}$  compounds, since  $R_3Sn^+$  compounds also precipitate, so that titrations of mixtures of such compounds do not give satisfactory results. This problem may be solved by using 8-hydroxyquinoline.

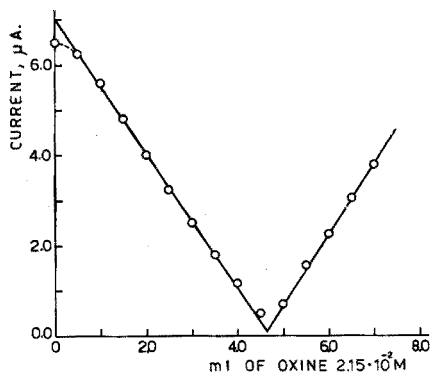


Fig. 1. Amperometric titration curve of  $(C_2H_5)_2SnCl_2$  with oxine (0.05 mmole of  $(C_2H_5)_2SnCl_2$ ; conditions as in Table II).

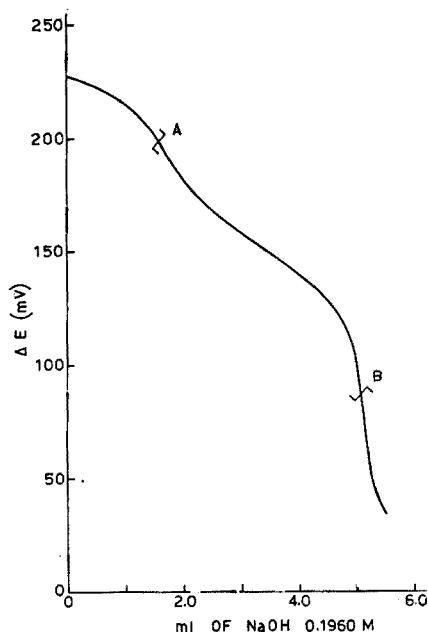


Fig. 2. Potentiometric titration curve of a mixture of  $(CH_3)_2SnCl_2$  and  $(CH_3)_3SnCl$  with sodium hydroxide (0.3 mmole of  $(CH_3)_2SnCl_2$  + 0.4 mmole of  $(CH_3)_3SnCl$  in 50 ml of water).

*Amperometric titrations of R<sub>2</sub>Sn<sup>2+</sup> compounds (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) with 8-hydroxyquinoline*

OKAWARA *et al.*<sup>4</sup> reported that dialkyltin compounds in ammoniacal medium yield fine yellow precipitates with oxine having the composition R<sub>2</sub>SnOx<sub>2</sub>; accordingly, in the present work an attempt was made to develop an amperometric method for the direct titration of diorganotin ions.

In ammonia-ammonium nitrate buffer (0.2 M) at an applied potential of -1.4 V *vs.* S.C.E., both R<sub>2</sub>SnCl<sub>2</sub> and oxine gave diffusion currents proportional to concentration up to 2 · 10<sup>-3</sup> M; a titration curve is shown in Fig. 1. It is apparent that a small excess of oxine is necessary to initiate precipitation; nevertheless, excellent results, precise and accurate within 1%, were obtained in titrations of 2 · 10<sup>-3</sup>-2 · 10<sup>-4</sup> M solutions of dialkyltin ions. Some of the results obtained are given in Table II. No detectable reaction occurred under the same conditions with compounds of the R<sub>3</sub>SnCl type; however, at an potential of -1.4 V, trialkyltin ions also gave a diffusion current; accurate amperometric titrations were thus possible provided that  $[R_3Sn^+]/[R_2Sn^{2+}] \leq 10$ .

TABLE II

AMPEROMETRIC TITRATION OF R<sub>2</sub>SnCl<sub>2</sub> COMPOUNDS WITH OXINE  
(2.15 · 10<sup>-2</sup> M titrant. Ratio R<sub>2</sub>Sn<sup>2+</sup>/oxine = 0.5. Each sample contained 2-5 ml of 1.0 · 10<sup>-2</sup> M R<sub>2</sub>SnCl<sub>2</sub> in 50 ml of solution. Background electrolyte: pH 9.2, 0.2 M ammonia-ammonium nitrate buffer + 0.002% gelatin. Applied potential: -1.40 V *vs.* S.C.E.)

Species	R <sub>2</sub> SnCl <sub>2</sub> taken (mmole)	Obs. end-point (ml)	Calc. end-point (ml)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn <sup>2+</sup>	0.050	4.65	4.65
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn <sup>2+</sup>	0.050	4.65	4.65
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn <sup>2+</sup>	0.030	2.84	2.79
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn <sup>2+</sup>	0.020	1.84	1.86
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Sn <sup>2+</sup>	0.020	1.83	1.86
(CH <sub>3</sub> ) <sub>2</sub> Sn <sup>2+</sup>	0.050	4.63	4.65
(CH <sub>3</sub> ) <sub>2</sub> Sn <sup>2+</sup>	0.030	2.79	2.79

*Amperometric titrations of R<sub>3</sub>PbCl compounds with NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>*

Numerous procedures for the determination of potassium and other univalent ions, based on precipitation with sodium tetraphenylboron (TPB), have been described. The precipitation of [(CH<sub>3</sub>)<sub>2</sub>Sn(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sup>-</sup> has been reported by WADA AND OKAWARA<sup>12</sup>. In the present work, it was found that various organometallic ions of the R<sub>3</sub>M<sup>+</sup> type yield sparingly soluble compounds with NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>. Exploratory experiments showed that organotin ions, because of the appreciable solubility of their TPB salts, could not be titrated amperometrically. The precipitation of R<sub>3</sub>Pb<sup>+</sup> compounds by TPB was too slow for satisfactory amperometric titration, but good results were obtained when an excess of TPB was added to the organolead solution and back-titrated amperometrically with a standard solution of thallium(I) nitrate at an applied potential of -0.475 V *vs.* S.C.E. as reported by KEMULA AND KORNAKCI<sup>13</sup>.

When the titration was carried out in 10<sup>-2</sup> N perchloric acid, it was unnecessary to remove the precipitate. The following procedure is suggested: the precipitation is carried out in as small a volume as possible by adding excess of standard TPB

solution, and allowing the solution to stand for at least 15 min, before dilution to the required volume with a mixture of  $10^{-2}$  *N* perchloric acid and 0.5 *M* sodium perchlorate; the excess of TPB is then titrated with standard thallium(I) solution as above. The results are summarized in Table III.

No precipitation occurs with  $R_2Pb^{2+}$  ions so that the above method is selective for  $R_3Pb^+$  compounds.

TABLE III

AMPEROMETRIC BACK-TITRATION OF  $R_3PbCl$  COMPOUNDS

(Each sample contained 1–5 ml of  $1.0 \cdot 10^{-2}$  *M*  $R_3PbCl$  and 3–10 ml of  $1.0 \cdot 10^{-2}$  *M* TPB + 0.002% gelatin in 50 ml of solution. Back-titration with  $5.0 \cdot 10^{-3}$  *M* thallium(I) nitrate. Background electrolytes: pH 2.0, 0.5 *M*  $NaClO_4$  +  $HClO_4$ . Applied potential:  $-0.475$  V vs. S.C.E.)

$R_3PbCl$ taken (mmole)	TPB added (mmole)	Obs. end-point (ml)	Calc. end-point (ml)
0.010	0.030	4.03	4.00
0.010	0.030	4.00	4.00
0.010	0.040	6.05	6.00
0.020	0.050	5.96	6.00
0.020	0.050	6.01	6.00
0.030	0.050	3.98	4.00
0.050	0.100	10.02	10.00

*Potentiometric titration of mixtures of  $R_3SnX$  and  $R_2SnX_2$  compounds with alkali*

The methods described above make it possible to titrate  $R_2Pb^{2+}$  and  $R_3Pb^+$  in admixture, but, for organotin ions, only  $R_2Sn^{2+}$  compounds may be titrated separately. For mixtures of such organotin ions, it was therefore necessary to determine the sum of *z* compounds, and thus calculate the amount of  $R_3Sn^+$  indirectly, knowing the amount of  $R_2Sn^{2+}$ . For this purpose, potentiometric titration with alkali, based on the known acidic properties of these compounds<sup>14</sup>, proved satisfactory.

The acidity of organotin ion solutions results from the following reactions:



Figure 2 shows the titration curve of a solution containing  $R_2SnCl_2$  and  $R_3SnCl$ . At the inflection point (B), the acidity resulting from the reactions (1)–(3) was completely titrated. The results were reproducible to within  $\pm 1\%$  for concentrations greater than  $2 \cdot 10^{-3}$  *M*. The first end-point (A) corresponded to the neutralization of the acidity resulting from reaction (1), but the acidities arising from the equilibria (2) and (3) could not be distinguished. Since the first end-point could be located only imprecisely, the method was not sufficient in itself to solve the problem.

*Determination of lead chloride in the presence of organolead chlorides*

In a previous paper<sup>6</sup> it was shown that more than 5% of lead chloride present in a mixture with  $(C_2H_5)_2PbCl_2$  could be determined by spectrophotometric titration with EDTA, since the absorbance of  $(C_2H_5)_2Pb$ –PAR complex did not change on addition of EDTA, whereas the  $Pb$ –PAR complex was destroyed quantitatively.

Because of the relatively common occurrence of alkyllead chlorides and  $\text{PbCl}_2$  in mixtures, it seemed highly desirable to develop a fairly rapid and simple procedure for the analysis of samples containing smaller amounts of lead chloride.

The method finally developed is analogous to that described by KIES<sup>15</sup> for the indirect titration of many metals with EDTA. Titrations were performed in ammoniacal medium and the end-points were detected by the potentiometric-galvanostatic technique. The procedure was as follows: to the sample containing organolead chloride and small amounts of lead chloride, a known excess of standard EDTA solution was added and the pH was adjusted to 9 by addition of ammonia-ammonium nitrate buffer; the free EDTA was then titrated with standard mercury(II) nitrate solution, measuring after each addition the potential difference across 2 indicator electrodes (amalgamated silver wires, 2 cm long and 1 cm diam.) polarized at a constant current of 6  $\mu\text{A}$ . The sharp depolarization of the electrodes, owing to the free mercury(II), allowed the end-point to be determined with excellent accuracy. Typical results are shown in Table IV. The method described allows the determination of more than 0.2% of lead chloride in presence of any trialkyllead or dialkyllead chlorides with relative error of 0.5–1%.

TABLE IV

VOLTAMMETRIC BACK-TITRATION OF LEAD CHLORIDE IN  $(\text{C}_2\text{H}_5)_2\text{PbCl}_2$   
(Each sample contained 5 ml of  $5.0 \cdot 10^{-2} M$   $(\text{C}_2\text{H}_5)_2\text{PbCl}_2$ , 10 ml of  $1.0 \cdot 10^{-3} M$  EDTA and 2–5 ml of  $5.0 \cdot 10^{-4} M$   $\text{PbCl}_2$  in 50 ml of solution. Back-titration with  $1.11 \cdot 10^{-3} M$  mercury(II) nitrate. Background electrolytes: pH 9.2, 0.2 M ammonia-ammonium nitrate buffer. Applied current: 6  $\mu\text{A}$ ).

$(\text{C}_2\text{H}_5)_2\text{PbCl}_2$ taken (mmole)	$\text{PbCl}_2$ taken (mmole)	% of $\text{PbCl}_2$ in mixture	$\text{PbCl}_2$ found (mmole)
0.250	—	0.0	0.0005 <sup>a</sup>
0.250	0.0010	0.4	0.0014
0.250	0.0015	0.6	0.0021
0.250	0.0020	0.8	0.0025
0.250	0.0025	1.0	0.0029

<sup>a</sup> Shows that 0.2% of  $\text{PbCl}_2$  is present in the  $(\text{C}_2\text{H}_5)_2\text{PbCl}_2$  blank solution.

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## SUMMARY

Mixtures of  $\text{R}_2\text{Sn}^{2+}$  and  $\text{R}_3\text{Sn}^+$  compounds can be analysed by titrating their total amount potentiometrically with alkali, and then determining  $\text{R}_2\text{Sn}^{2+}$  in another aliquot by amperometric titration with standard 8-hydroxyquinoline solution. In mixtures of  $\text{R}_2\text{Pb}^{2+}$  and  $\text{R}_3\text{Pb}^+$  compounds, dialkyllead ion can be titrated amperometrically with ferrocyanide solution and trialkyllead ions with tetraphenylboron solution. A potentiometric method is described for the determination of small amounts of lead chloride in the presence of any alkyllead chloride.

## RÉSUMÉ

Une méthode est proposée pour l'analyse de mélanges de composés  $R_2Sn^{2+}$  et  $R_3Sn^+$ . On dose la quantité totale des 2 composés sur une partie aliquote, par titrage potentiométrique au moyen d'un alcali; sur une autre partie, on effectue un titrage ampérométrique des ions  $R_2Sn^{2+}$ , à l'aide d'hydroxy-8-quinoléine. Dans les mélanges de composés  $R_2Pb^{2+}$  et  $R_3Pb^+$ , l'ion plomb-dialcoyle peut être titré ampérométriquement au moyen de ferrocyanure de potassium et les ions plomb-trialcoyle avec une solution de tétraphénylbore. On décrit également une méthode pour le dosage de faibles teneurs de chlorure de plomb, en présence de chlorure de plomb-alkoyle.

## ZUSAMMENFASSUNG

Es wird eine Methode zur Analyse von Mischungen aus  $R_2Sn^{2+}$ - und  $R_3Sn^+$ -Verbindungen vorgeschlagen. Die Gesamtmenge dieser Verbindungen wird potentiometrisch mit Alkali titriert und  $R_2Sn^{2+}$  durch amperometrische Titration mit 8-Hydroxychinolin bestimmt. In Mischungen entsprechender Bleiverbindungen können Dialkylblei-Ionen amperometrisch mit Hexacyanoferrat(II) und Trialkylblei-Ionen mit Tetraphenylborat bestimmt werden. Eine potentiometrische Methode zur Bestimmung kleiner Anteile Bleichlorid in Gegenwart von Alkylbleichlorid wird angegeben.

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## SHORT COMMUNICATIONS

### Spectrophotometric determination of vanadium in steel

It is customary practice to separate vanadium from iron and other interfering metals by precipitation with sodium bicarbonate followed by mercury cathode electrolysis before attempting the spectrophotometric determination of vanadium in steel<sup>1</sup>. Since these separations are time-consuming, it has seemed worthwhile to search for a more rapid and convenient means of isolating the vanadium. Recent work<sup>2</sup> has suggested that it might be possible to adapt the  $\alpha$ -benzoinoxime extraction-spectrophotometric oxine method proposed by HOENES AND STONE<sup>3</sup> to the analysis of steel. Tests have shown this to be true and, as a result, a rapid method for the determination of vanadium has been developed. Analysis of several NBS standard samples of steel shows the method to be very satisfactory.

#### Reagents

*Standard vanadium solution (100  $\mu\text{g/ml}$ ).* Dissolve 0.100 g of pure vanadium metal in 10 ml of nitric acid by heating gently, cool and dilute to 1 l; or dissolve 0.2296 g of c.p. ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) in 25 ml of (1+9) sulfuric acid and dilute to 1 l.

*$\alpha$ -Benzoinoxime-chloroform solution.* Dissolve 2 g of  $\alpha$ -benzoinoxime in 20 ml of ethanol by warming gently. Dilute to 200 ml with chloroform.

*Oxine-ethanol solution.* Dissolve 0.200 g of oxine (8-quinolinol) in 200 ml of ethanol.

#### Preparation of calibration graph

Transfer 0, 0.2, 0.4 and 0.6 ml of standard vanadium solution (100  $\mu\text{g/ml}$ ) to 125-ml conical flasks. Add 1 ml of perchloric acid and evaporate to about 0.5 ml volume on a flame. Cool and add 45 ml of water. Add 5 ml of hydrochloric acid and extract in a 125-ml separating funnel for 1 min with 10.0 ml of  $\alpha$ -benzoinoxime solution. Drain all of the lower layer into 25 ml of (1+99) hydrochloric acid in a 75-ml separating funnel. Shake for 10 sec and then drain all of the lower layer into a dry 50-ml conical flask. Add 5.0 ml of oxine solution, swirl, and then measure spectrophotometrically in a stoppered 5-cm absorption cell at 550  $\text{m}\mu$ , using distilled water as the reference solution, 5 min after adding the oxine solution.

#### Analysis of steel

Dissolve a 0.100–0.500 g sample of steel, containing up to 50  $\mu\text{g}$  of vanadium and no more than 1.25 mg of molybdenum, in 5 ml of hydrochloric-nitric acid mixture (4+1), plus 2–10 drops of hydrofluoric acid, by warming gently in a covered 125-ml conical flask. Add 3 ml of perchloric acid and evaporate to white fumes to oxidize carbides. Finally remove the cover and evaporate to about 0.25 ml (*i.e.*, almost to complete dryness) to expel excess acid. Cool, add 5 ml of hydrochloric acid and warm and swirl to dissolve salts. Cool, add about 150 mg of sodium metabisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ), heat to 70° or until gas bubbles start to form and allow to digest for 1 min. Heat to

vigorous boiling on a Meker type flame for exactly 10 sec. Cool quickly in a cold water bath to room temperature and add 45 ml of water. Add 0.3% potassium permanganate solution (w/v) dropwise until the solution just shows a definite color due to the permanganate; then add 1 drop in excess. Usually a total of 3 drops will be required. Pour into a 125-ml separating funnel and allow to stand for 5 min. Add 10.0 ml of  $\alpha$ -benzoinoxime solution, extract and proceed as directed in *Preparation of calibration graph*. If the sample contains sufficient molybdenum so that the extract remains cloudy after adding the oxime solution, warm and swirl the extract on a hot plate until complete solution of the molybdenum compound occurs and then cool to room temperature in a cold water bath. Measure spectrophotometrically 5 min after the addition of the oxime solution.

### Discussion

In attempting to adapt the method of HOENES AND STONE to the analysis of steel it was found that chromium(VI) or large amounts of molybdenum caused trouble. Chromium(VI) oxidizes the  $\alpha$ -benzoinoxime during the extraction and the colored oxidation products produced cause high results for vanadium. Hence, it is necessary to remove chromium quantitatively or to devise a method for obtaining the vanadium quantitatively in the pentavalent state, while retaining the chromium in the trivalent state, before attempting the extraction. In the present investigation, quantitative removal of chromium by distillation as chromyl chloride or by extraction of chromium(VI) with methyl isobutyl ketone failed<sup>4</sup>. Eventually a method for the selective oxidation of vanadium(IV) with potassium permanganate was used. In order to obtain quantitative oxidation of the vanadium with permanganate the acidity of the solution must be controlled. For this reason the instructions given in the method above must be followed closely. For reasons unknown, oxidation of the vanadium with permanganate appears to be incomplete when dealing with vanadium alone. For this reason it is necessary to oxidize with perchloric acid when preparing a calibration graph.

Molybdenum accompanies vanadium in the  $\alpha$ -benzoinoxime extraction but fortunately the yellow colored molybdenum-oxime compound subsequently produced

TABLE I  
ANALYSIS OF NBS STANDARD STEEL SAMPLES

Sample	Percent vanadium	
	Present	Found
101c (18 Cr-9 Ni)	0.049	0.047, 0.047
121a (18 Cr-10 Ni-0.4 Ti)	0.035	0.034, 0.034
161 (64 Ni-17 Cr-15 Fe)	0.029	0.030, 0.030
169 (77 Ni-20 Cr)	0.018	0.020, 0.020
123a (Cr-Ni-Nb)	0.037	0.033, 0.033
123b (Cr-Ni-Nb-Ta)	0.050	0.051, 0.049, 0.050
106a (1 Cr-1 Al-0.2 Mo)	0.002	0.003, 0.003, 0.003
125 (5 Si)	0.001	0.001, 0.001
111b (0.26 Mo)	0.003	0.002, 0.002
170 (0.23 Ti)	0.003	0.002, 0.002, 0.002
19f	0.007	0.007, 0.007, 0.007
22b	0.005	0.005, 0.005, 0.004
51a	0.002	0.002, 0.001
11g	0.001	0.001, 0.001, 0.001

does not interfere in the vanadium analysis. However, since the  $\alpha$ -benzoinoxime compound of molybdenum is not very soluble in chloroform, not much more than about 1.25 mg of molybdenum can be tolerated in the sample to be analyzed.

In the proposed method, the  $\alpha$ -benzoinoxime extract is washed with 25 ml of (1 + 99) hydrochloric acid to remove excess acid and the last traces of iron. The washing also removes any precipitate of tungsten, niobium or tantalum that may accompany the vanadium in the first extraction.

In order to demonstrate the validity of the proposed method, several NBS standard steel samples have been analyzed. The results obtained are shown in Table I. It will be seen that the reproducibility of the analyses is good. However, the figures for percent vanadium found do not always agree too well with the NBS recommended values. In spite of this there is reason to believe that the results shown are reliable since the figures given usually check well with those obtained by the ferrous laboratory of the National Bureau of Standards.

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### Determination of ring phosphates in sodium phosphate glass

Sodium phosphate glass, commonly known as Graham's salt, is formed by heating sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) above  $650^\circ$  and quenching the melt between stainless steel plates<sup>1</sup>. The resulting glass invariably contains small amounts of ring phosphates, also known as true metaphosphates<sup>2</sup>. In presence of acids, ring phosphates as well as linear polyphosphates are hydrolysed and ultimately converted to the orthophosphate<sup>2</sup>. There is therefore, a definite problem in determining the amount of ring phosphates present in a sample of Graham's salt. According to MARTENS AND RIEMAN<sup>3</sup>, long-chain, linear phosphates are precipitated by barium chloride but the ring phosphates remain in solution. After this precipitation, the ring phosphates can be converted to orthophosphate, which can be determined by the isobutanol extraction method as suggested by BERENBLUM AND CHAIN<sup>4</sup> and modified by WEIL-MALHERBE<sup>5</sup>. In the present paper, a technique is described for determining the amount of phosphorus present as ring phosphates in a solution containing a mixture of linear and ring phosphates.

#### *Reagents and apparatus*

All the chemicals used were of analytical grade. Organic chemicals were further purified by standard methods.

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*Tin(II) chloride.* Prepare a stock solution by dissolving 10 g of tin(II) chloride in 25 ml of concentrated hydrochloric acid. Prepare a dilute solution fresh for each measurement by diluting 0.5 ml of the stock solution to 20 ml with *N* sulphuric acid.

*Acid ethanol.* Dissolve 10 ml of concentrated sulphuric acid in 490 ml of 99.9% ethanol.

*Spectrophotometer.* A Carl-Zeiss spectrophotometer (Model PMQ II 2903) was used. Absorption was measured in 1-cm cells at 630 m $\mu$ .

#### *Procedure*

To 10 ml of a 1% solution of Graham's salt in pure water, add an excess of a saturated solution of barium chloride in conductivity water, while stirring vigorously. Filter on a sintered glass crucible and wash the precipitate thoroughly with water. Reject the precipitate and add about 2 ml of concentrated hydrochloric acid to the collected filtrate. Then digest on a water-bath for 4 h before evaporating to dryness. Redissolve the dried material in a small amount of water and precipitate the excess of barium chloride present as sulphate. It is essential to remove all the barium at this stage; barium chloride reacts with ammonium molybdate and thus interferes with the later spectrophotometric analysis. Filter off the barium sulphate and collect the filtrate in a 50-ml measuring flask. Dilute the solution to the mark.

To 5 ml of the solution containing the orthophosphate, add 6 ml of isobutanol and 1 ml of 5% (w/v) ammonium molybdate solution in 4 *N* sulphuric acid, and shake for about 15 sec. Transfer the organic layer as completely as possible to another bottle containing a pinch of sodium sulphate to absorb water. When the water has been completely absorbed, transfer 0.25 ml of the extract to another bottle and add 12.5 ml of the acid ethanol and 0.2 ml of the tin(II) solution. Shake for a few minutes and measure the absorbance of the homogeneous solution at 630 nm in a 1-cm cell. (The colour stability was exceptionally good; percent transmittance readings even after 24 h were identical with the initial value.) Construct a calibration curve by using

TABLE I

PHOSPHORUS AS RING PHOSPHATES IN SAMPLES OF GRAHAM SALT

<i>Time of heating NaPO<sub>3</sub> melt (h)</i>	<i>Temp. of melt (°)</i>	<i>Wt.-average mol. wt.</i>	<i>Amount of P as ring phosphates (%)</i>
6	700	7010	3.1
6	700	7780	4.9
6	700	9140	2.5
6	800	8980	3.9
6	800	9840	2.1
6	800	10640	2.4
9	700	9800	3.6
9	700	9950	2.0
9	700	9180	1.2
12	700	9660	3.5
12	700	9890	3.7
12	800	12040	2.8
12	800	11990	3.2
12	800	12040	3.3

standard sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) solutions. The Lambert-Beer law was applicable over the range 0.0049–0.049 g P as phosphate.

### *Results and discussion*

Results obtained for fourteen samples are given in Table I. The temperature and the time of heating the melt obtained from sodium dihydrogen phosphate which gave the glass on quenching, are also recorded. The weight-average molecular weights obtained by the viscosity method<sup>1</sup> are also given.

The amount of phosphorus present as ring phosphate in various samples of Graham's salt appears to be quite reasonable<sup>2</sup>. This method is an improvement over other methods, *e.g.* the chromatographic method<sup>3</sup>, which are less quantitative.

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## **The rapid determination of phosphorus in presence of arsenic, silicon and germanium**

The determination of phosphorus by the molybdenum blue method has lately been modified by several authors. ZINZADZE<sup>1</sup> showed the possibility of working with a "single solution" in which the molybdenum ions were present in a correct Mo(V):Mo(VI) ratio for the formation of the phosphorus-molybdenum blue complex. HAHN AND LUCKHAUS<sup>2</sup> simplified this reagent considerably by introducing hydrazine sulphate into the single solution. MURPHY AND RILEY<sup>3</sup> used ascorbic acid for the same purpose.

The slow development of the final phosphomolybdenum blue colour remained a problem until JEAN<sup>4</sup> showed that Ti, Zr and Bi, by association with the central phosphorus atom, catalyzed this reaction considerably. MURPHY AND RILEY<sup>5</sup> finally combined the suggestion of JEAN with their single solution method, but had to use antimony as a catalyst instead of bismuth due to the lower acidity of their medium; bismuth interfered by producing a cloudy precipitate.

Since the method proposed by MURPHY AND RILEY combined the advantages of both the single solution and the catalyst, it was tested in this laboratory for its

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applicability to the determination of phosphorus in soils and plant material.

MURPHY AND RILEY<sup>5</sup> reported a very strong interference from arsenic. Under normal conditions the arsenic level in plant material and in soils will be too low to cause an interference, but if arsenic-containing sprays have been used, a serious interference is to be expected. Therefore a method is proposed here in which arsenic does not interfere.

It is possible to remove arsenic beforehand either by liquid-liquid extraction<sup>6-9</sup> or by volatilization with perchloric acid and bromide<sup>7</sup>; these procedures are, however, time-consuming. It is well-known<sup>10</sup> that in a suitably acidic medium arsenic(V) liberates iodine from iodide, and that the iodine can be titrated with thiosulphate. The reactions are always carried out in two stages but the overall reaction suggests that the reduction of arsenic(V) can take place without iodide. Preliminary experiments showed that an excess of thiosulphate must be added, which, under these acidic conditions, leads to turbid solutions caused by the liberation of sulphur. This can be prevented by the addition of sulphite ions; sulphite alone does not reduce arsenic(V) quantitatively at room temperature<sup>10</sup> and on heating, a slight time effect was found. The use of the mixed reducing agent is thus an essential part of the procedure.

#### *Reagents*

*Mixed reagent.* Mix 50 ml of 5 *N* sulphuric acid, 15 ml of 4% (w/v) ammonium molybdate, 30 ml of freshly prepared 0.1 *M* ascorbic acid and 5 ml of potassium antimonyl tartrate solution (1000 p.p.m. Sb; 0.2743 g  $\text{KSbOC}_4\text{H}_4\text{O}_6/100$  ml). Prepare fresh daily.

*Reducing agent.* Mix 20 ml of 5 *N* sulphuric acid, 40 ml of 10% (w/v) sodium metabisulphite and 40 ml of 1% (w/v) sodium thiosulphate solution. Prepare fresh daily.

#### *Apparatus*

Measurements were made with an Optica CF4 spectrophotometer.

#### *Procedure*

Pipette a maximum of 30 ml of a neutral sample into a 50-ml volumetric flask. Add 5 ml of the reducing agent and mix thoroughly. After 15 min, add 8 ml of the mixed reagent, dilute the contents of the flask with water to the mark and again mix thoroughly. After not less than 40 min measure the optical density at a wavelength of 720 nm.

#### *Results*

Beer's law was obeyed to at least 150  $\mu\text{g}$  of phosphate per 50 ml of final volume. The readings remained virtually constant for at least 42 h (variations being smaller than 2%). The molar extinction coefficient, according to the definition of SANDELL, was 16150 at 720 nm and 20100 at 890 nm. With the quality of ascorbic acid used (p.a. Merck), the mixed reagent produced reliable results even when 24-h old; with other products, however, it was usually advisable to prepare a fresh mixed reagent just before use.

All experiments with interfering ions were done on both a blank and a solution

containing 75  $\mu\text{g}$  of phosphate. No interference could be detected from 2000  $\mu\text{g}$  of  $\text{Cu}^{2+}$ , 8000  $\mu\text{g}$  of  $\text{Ce}^{4+}$ , 4000  $\mu\text{g}$  of  $\text{Hg}^{2+}$ , 4000  $\mu\text{g}$  of  $\text{Si}^{4+}$ , 2000  $\mu\text{g}$  of  $\text{Bi}^{3+}$ , 1000  $\mu\text{g}$  of  $\text{As}^{5+}$ , or 8000  $\mu\text{g}$  of  $\text{SCN}^-$ . Gold(III) showed no interference at the 3000- $\mu\text{g}$  level; higher levels produced a green discoloration. Iron(III) produced a yellow discoloration which disappeared within 20 min; even 8000- $\mu\text{g}$  quantities did not interfere. Vanadium(V) showed a very slight positive influence, which did not exceed 5% at the 2000- $\mu\text{g}$  level; at higher levels a positive time influence could be detected but this stabilized after 2 h. Tungstate ion showed a negative influence: -20% at the 200- $\mu\text{g}$  level after 30 min, which was reduced to -12% after a period of 18 h. Titanium(III) did not interfere at the 1250- $\mu\text{g}$  level but produced turbid solutions with 2500  $\mu\text{g}$  Ti.

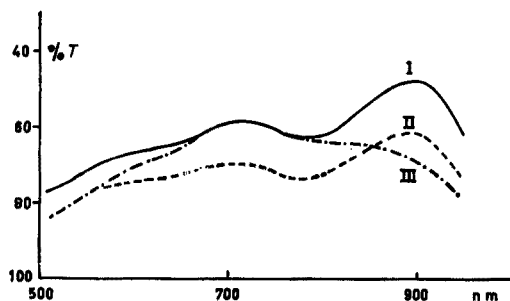


Fig. 1. Absorption curves of the phosphomolybdenum blue complex (I) in the presence of  $\text{Sn}^{4+}$  (II) or  $\text{Sn}^{2+}$  (III).

Germanium(IV) did not interfere up to the 2500- $\mu\text{g}$  level, but showed a slight positive interference of 8% after a period of 18 h; after 2.5 h this interference was still negligible. The interference of tin was remarkable (Fig. 1). Absorption curves were made for 75  $\mu\text{g}$  of phosphate in the presence of 200  $\mu\text{g}$  of  $\text{Sn}^{4+}$  or  $\text{Sn}^{2+}$  after a period of 1-2 h. The transmission minimum at about 890 nm represents the association of antimony with the central phosphorus atom. The figure clearly shows that tin(II) blocks this association, but measurements at 720 nm avoid this difficulty. The behaviour of tin(IV) is entirely different as it retards colour development. After a period of 20 h no influence of 200  $\mu\text{g}$  of tin(IV) could be detected. Spectra for 75  $\mu\text{g}$  of phosphate in the presence of 1250  $\mu\text{g}$  of titanium or 2000  $\mu\text{g}$  of bismuth showed no signs of a special behaviour, although an association of these ions with the central phosphorus atom could be expected.

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## BOOK REVIEWS

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M. A. BLOKHIN, *Methods of X-Ray Spectroscopic Research*, Translated from the Russian, Pergamon Press, Oxford, 1965, xv + 447 pp., price 90 s.

In his foreword the author states that "The aim of the present book is . . . to acquaint scientific workers, engineers, laboratory assistants and students who specialize in the field of X-ray spectroscopy, with present-day methods of investigation and with apparatus". However, the most recent literature reference is dated 1958, although some modernisation is achieved by a supplementary bibliography up to 1961 added by the translation editor.

The first 4 chapters (250 pp.) deal with instrumentation and include detailed descriptions of X-ray tubes for analysis both by direct electron excitation and by fluorescent spectra, power supplies for X-ray tubes, measurement of high voltage, production and measurement of high vacuum, and measurement of X-ray intensity. The chapter on the resolution of X-rays deals with various dispersive geometries and contains descriptions of some 18 long- and short-wave spectrographs and spectrometers together with certain multichannel systems under the heading of "quantometers". Some early electron probe microanalysers are also briefly described. The 5th chapter contains a detailed discussion of procedures by which the observed profiles of absorption and emission spectra may be corrected for various forms of distortion by use of Fourier series. The remaining 4 chapters (93 pp.) treat such topics as qualitative analysis, quantitative analysis using primary and fluorescent spectra and absorption analysis, and the effect of interfering elements in quantitative fluorescence analysis.

There appear to be few errors, but the age of the book becomes rather apparent in some places. Since X-ray spectrometers for routine determination of most elements are widely available commercially, the latter part of the book dealing with techniques should be of greater interest.

T. A. HAMOR (Birmingham)



H. SUHR, *Anwendungen der kernmagnetischen Resonanz in der organischen Chemie*, Chemie, Organische, in Einzeldarstellungen, Hrsg. von H. BREDERECK UND E. MÜLLER, Band 8, Springer-Verlag, Berlin, 1965, viii + 424 S., Ganzleinen DM 68.—

This is a companion volume to *Die kernmagnetische Resonanz und ihre Anwendung in der anorganischen Chemie* by E. FLUCK, published in 1963. The standard of presentation of the book is good, although the subject matter is rather variable. Chapter V on proton resonance gives a particularly detailed review of the chemical shifts of methyl, ethyl, isopropyl, *t*-butyl and cyclopropyl groups. The chemical shifts of a fairly extensive series of hydrocarbons, alkyl halides, aliphatic nitro, azo and diazo compounds, amines, alcohols and esters are also recorded. For the organic and analytical chemist, the 170 pages devoted to the correlation of proton shifts contains a great deal of very useful information. On the other hand, in the section on "other nuclei" the tabulated data for boron and phosphorus are out-of-date, though it must be admitted that many of the more recent references are listed.

The final Chapter (70 pp.) deals very ably with the application of NMR to quantitative analysis, the study of hindered rotation and conformational analysis, etc. The reviewer sees little advantage in reproducing 25 pages of intensity/frequency relationships for various spin systems, all of which have been more fully covered in earlier articles and books.

In summary, this is a very useful book which is thoughtfully presented; however, for English-speaking chemists its value is diminished by the recent availability of much more extensive works on NMR.

E. F. MOONEY (Birmingham)

*Anal. Chim. Acta*, 37 (1967) 275

H. GINSBERG, *Leichtmetallanalyse*, 4. völlig neubearbeitete Auflage (von H. BENSCH, M. KÖSTER UND H. PFUNDT), Walter de Gruyter, Berlin, 1965, 338 S., 60 Abb., Geb. DM 48.--

Diese neubearbeitete Auflage gibt im Teil A eine knapp gefasste Darstellung der modernen Verfahren auf dem Gebiet der Leichtmetallanalyse. Nahezu 2/3 des Buches behandeln die Analyse des Aluminiums und seiner Legierungen, wobei das Reinstaluminium und seine Legierungen der zahlreichen Spurenanalysen wegen eine besondere Berücksichtigung fand. Die weiterhin behandelten Analyseverfahren der Leichtmetalle Beryllium, Magnesium und Titan wurden zu Kapiteln zusammengestellt, in denen jeweils auch die Analyse der reinen Metalle eine besondere Behandlung gefunden hat.

In einem Teil B sind die emission-spektralanalytischen- und röntgen-fluoreszenz-spektrometrischen Verfahren in Grundlage und Arbeitsanweisungen beschrieben.

Das Buch wird jedem Analytiker, der sich mit den Leichtmetallen zu befassen hat, von grossem Wert sein.

W. KOCH (Duisburg-Hamborn)

*Anal. Chim. Acta*, 37 (1967) 275

**PUBLICATIONS RECEIVED**

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G. EISENMAN, R. BATES, G. MATTOCK AND S. M. FRIEDMAN, *The Glass Electrode*, Interscience—Wiley, New York, 1966, price 53 s (paperback).

This book contains previously published articles dealing with glass electrodes: The Electrochemistry of Cation-Sensitive Glass Electrodes (G. EISENMAN); The Glass Electrode in the Determination of pH (R. BATES); Laboratory pH Measurements (G. MATTOCK); Measurement of Sodium and Potassium by Glass Electrodes (S. M. FRIEDMAN).

C. J. NYMAN AND G. B. KING, *Problems for General Chemistry and Qualitative Analysis*, J. Wiley and Sons, New York, 1966, viii + 274 pp., price 23 s (paperback).

Chapter heads: Introduction; Units of Measurement; Atomic and Molecular Weights; Formulas and Percentage Composition; Methods of Balancing Equations; Gas Laws; Stoichiometry; Solids; Expressing Concentrations of Solutions; Colligative Properties of Solutions; Thermal Changes in Chemical Processes; Titrations; Rates of Chemical Reactions; Molecular Equilibrium; Equilibrium in Saturated Solutions; Hydrolysis and Complex Ion Formation; Nuclear Changes; Electrochemistry.

M. T. BECK (Ed.), *Proceedings of the Symposium on Coordination Chemistry*, Akademiai Kiado, Budapest, 1965, 481 pp., price \$ 15.0.

The Proceedings of an international symposium held in Tihany, Hungary, in 1964.

D. A. YOUNG, *Decomposition of Solids (International Encyclopedia of Physical Chemistry and Chemical Physics, Topic 21, Vol. 1)*, Pergamon Press, Oxford, 1966, xi + 209 pp., price 55 s.

Chapter heads: Introduction; Formal Theory; Endothermic Decompositions; The Photolysis of Solids; Exothermic Decompositions.

J. E. STRAIN, *Use of Neutron Generators in Activation Analysis* (H. A. ELION AND D. C. STEWART (Eds.), *Progress in Nuclear Energy, Series IX, Analytical Chemistry*, Vol. 4, Part 3) Pergamon Press, Oxford, 1965, 18 pp., price 10 s.

*Proceedings of the Second Conference on Silicate Analysis, Sept., 1965*, Special Publication No. 50, The British Ceramic Research Association, Stoke-on-Trent, England, 1966, ix + 168 pp., price 40 s.

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## ANNOUNCEMENT

### concerning the JOURNAL OF ELECTROANALYTICAL CHEMISTRY

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The boundaries between what are regarded as electroanalytical chemistry, electrochemistry and colloid chemistry are becoming increasingly diffuse. This has been reflected in the pages of the journal, where many of the papers published are of interest to chemists who consider themselves as falling under any of these three broad divisions.

The linking phenomena are those associated with the electrical double layer, and it is felt that it would be both useful and appropriate to acknowledge these broader interests by extending the scope of the journal to include all phenomena in which the electrical double layer plays an essential role.

These extend from applications in analytical chemistry through the fundamentals of electrode reactions, which are already the staple part of the journal, to studies of the double layer around colloidal particles, the stability of dispersions and electrokinetic phenomena as well as other surface chemical problems such as monolayers and soap films.

Since this broadening of the scope does not involve any change in the basic interests of the journal, the title has been only slightly modified. From January 1967 it has become:

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Papers for publication should be sent to one of the following addresses:

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Dr. R. H. OTTEWILL, Department of Chemistry, The University, Bristol 8, England;

Dr. R. PARSONS, Department of Chemistry, The University, Bristol 8, England;  
(Until July, 1967: Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, Calif. 91109, U.S.A.)

Professor C. N. REILLEY, Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27515, U.S.A.

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