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

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 29, No. 6, p. 489–598, December 1963

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UMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 29, No. 6, December 1963

THE DETERMINATION OF ALUMINUM BY ATOMIC ABSORPTION SPECTROSCOPY

A study of the determination of aluminum by atomic absorption spectroscopy has been made using a solution of aluminum cupferrate in 4-methyl-2-pentanone to feed oxy-acetylene or oxy-hydrogen flames. Investigations were made on the effect of the variables, *viz.*, slit-width, flow rates, flow ratios and flame positions, on the intensity of aluminum absorption. The data were studied to determine the optimum conditions. These investigations brought out the comparative merits of the two flames for the determination of aluminum, and also elucidated the mechanism of aluminum absorption in an oxy-acetylene flame.

C. L. CHAKRABARTI, G. R. LYLES AND F. B. DOWLING,

Anal. Chim. Acta, 29 (1963) 489–499

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH 2-MERCAPTOBENZOXAZOLE

A new spectrophotometric method for the determination of palladium is described using 2-mercaptobenzoxazole as reagent. The color reaction has a sensitivity of 0.08 μg of Pd per cm^2 for log $I_0/I = 0.001$ and obeys Beer's law from 2 to 40 p.p.m. The effects of pH time, order of addition of the reagents, temperature and diverse ions were investigated. The procedure was applied to synthetic solutions containing palladium plus a variety of foreign ions.

T. ARITA AND J. H. YOE,

Anal. Chim. Acta, 29 (1963) 500–504

ANALYSIS OF STYRENE–BUTADIENE COPOLYMERS BY NMR SPECTROSCOPY

A method for determining styrene–butadiene copolymer composition has been developed using NMR spectroscopy. The composition is determined in terms of mole per cent styrene, 1,2-butadiene addition and 1,4-butadiene addition. The NMR absorption bands derived from the aromatic and olefinic protons incorporated into the copolymer are used for this determination. Calibration is not required for the application of this method.

W. L. SENN, Jr.,

Anal. Chim. Acta, 29 (1963) 505–509

A SENSITIVE METHOD FOR THE MICRODETERMINATION OF CHOLINE

A sensitive method for the determination of choline (0.1–3 μmoles), particularly in phospholipids, is described. Choline is precipitated as the insoluble phosphomolybdate, the excess phosphomolybdic acid is carefully removed and phosphorus determined spectrophotometrically in the precipitate by reduction to molybdenum blue. Compounds capable of forming insoluble phosphomolybdates interfere. Interference of ammonia can be prevented by the addition of formaldehyde.

A. J. DE KONING,

Anal. Chim. Acta, 29 (1963) 510–516

THE DETERMINATION OF VANADIUM, MOLYBDENUM AND TUNGSTEN BY INFRARED SPECTROSCOPY

The infrared spectra of the 8-hydroxyquinolinates of molybdenum, vanadium and tungsten in the region 3–15 μ were investigated. It was found possible to determine the elements quantitatively, singly or in pairs, with an error of about 3%. Molybdenum was determined at 10.80 μ and 10.93 μ, vanadium at 10.50 μ, and tungsten at 10.61 μ or 10.90 μ.

R. J. Magee and A. S. Witwit,
Anal. Chim. Acta, 29 (1963) 517–523

MAGNETIC TITRATIONS

Magnetic titrations using a new titration cell and procedure are described. The paramagnetism of a hexammine nickel nitrate solution decreases linearly upon the addition of cyanide up to the end-point (complete formation of $Ni(CN)_4^{2-}$); there is no evidence of the formation of intermediate complexes. Intermediate complexes are evident in the titrations of iron(II) with 1,10-phenanthroline and with 2,2'-bipyridyl; log K_1 values, calculated from the magnetic data, are 6.0 and 5.0 respectively.

M. L. Heit and D. E. Ryan,
Anal. Chim. Acta, 29 (1963) 524–531

DIRECT SPECTROPHOTOMETRIC DETERMINATION OF INDIUM IN TIN

Indium is separated from tin by an anion-exchange process in 0.5 *M* hydrochloric acid solution. Subsequently, the indium is extracted into 1,2-dichlorobenzene as its complex with 5,7-dichloro-8-quinolinol. The complex forms and extracts quantitatively in the pH range 3–7. The yellow, organic phase is measured spectrophotometrically at 415 mμ; its absorbancy is directly proportional to the indium content of the aqueous phase up to a total of 1.5 mg of indium per 50 ml. This procedure quantitatively separates the two metals, allows one to determine the indium content of indium(<5%)–tin alloys with a relative error less than 0.7%, and considerably reduces color fading errors inherent in some previously reported spectrophotometric methods for indium.

B. A. Raby and C. V. Banks,
Anal. Chim. Acta, 29 (1963) 532–538

A DIFFERENTIAL THERMAL ANALYSIS (DTA) AND THERMOGRAVIMETRIC ANALYSIS (TGA) STUDY OF SOME ORGANIC ACIDS. PART II

The differential thermal analysis and thermogravimetric analysis curves of 16 organic acids are presented. The "procedural weight-loss temperatures" for the anhydrous acids ranged from 115° for salicylhydroxamic acid to 250° for 5-aminosalicylic acid. The DTA curves were characterized by endothermic and exothermic peaks which were caused by fusion, vaporization, sublimation, and decomposition reactions.

W. W. Wendlandt and J. A. Hoiberg,
Anal. Chim. Acta, 29 (1963) 539–544

A SYSTEMATIC STUDY OF THE SOLVENT EXTRACTION OF METAL CUPFERRATES

The extraction of the cupferrates of 33 metals (Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Sc, Y, La, Ti, Zr, Th, V, Nb, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Pb, Sb and Bi) with chloroform was studied in relation to pH values. The extraction constants and two-phase stability constants of the cupferrates were calculated; these can be used to determine the optimum conditions for the separation of many metals.

J. Starý and J. Smižanská,
Anal. Chim. Acta, 29 (1963) 545–551

THEORY OF PHOTOMETRIC MICROTITRATIONS

A METALLOCHROMIC INDICATOR FORMING A STEP-WISE SYSTEM OF COMPLEXES

The theory of photometric titrations is developed to cover a step-wise system of indicator complexes, the simultaneous presence of the last three steps being considered. A general expression for the dependence of the equivalent fraction on the fraction of the free indicator form is derived. This allows: (*1*) easy calculation of the theoretical shapes of curves for different values of all parameters involved; (*2*) critical consideration of the specific effect of these parameters on the shape of the curve. Noticeable dissociation of the metal complexan due to the competitive equilibrium is shown in more or less pronounced rounding off at the end-point; in extreme cases the accuracy of the end-point evaluation may be decreased. Increased indicator concentrations help to extend the portion of the curve suitable for linear extrapolation of the end-point. It is also shown that the step-wise equilibrium is reflected by changes in the shape of the titration curves at different wavelengths. If only the last two step-complexes prevail before the end-point, it is possible to find a wavelength at which this portion of the curve has a linear course suitable for accurate end-point evaluation.

S. Kotrlý,
Anal. Chim. Acta, 29 (1963) 552–563

THE ISOLATION OF CAESIUM-137 FROM LIQUID RADIOACTIVE FALL-OUT

A method is suggested for the isolation of caesium-137 from liquid radioactive fall-out, suitable for the treatment of up to 1 l of water in one batch. Caesium is coprecipitated with Prussian blue and dissolution of the precipitate in a saturated EDTA solution at pH 10, is followed by extraction of caesium as its dipicrylaminate, by nitrobenzene.

J. Beneš and M. Kyrš,
Anal. Chim. Acta, 29 (1963) 564–568

SOLVENT EXTRACTION OF CHROMIUM(VI) WITH TRIBENZYLAMINE

The use of tribenzylamine as an extracting agent is recommended for a simple and selective separation of chromium(VI). Interferences from foreign elements were investigated by means of radioactive tracers and spectrophotometric techniques. The method is applied to neutron activation analysis of chromium traces in various materials.

G. B. Fasolo, R. Malvano and A. Massaglia,
Anal. Chim. Acta, 29 (1963) 569–573

TETRAPHENYLPHOSPHONIUM CHLORIDE AS A REAGENT FOR THE DETERMINATION OF VANADIUM(V) (DECAVANADATE)

The extraction and spectrophotometric determination of vanadium (V) (decavanadate) by means of tetraphenylphosphonium chloride (TPP) is described. The yellow TPP–decavanadate solution in ethylene chloride obeys Beer's law at 350 mμ and at 400 mμ over the range 4–60 μg of vanadium(V) per ml. At pH 3.8 a single extraction with 0.1 *M* aqueous TPP solution and ethylene chloride is satisfactory. Zn, Al, Cu, Co and Ti do not interfere.

C. Liteanu, I. Lukács and C. Strusievici,
Anal. Chim. Acta, 29 (1963) 574–579

DETECTION OF α-AMINO- AND α-HALOGENO-FATTY ACIDS BY SPOT TESTS

(Short Communication)

F. Feigl and S. Yariv,
Anal. Chim. Acta, 29 (1963) 580–582

INTENSIFICATION OF COLOUR REACTIONS BETWEEN COPPER IONS AND POLYAMINES BY MONTMORILLONITE

(Short Communication)

W. Bodenheimer, B. Kirson and S. Yariv,
Anal. Chim. Acta, 29 (1963) 582–585

SIMPLE VAPOR SORPTION METHOD FOR DETERMINATION OF WATER IN LIQUIDS

(Short Communication)

S. D. Christian and H. E. Affsprung,
Anal. Chim. Acta, 29 (1963) 586–588

THE DETERMINATION OF ALUMINUM BY ATOMIC ABSORPTION SPECTROSCOPY

CHUNI L. CHAKRABARTI

Coates Chemical Laboratories, Louisiana State University, Baton Rouge 3, Louisiana (U.S.A.)

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(Received May 14th, 1963)

A survey of the literature reveals that atomic absorption spectroscopy has not been successful when applied to the determination of aluminum[1-6]. One of the reasons for this failure appears to be the formation of the refractory AlO molecule in the flame, thus leaving virtually no free atoms for atomic absorption. In an earlier communication[7], the present authors reported that they succeeded in determining aluminum by atomic absorption spectroscopy using either oxy-acetylene or oxy-hydrogen flames fed with an organic aerosol containing an aluminum complex. The present paper deals with the determination of aluminum with both the flames. Since the oxy-acetylene flame was found to be more sensitive (absolute) then the oxy-hydrogen flame, final experiments were made with the former flame. This paper presents the results of the investigation of the parameters which govern the intensity of aluminum absorption when an oxy-acetylene flame is used. The parameters investigated include flow rates, flow ratios of oxygen and fuel gas, slit-widths and flame positions (vertical and lateral). The results bring out the comparative merits of oxy-acetylene and oxy-hydrogen flames for the determination of aluminum and also help in understanding the mechanism of aluminum absorption with an oxy-acetylene flame.

EXPERIMENTAL

Apparatus

The atomic absorption spectrophotometer used in these studies was designed and built by Kem-Tech Laboratories. A Sargent Recorder, Model SR, 0–125 mV range, was used for absorption measurements. A Beckman Zeromatic pH-meter with glass and calomel electrodes was used for pH measurements.

Reagents

Aluminum standard solutions were prepared by dissolving aluminum metal (chemically pure) in concentrated hydrochloric acid. The solution was diluted to known volumes with demineralized water. Aliquots of organic extracts were prepared by diluting the extracts with pure organic solvents and volumes made up to the marks in volumetric flasks. Integral types of aspirator-burners made by Beckman were used for sample atomization. The ammonium salt of N-nitrosophenylhydroxylamine (cupferron) solution was prepared fresh as a 0.1 M aqueous solution; 4-methyl-2-pentanone (pure) was used as the organic solvent for extraction purposes. All other chemicals used were of reagent grade.

Procedure

Aluminum was extracted into an organic solvent as follows. An aqueous solution of aluminum was buffered with ammonium acetate and its pH adjusted to 3.5. A freshly prepared aqueous solution of the ammonium salt of N-nitrosophenylhydroxylamine (cupferron) was added, and the aluminum cupferrate chelate extracted into 4-methyl-2-pentanone. The organic phase was then separated and aspirated into an oxy-acetylene or oxy-hydrogen flame. The absorption was measured at 3962–3944 Å. The lamp current was 17 mA and the photomultiplier voltage was 600 V. The amplifier gain was held constant and buck-out controls coupled with assorted range plugs were used to vary the sensitivity of the SR recorder.

The aluminum resonance lines at 3944 and 3962 Å were used jointly for absorption measurements. However, the monochromator currently used in the atomic absorption spectrophotometer is not capable of resolving these two lines without unduly reducing the intensity. Since these lines could not be resolved with the monochromator being used, and because they may have different absorption characteristics, it was not possible to establish whether or not Beer's law applies.

RESULTS AND DISCUSSION

The following results were obtained by atomizing the standard aluminum solution into the flame and a systematic study of each variable was made while the other variables were held constant.

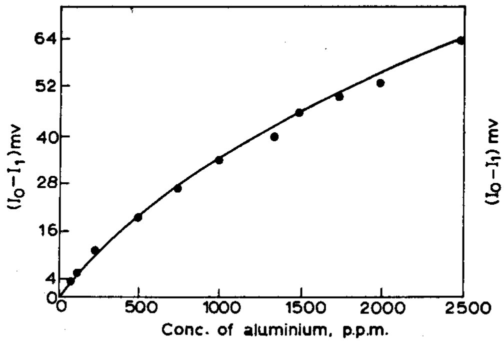

Fig. 1. Calibration curve; oxy-acetylene flame.

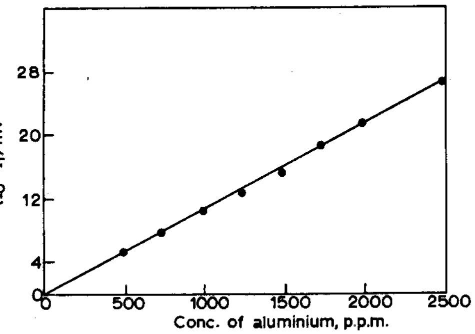

Fig. 2. Calibration curve; oxy-hydrogen flame.

In Fig. 1 with an oxy-acetylene flame, the calibration graph plotted on linear coordinates becomes curved toward the concentration axis with increasing concentrations of aluminum. However, a nearly linear graph is obtained if logarithmic coordinates are used instead of linear coordinates. Hence, logarithmic coordinates should be used if linear calibration graphs are desired for quantitative work. In Fig. 2, the oxy-hydrogen flame gives a nearly linear calibration graph in the concentration range 0–2500 p.p.m. when plotted on linear coordinates.

Figures 3 and 4, which are Ringbom curves, show that the maximum differential sensitivity is obtained in the concentration range 1500–2500 p.p.m. (or higher) when an oxy-hydrogen flame is used, but the range shifts to 500–1500 p.p.m. when an oxy-acetylene flame is used. The range of maximum differential sensitivity constitutes the optimum range of concentration, in which the relative errors are at a minimum. From Figs. 3 and 4, it can be calculated that within the optimum ranges the relative analysis errors that would result from 1% error in photometer readings are as follows:

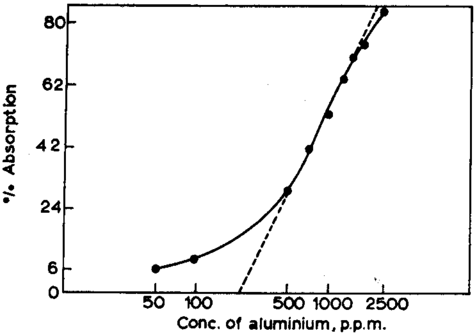

Fig. 3. Ringbom curve; oxy-acetylene flame.

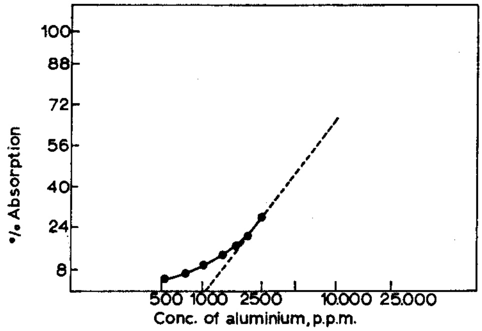

Fig. 4. Ringbom curve; oxy-hydrogen flame.

Oxy-acetylene flame

$$\frac{\%\ \text{relative analysis error}}{1\%\ \text{absolute photometric error}} = \frac{230}{\text{slope}} = \frac{230}{83} = 2.8$$

Oxy-hydrogen flame

$$\frac{\%\ \text{relative analysis error}}{1\%\ \text{absolute photometric error}} = \frac{230}{\text{slope}} = \frac{230}{82} = 2.8$$

Since the reading error in a good spectrophotometer is of the order of 0.2% on the transmittance scale, the relative analysis error is $2.8 \cdot 0.2 = 0.56\%$. However, other factors involved in the analysis, *e.g.*, separation by solvent extraction, dilution, etc. would probably make the over-all analysis error larger than the figures quoted above.

The results indicate that the absorptivity varies with the aluminum concentration when an oxy-acetylene flame is used — which means that calibration curves must be used to obtain accurate results. However, an oxy-acetylene flame has been found to be much more sensitive (absolute) than an oxy-hydrogen flame for this system.

The following studies were made on the effect of variables on aluminum absorption using an oxy-acetylene flame.

Slit-width

Previous work[7] indicated that an optimum concentration of 1250 p.p.m. of aluminium produced adequate sensitivity for the study of variables. Fuel ratios and flow rates were established and held constant. The burner position was adjusted to give maximum sensitivity and held constant. The slit-width was then varied from 0.1 mm to 0.3 mm as shown in Fig. 5. The absorption increased with an increase in slit-width until the slit-width became sufficiently wide to allow turbulence of the flame absorption zone to make the readings erratic. This point was reached at 0.25 mm, and above this slit-width the signal-to-noise ratio was unsatisfactory. To minimize the influence of the absorption zone turbulence, a slit-width less than 0.25 mm was used. A slit-width of 0.20 mm (a spectral slit-width of 6.2 mμ) produced adequate response with a high signal-to-noise ratio. A slit-width of 0.20 mm was, therefore, selected for the remaining investigations and held constant.

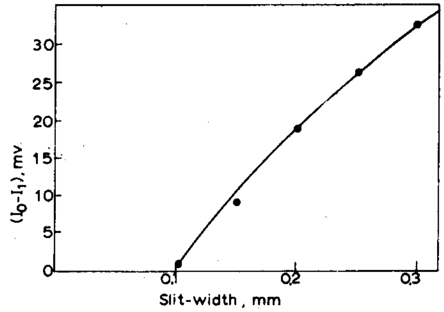

Fig. 5. Intensity of aluminum absorption as a function of slit-width; oxy-acetylene flame.

Flame position

Figure 6 is a plot of the intensity of aluminum absorption as a function of burner height measured from the fixed hollow-cathode beam. The burner position was varied by the use of three-dimensional positioning mechanisms which allowed the burner to be moved in a horizontal, vertical and lateral position, one mm per full turn of the adjustment knob. The tip of the burner, when placed in the hollow-cathode beam, was taken as the zero position. The burner was then moved in a downward direction in

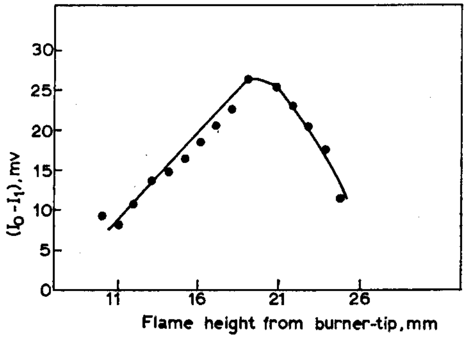

Fig. 6. Intensity of aluminum absorption as a function of flame-height; oxy-acetylene flame.

steps of 1 mm. The absorption was measured at each step. Maximum absorption was reached at 19 mm from the tip of the burner to the center of the hollow-cathode light beam.

The lateral displacement of the flame position as a function of absorption depends on the dimension of the focal point of the hollow-cathode lens. The smaller the cross-section of the light beam at the focal point, the more critical is the flame lateral position. The optimum condition is to have the entire beam focussed in the absorption zone. The instrument as designed by Kem-Tech Laboratories produces a beam which fulfils the above condition. Fig. 7 graphically shows the effect of lateral movement of the flame position on the aluminum absorption. Two maxima are observed in Fig. 7, which indicates that the maximum absorption takes place on the fringes of the inner cone. A broader beam may not show the above absorption characteristics — it may even show a decrease in over-all absorption. The above studies were performed with the burner fixed at 19 mm below the center point of the hollow-cathode beam, thus ensuring maximum vertical absorption.

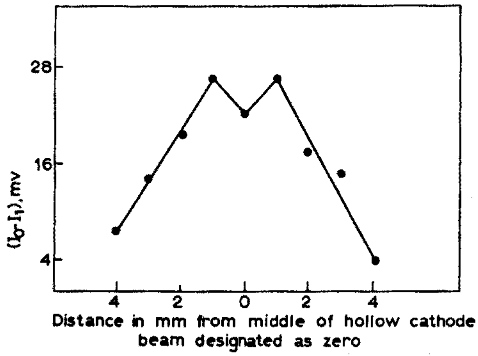

Fig. 7. Intensity of aluminum absorption as a function of flame position (lateral); oxy-acetylene flame.

The above studies emphasize the need for meticulous care in setting the flame position to obtain the maximum absorption.

Oxygen/fuel ratio

Figure 8 presents a family of curves drawn with the results obtained by holding the oxygen flow constant and varying the acetylene flow. The design of the Beckman burner is such that the limiting orifices present in the burner limit the flow rates. This burner design precludes the use of certain flow rates with certain oxygen/fuel ratios. The curves in Fig. 8 indicate that an oxygen/fuel ratio of about 2 would give the maximum absorption. Because of the limitations inherent in the burner and the increased aspiration of the organic solvent at higher oxygen flow rates, it was impossible to reach the oxygen/fuel ratio of even 2.1 until the oxygen flow rate was reduced to 3.5 l/min. Oxygen flow rates of 3.5 l/min and lower would approach this oxygen/fuel ratio. It is evident from the curves that an oxygen flow rate of 3.5 l/min or 3.0 l/min with an oxygen/fuel ratio of about 2 would give the maximum sensitivity.

However, at these settings the turbulent nature of the flame, caused by aspiration rates, luminescence, etc., becomes an important consideration. The high noise introduced by these factors makes the above ratio and flow rate unsuitable. For the burner used, the greatest signal-to-noise ratio is obtained with an oxygen/fuel ratio of 3.63. Analysis of Fig. 8 would indicate that it may be desirable to sacrifice 10% of the sensitivity at this oxygen/fuel ratio and use an oxygen flow of 3.5 rather than 3.0 l/min.

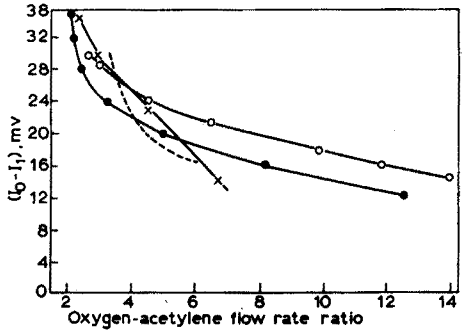

Fig. 8. Intensity of aluminum absorption as a function of ratio of flow rates of oxygen to acetylene at various oxygen flow rates.

This would then cause minor variations in acetylene flow rates to have less effect on the sensitivity. At an oxygen flow rate of 3.5 l/min and a fuel ratio of 3.63, the signal-to-noise ratio is not as good as that with the same ratio and an oxygen flow rate of 3.0 l/min. The oxygen flow rate of 3.0 l/min with an oxygen/fuel ratio of 3.63 was, therefore, finally selected. This oxygen/fuel ratio gives adequate sensitivity with optimum signal-to-noise ratio.

The turbulence in the flame at various oxygen/fuel ratios is caused by several factors. The oxygen flow rate determines the rate of aspiration of the sample. Higher flow rates introduce more organic solvent into the flame, the vigorous combustion of which creates turbulence in the flame. The carbon particles in the fuel-rich flame produce luminosity, incandescence, and instability of the flame. Such a fuel-rich flame gives strong emission from the C_2-band systems[8]. The above studies were extended using various acetylene flow rates and varying the oxygen flow rates. The results of this investigation (Fig. 9) confirmed those presented in Fig. 8.

Figure 9 shows that the absorption increases with increasing acetylene flow rates — it reaches the maximum with an acetylene flow rate of 1.38 l/min, and the minimum with an acetylene flow rate of 0.3 l/min (the latter gives an entirely flat graph). The reverse tendency can be noted with the oxygen flow rate as shown in Fig. 8. The absorption increases with decreasing oxygen flow rates. It should be noted that the ratio of 2.1 is smaller than the stoichiometric ratio of 2.5 for the reaction

$$2\,C_2H_2 + 5\,O_2 = 4\,CO_2 + 2\,H_2O$$

However, all ratios were calculated without taking into consideration the additional oxygen required for combustion of the organic solvent, nor the large amount of air entrained at the base of the flame.

From these two curves it can be seen that the higher the acetylene flow rate and the lower the oxygen flow rate, the higher is the absorption. Both of these flow rates have their practical limits, and the maximum absorption takes place when these limits make the flow rate ratio equal to about 2.1. However, with this ratio the flame background becomes too noisy and the readings become too erratic for accurate measurement.

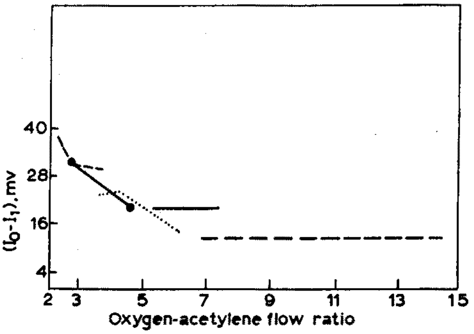

Fig. 9. Intensity of aluminum absorption as a function of ratio of flow rates of oxygen to acetylene at various acetylene flow rates.

Precision, detection limit and sensitivity

It can be seen from Table I that the average standard deviation is 53 p.p.m. at the level of aluminum concentrations of 750 p.p.m. and above. This high value of standard deviation is mainly due to the enhanced production of flame gases caused by the vigorous combustion of the organic solvent, which is the major source of fuel in such a flame.

TABLE I

PRECISION DATA

Aluminum concentration (p.p.m.)	*Standard deviation (p.p.m.)*		*Number of determinations*
78	13		17
100	18		12
500	37		11
750	59	Average = 53	11
1000	44		5
1250	51		11
1750	58		6

Assuming the detection limit is twice the standard deviation found at very low levels of concentration and taking the standard deviation of 13 p.p.m. at the concentration level of 78 p.p.m., the detection limit for aluminum may be set at 26 p.p.m. This detection limit has been confirmed experimentally by direct determination with a solution of 26 p.p.m. aluminum. The concentration of aluminum required to produce 1% absorption has been found to be 8 p.p.m.

Interference study

Atomic absorption spectroscopy with a modulated radiation source is free from radiation interference and virtually free from physical interference[1,9] — only chemical interferences present a problem. Since aluminum was isolated from associated elements by complex formation and extracted with the organic solvent, 4-methyl-2-pentanone, at the controlled pH of 3.5, the chemical interference from other cations and anions can only come from those which co-extract at this pH. Although no systematic study of such interference was made, it was considered unlikely that any cations and anions would co-extract in quantities exceeding their tolerance limits in atomic absorption spectroscopy. Even if they are co-extracted, they can be partly removed by backwashing the organic extracts with water before the extracts are atomized into the flame.

Mechanism of metal atom production in flames

The mechanism of metal atom reduction in flames has been explained by ROBINSON AND KEVAN[10]. The flame consists of four parts: (*1*) base, (*2*) inner cone, (*3*) reaction zone, and (*4*) outer mantle. The reactions that occur in these four zones are respectively (*1*) evaporation, (*2*) decomposition, (*3*) oxidation, and (*4*) equilibrium with metal atoms. Of the factors that control these reactions, the most important ones are the feed rate in (*1*), the flame temperature in (*2*), the flame composition and the stability of AlO in (*3*), and the flame composition and the equilibrium constant of the reaction $Al + O \rightleftarrows AlO$ in (*4*).

It is seen that the population of aluminum atoms depends on step *3* and Kp (equilibrium constant) in step *4*. Kp depends on temperature and dissociation energy and determines whether or not enough atoms actually exist long enough to absorb radiation. The attainment of equilibrium depends on the temperature and the residence time of the particles passing through the flame. It must be noted that the flame gases are never in complete equilibrium. However, the experimental evidence that the sensitivity is low and the flame position is critical indicates that the life of the ground state aluminum atoms (*i.e.*, before oxidation to AlO) is extremely short. In step *2*, it is also possible that this particular chelating agent, cupferron, facilitates the process of detection by the ease with which aluminum cupferrate complex is decomposed in the flame yielding aluminum atoms.

Molecular compounds and thermal dissociation

A high reducing flame[9] is calculated to be the most favorable medium to inhibit AlO formation. A rich acetylene flame containing acetylene less than the stoichiometric ratio (equal to 2.5 for the reaction $2\ C_2H_2 + 5\ O_2 = 4\ CO_2 + 2\ H_2O$) should thus be the most favorable medium. As shown in Figs. 7 and 8, the maximum aluminum absorption takes place when the ratio of oxygen/acetylene flow rate is about 2.1. It must be remembered that the organic solvent is the major fuel at this ratio and requires additional oxygen for its combustion. This should be set against the fact that there is a large body of air entrained at the base of the burner. On the whole, for the maximum absorption, the oxygen/fuel ratio corresponds more closely to a burned gas composition which consists of $CO + H_2O$ (rather than $CO_2 + H_2O$) and approaches 1.5 which is the theoretical ratio of oxygen/acetylene for the reaction

$$2\ C_2H_2 + 3\ O_2 = 4\ CO + 2\ H_2O$$

The bulk of the burned flame gases may be regarded as a combined high-temperature solvent and thermostat for chemical reactions involved, *e.g.*, formation, dissociation of AlO and re-combination, which involves evolution or absorption of large quantities of energy. The extent of these processes of formation, dissociation and re-combination depends on the temperature, the composition of the flame gases and the velocity of the reacting species; they also determine the locations within the flame where the aluminum atoms are produced. In the flames used, atomic or molecular oxygen is always present, especially in the outer mantle. As can be seen from Fig. 7, aluminum absorption is maximum in the reaction zone of the flame and falls off sharply, reaching the minimum value in the outer mantle. When the ground state aluminum atoms reach the outer mantle of the flame, where there is an abundance of atomic or molecular oxygen, they form AlO with consequent decrease in atomic absorption. Flame composition thus appears to play a decisive role in the detection process, but the mechanism is only partly understood. HERZBERG[11] reports that AlO bands are emitted by the outer layers of an electric arc, which means that high temperature alone does not dissociate AlO sufficiently. Also, ROBINSON[2-4] could not detect aluminum absorption, even by using an oxy-cyanogen flame (4550°). A lower temperature in conjunction with a highly reducing medium has been found to produce aluminum atoms[7,12]. This lends support to the hypothesis that the aluminum atoms are produced by chemical reactions, and the flame composition is a more potent factor than the flame temperature in production of the aluminum atoms. It may also be noted that an increase in temperature will inevitably alter the composition of the flame gases, and this may well result in a shift of the equilibrium $Al + O \rightleftarrows AlO$ to the right, with consequent decrease in the aluminum atom population. Further work is necessary to elucidate fully the role played by flame composition in the detection process, and here may be found the key to the problem: the part played by flames in forming refractory compounds with many elements, which are, therefore, not amenable to analysis by atomic absorption spectroscopy. This problem is indeed one created by flames because it is absent in flameless atomization[13] in non-oxidizing medium, and therefore, the flame composition should hold the key for its solution or else the problem can be eliminated by avoiding flames altogether as a means of sample atomization.

To explain the absorption by aluminum in flames, the following points must be considered. In order to obtain aluminum absorption in a flame, aluminum must be obtained as atoms in the ground state. It has been established experimentally[14] that extremely small quantities of the ground state aluminum atoms are produced when aqueous solutions are atomized into an air-acetylene flame (concentration in p.p.m. giving 1% absorption > 1000). Aqueous solutions of oxy-hydrogen and oxy-acetylene flames fed with water have an energy equivalent to about 5 eV and 5.5 eV, respectively. The dissociation energy[15,16] of AlO is around 6 eV. It can, therefore, be predicted that AlO will readily form and remain predominantly undissociated in an oxy-hydrogen or an oxy-acetylene flame fed with aqueous solutions. Oxy-hydrogen and oxy-acetylene flames fed with an aerosol containing 4-methyl-2-pentanone have an energy equivalent to about 6 eV and 6.3 eV, respectively (these figures[17] are only indicative, depending as they do on many factors, *e.g.*, flowrates of aerosol, oxygen and fuel gases, particular elements present in the aerosol, etc.). It can be seen that AlO will tend to dissociate ($AlO \rightarrow Al + O$) in an oxy-hydrogen flame and more so in an oxy-acetylene flame, when both of them are fed with an aerosol containing 4-methyl-2-pentanone.

Although the molecular dissociation of AlO increases, the large values for the dissociation energy of AlO and Kp make the bulk of aluminum still exist as undissociated AlO molecules. This is substantiated by the experimental evidence[12] that under identical experimental conditions, when an oxy-acetylene flame was used, with enhancement of the ground state alunimum atom population, there was also simultaneously an enhancement of AlO band emission (*i.e.*, enhancement of AlO population); the intensity of emission of the 396.2 mμ aluminum line is equal to the intensity of the strongest AlO band head at 484 mμ of the AlO molecular band systems. However, the flame composition and the organic solvent play more decisive roles than the flame temperature in the production of the aluminum atoms. The function of 4-methyl-2-pentanone appears to be (*1*) to increase the feed rate of the aluminum complex, which results in an increased population of both the ground state aluminum atoms and AlO molecules; (*2*) to increase the rate of evaporation of the solution resulting in faster release of solid salts available for decomposition; (*3*) to increase the flame temperature.

The last is also the least. The experimental evidence[2-4,14] that absorption by aluminum atoms in flames which were fed with aqueous solution was small or non-existent points to the fact that the equilibrium of the reaction $Al + O \rightleftarrows AlO$ shifts predominantly to the right and also that the life of the ground state aluminum atoms is extremely short. With a strongly reducing flame coupled with temperature enhancement with an organic aerosol, both the ground state aluminum atoms and the AlO molecules were observed in flames [7,12].

This work was sponsored by the U.S. Air Force Contract AF 30(602)-2426 and the U.S. Public Health Service Contract AP 00128-02.

Note

When this paper was in its final form, a scientific communication[18] was published, which reported, inter alia, detection of aluminum with a sensitivity of 6 p.p.m./1% absorption when a solution of aluminum chloride in ethanol was aspirated into a strongly reducing oxy-acetylene flame.

SUMMARY

A study of the determination of aluminum by atomic absorption spectroscopy has been made using a solution of aluminum cupferrate in 4-methyl-2-pentanone to feed oxy-acetylene or oxy-hydrogen flames. Investigations were made on the effect of the variables, *viz.*, slit-width, flow rates, flow ratios and flame positions, on the intensity of aluminum absorption. The data were studied to determine the optimum conditions. These investigations brought out the comparative merits of the two flames for the determination of aluminum, and also elucidated the mechanism of aluminum absorption in an oxy-acetylene flame.

RÉSUMÉ

Une étude a été effectuée sur le dosage spectroscopique par absorption atomique de l'aluminium, sous forme de cupferrate dans la méthyl-4-pentanone-2. Les auteurs ont examiné l'influence de divers facteurs (largeur de la fente, position de la flamme, etc.) sur l'intensité de l'absorption de l'aluminium. Ces recherches permettent de comparer les avantages des deux flammes (oxy-acétylène et oxy-hydrogène) pour le dosage de l'aluminium et également d'élucider le mécanisme de l'absorption de l'aluminium dans la flamme oxy-acétylénique.

ZUSAMMENFASSUNG

Zur Bestimmung des Aluminiums mit der atomaren Absorptionsspektroskopie wurden Versuche durchgeführt, bei denen eine Lösung von Aluminiumkupferronat in 4-Methylpentanon-2 in einer

Sauerstoff-Acetylen-oder einer Sauerstoff-Wasserstoff-Flamme versprüht wurde. Verschiedene Faktoren, die die Intensität der Absorption beeinflussen, wie z.B. die Flammenposition, die Zusammensetzung der Gasgemisches oder die Spaltbreite, wurden untersucht und die optimalen Bedingungen bestimmt. Die Versuche zeigen die Vorteile der beiden Flammen und ergeben ferner eine Deutung für den Mechanismus der Absorption in der Sauerstoff-Acetylen-Flamme.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH 2-MERCAPTOBENZOXAZOLE

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(Received May 14th, 1963)

A number of compounds have been proposed as reagents for the spectrophotometric determination of palladium. *p*-Nitrosodiphenylamine, *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline have been reported by OVERHOLSTER AND YOE[1,2] as highly sensitive reagents for the spectrophotometric determination of palladium. WEST AND AMIS[3] studied the reaction of *para*rosaniline hydrochloride (*p*-fuchsin) with palladium(II) ions and developed a useful spot-test procedure. Positive interferences are easily obviated and there is no interference caused by other members of the platinum group under their test conditions. CHENG[4] states that 2-nitroso-1-naphthol gives a color reaction with palladium ions which shows tolerance to many ions that usually interfere with its spectrophotometric determination. Certain mercapto or thiol compounds were used by MAJUMDAR AND CHAKRABARTTY[5]. AYRES AND JANOTA[6] used quinoxaline-2,3-dithiol as a spectrophotometric reagent for this metal.

2-Mercaptobenzoxazole (2-benzoxazolethiol) is reported by DUVAL *et al.*[7] to give a precipitate with rhodium. The compound also gives a sensitive colour reaction with palladium(II) ions but no previous attempt has been made to use it as a spectrophotometric reagent for palladium.

This paper presents an extensive study of the reaction of palladium(II) with 2-mercaptobenzoxazole and its use in a spectrophotometric method for the determination of small amounts of palladium. The reagent is not as sensitive as the *p*-nitrosophenylamino-type of compound but is quite satisfactory for the determination of palladium in concentrations as low as a few tenths p.p.m.

EXPERIMENTAL

Apparatus

Absorbance curves were obtained with a Beckman ratio recording spectrophotometer, Model DK-2. For measurements at a single wave-length a Beckman spectrophotometer, Model DU, was used. Measurements were made in matched 1.00-cm Corex cells.

A Beckman pH meter, Model G, was used for all pH measurements. It was checked with certified standard buffer solutions.

Reagents

Standard palladium solution. Dissolve 0.843 g of palladium chloride, $PdCl_2$, in 25 ml of 0.2 *N* hydrochloric acid and dilute to 1 l with distilled water. The solution contains 0.5 mg of palladium per ml. Standardize the solution gravimetrically by the dimethylglyoxime method[8].

Pure palladium metal is also satisfactory for preparing standard palladium solutions. Dissolve 0.5 g of metallic palladium in 6 ml of 12 *N* hydrochloric acid. Add 5 ml of concentrated nitric acid and evaporate to dryness to remove the acids. Dissolve the residue in 25 ml of 0.2 *N* hydrochloric acid and dilute to 1 l with distilled water.

More dilute standard solutions are made by diluting the standard stock solution with 0.005 *N* hydrochloric acid.

2-Mercaptobenzoxazole, 0.15% (0.011 M). Dissolve 0.15 g of 2-mercaptobenzoxazole (Eastman 5311) in 100 ml of a 1 : 1 mixture of dioxane and distilled water.

Solutions of diverse ions. Reagent-grade salts were used to prepare solutions of various ions in 0.005 *N* hydrochloric acid. These solutions generally contained 1 mg of the ion per ml of solution.

Other reagents. All other reagents were analytical grade and were used without further purification.

PRELIMINARY STUDIES

Properties of the reagent

2-Mercaptobenzoxazole is practically insoluble in water but dissolves in many organic solvents to give a clear pale yellow solution. It is highly soluble in dioxane.

Fig. 1 shows the absorbance curve of the reagent and the palladium complex in the visible and near ultraviolet regions. In order to obtain a low reagent blank and a useful range of palladium concentration, a 0.15% reagent solution is required. The reagent solution is not very stable and a fresh one should be prepared daily.

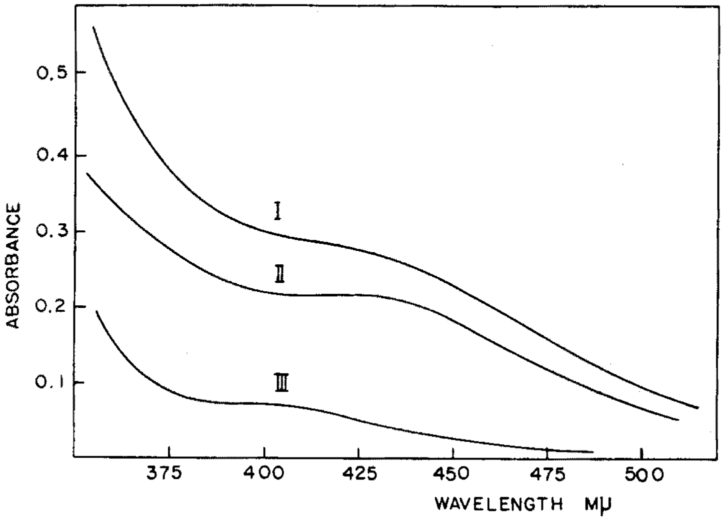

Fig. 1. Absorbance of the palladium complex. Curve I, Pd complex *vs.* water; curve II, Pd complex *vs.* reagent; curve III, reagent *vs.* water.

Properties of the complex

Colour. The reagent reacts instantly with palladium ions and forms an orange yellow precipitate which is not very soluble in water, ethanol and acetone. The complex gradually precipitates from a dioxane solution, but this can be avoided by using a mixture of cyclohexanone and dioxane as the diluting solvent, and a yellow coloured solution is obtained.

The ratio of cyclohexanone to dioxane is not critical, and 30% of cyclohexanone is satisfactory in our method.

The absorbance of the complex against the reagent solution is shown in Fig. 1 (curve II). The curves show that the absorbance of the complex and that of the reagent (Fig. 1, Curve III) decrease sharply above 340 mμ and the colour of the complex is partially masked by the yellow colour of the reagent. For this reason, absorbance measurements were made at 375 mμ.

Effect of acidity. The complex is formed over the entire pH range. If the pH is increased, the colour intensity is increased but the stability of the complex is decreased. The use of a buffer solution to control the pH was not advisable because of the tendency of the complex to precipitate. For this reason, a 0.005 *N* hydrochloric acid solution of the palladium sample was used without further adjustment of the pH.

Reaction rate and stability. The reaction is instantaneous but the complex is slightly unstable. After 15 min, the colour intensity decreases slowly, but the decrease is only 1% in 10 min.

Order of addition of reagents. The order of addition of the reagents was found to have no effect on the absorbance of the complex.

Effect of temperature. Absorbance measurements at 15°, 25° and 35°, respectively, showed the complex to be independent of normal variations in laboratory temperature.

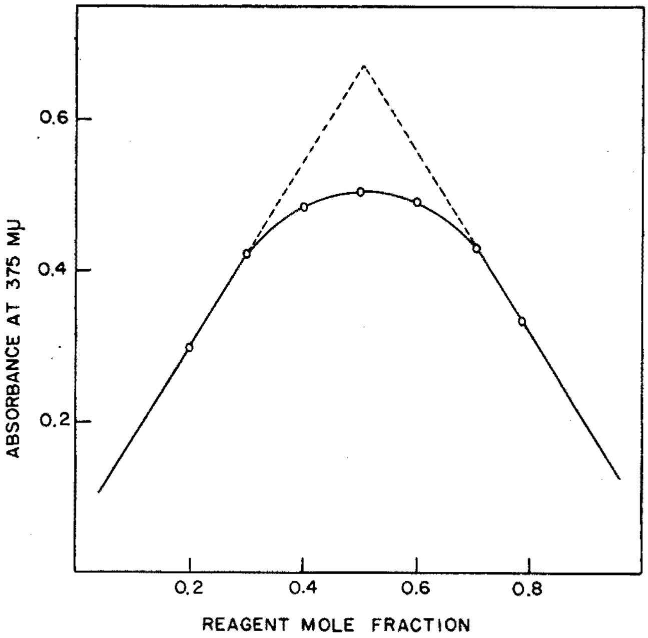

Fig. 2. Mole ratio determination by the method of continuous variations.

Mole ratio studies. In order to study the ratio of palladium to organic ligand, the continuous variations method of JOB[9] as modified by VOSBURGH AND COOPER[10] was used. It showed the complex to have a 1 : 1 ratio of palladium to organic ligand. The same ratio was found by the method of YOE AND JONES[11]. The graph for the continuous variations method is shown in Fig. 2.

Effect of diverse ions. The tolerances to diverse ions are summarized in Table I.

TABLE I

TOLERANCE OF DIVERSE IONS

(20.0 p.p.m. Pd)

Ion	*Added as*	*Limiting concentration (p.p.m.)*	
		± 2%	± 5%
Pt^{4+}	H_2PtCl_6	3	7
Au^{3+}	$AuCl_3$	1	3
Cu^{2+}	$Cu(NO_3)_2$	0.7	2
Ru^{3+}	$RuCl_3$	1	3
Co^{2+}	$Co(NO_3)_2$	>100	>100
Os^{6+}	K_2OsO_4	4	10
Ni^{2+}	$Ni(NO_3)_2$	14	35
Cd^{2+}	$Cd(NO_3)_2$	13	32
Fe^{3+}	$Fe(NO_3)_3$	0.4	1
Th^{4+}	$Th(NO_3)_4$	16	40

Beer's law. Beer's law is obeyed over the concentration range 2 to 40 p.p.m. palladium, the most sensitive range being 15 to 30 p.p.m.

Sensitivity. The sensitivity of the color reaction is 0.08 μg of Pd per cm^2 for $\log I_0/I = 0.001$, corresponding to 1 part of palladium in 12.5 million parts of solution. A more practical sensitivity, *i.e.*, an absorbance of 0.005, is 0.4 p.p.m. The spot-plate sensitivity is 0.05 μg of Pd per 0.05 ml of test solution and the dilution limit is 1 to 1,000,000.

PROCEDURE

The sample weight should be chosen so that 1 ml of sample solution will contain 100 to 300 p.p.m. of palladium. Mix 1 ml of sample solution, 3 ml of dioxane and 3 ml of cyclohexanone in a 10-ml volumetric flask. Add 2 ml of 2-mercaptobenzoxazole reagent solution to the flask, thoroughly mix and immediately dilute with dioxane to 10 ml. Again mix, allow the solution to stand for 20 min and measure the absorbance at 375 mμ using the reagent as a blank. Read the amount of palladium from a standard graph.

Analysis of synthetic solutions

The results of analysis of synthetic solutions are summarized in Table II. Each sample was analyzed in duplicate or triplicate. The values were in close agreement; the averages are recorded in the Table.

Precision

The precision of the method was determined for a solution containing palladium alone (20 p.p.m.) and for synthetic solution No. 1 (Table II). For each solution 11

TABLE II

ANALYSIS OF SYNTHETIC SOLUTIONS

Series A

No.	*Pd present (p.p.m.)*	*Other ions present (p.p.m.)*					*Pd found (p.p.m.)*
		Pt^{4+}	Au^{3+}	Cu^{2+}	Ru^{3+}	Co^{2+}	
1	21.3	1	0.4	0.1	—	10	21.5
2	21.3	2	—	—	0.1	20	21.7
3	21.3	—	0.5	0.2	—	20	21.6
4	21.3	1	—	0.1	0.1	40	21.5

Series B

No.	*Pd present (p.p.m.)*	*Other ions present (p.p.m.)*						*Pd found (p.p.m.)*
		Pt^{4+}	Os^{6+}	Ni^{2+}	Cd^{2+}	Fe^{3+}	Th^{4+}	
5	21.3	1	1	2	—	—	2	21.6
6	21.3	1	—	4	—	—	3	21.5
7	21.3	2	—	—	—	0.1	2	21.5
8	21.3	2	—	4	3	—	1	21.6

determinations were made. From these data the standard deviation, σ, was calculated from the formula $\sigma = \sqrt{d^2/(n-1)}$, where d is the deviation from the mean and n is the number of determinations. The results are as follows: 20.0 p.p.m. Pd, $\sigma = \pm 0.165$ p.p.m., *i.e.*, ± 0.88%. Synthetic solution No. 1, $\sigma = \pm 0.184$ p.p.m., *i.e.*, ±0.91%.

SUMMARY

A new spectrophotometric method for the determination of palladium is described using 2-mercaptobenzoxazole as reagent. The color reaction has a sensitivity of 0.08 µg of Pd per cm² for log $I_0/I = 0.001$ and obeys Beer's law from 2 to 40 p.p.m. The effects of pH, time, order of addition of the reagents, temperature and diverse ions were investigated. The procedure was applied to synthetic solutions containing palladium plus a variety of foreign ions.

RÉSUMÉ

Une nouvelle méthode spectrophotométrique est proposée pour le dosage du palladium, au moyen de 2-mercaptobenzoxazole. A 375 mµ, la loi de Beer est suivie pour des concentrations en palladium allant de 2 à 40 p.p.m.

ZUSAMMENFASSUNG

Es wird eine spektralphotometrischen Methode zur Bestimmung von Palladium mit Hilfe von 2-Mercaptobenzoxazol beschrieben. Der Einfluss verschiedener Faktoren wurde untersucht. Bei 375 mµ gilt das Beersche Gesetz für einen Konzentrationsbereich von 2 bis 40 p.p.m. Pd.

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ANALYSIS OF STYRENE–BUTADIENE COPOLYMERS BY NMR SPECTROSCOPY

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(Received May 26th, 1963)

The initial application of high-resolution nuclear magnetic resonance (NMR) to the study of polymers was made by BOVEY, TIERS AND FILIPOVICH[1]. In their study it was noted that the line widths obtained in NMR spectra of polymer solutions were dependent on the local viscosity in the direct vicinity of the chain segments and not on the macroscopic viscosity of the sample. This observation was responsible for the applications of NMR techniques to the determination of tacticities and functional groups in polymeric systems. An example of the former is the determination of the relative amounts of *iso*, *syndio-* and *atactic* triads in polymethylmethacrylate[2–5]. Recently, CHEN[6] has used high-resolution NMR to determine the functional groups in butadiene–isoprene copolymers. This study is concerned with the application of high-resolution NMR to the determination of styrene, 1,2-butadiene addition and 1,4-butadiene addition in styrene–butadiene copolymers.

EXPERIMENTAL

Apparatus

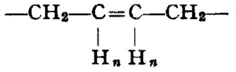
Spectra were obtained at a frequency of 60 megacycles per sec using a Varian A-60 NMR spectrometer. Spectral calibration was checked using a SIE Model M-2 R-C Oscillator in conjunction with a Hewlett-Packard 5243L electronic counter. The spectra were calibrated for tetramethylsilane equal to zero p.p.m. The temperature of the probe was maintained at 40 ± 2° by use of a V-6040 A-60 temperature controller. The electronic integrator of the A-60 was used to measure the areas of the absorption mode signals. Each of the pertinent bands was integrated five times and the average value used in the calculations.

Sample preparation

Polymer solutions were prepared by dissolving approximately 5 to 15% weight of the sample in spectroquality-grade carbon tetrachloride. Dissolution of the polymer was facilitated by gently heating on a steam bath or in some cases by ultrasonic vibration. A styrene–butadiene copolymer of known composition (by infrared analysis) was used as the base stock solution. This copolymer was blended with varying amounts of 98% *cis*-1,4-polybutadiene in order to obtain an effective range of compositions. Tetramethylsilane was added as an internal standard.

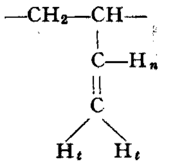
Peak assignments

The olefinic proton introduced into the polymer by butadiene can be designated as follows:



$$-CH_2-\underset{H_n}{C}=\underset{H_n}{C}-CH_2-$$

(1,4-addition *cis* or *trans*)



(1,2-addition)

The non-terminal olefinic hydrogens (H_n) resonate at a lower primary field than the terminal olefinic protons (H_t)[7]. In Fig. 1 three NMR spectra of styrene–butadiene copolymers varying in composition are shown. In these polymers the chemical shift for

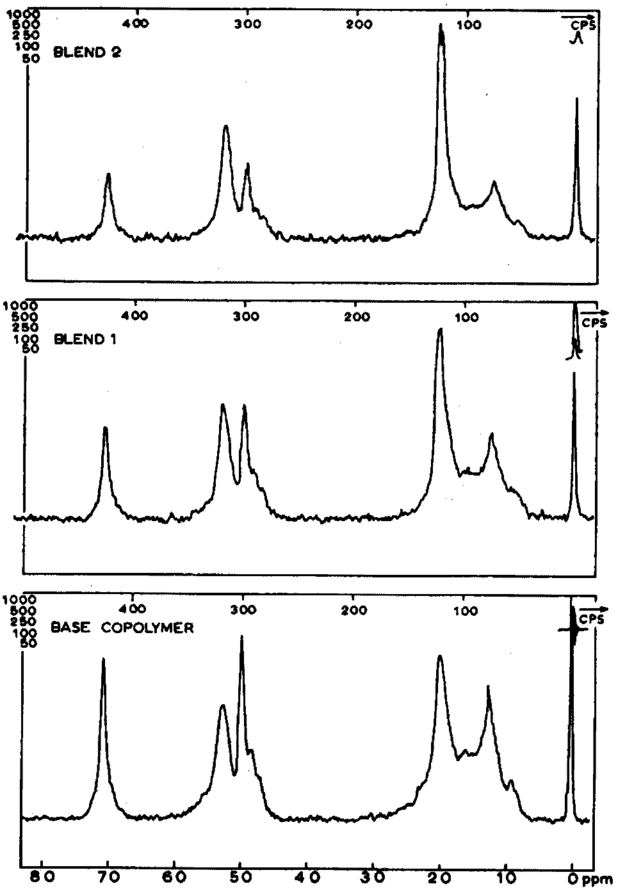


Fig. 1. NMR spectra of styrene–butadiene copolymers.

H_n is 5.3 to 5.4 p.p.m. and that for H_t 5.0 to 5.1 p.p.m. The terminal protons of the 1,2-butadiene addition segment are spin-coupled to the non-terminal proton. The coupling constants are approximately 10 c/s for *cis* and 18 c/s for *trans*. This is the origin of the two small peaks adjacent to the main H_t absorption band. The corresponding splitting of the internal olefinic absorption of the 1,2-addition product is masked by the broad absorption band of the 1,4-addition olefinic hydrogens.

The aromatic protons derived from the styrene segment of the polymer resonate at 7.2 p.p.m. This is in agreement with chemical shift values tabulated for monoalkylbenzenes[8]. The extremely low field position for this resonance is due to the "ring-current" effect[9].

The remaining portion of the spectrum between approximately 1 and 2.5 p.p.m. is contributed by methylene and methine protons present in the polymer backbone structure. The band at *ca.* 2 p.p.m. arises from moieties alpha to the double bond and that at *ca.* 1.3 p.p.m. from those beta to the double bond. However, depending upon the manner in which the mononer units are joined together, it is possible for these moieties to experience small differences in their magnetic environments. This, coupled with the somewhat restricted motion of the polymer backbone, leads to peak broadening. As a result, this region cannot be used for quantitative analysis, although it can be used for diagnostic purposes. The peak at *ca.* 2 p.p.m. will roughly correlate with 1,4-addition and that at *ca.* 1.3 p.p.m. with 1,2-addition.

On the basis of these peak assignments, the bands pertinent to this analysis are designated as follows:

Hydrogen type	*Band maxima (p.p.m.)*
Aromatic	7.2
Non-terminal olefinic	5.3–5.4
Terminal olefinic	5.0–5.1

Calculations

Let

A_a = relative area of aromatic absorption

A_t = relative area of terminal olefinic absorption

A_n = relative area of non-terminal olefinic absorption

M_1 = moles of styrene segment in effective sample volume

M_2 = moles of 1,2-butadiene addition segment in effective sample volume

M_3 = moles of 1,4-butadiene addition segment in effective sample volume

Then

Relative areas	*Styrene*	*1,2-Addition*	*1,4-Addition*
A_a	$= 5\,M_1$	$+ \;0\,M_2$	$+ \;0\,M_3$
A_t	$= 0\,M_1$	$+ \;2\,M_2$	$+ \;0\,M_3$
A_n	$= 0\,M_1$	$+ \;1\,M_2$	$+ \;2\,M_3$
—	——	——	——
1	$= 5\,M_1$	$+ \;3\,M_2$	$+ \;2\,M_3$

From which the following calculation is derived:

Component	*Relative number moles*	*Mole fraction*
Styrene	$M_1 = A_a/5$	$X_1 = A_a/5T$
1,2-Butadiene addition	$M_2 = A_t/2$	$X_2 = A_t/2T$
1,4-Butadiene addition	$M_3 = (A_n/2)\text{-}(A_t/4)$	$X_3 = (A_n/2T)\text{-}(A_t/4T)$
Total	T	1.00

In order to obtain proper results using this technique it is necessary that the area integration be carried out under conditions such that $(\gamma H_1)^2 T_1 T_2 \ll 1$, where γ is the magnetogyric ratio, H_1 the radio-frequency driving field, T_1 the spin–lattice relaxation time and T_2 the spin–spin relaxation time. Under these conditions the area of the absorption band becomes proportional to the number of absorbing nuclei and independent of relaxation effects. Results of some analyses are shown in Table I.

TABLE I

COMPOSITIONS OF STYRENE–BUTADIENE AND POLYBUTADIENE BLENDS

		Styrene	*1,2-Addition*	*1,4-Addition*
Base copolymer[a]		15	56	29
Blend 1[a]	Found	12	44	44
	Calc.	12	42	46
Blend 2[a]	Found	10	39	51
	Calc.	11	39	50
Blend 3	Found	8	26	66
	Calc.	8	30	62
Blend 4	Found	6	24	70
	Calc.	6	25	69
Blend 5	Found	4	19	77
	Calc.	5	21	74

[a] Analyses calculated from spectra shown in Fig. 1.

DISCUSSION

This technique has been used routinely for the analysis of styrene–butadiene copolymers. The major time-consuming step is the dissolution of the sample. This operation is normally carried out in batches. The time required for analysis after dissolution is approximately 20 min. Although this approach will determine styrene, 1,2-butadiene addition and 1,4-butadiene addition, it will not differentiate between the *cis* and *trans* modes arising in 1,4-addition. No calibration is required for these analyses.

The author wishes to thank Esso Research Laboratories, Humble Oil & Refining Co. for permission to publish this material. The author is also indebted to Mr. W. E. HUNTER and Mrs. BLANCHE D. FOSTER for experimental work contributed to this study.

SUMMARY

A method for determining styrene–butadiene copolymer composition has been developed using NMR spectroscopy. The composition is determined in terms of mole per cent styrene, 1,2-butadiene addition and 1,4-butadiene addition. The NMR absorption bands derived from the aromatic and olefinic protons incorporated into the copolymer are used for this determination. Calibration is not required for the application of this method.

RÉSUMÉ

L'auteur propose une méthode d'analyse de copolymères styrène–butadiène par spectroscopie NMR ("nuclear magnetic resonance"). Les bandes d'absorption dérivées des protons aromatiques et oléfiniques, incorporés au copolymère sont utilisées pour cette détermination. Un calibrage n'est pas nécessaire.

ZUSAMMENFASSUNG

Es wurde ein Verfahren entwickelt, das mit Hilfe von kernmagnetischen Resonanzspektren die Analyse von Mischpolymerisaten aus Butadien und Styrol ermöglicht. Zur Bestimmung wurden Absorptionsbanden, die auf aromatische und olefinische Protonen zurückzuführen sind, benutzt. Eine Eichung ist bei dieser Methode nicht notwendig.

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A SENSITIVE METHOD FOR THE MICRODETERMINATION OF CHOLINE

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(Received June 4th, 1963)

A quantitative study of the composition of the phospholipids of the South African pilchard (*Sardina ocellata* Jenyns) necessitated the determination of small quantities of choline. Of the published methods for the determination of choline, one will be briefly mentioned here; a second will be discussed in more detail. Choline is frequently precipitated as choline reineckate [$C_5H_{14}ON \cdot Cr(NH_3)_2(SCN)_4$] and determined spectrophotometrically by dissolving the reineckate in acetone[1,2]. This method has proved unreliable with fractions of fish lipids in LOVERN's laboratory[3] as well as in ours.

LEVINE AND CHARGAFF[4] determine between 20–100 μg of choline by chromatography on filter paper, followed by conversion of choline to the insoluble choline phosphomolybdate and reduction of the latter to molybdenum blue by means of stannous chloride. The area of the blue spot thus produced is measured with a planimeter and the amount of choline read from a suitable calibration curve. Two factors are important in this method. Firstly, choline phosphomolybdate is by no means completely insoluble in water (under the conditions described, less than 20 μg of choline fails to form choline phosphomolybdate), thus the removal of excess phosphomolybdic acid from the paper by washing with running water has to be strictly standardized for temperature and time, in order to prevent loss of choline. Secondly, several workers have observed the presence of two blue spots when testing for choline according to LEVINE AND CHARGAFF[4,5]. Recently, it has been shown that this second spot is due to (2-chloroethyl)-trimethylammonium chloride (2-chlorocholine), an artifact formed from choline during the hydrolysis with aqueous hydrochloric acid[6]. This second spot, therefore, ought to be included in the calculation. This factor is, of course, of no consequence when alkaline hydrolysis is applied.

The present paper describes the determination of 0.1–3 μmoles (12–350 μg) of choline by precipitation of choline with phosphomolybdic acid in a small volume (less than 0.3 ml). The precipitate, after centrifuging and careful removal of excess phosphomolybdic acid, is dissolved in 1 N sulphuric acid and assayed spectrophotometrically for phosphorus. Phosphorus is determined by BARTLETT's modification of the FISKE AND SUBBAROW method[7]. The method determines the total quantity of choline plus 2-chlorocholine and is extremely sensitive and accurate. It can be conveniently adopted in laboratories working in the phospholipid field, since it is essentially a phosphorus determination. In addition, the application of the method in the analysis of pilchard phospholipids is demonstrated.

EXPERIMENTAL

Reagents

Choline chloride. This reagent (BDH Laboratory Reagent; at least 99% pure) was recrystallized from ethanol and dried over P_2O_5 in vacuo. Two solutions containing respectively 22.92 µmole and 4.57 µmole of choline/ml were prepared by dissolving the appropriate amount of choline chloride in 0.1 *N* hydrochloric acid.

2-Chlorocholine chloride. This compound was prepared as described by TAKETOMO[8]. Titratable chloride (argentometric) 22.36%; calculated for $C_5H_{13}NCl_2$ (158.07) 22.43%. Two solutions containing 17.99 µmole and 3.59 µmole of 2-chlorocholine/ml were prepared in 0.1 *N* hydrochloric acid.

Phosphomolybdic acid ($H_3PO_4 \cdot 12\, MoO_3 \cdot 24\, H_2O$, A.R.). A 10% solution in water was prepared. This solution was filtered before use.

All other chemicals were of A.R. grade.

Calibration curves

Choline. Quantities of 0.1 to 4 µmoles of choline were pipetted with an Agla micrometer syringe (Burroughs Wellcome & Co., London) into graduated 10-ml centrifuge tubes. The volume was kept as small as possible (less than 0.2 ml). If a micrometer syringe is not available, an ordinary pipette may be used and the volume subsequently reduced in a boiling water bath. To the solution was added 0.1 ml of 10% phosphomolybdic acid. A yellow precipitate appeared immediately; the tubes were covered with aluminium foil and put in ice for 1 h. Thereafter the tubes were centrifuged for 2 min at 4000 r.p.m. The liquid in the centrifuge tubes was removed with a small capillary pipette, without disturbing the precipitate. The precipitate was washed twice, without disturbing it, with 1 ml of cold (10°) aqueous 10% sodium sulphate solution in water, centrifuging in between. Great care was taken to remove all traces of phosphomolybdic acid by rinsing the walls of the tubes. After the removal of the washing liquid, the tubes were filled to 4.1 ml with distilled water, and 0.5 ml of 10 *N* sulphuric acid was added. The tubes were provided with a small pointed glass rod and arranged in a boiling water bath. The choline phosphomolybdate was dissolved slowly in the hot 1 *N* sulphuric acid with continual stirring. The tubes were cooled to room temperature, and the phosphorus determination was started by the addition of 0.2 ml of aqueous 5% ammonium molybdate tetrahydrate and 0.2 ml of FISKE AND SUBBAROW solution; the latter was prepared as described by BARTLETT[7].

The molybdenum blue colour was developed by placing the tubes in the boiling water bath for 7 min. The tubes were cooled in cold water, and the solution in each tube was transferred to a 50-ml volumetric flask, and diluted to volume with distilled water. The optical density at 830 mµ was determined against a reagent blank in a Unicam S.P. 500 spectrophotometer. The optical density of the reagent blank determined against distilled water was between 0.004 and 0.008.

2-Chlorocholine. The same procedure as that described for choline was followed. The dissolution of 2-chlorocholine phosphomolybdate, however, was accomplished in alkaline medium by the addition of 4.1 ml of 0.1 *N* sodium hydroxide. After the precipitate had completely dissolved (heating if necessary), the solution was acidified with 0.5 ml of 10 *N* sulphuric acid and phosphorus determined as described for choline.

Phosphorus. Amounts of 0.3 to 1 µmoles of phosphorus were used in preparing this curve, after a solution of potassium dihydrogen phosphate containing 0.323 μmole of phosphorus/ml had been prepared.

Determination of choline in a phospholipid

In general, choline determinations can be divided into two parts. Firstly, the hydrolytic procedure, which liberates choline from the phospholipid; secondly, the determination of liberated choline. Hydrolysis in acid (HCl) as well as alkaline ($Ba(OH)_2$) medium has been employed by different workers[1,4,5,9,10].

Hydrolysis. 50–200 mg of the phospholipid was hydrolysed with 2–12 ml of 2 *N* hydrochloric acid in a sealed ampoule at 120° for 24 h. The ampoule was opened and the solution was filtered. The residual tar was thoroughly leached with hot water and poured into the same filter. If the residual tarry material passed through the filter, the water phase was extracted with some light petroleum. After evaporation of the filtrate on the steam-bath and drying in a vacuum desiccator, the material was taken up in 1.0–4.0 (exact) ml of water and an aliquot taken for analysis. Larger or smaller quantities of material can of course be hydrolysed. For instance, the total amount of choline liberated by hydrolysis of as little as 1 mg of phospholipid can be conveniently determined in this way.

Hydrolysis with 6 *N* hydrochloric acid or barium hydroxide was carried out as described by LEVINE AND CHARGAFF[4] and MCKIBBIN AND TAYLOR[10], respectively.

Determination. An aliquot (*e.g.* 0.1 ml) containing between 0.1 to 3 μmoles of choline was treated as described for the preparation of the choline calibration curve. The amount of choline was obtained by reference to the choline calibration curve. If the presence of ammonia was suspected, 2 drops of a 38% formaldehyde solution in water were added 30 min before the introduction of phosphomolybdic acid.

Removal of amino acids. In some experiments it was necessary to remove amino acids before a choline determination. This was accomplished by adding to the solution in the centrifuge tube 0.02 ml of a 2% sodium nitrite solution and 1 drop of 4 *N* hydrochloric acid. The mixture was placed in a boiling water bath for approximately 15 min and subsequently analysed for choline.

Paper chromatography. Paper chromatograms were prepared as described previously[6]. In one instance the staining procedure of BRANTE[11] with iodine vapour was employed.

RESULTS AND DISCUSSION

Calibration curves

Fig. 1 shows the optical density of the molybdenum blue solution at 830 mμ *vs.* μmoles of choline, 2-chlorocholine and phosphorus. The figure shows that under the conditions of the test choline phosphomolybdate was soluble to a very small extent. An amount of 0.05 μmoles (6 μg) of choline dissolved during the procedure; this figure represents the lower limit of detection. The phosphomolybdate of 2-chlorocholine was completely insoluble, dissolving only on prolonged heating in 1 *N* sulphuric acid, which was the method applied in the determination of choline in phospholipids. In the preparation of the calibration curve it was dissolved, in the first instance, in 0.1 *N* sodium hydroxide; subsequent addition of sulphuric acid did not result in re-precipitation of the phosphomolybdate. It can be seen from the curves that any conversion of choline to 2-chlorocholine during hydrolysis with hydrochloric acid does not introduce any error in the determination.

From the three calibration curves it can be calculated that one mole of phosphorus produces the same colour density as 3.1 moles of choline and 3.04 moles of 2-chlorocholine. The molar ratio of choline and 2-chlorocholine to phosphorus in their respective phosphomolybdates is therefore 3. At this stage it should be mentioned that reduction of choline phosphomolybdate to molybdenum blue, without prior addition of excess ammonium molybdate did not produce a straight line calibration curve. In our initial experiments the addition of ammonium molybdate was omitted, but the blue colours produced were very weak and did not follow Beer's law. WHEELDON AND COLLINS[12], however, obtained a linear calibration curve at 630 mμ on reduction of choline phosphomolybdate without the addition of ammonium molybdate, by means of stannous chloride in acetone–alcohol (1 : 2) solution.

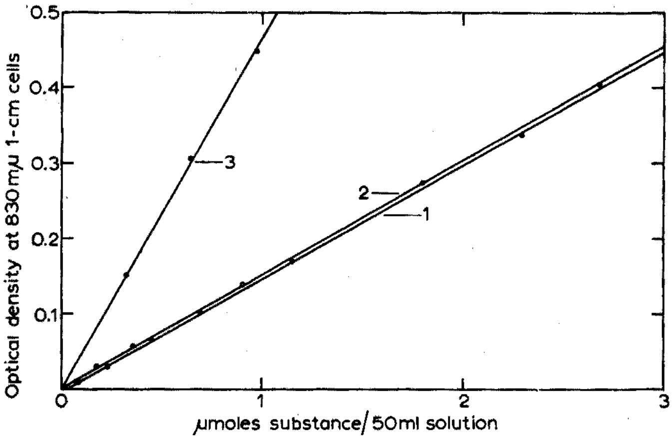

Fig. 1. Calibration curve showing optical density of the molybdenum blue colour at 830 mμ *vs.* μmoles of choline(1), 2-chlorocholine(2) and phosphorus(3).

Recovery of choline

Different quantities of choline chloride were added to a commercial cooking oil; the material was hydrolysed with 2 *N* hydrochloric acid as described in the experimental section. The recovery of choline was shown to be approximately 100% (Table I).

TABLE I

RECOVERY OF CHOLINE ADDED TO A COOKING OIL

Choline added (%)	*Choline recovered (%)*	*% Recovery*
2.73	2.74	100
6.31	6.25	99
8.75	8.90	102
10.57	10.83	103

Interference by compounds forming insoluble phosphomolybdates

Many nitrogenous compounds are capable of forming phosphomolybdates[13-15]. Extremely insoluble phosphomolybdates are found in the class of quaternary ammonium compounds[13-15]. These latter compounds, if present, will interfere in the determination of choline. It is shown below that, apart from ammonia, which is dealt with separately, no interfering compounds were present in hydrolysates of phospholipids.

Hydrolysates of pilchard phospholipids revealed on paper chromatograms one or two compounds forming an insoluble phosphomolybdate. The major compound was choline; the second compound, which sometimes occurred in small quantities on hydrolysis with aqueous hydrochloric acid, was 2-chlorocholine[6]. The remainder of the nitrogenous compounds in the hydrolysate consisted of amino acids and ethanolamine.

Only the basic amino acids lysine, histidine, arginine, the sulfur-containing amino acid cystine and ethanolamine were capable of precipitating a reasonably insoluble phosphomolybdate (*cf.*[16]). These precipitates, however, were formed with quantities far in excess of those found in the hydrolysates. It was nevertheless decided to test for a possible interference of these substances. It was found that a choline calibration curve prepared from choline, to which lysine, histidine, arginine, cystine and ethanolamine were added, was identical to a curve prepared from choline only. The quantities of amino acid added to choline were more than ten times the actual amount found in a hydrolysate, while ethanolamine was added in approximately twice this amount. Moreover, the determination of choline, in a hydrolysate before and after treatment with nitrous acid gave identical results. This is clearly shown in Table II.

Betaine, which, as pointed out by Lovern[3], is a likely interfering substance in the precipitation of choline as its reineckate was not detected. The staining procedure of Brante[11] failed to detect betaine on chromatograms of pilchard phospholipid hydrolysates treated with nitrous acid.

TABLE II

CHOLINE DETERMINATION IN A PILCHARD PHOSPHOLIPID

Hydrolytic procedure	*% Choline*	*Average*
2 *N* HCl at 120° for 24 h (*cf.* Lovern, Olley and Watson[9])	7.84, 7.93	7.9
	7.93, 8.04 (addition of HCHO)	8.0
	7.88, 7.79, 7.82 (HNO_2 treatment)	7.8
6 *N* HCl at 100° for 48 h (Levine and Chargaff[4])	8.03, 7.92, 8.03	8.0
	7.89, 8.06 (addition of HCHO)	8.0
	8.06, 8.06, 8.06 (HNO_2 treatment)	8.1
Saturated $Ba(OH)_2$ at 100° for 10 h; followed by ± 1 *N* HCl for $1^2/_3$ h at 100° (McKibbin and Taylor[10])*	7.36, 7.51, 7.40, 7.48	7.4
	6.97, 7.13, 6.82 (addition of HCHO)	7.0
	7.32, 7.28, 7.32 (HNO_2 treatment)	7.3
		Standard deviation = 0.06

* Determination of choline by the method of Entenman *et al.*[2] in this sample, *i.e.* reineckate precipitation, gave figures ranging from 8.8 to 12.7.

Interference by ammonia

Ammonium phosphomolybdate precipitates only slowly, hence it does not appear as a spot on paper chromatograms which are prepared by dipping the paper in a phosphomolybdic acid solution. The precipitate is much more soluble than choline phosphomolybdate. A calibration curve prepared with ammonium chloride appeared to be approximately a straight line parallel to the choline and 2-chlorocholine curves but cutting the abscissa at 0.3 μmoles. Serious discrepancies were observed if, for instance, 2 μmoles of ammonium chloride were added to choline in the preparation of the calibration curve. No interference, however, was noticed if formaldehyde was added before the precipitation with phosphomolybdic acid. Hexamethylenetetramine, the reaction product of ammonia and formaldehyde, did not precipitate as a phosphomolybdate, at least under the conditions of the test. The results in Table II demonstrate that hydrolysis in an alkaline medium[10] probably gave rise to ammonia formation.

Effect of acidity

The effect of acidity in the precipitation of choline phosphomolybdate was studied by preparing calibration curves in 0.1 *N* and 1 *N* hydrochloric acid solutions. The precipitate in the latter solution settled more quickly, but identical curves were obtained.

Upper limit of determination

The molybdenum blue colour produced in a phosphorus determination is, according to BARTLETT[7], proportional to the concentration of phosphorus up to 1.5 μmoles (corresponding to 4.5 μmoles of choline) in the reaction mixture. We observed above 5 μmoles of choline deviations from Beer's law and prefer to work in the range 0.1–3 μmoles of choline.

Choline determination in a phospholipid

The results obtained in the determination are shown in Table II. Hydrolysis with 2 *N* hydrochloric acid, which shows approximately 100% recovery of choline added to a commercial cooking oil (Table I), is preferred. It should be noted that hydrolysis in an alkaline medium gave lower results than in an acid medium. This is undoubtedly due to decomposition of choline under alkaline conditions; it is well known that the free base is susceptible to heat, in contrast to choline chloride[17].

The author wishes to thank Dr. G. M. DREOSTI for his permission to publish this paper, and Miss M. J. NIELSEN for help in some of the experiments.

SUMMARY

A sensitive method for the determination of choline (0.1–3 μmoles), particularly in phospholipids, is described. Choline is precipitated as the insoluble phosphomolybdate, the excess phosphomolybdic acid is carefully removed and phosphorus determined spectrophotometrically in the precipitate by reduction to molybdenum blue. Compounds capable of forming insoluble phosphomolybdates interfere. Interference of ammonia can be prevented by the addition of formaldehyde.

RÉSUMÉ

Une méthode est décrite pour le dosage de microquantités de choline (0.1–3 μmoles). La choline est précipitée sous forme de phosphomolybdate, dont on dose la teneur en phosphore, spectrophotométriquement, par réduction en bleu de molybdène.

ZUSAMMENFASSUNG

Es wird eine sehr empfindliche Methode zur Bestimmung von Cholin (0.1–3 μmol) beschrieben. Das Cholin wird als Phosphormolybdat ausgefällt und über die spektralphotometrische Bestimmung des durch Reduktion gebildeten Molybdänblaus bestimmt.

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THE DETERMINATION OF VANADIUM, MOLYBDENUM AND TUNGSTEN BY INFRARED SPECTROSCOPY

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(Received May 6th, 1963)

Until quite recently infrared absorption spectroscopy had few applications in analytical chemistry. The development of the potassium bromide disc technique[1] has, however, improved the position.

MAGEE AND AL-KAYSSI[2] used the technique in the systematic identification of fourteen anions, and later for the determination of rhenium and technetium[3]. In both investigations tetraphenylarsonium chloride was used as the precipitating agent for the polyatomic anions and the compounds formed showed strong, sharp absorption bands in the region 9–13 μ, which were assignable to metal–oxygen stretching frequencies.

In the present work a reagent was sought which, in the complex formed, preserved the metal–oxygen band; a further criterion was that the reagent should show an absorption spectrum having as few strong absorption bands as possible,particularly in the region 9–13 μ.

Among the reagents investigated 8-hydroxyquinoline possessed the necessary requirements. Little previous work has been carried out with this reagent in the infrared region of the spectrum. CHARLES *et al.*[4] and PHILLIPS AND DEYE[5] studied the infrared spectra of a number of metal 8-hydroxyquinolinates and came to the conclusion that a band in the region of 11 μ was assignable to the metal–oxygen stretching frequency. STONE[6] examined the infrared spectra of bismuth and magnesium 8-hydroxyquinolinates. The only infrared work of a quantitative nature using 8-hydroxyquinoline is that of MAGEE AND MARTIN[7] who used the reagent for the determination of niobium and tantalum.

In the present work the 8-hydroxyquinolinates of chromium, vanadium, molybdenum and tungsten were examined by the infrared technique with a view to their use in the qualitative and quantitative analysis of the elements. The results of these investigations are reported below.

EXPERIMENTAL

The 8-hydroxyquinolinates of chromium, vanadium, molybdenum and tungsten were prepared as follows.

Vanadium and chromium

To the aqueous solution of vanadium or chromium, 5 g of ammonium acetate were added, and the solution was heated. A 4% 8-hydroxyquinoline solution in glacial acetic acid was then added dropwise, and the solution was filtered, while hot, through a sintered glass crucible (porosity 4). The precipitate was washed thoroughly with hot water to remove excess of the reagent, and finally dried at 135–140°.

Molybdenum and tungsten

An aqueous solution of sodium molybdate or tungstate was made slightly alkaline with sodium hydroxide solution. A 4% 8-hydroxyquinoline solution in alcohol was then added, and the solution was heated to dissolve the precipitate formed.

The solution was now made acidic by the addition of 10% acetic acid and the precipitated molybdenum 8-hydroxyquinolinate or tungsten 8-hydroxyquinolinate filtered, while hot, through a sintered glass crucible. The precipitate was washed thoroughly with hot water to remove excess of the reagent, and dried at 135–140°.

Preparation of the disc

Samples (2 mg) of the dried complexes were mixed with 200 mg of potassium bromide (spectroscopic grade, dried at 140° for 24 h before use), and the mixture was ground as fine as possible with an agate pestle and mortar. The ground mixture was transferred to a Perkin-Elmer die. The assembled die was placed in the hydraulic press and evacuated for 2 min, and a total pressure of ten tons was applied for 5 min. The die was then dismantled and the disc removed, transferred to the disc holder and placed in position in the beam of a Perkin–Elmer ("Infracord") Spectrophotometer, Model 137. A potassium bromide disc of the same dimensions was placed in the reference beam. The spectrum was recorded over the range 3–15 μ.

RESULTS AND DISCUSSION

The spectra obtained for 8-hydroxyquinoline, three metal chelates, and mixtures of the chelates are shown in Figs. 1 and 2.

In the region 3–9 μ all the elements show similar absorption. This is probably due to the vibrations of the ring parts of the molecule. In the region 6–8 μ, however, bands are much sharper than in 8-hydroxyquinoline itself. Around 9 μ a sharp band occurs, which is not present in 8-hydroxyquinoline. According to CHARLES *et al.*[4], the 9 μ peak, which occurs in the spectra of all the elements investigated by them, but not in 8-hydroxyquinoline, is associated with C–O vibration in the molecule. These workers found that this peak varied by a small amount from one metal 8-hydroxyquinolinate to another, being displaced to lower frequencies as the atomic weight of the metal increased.

For all the metal 8-hydroxyquinolinates, it will be seen that a strong peak occurs at about 12 μ. It is suggested[8] that it is due to diatomic vibration, possibly metal–oxygen stretching frequency.

Molybdenum, tungsten and vanadium 8-hydroxyquinolinates all exhibit absorption in the region 10–12 μ (Figs. 1 and 2). These bands are very strong. Chromium 8-hydroxyquinolinate does not show absorption in this region, possibly because of the lack of metal–oxygen bonding in the chelate.

The number and positions of the bands in the region 10–12 μ are shown in Table I.

The region from 12–15 μ shows differences in the various spectra. The bands in this region are, however, generally broad, expecially in the case of vanadium.

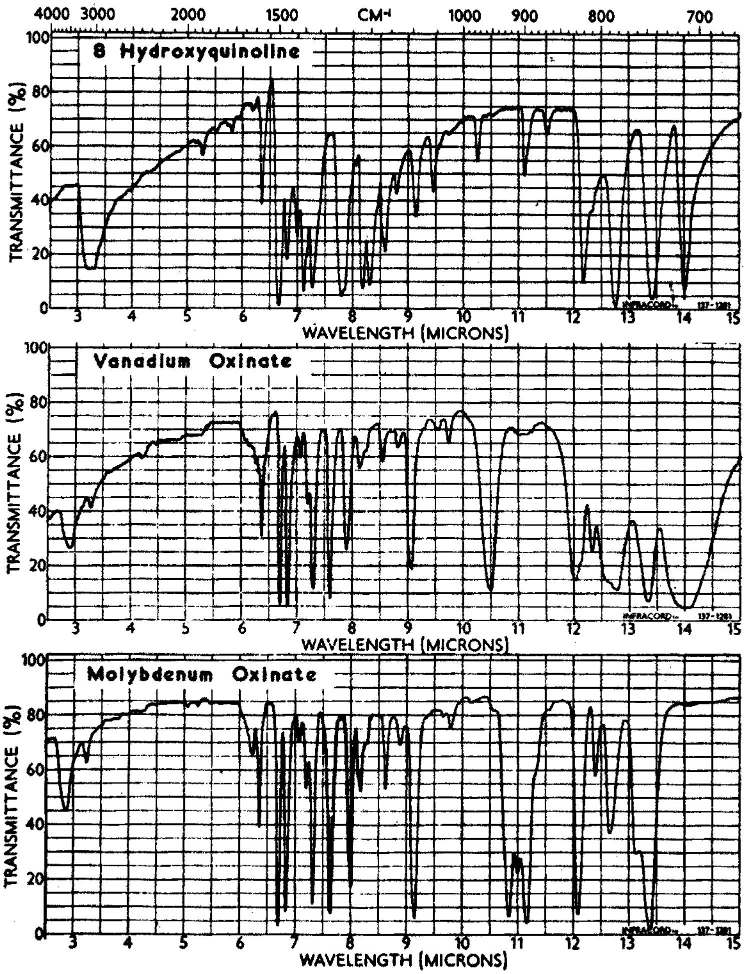

Fig. 1. The infrared spectrum in the region 3–15 μ of: (a) 8-hydroxyquinoline; (b) vanadium 8-hydroxyquinolinate; (c) molybdenum 8-hydroxyquinolinate.

TABLE I

BANDS FOR METAL 8-HYDROXYQUINOLINATES

Metal	*Peaks (μ)*
Mo	10.80, 10.93, 11.12
W	10.61, 10.90, 11.10
V	10.5 (14 μ – a broad peak)
Cr	—

From the above results it appeared that the infrared absorption spectra of the 8-hydroxyquinoline derivatives of molybdenum, tungsten and vanadium might form the basis of a useful method for the identification of these elements either alone or in a mixture. Vanadium is readily identifiable by the peak at 10.5 μ, and also by the

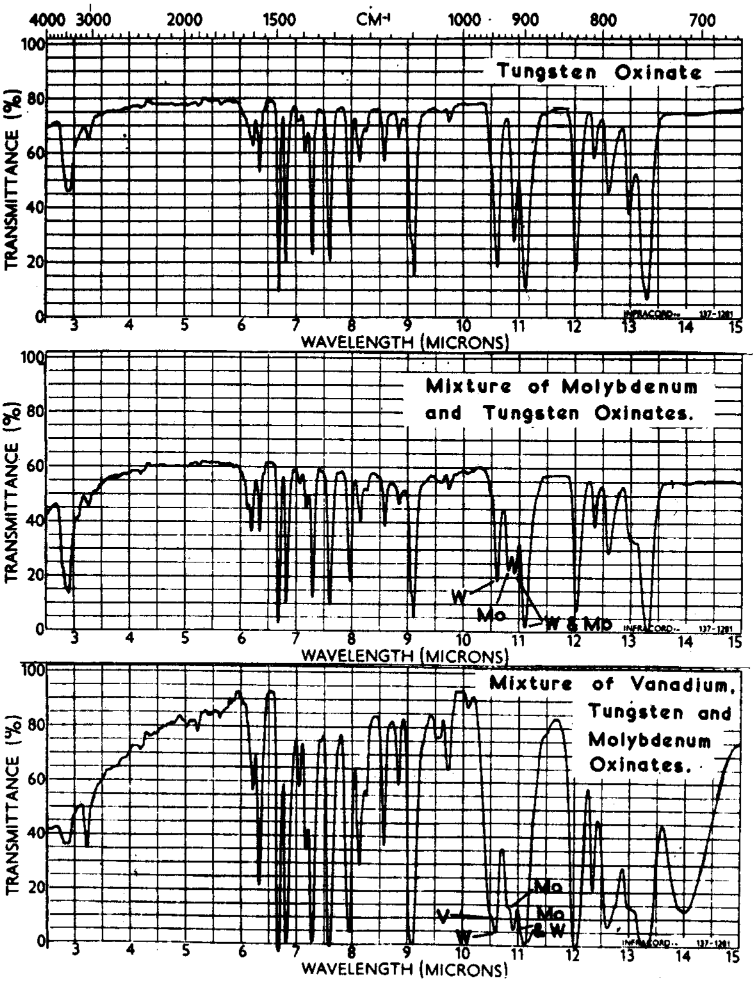

Fig. 2. The infrared spectrum in the region 3–15 μ of: (a) tungsten 8-hydroxyquinolinate; (b) a mixture of molybdenum and tungsten 8-hydroxyquinolinates; (c) a mixture of vanadium, tungsten and molybdenum 8-hydroxyquinolinates.

broad peak around 14 μ. Molybdenum and tungsten are also easily identified by the peaks at 10.8 μ and 10.61 μ, respectively.

Analytical applications

In order to apply the infrared technique to the quantitative analysis of vanadium, molybdenum and tungsten, it was clear that certain conditions should be fulfilled: (*1*) complete precipitation of the 8-hydroxyquinolinates of these elements should be easily achieved, (*2*) each of the metal 8-hydroxyquinolinates should have constant composition. According to WELCHER[9], the above requirements are easily attained for the elements under investigation.

The use of KBr as a supporting medium for the sample in quantitative work, introduces the possibilitity of complications. Two main factors may influence the results: (*1*) the CHRISTIANSEN filter effect, and (*2*) variation of the disc thicknesses. The first effect can be largely minimised if the particle size of the powder is reduced below the wave length of the radiation. Secondly, the disc diameter is constant (controlled by the dimensions of the die); the thickness is thus proportional to the weight of the disc. Consequently, both these effects can be largely minimised by grinding the disc components to a very fine size below that of the wavelength of the radiation, and weighing the disc before correcting to a unit weight, *i.e.* 200 mg.

There are a number of other factors which can cause errors but it is possible to overcome any difficulties by using only transmittance values between 20% and 70%, and keeping the instrument settings constant during the experimental work. The slit width should be held at a minimum, *i.e.* 0.25 μ, throughout the work.

If the precautions outlined above are strictly adhered to, the total error in the measurement of concentration should not exceed 2–3% and analytical application of the technique becomes possible.

Calibration curves

As the conversion of vanadium, molybdenum and tungsten to their 8-hydroxyquinolinate complexes is quantitative, calibration curves were prepared from pure samples of the substances.

From the dried precipitates KBr discs were obtained by weighing 0.2–2 mg of the metal 8-hydroxyquinolinate, and mixing with about 200 mg of accurately weighed potassium bromide. Spectra were recorded over the range 3–15 μ, using a KBr disc of the same weight in the reference beam.

The disc was weighed and the amount of metal 8-hydroxyquinolinate corrected to a total disc weight of 200 mg.

For molybdenum the optical densities at 10.80 μ and 10.93 μ were determined. For tungsten the values at 10.61 μ or 10.90 μ, and for vanadium those at 10.50 μ were used. In all cases the base-line technique was employed[3].

The calibration curves were linear and showed adherence to BEER's law, except where the amount of metal 8-hydroxyquinolinate present in the disc was over 2 mg. This may be due to the formation of less sharp bands, when it became difficult to measure the optical density exactly.

For the metal 8-hydroxyquinolinates of the three elements, this procedure yielded an error of ±3%.

Synthetic mixtures

The procedure was applied to the determination of vanadium, molybdenum, and tungsten in synthetic mixtures. The results obtained are presented in Table II, from which it can be seen that the maximum percentage error for vanadium, molybdenum, or tungsten was about 7%. In most cases satisfactory results were obtained, but, when the ratio of vanadium to molybdenum or tungsten was larger than 1:4, the error obtained was about 5%. This may be due to the fact that the 8-hydroxyquinolinates of these elements show maximum absorption in the region 10.5–11.2 μ, so that the presence of relatively large amounts increases the background absorption significantly. This, in turn, would cause the transmittance value to decrease, making it difficult to keep the readings within the optimum transmittance range.

From the spectra shown in Fig. 2 it can be seen that the presence of vanadium, molybdenum and tungsten can readily be detected. The vanadium peak at 10.5 µ appears as a shoulder on the tungsten peak (that is, the peak at 10.61 µ). The peak at 10.80 µ is due to molybdenum, while the other two peaks at 10.90 µ and 11.1 µ are due both to tungsten and molybdenum.

TABLE II

ANALYSIS OF SYNTHETIC MIXTURES

µg Vanadium			*µg Molybdenum*			*µg Tungsten*		
Present	*Found*	*% Error*	*Present*	*Found*	*% Error*	*Present*	*Found*	*% Error*
84.21	82.97	− 1.5	92.28	89.97	−2.4	—	—	
119.34	119.48	+0.11	161.49	165.87	+2.6	—	—	
42.12	44.26	+5	253.77	249.15	−1.4	—	—	
60.37	58.68	−2.7	—	—		219.0	221.19	+1
112.32	112.88	+0.49	—	—		456.25	485.45	+6.4
70.20	65.98	−6	—	—		401.5	397.12	−1.09
—	—		101.50	105.89	+4.3	182.5	168.63	−7.6
—	—		115.35	115.35	0	182.5	189.8	+4
—	—		184.56	175.33	−5	270.1	277.4	+2.7

A series of experiments was carried out to determine the three elements in the presence of each other, but errors were found to be rather large (up to ± 10%). Experience has shown however, that it is possible to determine vanadium, molybdenum and tungsten individually as the metal 8-hydroxyquinolinates. It is also possible to determine pairs of the elements.

In general the greatest amount of metal chelate that can be used within the optimum transmittance range is 1.6 mg. The smallest amount of chelate that could be detected was 0.2 mg.

SUMMARY

The infrared spectra of the 8-hydroxyquinolinates of molybdenum, vanadium and tungsten in the region 3–15 µ were investigated. It was found possible to determine the elements quantitatively, singly or in pairs, with an error of about 3%. Molybdenum was determined at 10.80 µ and 10.93 µ, vanadium at 10.50 µ, and tungsten at 10.61 µ or 10.90 µ.

RÉSUMÉ

Les spectres infra-rouges des hydroxyquinoléates de molybdène, vanadium et tungstène ont été examinés entre 3–15 µ. Il est possible de doser ainsi ces éléments, soit isolés, soit deux par deux avec une erreur de ± 3%.

ZUSAMMENFASSUNG

Die Infrarotspektren der 8-Hydroxychinolate des Molybdäns, Vanadins und Wolframs im Bereich von 3–15 µ wurden untersucht. Es ist möglich, die Elemente quantitativ, einzeln oder zu zweien mit einem Fehler von etwa 3% zu bestimmen.

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MAGNETIC TITRATIONS

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(Received March 11th, 1963)

If a change in orbital moment occurs upon the addition of a complexing ligand to a metal ion solution, a quantitative study of the reaction can be made by a titration technique. CORYELL *et al.*[1] by such a procedure, showed that the susceptibilities of intermediate compounds in hemoglobin reactions are linearly related to the number of hemes that have undergone reaction; difficulties of titrant additions, stirring, and of re-setting titration apparatus in the magnetic field, however, necessitated 4–7 h for a titration. This paper describes a cell and procedure that permits a titration to be carried out in 30 to 75 min. The results of magnetic titrations of nickel with cyanide and of iron(II) with 1,10-phenanthroline and with 2,2'-bipyridyl are recorded; formation constants for the mono-iron(II) complexes are calculated from the titration data.

EXPERIMENTAL

Titration apparatus

The simplest and most convenient method for determining the bulk susceptibility of a solution is that of GOUY[2]. The use of a GOUY balance in a titration procedure necessitates a titration cell that, in addition to being a closed system to eliminate weight losses from solvent evaporation, should permit simple addition of titrant and allow rapid mixing of the reactants to enable titrations to be completed in a reasonable time. The cell design finally employed consisted of two units and is shown in Fig. 1; one unit (C) holds the metal ion being titrated while the titrant is contained in a modified weight burette (B). The two units are connected through ground glass joints so that both the titrant and the solution to be titrated are enclosed in the one system (A); the weight of the entire cell and its reacting solutions, in air, remains constant throughout the titration and changes in weight in the magnetic field, when corrected for dilution, are due entirely to changes in the magnetic moment of the solution being titrated.

Gouy balance

The unit employed in the present work consisted of an HO 3 Oertling semi-micro single pan balance and a permanent magnet with a field strength of 5500 gauss.

Stirring

The problem of efficient stirring of the solution in the cell after addition of each reagent aliquot was solved by using a Vortex Jr. Mixer obtained from Scientific Industries Inc., Springfield, Massachusetts. This machine gave rapid efficient mixing.

Titration procedure

Approximately 1 ml of the metal ion solution was added to the glass cell, the titrant placed in the weight burette, and the two units were joined. The titration assembly was weighed in air and in the magnetic field. The apparatus was then removed from the suspension by means of a wooden test tube holder, a known number of reagent drops added, the solution stirred, and the apparatus replaced in the magnetic field. Weighings and reagent additions were made every 5 min. A titration took about 75 min but by decreasing the number of reagent additions and the time interval between weighings, a titration could be carried out in less than 30 min. All titrations were done at room temperatures.

Although the weight of the titration apparatus and contents in air remains constant throughout the titration, a correction for sample dilution must be applied (for accurate results) for magnetic field weighings since the magnetic gradient with respect to the

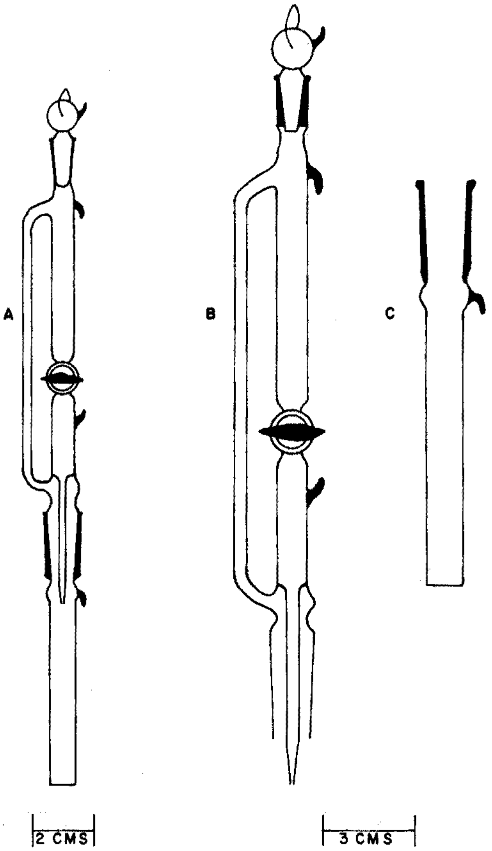

Fig. 1. Titration apparatus: A, complete titration unit; B, modified weight burette for titrant; C, cell container for solution being titrated.

solution has changed due to the volume increase. The dilution effect was determined by following the decrease in paramagnetism as water was added to another sample of metal ion using the above procedure; if the dilution effect is the same as that caused by reagent addition, no orbital change during complex formation has taken place. The data obtained from a typical magnetic titration are given in Table I; these results are discussed under *o*-phenanthroline titrations.

TABLE I

TITRATION OF $0.218 \cdot 10^{-3}$ MOLES IRON WITH *o*-PHENANTHROLINE

Wt. of cell in air (g)	*Wt. of cell in field (g)*	*ΔW (mg)*	*Dilution effect (mg)*	*Corrected ΔW (mg)*	*Moles o-phenanthroline added$\cdot 10^5$*
61.46239	61.47040	+8.01	—	+8.01	0
61.46239	61.46761	+5.22	1.25	+6.47	6.12
61.46239	61.46487	+2.48	2.22	+4.70	12.24
61.46239	61.46237	−0.02	3.13	+3.11	18.36
61.46239	61.46020	−2.19	3.94	+1.75	24.48
61.46239	61.45838	−4.01	4.69	+0.68	30.60
61.46239	61.45555	−6.84	5.84	−1.00	40.80
61.46239	61.45275	−9.64	6.74	−2.90	51.00
61.46239	61.45033	−12.06	7.40	−4.66	61.20
61.46239	61.44902	−13.37	7.90	−5.47	71.40
61.46239	61.48855	−13.84	8.33	−5.51	81.60

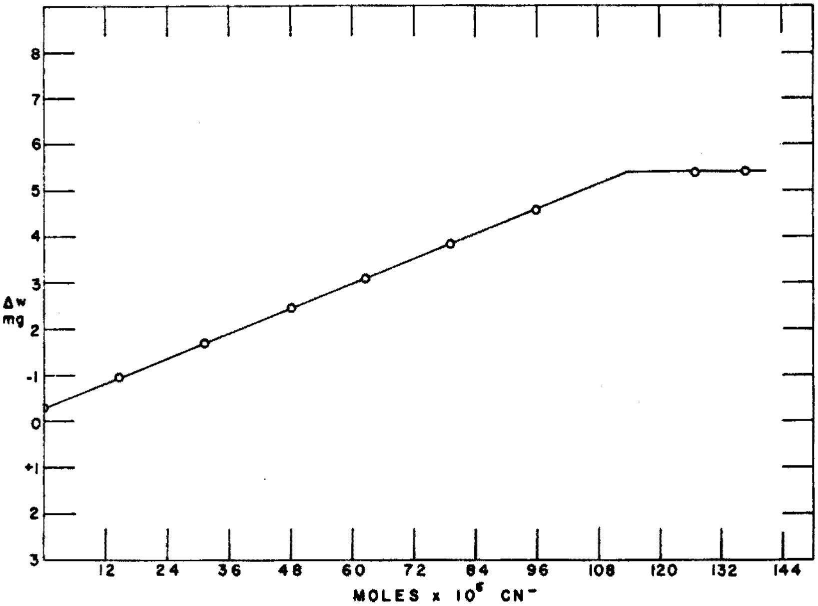

Fig. 2. Cyanide titrations: $2.81 \cdot 10^{-4}$ moles hexammine nickel(II) nitrate with 0.9600 *M* potassium cyanide.

Nickel-cyanide titrations

The standard procedure for magnetic titrations was carried out by adding 0.9600 *M* potassium cyanide to a standard hexammine nickel nitrate solution. The paramagnetism of the solution decreased steadily upon reagent addition up to the end-point; no change in paramagnetism was observed after adding $1.13 \cdot 10^{-3}$ moles of cyanide to $0.281 \cdot 10^{-3}$ moles of hexammine nickel nitrate. The results obtained are shown in Fig. 2.

A straight line plot was obtained and the only break in the titration curve occurred at the end-point when $1.13 \cdot 10^{-3}$ moles of cyanide had been added to give complete formation of the diamagnetic $Ni(CN)_4^{2-}$. Since the decrease in paramagnetism of the solution was linearly related to the amount of $Ni(CN)_4^{2-}$ formed, there was no evidence of the formation of intermediate complexes.

Titrations were done in ammoniacal solution to avoid precipitation of $Ni[Ni(CN)_4] \cdot 2H_2O$; accurate measurement of the magnetic moment of solutions containing precipitates is extremely difficult since the precipitate cannot be homogeneously suspended throughout the solution.

Iron–1,10-phenanthroline titrations

1,10-Phenanthroline is known to form mono-, bis-, and tris-complexes with transition metal ions[3]. Since *o*-phenanthroline is only slightly soluble in water, the dihydrochloride was used as titrant.

The standard procedure for a magnetic titration was followed using a 0.2205 *M* ferrous iron solution, and an approximately 0.6 *M* *o*-phenanthroline solution. The solution became bright red on the first addition of reagent, and there was a steady decrease in the paramagnetism of the solution up to the end-point. From a plot of the titration data, without a correction for dilution, it is seen that the final product is a three-to-one complex (Fig. 3). When the dilution effect was considered, the end-point occurred at the exact stoichiometric point. (The values used are given in Table I.) The corrected plot shows also a break at a 1 : 1 mole ratio of reagent to metal ion.

If only one complex, which is diamagnetic, is formed during a titration, the decrease in paramagnetism of the solution would be directly proportional to the amount of reagent added, and a straight line plot would result (following correction for dilution) with a break occurring at the equivalence point only. The occurrence of more than one break in the iron–phenanthroline titration curve, is indicative, therefore, of the formation of more than one complex—complexes that must differ in their magnetic moment.

Mono-, bis- and tris-1,10-phenanthroline complexes with iron(II) are known[4–8]. The solid mono-complex reported by BROOMHEAD AND DWYER[4] to be paramagnetic was prepared in this laboratory and found to contain four unpaired electrons. The bis-complex has been reported as more unstable in aqueous solution than the mono- and tris-complexes[8]. The solid tris-complex is well known to be diamagnetic[5] and the results of the magnetic titration confirm that the 3 : 1 phenanthroline–iron complex is diamagnetic in solution. Considering, therefore, the titration (and assuming that the concentration of the bis-complex is negligible), one can calculate the concentration of the mono- and tris-complexes present throughout the titration; the formation constant for the mono-complex can also be calculated, knowing the value for the overall formation constant K_3. It is necessary to assume that the diamagnetic contribution of free phenanthroline is essentially the same as water and that the paramagnetic iron behaves the same magnetically as the free iron or as Fe(phen)$^{2+}$; since both the amount of unreacted phenanthroline and Fe(phen)$^{2+}$ formed is small (see below), these assumptions are valid.

In order to obtain ΔW values that are significant for a given concentration of iron, comparisons must be made at the same field strength. This can be done if comparisons are made at the same solution volume and corrections are considered for diamagnetic constituents.

The titration is begun with a known concentration of iron. This initial concentration of paramagnetic iron in the given volume causes a ΔW change, which is used to determine the paramagnetic iron concentration in the solution as the titration proceeds. To make this calculation after reagent has been added, it is necessary to know the ΔW for iron at the dilution used; if the ΔW for solvent plus added reagent (both diamagnetic) is also known, then the concentration of paramagnetic iron can be found. The following measurements permit the calculation of the concentration of iron complexes in solution and the formation constant of the mono-complex.

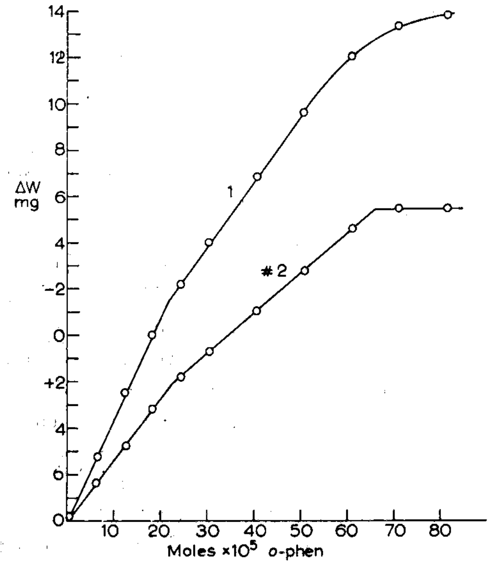

Fig. 3. Phenanthroline titrations: 1, 2.18·10^{-4} moles iron(II) with a solution containing 4.4563 g o-phenanthroline dihydrochloride in 26.812 g solution; 2, as above corrected for dilution.

Thus:

A { (a) One ml of water + n ml of water $\Delta W_a = -\text{a mg}$
(b) One ml of iron + n ml of water $\Delta W_b = \text{b mg}$

Y moles of iron(II) in the above volume causes a change of (a + b) mg

B { (c) One ml of water + n ml of reagent $\Delta W = -\text{c mg}$
(d) One ml of iron + n ml of reagent $\Delta W = \text{d mg}$

Since the volumes of A and B are the same, comparisons of paramagnetic iron concentrations in solution are possible. The overall change must be due to a change in the amount of paramagnetic iron resulting from the formation of the tris-complex, since the other constituents (diamagnetic) are considered. Inasmuch as (a+b) mg is the ΔW for Y moles of iron in the volume taken, then (c+d) mg is the ΔW for Y (c+d)/(a+b) moles of iron. The calculation for the addition of $6.12 \cdot 10^{-5}$ moles of *o*-phenanthroline to $2.18 \cdot 10^{-4}$ moles of iron is shown below; the measured values for a, b, c and d were 9.60, 6.76, 9.60 and 5.34 mg respectively. (A diamagnetic contribution of 0.12 mg for the tris-complex is included in the d value.)

Paramagnetic iron present = $(2.18 \cdot 10^{-4})$ 14.94/16.36 moles = $2.00 \cdot 10^{-4}$ moles.
Therefore iron complexed as 3 : 1 = $1.8 \cdot 10^{-5}$ moles
iron complexed as 1 : 1 = $0.72 \cdot 10^{-5}$ moles
iron uncomplexed = $1.93 \cdot 10^{-4}$ moles.
Since $K_3 = (\mathrm{Fe(phen)_3}^{2+})/(\mathrm{Fe}^{2+})(\mathrm{phen})^3 = 2 \cdot 10^{21}$
then $(\mathrm{phen}) = 3.60 \cdot 10^{-8}$ and
$K_1 = (\mathrm{Fe(phen)}^{2+})/(\mathrm{Fe}^{2+})(\mathrm{phen}) = 1.03 \cdot 10^6$
$\log K_1 = 6.0$

A calculation for the addition of $18.4 \cdot 10^{-5}$ moles of *o*-phenanthroline to $2.18 \cdot 10^{-4}$ moles of iron showed that formation of the tris-complex was complete within the limits of detection by the technique employed; only near the beginning of the titration is the mono-complex detectable. A $\log K_1$ value of 5.9 has been reported[8].

Iron-bipyridyl titrations.

Magnetic titrations were performed to compare results with the *o*-phenanthroline–iron system; an alcoholic solution of bipyridyl was used as the titrant. The standard procedure for magnetic titrations was followed. The iron solution became deep red

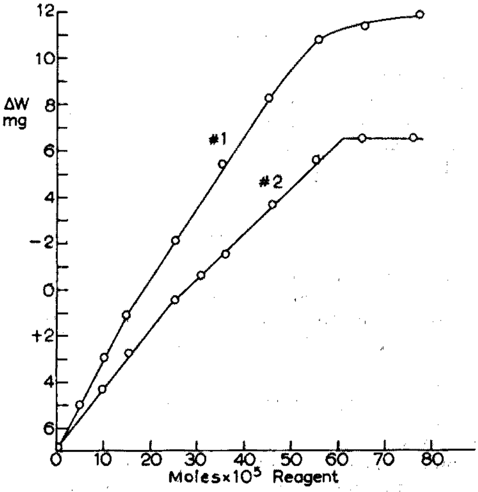

Fig 4. Bipyridine titrations: 1, $2.02 \cdot 10^{-4}$ moles iron(II) with an alcoholic solution containing 3.2671 g bipyridine in 19.466 g solution; 2, as above corrected for dilution.

on the first addition of reagent, and the paramagnetism of the solution steadily decreased up to the end-point as the titration proceeded. Both corrected and uncorrected plots of the data (Fig. 4) show the final product to be the 3 : 1 complex. Another break is also found in plot 2 which occurs very nearly at a 1 : 1 mole ratio of reagent to iron. The presence of this break shows that more than one complex is present in solution.

The 1 : 1 complex[4] and the 2 : 1 complex[6] are both paramagnetic; the 3 : 1 complex is diamagnetic[9]. Calculations similar to those for the *o*-phenanthroline system showed the presence of more than one complex; neglecting the formation of the 2 : 1 complex, the following results were obtained for the addition of $5.10 \cdot 10^{-5}$ moles of bipyridine to a solution containing $2.02 \cdot 10^{-4}$ moles of iron.

$$(\mathrm{Fe(bipyridyl)_3^{2+}}) = 0.13 \cdot 10^{-4} \text{ moles}$$
$$(\mathrm{Fe(bipyridyl)^{2+}}) = 0.12 \cdot 10^{-4} \text{ moles}$$
$$(\mathrm{Fe^{2+}}) = 1.77 \cdot 10^{-4} \text{ moles}$$

From the above data and the reported value of 17.7 for log K_3[10], the calculated value for log K_1 is 5.0. A calculation for the addition of $15.3 \cdot 10^{-5}$ moles of reagent to the iron solution showed that, within limits of detection, all the bipyridine was present as the 3 : 1 complex.

CONCLUSIONS

The titration apparatus and the procedure described allow magnetic titrations to be carried out simply and relatively quickly. The formation of intermediate complexes may be detectable from the titration curve and the formation constants, for such lower complexes, calculated from the magnetic data. The usefulness of the method is restricted by its application to homogeneous solutions only and by the detection limits of the technique; in our titrations metal ion concentrations of 0.2 *M* gave weight differences of from 6 to 18 mg (depending upon the number of unpaired electrons in the metal ion) so that the differences in the amount of metal ion detectable were approximately 10^{-5} moles.

SUMMARY

Magnetic titrations using a new titration cell and procedure are described. The paramagnetism of a hexammine nickel nitrate solution decreases linearly upon the addition of cyanide up to the end-point (complete formation of $\mathrm{Ni(CN)_4^{2-}}$); there is no evidence of the formation of intermediate complexes. Intermediate complexes are evident in the titrations of iron(II) with 1,10-phenanthroline and with 2,2'-bipyridyl; log K_1 values, calculated from the magnetic data, are 6.0 and 5.0 respectively.

RÉSUMÉ

Des titrages magnétiques, utilisant une nouvelle cellule de titration, sont décrits. Le paramagnétisme d'une solution de nitrate de nickel hexammine décroit linéairement avec l'addition de cyanure, jusqu'au point final (formation de $\mathrm{Ni(CN)_4^{2-}}$, sans complexes intermédiaires). Des complexes intermédiaires se forment lors des titrages du fer(II) par la 1,10-phénanthroline et le 2,2'-bipyridyle.

ZUSAMMENFASSUNG

Es wird eine magnetische Titration, die eine neuartige Titrationszelle und Arbeitsweise benutzt, beschrieben. Der Paramagnetismus einer Hexammin-Nickelnitratlösung nimmt linear mit der Zugabe des Cyanids bis zur vollständigen Bildung von $\mathrm{Ni(CN)_4^{2-}}$ ab. Es gibt keinen Hinweis für die Entstehung anderer Komplexe. Unterschiedliche Komplexe bilden sich im Verlauf der Titration von Eisen(II) sowohl mit 1,10-Phenanthrolin als auch mit 2,2'-Bipyridyl.

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DIRECT SPECTROPHOTOMETRIC DETERMINATION OF INDIUM IN TIN*

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(Received May 3rd, 1963)

The binary system, indium and tin, has several interesting properties. Because these properties correlate with alloy composition, there is need for a method to determine indium in tin. The particular alloys for which the method described below was developed contained less than five weight per cent of indium.

A major obstacle to the analysis for indium is that tin interferes with most methods available for the determination of indium. Actually, analyses for indium in indium–tin systems can be performed without the separation of the two metals by polarographic[1], spectrographic[2], and anodic stripping voltammetric[3] methods.

However, because many laboratories are not equipped with the instruments necessary for the above-mentioned methods, it becomes desirable to separate indium from tin before the determination of indium. Furthermore, until recently, it has been extraordinarily difficult to separate the two metals in order to avoid the interference of tin.

SEPARATION OF TIN AND INDIUM

Because tin is a serious interference to the determination of indium, it is important to separate the two metals quantitatively before attempting to determine indium. Several procedures have been proposed to accomplish this separation, but either the separation is incomplete or the procedure is inconvenient.

Ion exchange, particularly anion exchange, seems to offer the most promising approach to the problem of separating indium from tin. Polarographic, potentiometric, ion-exchange, and solvent extraction studies have given data about the stabilities of the various indium-chloride and tin-chloride species. The ion-exchange distribution behavior of indium and tin in hydrochloric acid solutions is known[4,5]. Actual separations of indium and tin from each other[6,7] and from other metals[8–10] have been performed in hydrochloric acid media.

If indium and tin are placed on a Dowex A2 resin column in 12 M hydrochloric acid solution, both elements are adsorbed[11]. Indium and tin(IV) are not desorbed with an eluant which is greater than 3 M in hydrochloric acid, but they will desorb when the solution is between 1 M and 3 M. Tin(II) begins to desorb when the hydrochloric acid

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* Contribution No. 1312. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

concentration is reduced below 0.1 *M*. The distribution coefficients for indium(III), tin(II), and tin(IV) with respect to Dowex 1-X10 resin in hydrochloric acid solutions have been published[5]; indium consistently has a much smaller distribution coefficient than either oxidation state of tin and the difference is greatest in solutions less than 1 *M* in hydrochloric acid.

On the basis of the above information, studies were made with indium and tin(II) in 0.5 *M*, 0.75 *M*, and 1.5 *M* hydrochloric acid solutions. These solutions also contained 0.1% hydroxylammonium chloride to ensure the retention of tin as tin(II).

All the work was done on Dowex 1-X8, 50–100 mesh, anion-exchange resin. Because tin adsorbs strongly on the resin and is difficult to remove, a fresh portion of resin was used for each run. The procedural details for the separation of indium from tin, which have been derived from our studies, are given in the section DETAILED PROCEDURE FOR THE SEPARATION AND DETERMINATION OF INDIUM. Table I summarizes the observations of the present authors.

TABLE I

ELUTION BEHAVIOR OF INDIUM AND TIN

Molarity of HCl	*Start of indium elution (ml)*	*End of indium elution (ml)*	*Start of tin(II) elution (ml)*	*End of tin(II) elution (ml)*
0.5	5–10	75	> 200	> 1000
0.75	25	450	250	> 1000
1.5	50–100	> 1000	> 300	> 1000

DETERMINATION OF INDIUM

Although a considerable number of methods have been employed for the determination of indium, spectrophotometry seemed especially pertinent because of the small sample sizes. The most thoroughly studied color-forming complexes of indium are its compounds with 8-quinolinol, the 5,7-dihalo-8-quinolinols, and other 8-quinolinol derivatives. The characteristic absorption bands of their spectra occur in the visible region from 390 to 420 mμ.

The published procedure is simple[12]. A dilute hydrochloric acid solution is buffered to pH 3.8–4.0 with potassium acid phthalate. Indium is then extracted into a chloroform solution of the reagent. There is one claim that the 5,7-dihalo-8-quinolinols are insoluble in chloroform[13], but the present authors found good solubility. The yellow organic phase is measured spectrophotometrically. The method is good for 0.1 to 100 μg of indium in the aqueous phase. By using a larger aqueous volume, the present authors have extended the range up to 1.5 mg of indium.

Choice of reagent

8-Quinolinol and its three dihalo derivatives, 5,7-dichloro-8-quinolinol, 5,7-dibromo-8-quinolinol, and 5,7-diiodo-8-quinolinol, were investigated as reagents for the determination of indium. Table II compares the absorbancies (related to sensitivities) of the four compounds complexed with indium. The organic phase, in all cases, contained 0.1% of the reagent in chloroform. All aqueous phases were identical in every respect and contained 1.00 mg of indium. These results agree with the findings of

MOELLER *et al.*[14], that absorption intensity increases with the atomic weight of the halogen substituent.

5,7-Dichloro-8-quinolinol was chosen as the reagent in case there is any possibility of halogen exchange with the chlorinated solvent. A probably more serious error occurs because of photochemical dehalogenation of the reagent. Some of the reagent solutions prepared in this laboratory have shown obvious visual evidence of free halogen being present. Similar observations have been made by others[15]. 5,7-Diiodo-8-quinolinol was the worst offender and 5,7-dichloro-8-quinolinol was the least offender in this respect. It is consequently recommended that the reagent solution be prepared a relatively short time before it is needed. The solutions appear to be stable for at least one week.

TABLE II

ABSORBANCIES OF INDIUM COMPLEXES IN CHLOROFORM

Reagent	*Absorbancy*
8-Quinolinol	1.21
5,7-Dichloro-8-quinolinol	1.44
5,7-Dibromo-8-quinolinol	1.50
5,7-Diiodo-8-quinolinol	1.65

Choice of solvent

A considerable amount of difficulty was encountered with color stability in the chloroform solutions. Chloroform decomposes photochemically to form acidic products and these apparently cause some decomposition of the indium complex. Carbon tetrachloride is quite stable, but the indium complexes have low solubility in that solvent. 1,2-Dichlorobenzene was found to be a satisfactory solvent for the reagent and the complexes. Table III compares the absorbancy of indium tris (5,7-dibromo-8-quinolinolate) in the three solvents. The composition of the aqueous phases was the same as that used to obtain the data in Table II. The organic phases all contained 0.1% of 5,7-dibromo-8-quinolinol.

TABLE III

ABSORBANCY OF INDIUM TRIS(5,7-DIBROMO-8-QUINOLINOLATE) IN VARIOUS SOLVENTS

Solvent	*Absorbancy*
Chloroform	1.50
Carbon tetrachloride	0.31
1,2-Dichlorobenzene	1.48

It was found that the reagents 5,7-dichloro-8-quinolinol and 5,7-dibromo-8-quinolinol in 1,2-dichlorobenzene form the systems which fade most slowly and linearly. It has been suggested that it might be possible to buffer the organic phase in order to maintain a constant acid strength and, therefore, stabilize the color even more. In the present system indium can be determined with a quite small error from color fading, if the absorbancy is measured within a few hours after extraction. The error is less than 2% after 20 h. It is the usual practice in this laboratory to measure the color within an hour of the extraction.

Choice of pH

To determine the optimum pH of the aqueous phase, a series of identical indium chloride solutions was prepared and the individual solutions were adjusted to different pH values. Solutions of 5,7-dibromo-8-quinolinol in 1,2-dichlorobenzene were used to extract the indium. It was observed that the complex forms and extracts equally well over the pH range 3–7. Below pH 3, the extraction is incomplete. The pH value 4.0 was chosen for the analytical procedure in order to minimize the possibility of precipitating indium hydroxide, which begins at pH 3.4–4.0 (ref. 16, 17).

An effort was made to reduce buffer competition for indium by choosing an acetic acid-sodium acetate buffer to replace the potassium acid phthalate because the indium acetate complexes are weak[18]. No significant changes were observed in the shape of the spectra or in the wavelength of maximum absorption when the buffer system was changed.

Equilibration time

This work confirmed that 5 min of vigorous shaking is usually sufficient for equilibration of the phases[12]. However, it was found that, in the presence of fluoride, the extraction of indium is slow and the amount extracted is a linear function of contact time. The results are shown in Table IV. The conditions were: 100 mg of fluoride, 1.00 mg of indium and/or 100 mg of tin(IV), the aqueous phase volume was 100 ml, the organic phase volume was 50 ml, the pH was 4.0, and the extractant was a 0.1% solution of 5,7-dibromo-8-quinolinol in 1,2-dichlorobenzene. It is interesting to note that indium extracts slowly in the presence of fluoride alone, but does not extract at all in the presence of both fluoride and tin(IV).

TABLE IV

EXTRACTION OF INDIUM FROM FLUORIDE SOLUTIONS

Contact time (min)	*Absorbancy of indium alone*	*Absorbancy of tin(IV) alone*	*Absorbancy of indium and tin (IV) together*
10	0.505	~0	~0
20	0.753	~0	~0
30	1.000	~0	~0

Interferences

The present authors observed that tin(IV) does not interfere with the determination of indium when present in amounts less than 5 mg. Tin(II) interferes seriously. This observation is corroborated by others[12,19–21]. Table V illustrates the difference in behavior of tin(II) and tin(IV).

Other interferences are Al(III), Bi(III), Co(II), Cu(II), Fe(III), Fe(II), Ga(III), Ni(II), Sb(III) and Tl(III)[12,20]. The lanthanon elements form complexes with 8-quinolinol and its 5,7-dihalo derivatives[22]. The present research has shown that zinc(II) interferes. It is claimed that Ag(I), As(V), As(III), Ca(II), Cd(II), Cr(III), Ce(?), Hg(II), Mg(II), Mn(?), Pb(?), Sr(II) and Zn(II) do not interfere[12,20]. The present work has shown that yttrium(III) apparently does not interfere. LUKE AND CAMPBELL give several tables of interference data[19]. The reader will be able to ascertain the nature of interference by other metals by referring to the table given in the text of KOLTHOFF AND SANDELL[23].

TABLE V

ABSORBANCIES OF TIN SOLUTIONS

Mg of tin	*Oxidation state of tin*	*Absorbancy*
1.01	II	0.832
3.04	II	> 2.0
5.07	IV	0.007

DETAILED PROCEDURE FOR THE SEPARATION AND DETERMINATION OF INDIUM

Reagents

Hydrochloric acid. 12 *M*, reagent grade.

Eluant solution. 0.5 *M* Hydrochloric acid which is 0.1% in hydroxylammonium chloride. Prepare the solution by dissolving 1.0 g of reagent-grade hydroxylammonium chloride in about 500 ml of distilled water, adding 41.6 ml of 12 *M* hydrochloric acid, and diluting to one liter.

Nitric acid. 15 *M*, reagent grade.

pH 4.0 Buffer solution. Dissolve 143 ml of reagent-grade glacial acetic acid and 61.2 g of reagent-grade sodium acetate trihydrate in enough distilled water to make one liter of solution.

Reagent solution. Dissolve 1.0 g of reagent-grade 5,7-dichloro-8-quinolinol in sufficient reagent-grade 1,2-dichlorobenzene to make one liter of solution.

Indium chloride standard solutions. Dissolve 1.000 g of indium metal in a minimum amount of hydrochloric acid and dilute the solution to exactly one liter with distilled water. This solution contains 1.00 mg of indium per ml. Solutions containing 10 or 100 μg per ml can be prepared by dilution.

Tin metal. Reagent grade.

Anion exchange resin. A convenient amount of Dowex 1-X8, 50–100 mesh, resin in the chloride form is very slowly reverse-flushed with distilled water to float off the fine particles. The largest particles are air-dried and stored in a capped jar.

Apparatus

The absorbancy measurements were made with a Beckman DU spectrophotometer. The cells were 1-cm Corex cells.

All volumetric glassware used in this work was class "A" glassware.

The ion-exchange column was made of Pyrex glass; at the bottom end was a stopcock with a 2-mm bore. A coarse fritted disc was sealed into the bottom of the column. About 9 cm above the frit, the column flared so that a rubber stopper could be inserted. The diameter of the column below the flare was 1 cm. A small funnel was attached into the flare with a suitable rubber stopper.

Procedure

The standard curve used for this work was obtained from standard, synthetic mixtures. The standards were prepared by measuring various known volumes of the standard indium solutions (containing from 0 to 5 mg of indium) into small beakers containing weighed amounts of tin metal (90 to 120 mg). These mixtures were treated with 12 *M* hydrochloric acid to dissolve the tin. Thereafter, the standards were treated in the manner detailed below.

Weigh out a sample of the indium–tin alloy. Dissolve the sample in a minimum amount of 12 *M* hydrochloric acid and evaporate nearly to dryness. Dilute the residue to a known volume, V_0 ml, in a volumetric flask. The diluent is the eluant solution. Either the amount of alloy or the volume of the flask should be chosen so that a 10- to 25-ml aliquot, V_1 ml, of the solution will contain less than 120 mg of total metal and less than 5 mg of indium.

Prepare the anion-exchange column by weighing 3.0 g of the dried and sorted resin into about 20 ml of the eluant solution to form a resin slurry. Transfer this slurry to the column and allow the liquid to drain out until the top of the resin bed (about 7–8 cm) is barely covered with liquid. Note that the effluent from this operation is discarded. Pipet a known volume, V_1 ml, of the indium–tin solution into the funnel and allow to flow through the resin bed at a flow rate of 5–10 ml per min. Pour additional eluant solution through the column to give a total effluent volume of about 75 ml. Collect the effluent in a 150-ml beaker.

After the addition of 10 ml of 15 *M* nitric acid, evaporate the effluent solution nearly to dryness in order to destroy hydroxylammonium chloride and to oxidize any tin which might have passed through the column. Take up the residue in 10 ml of 12 *M* hydrochloric acid and again evaporate nearly to dryness to convert the indium back to the chloride. Finally, transfer this residue quantitatively, using distilled water, into a volumetric flask and dilute the contents to volume, V_2 ml, with distilled water. The volume of this flask is so chosen that a 25.00-ml portion of the contents will contain less than 1.5 mg of indium.

Pipet the 25.00-ml portion into a 125-ml separatory funnel equipped with a Teflon stopcock. Also add to the funnel 10.0 ml of the pH 4.0 buffer and 15.0 ml of distilled water. Maintain the pH of the solution in the funnel at 4.0 by the addition of dilute sodium hydroxide or hydrochloric acid. Pipet into the funnel 50.00 ml of the reagent solution. Stopper the funnel and vigorously shake the contents for 5 min. Drain the yellow, organic layer through a filter paper to remove the water drops. Measure the absorbancy of the resulting clear solution with the spectrophotometer at 415 mμ against a reagent blank.

Calculations

The data obtained from the standard, synthetic mixtures are used to plot absorbancy, A, as a function of the mg of indium in the aqueous phase. This should be a straight line which phases through the origin. One can find the slope, S, of the line from the relation:

$$S = \Delta A/\Delta(\text{mg of In}) \tag{1}$$

Therefore:

$$\text{mg of In in sample} = \frac{A V_2 V_0}{25 V_1 S} \tag{2}$$

If W = g of sample:

$$\text{Weight per cent of In in sample} = \frac{AV_2V_0}{250\ WV_1S} \qquad (3)$$

SUMMARY

Indium is separated from tin by an anion-exchange process in 0.5 M hydrochloric acid solution. Subsequently, the indium is extracted into 1,2-dichlorobenzene as its complex with 5,7-dichloro-8-quinolinol. The complex forms and extracts quantitatively in the pH range 3–7. The yellow, organic phase is measured spectrophotometrically at 415 mμ; its absorbancy is directly proportional to the indium content of the aqueous phase up to a total of 1.5 mg of indium per 50 ml. This procedure quantitatively separates the two metals, allows one to determine the indium content of indium(< 5%)–tin alloys with a relative error less than 0.7%, and considerably reduces color fading errors inherent in some previously reported spectrophotometric methods for indium.

RÉSUMÉ

L'indium est séparé d'avec l'étain au moyen d'un échangeur d'anions, en solution acide chlorhydrique 0.5 M. Il est ensuite extrait dans le dichloro-1,2-benzène sous forme de dichloro-5,7-hydroxy-8-quinoléate, à un pH de 3 à 7. La phase organique jaune est mesurée spectrophotométriquement à 415 mμ; ce procédé permet de doser des teneurs en indium < 5%, dans des alliages indium–étain, avec une erreur relative inférieure à 0.7%.

ZUSAMMENFASSUNG

Indium lässt sich von Zinn in 0.5 M Salzsäure mit einem Anionenaustauscher trennen und anschliessend mit 1,2-Dichlorbenzol als Komplex des 5,7-Dichlor-8-Hydroxychinolins beim pH-Wert 3–7 quantitativ extrahieren. Die bei 415 mμ spektralphotometrisch gemessene Absorption ist bis zu einem Gehalt von 1.5 mg in 50 ml des wässrigen Phase der Indiumkonzentration direkt proportional. In Indium–Zinn-Legierungen lassen sich Indiumgehalte bis 5% mit einem relativen Fehler von 0.7% bestimmen.

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A DIFFERENTIAL THERMAL ANALYSIS (DTA) AND THERMOGRAVIMETRIC ANALYSIS (TGA) STUDY OF SOME ORGANIC ACIDS. PART II

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(Received May 24th, 1963)

The first part[1] of this series of investigations was an attempt to use differential thermal analysis (DTA) as a technique to "finger-print" organic acids. By this technique, an attempt was made to characterize these acids by means of a simple and easily obtained thermogram which could be used for detection and identification purposes. By use of a commercially available instrument, the Deltatherm, it was hoped that the experimental conditions would be such that the curves could be reproduced by use of a similar instrument in other laboratories. This investigation is a continuation of the above in which 16 additional organic acids were studied by DTA and, to provide thermal weight-loss data, by thermogravimetric analysis (TGA), as well.

EXPERIMENTAL

Reagents

The organic acids were obtained from commercially available sources such as Eastman Organic Chemicals, Rochester, N.Y.; Purkis Williams Ltd., London, Great Britain; Eastern Chem. Co., Newark, N.J.; Matheson, Coleman and Bell Co., East Rutherford, N.J.; Pilot Chem. Co., Waltham, Mass.; and the Aldrich Chem. Co., Milwaukee, Wisc. All of the acids were used without further purification, since their melting points all agreed quite well with the literature values.

Apparatus

The DTA apparatus and experimental techniques were the same as previously described[1].

The automatic recording thermobalance was similar to that previously described[2] except that the furnace and sample holder were mounted vertically above the balance. The samples, which ranged in weight from 28 to 35 mg, were placed in a No. 00000 Coors porcelain crucible and pyrolyzed in a static air atmosphere at a heating rate of 5° per min.

RESULTS AND DISCUSSION

The TGA thermograms are given in Figs. 1 and 2 while the DTA thermograms are shown in Figs. 3–5.

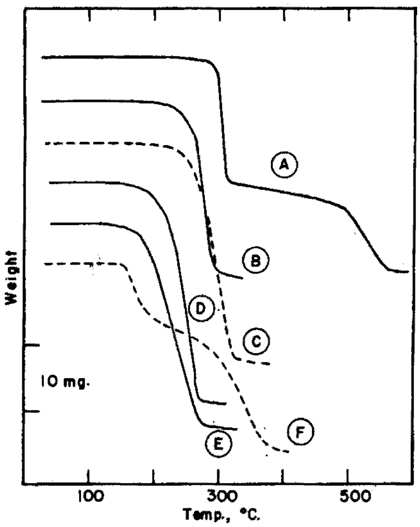

Fig. 1. TGA curves of organic acids in an air atmosphere. A, 5-aminosalicylic acid; B, 5-nitrosalicylic acid; C, picric acid; D, 5-bromosalicylic acid; E, salicylhydroxamic acid; F, acetylsalicylic acid.

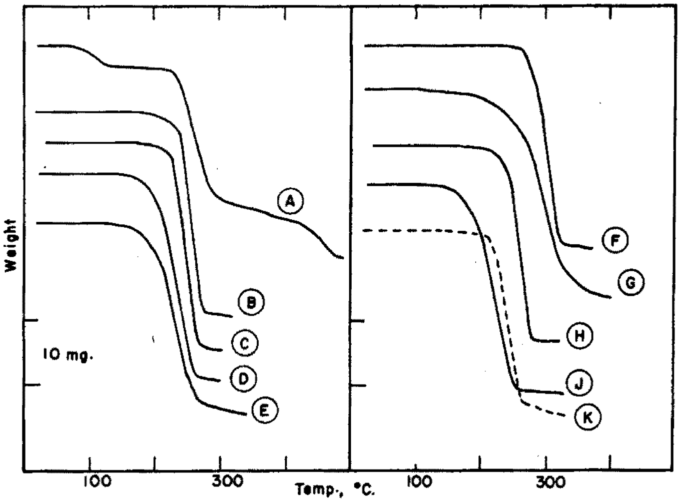

Fig. 2. TGA curves of organic acids in an air atmosphere. A, 3,4-dihydroxybenzoic acid·1.5 H_2O; B, 4-hydroxy-3-methoxybenzoic acid; C, *m*-hydroxybenzoic acid; D, 2,4-dimethoxybenzoic acid; E, tropic acid; F, diphenic acid; G, *p*-bromomandelic acid; H, α, β-dibromosuccinic acid; J, *m*-cresoxyacetic acid; K, *d*-camphoric acid.

Since the minimum weight-loss or decomposition temperatures obtained on the TGA thermograms depend on a number of factors, the term "procedural weight-loss temperature"[3] will be used to describe the curves. As was anticipated, the weight-loss curves consisted mainly of one continuous step or decrease in weight. This continuous

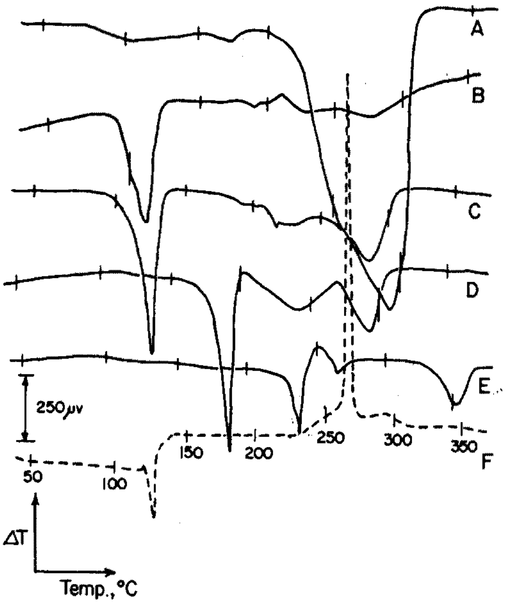

Fig. 3. DTA curves of organic acids in an argon atmosphere. A, α, β-dibromosuccinic acid; B, *m*-cresoxyacetic acid; C, *p*-bromomandelic acid; D, *d*-camphoric acid; E, diphenic acid; F, picric acid.

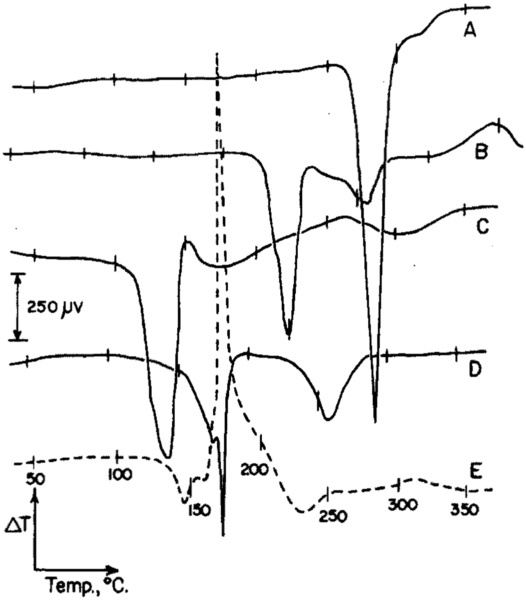

Fig. 4. DTA curves of organic acids in an argon atmosphere. A, 5-aminosalicylic acid; B, 5-nitrosalicylic acid; C, acetylsalicylic acid; D, 5-bromosalicylic acid; E, salicylhydroxamic acid.

weight loss was either the result of sublimation, vaporization, or decomposition reactions; probably in many cases the sum of all three of these reactions.

In the case of 3,4-dihydroxybenzoic and 5-aminosalicylic acids, various intermediate weight-loss regions were found in the curves. For the former, the weight loss from 70° to 140° corresponded closely to the loss of 1.5 moles of water per mole of organic acid (14.1% found; 14.92% theor.). Above 220° the anhydrous acid began to lose weight giving a break in the curve at about 300°. The composition of the compound in this region of the curve was not known. Likewise, for 5-aminosalicylic acid, a break in the curve was found at about 320° which resulted in a region of intermediate thermal stability until further rapid weight loss took place above 490°.

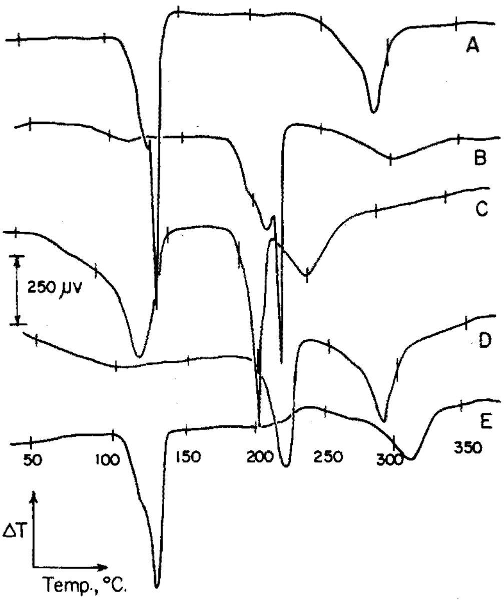

Fig. 5. DTA curves of organic acids in an argon atmosphere. A, 2,4-dimethoxybenzoic acid; B, *m*-hydroxybenzoic acid; C, 3,4-dihydroxybenzoic acid·1.5 H_2O; D, 4-hydroxy-3-methoxybenzoic acid; E, tropic acid.

To summarize the TGA thermogram results, the "procedural weight loss temperatures" are given in Table I.

The DTA thermogram peak maxima temperatures are given in Table I.

The DTA curves were characterized by a series of endothermic, and in the case of several of the acids, by exothermic peaks, which were caused by heat absorption or evolution due to fusion, sublimation, boiling, and decomposition reactions. Since the compounds were pyrolyzed in an argon atmosphere, oxidation peaks were absent from the curves except if the acids contained their own oxidizing groups.

Most of the endothermic peaks were fairly sharp and well defined with several notable exceptions. The peak for α, β-dibromosuccinic acid was extremely broad. This

TABLE I

PROCEDURAL WEIGHT-LOSS AND MAXIMA PEAK TEMPERATURES FOR THE ORGANIC ACIDS

Acid	*Weight-loss temperature (°)*	*Peak[a] temperatures (°)*
5-Aminosalicylic	250	275
5-Nitrosalicylic	200	250, 310
Acetylsalicylic	150	140, 175[b], 300[b]
5-Bromosalicylic	140	175[c], 180, 260
Salicylhydroxamic	115	145, 170[d], 235
α, β-Dibromosuccinic	200	175[b], 290[b]
m-Cresoxyacetic	140	110
p-Bromomandelic	100	125, 285
d-Camphoric	160	190, 240[b], 290
Diphenic	230	240, 260, 350
Picric	200	125, 260[d]
2,4-Dimethoxybenzoic	150	170[c], 180, 290
m-Hydroxybenzoic	180	210[c], 220, 300[b]
3,4-Dihydroxybenzoic $\cdot 1.5\ H_2O$	70, 220	135, 215, 250
4-Hydroxy-3-methoxybenzoic	180	220, 290
Tropic	140	130, 310

[a] All are endothermic peaks except as indicated.
[b] Broad peak.
[c] Shoulder peak.
[d] Exothermic peak.

would indicate that the heat of decomposition for this compound was much larger than for the other acids or that several simultaneous competing reactions were taking place. Generally, for a fusion transition, the peaks were quite sharp while the decomposition peaks were broader. In many cases, two peaks were present in the curve; one for the fusion transition, the other for the decomposition reaction. Several compounds had more than one decomposition peak such as *d*-camphoric, 5-nitrosalicylic, acetylsalicylic, and diphenic acids.

Several of the acids, such as 2,4-dimethoxybenzoic, *m*-hydroxybenzoic, 5-bromosalicylic, and tropic acids, contained shoulder peaks which could be the result of partial sublimation of the sample. This was then followed by a fusion transition of the remaining amount of acid in the sample well.

In the case of 3,4-dihydroxybenzoic acid, the first endothermic peak was probably the result of a dehydration reaction as indicated by the weight-loss curve for this compound. Also, since the melting point of this acid is 199°, the second peak represents the fusion transition.

Three of the acids studied had DTA curves which contained exothermic as well as endothermic peaks. In the case of picric acid, the first peak at 125° was due to the fusion of the compound while the second peak, at 260° was caused by the explosive decomposition of the molten acid. Likewise, for salicylhydroxamic acid, a small endothermic peak at 145° was followed by a large sharp exothermic peak at 170°. Although not as evident as the above two examples, the 5-nitrosalicylic acid curve had a small broad exothermic peak at about 400°.

SUMMARY

The differential thermal analysis and thermogravimetric analysis curves of 16 organic acids are presented. The "procedural weight-loss temperatures" for the anhydrous acids ranged from 115° for salicylhydroxamic acid to 250° for 5-aminosalicylic acid. The DTA curves were characterized by endothermic and exothermic peaks which were caused by fusion, vaporization, sublimation, and decomposition reactions.

RÉSUMÉ

Les auteurs présentent les courbes d'analyse thermique différentielle et les courbes d'analyse thermogravimétrique de seize acides organiques. Les courbes d'analyse thermique différentielle sont caractérisées par des pics endothermiques et exothermiques, causés par les réactions de fusion, vaporisation, sublimation et décomposition.

ZUSAMMENFASSUNG

Es werden die mit der Differentialthermoanalyse und der thermogravimetrischen Analyse erhaltenen Kurven von 16 organischen Säuren dargestellt. Die DTA-Kurven sind durch endotherme und exotherme Maxima gekennzeichnet, welche durch Schmelz-, Verdampfungs-, Sublimations- und Zersetzungsreaktionen verursacht werden.

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A SYSTEMATIC STUDY OF THE SOLVENT EXTRACTION OF METAL CUPFERRATES

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(Received June 10th, 1963)

Cupferron (the ammonium salt of N-phenylhydroxylamine) is one of the best known organic reagents which form extractable chelates with many metals. Although many qualitative data on cupferron extraction are available, very few authors[1-3] have studied the extraction procedures quantitatively. For this reason a systematic study of the extraction of 33 metals as cupferrates was carried out with chloroform as the organic solvent. From these results, the extraction constants and two-phase stability constants of the metal cupferrates were calculated; these can be used to determine the optimum conditions for the separation of many metals.

The present paper is a continuation of the systematic studies on solvent extraction of metal chelates which have been carried out in our laboratory. The general theoretical considerations involved in the solvent extraction of metal chelates were described in previous publication[4-6].

EXPERIMENTAL

Reagents

All reagents used were of A.R. quality. Chloroform was purified by shaking with concentrated sulfuric acid followed by distillation. The radioisotopes used were of radiochemical purity.

Procedures

The pH measurements were made with a Radiometer pH M4b (Copenhagen) equipped with a glass electrode and a saturated calomel electrode as a reference electrode. Spectrophotometric measurements were made on a Zeiss Universal Spectrophotometer. For radiometric measurements, an end-window Geiger-Müller counter was used.

Distribution measurements

Ten ml of chloroform were shaken on a mechanical shaker with an equal volume of aqueous phase containing the appropriate metal and cupferron. The total metal concentration for monovalent and divalent metals was 10^{-3} M; for the other metals investigated, 10^{-4} M solutions were used. The pH was adjusted by addition of sodium hydroxide and perchloric acid, and sodium perchlorate was added to give a constant ionic strength of 0.10 M (except, of course, in experiments below pH 1.2).

As cupferron decomposes relatively quickly in acid solutions, shaking for only 5 min was used in all cases. This time was found quite sufficient for attainment of equilibrium in most of the systems investigated (only nickel and a few other metals were extracted more slowly).

After the two phases were separated, the equilibrium concentration of the metal in the organic and/or aqueous phase was determined. A survey of the analytical methods used is given in Table I.

All distribution experiments were carried out at 20°.

TABLE I

ANALYTICAL METHODS USED FOR DETERMINATION OF DISTRIBUTION RATIO OF PERCENTAGE EXTRACTION

Metal	*Method*	*Metal*	*Method*
Be	Spectrophotometric with eriochrome cyanine R(500 mμ)	U	Spectrophotometric as dibenzoylmethanate (382 mμ)
Mg, Ca, Sr, Ba	Compleximetric	Mn	Compleximetric
Al	Compleximetric	Fe	Spectrophotometric as cupferrate (486 mμ) Radiometric (^{59}Fe)
Ga	Spectrophotometric as oxinate (395 mμ)	Co	Spectrophotometric as thiocyanate (in acetate medium 610 mμ)
In	Spectrophotometric as oxinate (400 mμ) Radiometric (^{114}In)	Ni	Spectrophotometric as dimethylglyoximate (448 mμ)
Tl	Radiometric (^{204}Tl)	Pd	Spectrophotometric as dimethylglyoximate (435 mμ) and as oxinate (420 mμ)
Sc	Spectrophotometric as oxinate (380 mμ)		
Y	Radiometric (^{91}Y)	Cu	Compleximetric
La	Radiometric (^{140}La)	Ag	Extractive titration with dithizone Radiometric (^{110}Ag)
Ti	Spectrophotometric as cupferrate (376 mμ)	Zn	Radiometric (^{65}Zn)
Zr	Radiometric (^{95}Zr)	Cd	Radiometric (^{115}Cd)
Th	Radiometric (^{234}Th)	Hg	Extractive titration with dithizone
V	Spectrophotometric as cupferrate (504 mμ).	Pb	Compleximetric Radiometric (^{210}Pb)
Nb	Radiometric (^{95}Nb)	Sb	Spectrophotometric with bismuthone (390 mμ in diethyl ether)
Mo	Spectrophotometric as thiocyanate (444 mμ) Radiometric (^{99}Mo)	Bi	Radiometric (^{210}Bi) Extractive titration with dithizone.
W	Radiometric (^{185}W)		

RESULTS

Beryllium

The pH conditions for the extraction of beryllium(II) are shown in Fig. 1. In the presence of 0.05 *M* cupferron solution, quantitative extraction of beryllium with chloroform took place in the pH region 3.8–8.7 (pH$_{1/2}$ = 2.07).

Magnesium, calcium, strontium and barium

These metals were not extracted with chloroform in the presence of an excess of cupferron (0.05 *M*) throughout the pH region investigated (0–12).

Aluminum, gallium, indium and thallium

The extraction curves of gallium(III), indium(III) and thallium(III) are given in

Fig. 2. In the presence of 0.005 *M* reagent solution, gallium and indium were completely extracted with chloroform at pH values higher than 1.5 and 2.8 respectively ($\text{pH}_{1/2}$ values are 0.66 and 1.5 respectively). Only 50% of thallium(III) was extracted under these conditions; the incomplete extraction was probably caused by hydrolysis. Aluminum was quantitatively[7] extracted with chloroform at pH 3.5–9 in the presence of 0.05 *M* reagent solution ($\text{pH}_{1/2}$ = 2.51).

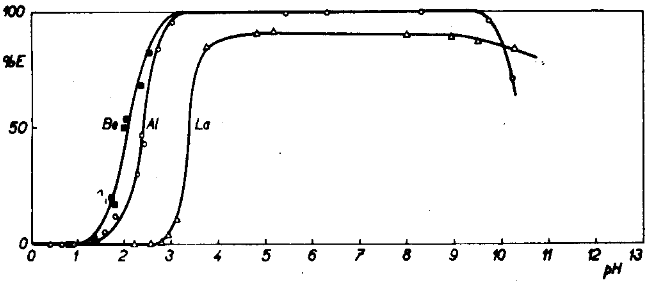

Fig. 1. Extraction of Be(II), Al(III) and La(III) with chloroform in the presence of 0.05 *M* cupferron *vs.* the pH value of the aqueous phase. ■ Be, ○ Al, △ La.

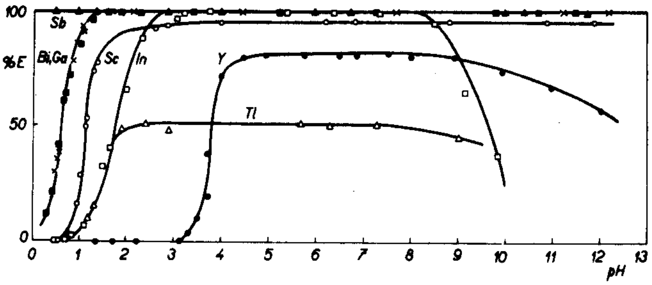

Fig. 2. Extraction of Ga(III), In(III), Tl(III), Sc(III), Y(III), Sb(III) and Bi(III) with chloroform in the presence of 0.005 *M* cupferron *vs.* the pH value of the aqueous phase, × Ga, □ In, △ Tl, ○ Sc, ● Y, ▲ Sb, ■ Bi.

Scandium, yttrium and lanthanum

The cupferrates of scandium(III), yttrium(III) and lanthanum(III) could be extracted with chloroform only incompletely (see Figs. 1 and 2). The extraction of the first two metals was carried out in the presence of 0.005 *M* cupferron ($\text{pH}_{1/2}$ = 1.2 and 3.9 for Sc and Y respectively); in the case of lanthanum, 0.05 *M* cupferron solution was used. Maximum extractibility (about 90%) of lanthanum was obtained in the pH region 4–10 ($\text{pH}_{1/2}$ = 3.4).

Titanium, zirconium and thorium

Titanium and zirconium could be quantitatively extracted with chloroform in the presence of 0.005 *M* cupferron, even from solutions of relatively high acidity (pH 0–3). The decrease in the extractibility of these metals at higher pH values (see Fig. 3) can probably be explained by hydrolysis. The extraction of thorium was investigated in detail by DYRSSEN[9] who found that quantitative extraction of thorium occurred at pH 2.5–9 ($\text{pH}_{1/2}$ = 1.2; 0.005 *M* cupferron solution).

Vanadium and niobium

Vanadium(V) formed with an excess of cupferron (0.005 *M* solution) at pH 0–3 a chelate which was quantitatively extracted into chloroform. At higher pH the extraction rate was decreased because of the formation of the non-extractable anion VO_3^- (see Fig. 4). The vanadium complex absorbed strongly at 540 mμ and thus cupferron extraction could be used for direct photometric determination of vanadium. Niobium was almost quantitatively extracted (> 98%) with chloroform in the presence of 0.005 *M* cupferron in the pH region 0–9.

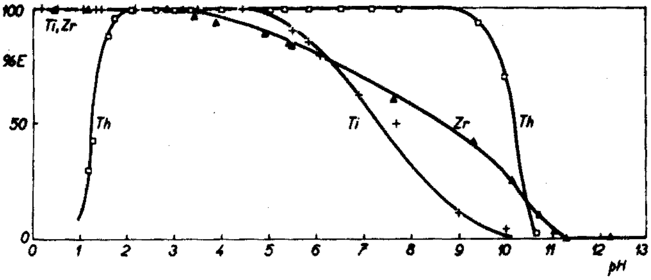

Fig. 3. Extraction of Ti(IV), Zr(IV) and Th(IV) with chloroform in the presence of 0.005 *M* cupferron *vs.* the pH value of the aqueous phase, + Ti, ▲ Zr, □ Th.

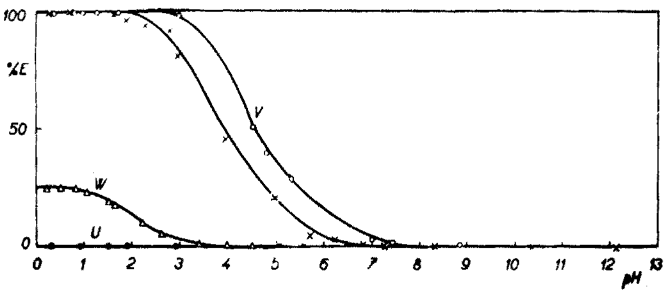

Fig. 4. Extraction of V(V), Mo(VI), W(VI) and U(VI) with chloroform in the presence of 0.005 *M* cupferron *vs.* the pH value of the aqueous phase. ○ V, × Mo, △ W, ● U.

Molybdenum, tungsten and uranium

The extraction curves of molybdenum(VI), tungsten(VI) and uranium(VI) are shown in Fig. 4. Of these metals, only molybdenum(VI) was quantitatively extracted with chloroform at pH 0–2; only 20% of tungsten was extracted under the above conditions (0.005 *M* cupferron solution). With higher reagent concentrations, the extraction of tungsten was increased. Uranium(VI) was not extracted with chloroform below pH 3 at all. At higher pH values emulsification occurred, so that it was impossible to determine the amount of uranium extracted into the organic phase.

Manganese, iron, cobalt and nickel

The pH dependence of the extraction of manganese(II), iron(III), cobalt(II) and nickel(II) with chloroform in the presence of 0.05 M cupferron is given in Fig. 5. Of these metals, only the cupferrates of iron(III) and cobalt(II) were quantitatively extracted; iron cupferrate was extracted at pH 0–5 (at higher pH values the results were not reproducible because of hydrolysis of iron(III)), and cobalt cupferrate was extracted at pH 5–12 ($\mathrm{pH}_{1/2} = 3.18$). The present data for iron agree very well with the results of SANDELL AND CUMMINGS[1] who found the extraction constant to be $7 \cdot 10^9$ (in 1 M perchloric acid).

The reaction between nickel and cupferron was slow and therefore the extraction curve of nickel had an atypical form (see Fig. 5). Manganese was extracted with chloroform in the pH region 4.5–9 only to the extent of 16%.

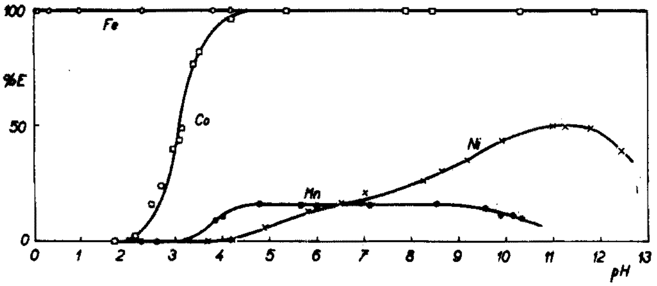

Fig. 5. Extraction of Mn(II), Fe(III), Co(II) and Ni(II) with chloroform in the presence of 0.05 M cupferron solution *vs.* the pH value of the aqueous phase. ● Mn, ○ Fe, □ Co, × Ni.

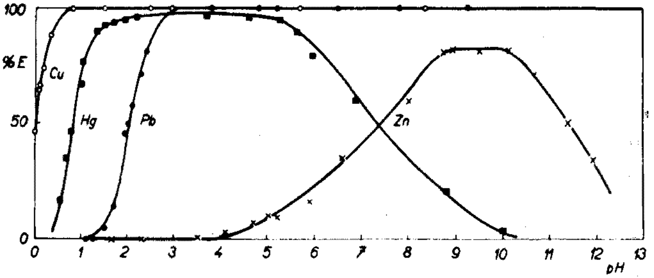

Fig. 6. Extraction of Cu(II), Zn(II), Hg(II) and Pb(II) with chloroform in the presence of 0.05 M cupferron *vs.* the pH values of the aqueous phase. ○ Cu, × Zn, ■ Hg, ● Pb.

Palladium

Palladium(II) was completely extracted in the presence of 0.005–0.05 M cupferron with chloroform over the whole pH region investigated (0–12).

Copper, silver, zinc, cadmium, mercury and lead

Quantitative extraction of copper(II) and lead(II) with chloroform in the presence of 0.05 M cupferron, occurred at pH values higher than 2 and 3 respectively ($\mathrm{pH}_{1/2} =$ 0.03 and 2.06 respectively). The present results for copper(II) are in complete agreement with data of FURMAN, MASON AND PECOLA[2].

The maximum extraction of mercury(II) — about 97% — and of zinc(II) — about 75% — occurred in the pH ranges 1–5 and 8.5–10.5 respectively ($\text{pH}_{1/2} = 0.85$ and 7.4 respectively). The cupferrates of silver(I) and cadmium(II) are only slightly soluble in chloroform[2] so that large amounts of these metals are practically not extracted into this solvent; by means of trace concentrations of radioactive silver and cadmium, partial extraction of both metals from neutral medium was observed.

Antimony and bismuth

The extraction curves of antimony(III) and bismuth(III) are shown in Fig. 2. In the presence of 0.005 *M* cupferron, antimony(III) was completely extracted with chloroform over the whole pH region investigated (0–11), whereas quantitative extraction of bismuth(III) took place only at pH values higher than 1.5 ($\text{pH}_{1/2} = 0.61$).

DISCUSSION

From the distribution data of the metals investigated, the composition and extraction constants were calculated[4–6]. In general, it was found that cupferron forms complexes of the type MA_n with metals (n is the charge of the metal ion). From the extraction constants, and from the distribution coefficient ($\log q_{HA} = 2.18$)[9] and dissociation constant ($pK_{HA} = 4.13$)[8] of cupferron, the two-phase stability constants, $Q_N K_N$, of the metal cupferrates were calculated. All the results obtained are summarized in Table II.

TABLE II

EXTRACTION DATA FOR METAL CUPFERRATES

Metal ion	$pH_{1/2}$*	$\log K_0$	$\log Q_N K_N$
Be^{2+}	2.07	−1.54	11.08
Al^{3+}	3.51	−3.5	15.43
Ga^{3+}	−0.3	4.92	23.85
In^{3+}	0.5	2.42	21.35
Tl^{3+}		~3	
Sc^{3+}	0.2	3.34	22.27
Y^{3+}	2.9	−4.74	14.19
La^{3+}	3.4	−6.22	12.71
Ti^{4+}	<0		
Zr^{4+}	<0		
Th^{4+}	0.2	4.44	29.68
VO_2^+	<0		
Nb(V)	<0		
Mo(VI)	<0		
Fe^{3+}	<0		
Co^{2+}	3.18	−3.56	9.06
Pd^{2+}	<0		
Cu^{2+}	0.03	2.66	15.28
Zn^{2+}	7.4		
Hg^{2+}	0.85	0.91	13.53
Pb^{2+}	2.06	−1.53	11.09
Sb^{3+}	<0		
Bi^{3+}	−0.4	5.08	24.01

* In the presence of 0.05 *M* cupferron solution.

From Table II it can be seen, that some metals (Ti(IV), Zr(IV), V(V), Fe(III), Mo(VI), Pd(II) and Sb(III)) were quantitatively extracted even from relatively highly acidic medium; hence it was impossible to determine their extraction constants. The extractability of the other metal cupferrates decreased in the following order: Bi(III), Ga(III), Cu(II), Th(IV), Sc(III), Tl(III) In(III), Hg(II), Pb(II), Be(II), Al(III), Co(II), Y(III) and La(III). The cupferrates of W(VI), Mn(II), Ni(II), Zn(II), Ag(I) and Cd(II) were extracted with chloroform only to small extent, whereas Mg(II), Ca(II), Sr(II), Ba(II) and U(VI) were not extracted at all.

SUMMARY

The extraction of the cupferrates of 33 metals (Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Sc, Y, La, Ti, Zr, Th, V, Nb, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Pb, Sb and Bi) with chloroform was studied in relation to pH values. The extraction constants and two-phase stability constants of the cupferrates were calculated; these can be used to determine the optimum conditions for the separation of many metals.

RÉSUMÉ

L'extraction des cupferrates de 33 métaux (Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Sc, Y, La, Ti, Zr, Th, V, Nb, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Pb, Sb et Bi) avec le chloroforme a été examinée en fonction du pH. Les constantes d'extraction et de stabilité des cupferrates ont été calculées; elles peuvent servir à déterminer les conditions optima de séparation de nombreux métaux.

ZUSAMMENFASSUNG

Es wurde die Extraktion folgender 33 Metalle als Cupferron-Komplex mit Chloroform in Abhängigkeit vom pH-Wert untersucht: Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Sc, Y, La, Ti, Zr, Th, V, Nb, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Pb, Sb und Bi. Die Extraktions- und Stabilitätskonstanten wurden berechnet. Mit ihnen lassen sich bei vielen Metallen die optimalen Bedingungen für die Trennung voraussagen.

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THEORY OF PHOTOMETRIC MICROTITRATIONS

A METALLOCHROMIC INDICATOR FORMING A STEP-WISE SYSTEM OF COMPLEXES

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(Received April 15th, 1963)

Photometric end-points are frequently employed for compleximetric microtitrations with metallochromic indicators even for microgram concentrations[1]. The accuracy of such a microdetermination is usually better than that of other analytical methods for similar concentrations, but it is heavily dependent on the shape of the titration curve, which is influenced markedly by the step-wise equilibrium of the metal–indicator complexes, especially when the concentration of the free indicator increases.

Although many thoroughly studied metallochromic indicators have been found to form a step-wise system of complexes[2,3], previous theories of photometric titrations have been simplified so that only the case of a single metal–indicator complex MI[4,5] or MI_n (ref. 6) has been considered. Similar simplifications have also been made in attempts to characterize theoretically the sharpness of indicator colour changes in visual titrations[7,8], which are also closely related to the theory of photometric titrations.

The present status of both these lines of theory suggested its further development for the overlooked equilibria of step-wise complexes under the concentration conditions which are typical for compleximetric microtitrations. One aim of this contribution is to explain the changes in the shapes of curves from the view point of the feasibility of accurate graphical end-point extrapolation, when a step-wise complex formation takes place.

LIST OF PRINCIPAL SYMBOLS

Symbol	*Definition*
C_Y	Total concentration of titrant
C_I	Total concentration of indicator
C_M	Total concentration of metal
[ ]	Equilibrium concentration of the species indicated within the square brackets
α	$= [I]/C_I$, fraction of the free form of the indicator
a	$= C_Y/C_M$, equivalent fraction of the titrant added
K_{MY}	$= [MY]/[M][Y]$, stoichiometric stability constant of the metal complexan, MY

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K_{n-i}	$= [MI_{(n-i)}]/[M][I]^{(n-i)}$, stoichiometric stability constant of the metal–indicator complex, $MI_{(n-i)}$
k_n	$= [MI_n]/[MI_{(n-1)}][I]$, stoichiometric step stability constant of MI_n
ε_{01}	Molar absorptivity of the free form I of the indicator
$\varepsilon_{1(n-i)}$	Molar absorptivity of a particular complex ion $MI_{(n-i)}$
V	Total volume of the titrated solution in ml
M	Molarity of the titrant
${}^{\;n}_{n-i}T$	Fraction of C_M present in forms of M and all steps from $MI_{(n-i)}$ to MI_n, eqns (13) and (18)
t_s	Partial function of ${}^{\;n}_{n-i}T$, a linear function of α, eqn. (18)
t_h	Partial function of ${}^{\;n}_{n-i}T$, a non-linear function of α, eqn. (18)
t	$= t_h/t_s$, ratio of both partial functions
${}^{\;n}_{n-i}U$	Ratio of the uncomplexed EDTA ion Y to C_M, considering the step equilibrium from $MI_{(n-i)}$ to MI_n, eqns. (13) and (15)
U_{n-i}	Partial function of ${}^{\;n}_{n-i}U$, corresponding to the presence of the step $n-i$, eqn. (16)
δ_a	Permissible experimental error in a

EQUATIONS OF THE STUDIED EQUILIBRIUM

The end-point indication of a compleximetric titration with metallochromic indicator is based upon a competitive reaction of a system of coloured indicator–metal complexes with the chelating ion. A list of the symbols used in the subsequent sections is given above.

If we limit our considerations only to a system of the last three steps of the complex formation $MI_{(n-2)}$, $MI_{(n-1)}$ and MI_n, the equilibrium of the indicator colour change may be written as follows:

$$MI_{(n-2)} + Y \rightleftharpoons MY + (n-2)\,I \qquad (1)$$

$$MI_{(n-2)} + I \rightleftharpoons MI_{(n-1)} \qquad (2)$$

$$MI_{(n-1)} + I \rightleftharpoons MI_n \qquad (3)$$

where M denotes the titrated metal, Y the free ethylenediamine-tetraacetate (EDTA) ion and MY, $MI_{(n-2)}$, etc., the complexes of the metal with EDTA and with the indicator respectively*.

The fundamental set of equations expressing all the variables of the equilibrium system includes the expressions for the stoichiometric stability constants of the complexes formed:

$$K_{MY} = \frac{[MY]}{[M][Y]} \qquad (4)$$

$$K_{n-2} = \frac{[MI_{(n-2)}]}{[M][I]^{(n-2)}} \qquad (5)$$

$$K_{n-1} = \frac{[MI_{(n-1)}]}{[M][I]^{(n-1)}} = K_{n-2}\cdot k_{n-1} \qquad (6)$$

$$K_n = \frac{[MI_n]}{[M][I]^n} = K_{n-2}\cdot k_{n-1}\cdot k_n \qquad (7)$$

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* For the sake of simplicity, the charges of the ions are omitted.

And it also includes the conditions for the total (analytical) concentrations of EDTA added (C_Y), of the titrated metal (C_M) and of the indicator (C_I):

$$C_Y = a \cdot C_M = [Y] + [MY] \tag{8}$$

$$C_M = [M] + [MY] + [MI_{(n-2)}] + [MI_{(n-1)}] + [MI_n] \tag{9}$$

$$C_I = [I] + (n-2)[MI_{(n-2)}] + (n-1)[MI_{(n-1)}] + n[MI_n] \tag{10}$$

If the maximum number of addends n is equal to one or two, the foregoing equations should be correspondingly simplified.

EQUATION OF A PHOTOMETRIC TITRATION CURVE

The photometric titration curve representing the change of absorbance during the titration is given as a sum of the absorbances of the individual ions involved in the equilibrium. If the indicator complexes and the free form of the indicator are the only ions which absorb light at the given wavelength, the total absorbance E is expressed by the equation

$$E = \varepsilon_{1(n-2)}[MI_{(n-2)}] + \varepsilon_{1(n-1)}[MI_{(n-1)}] + \varepsilon_{1n}[MI_n] + \varepsilon_{01}[I] \tag{11}$$

The concentrations of all individual indicator complex ions in eqn. (11) may be expressed as a function of the equilibrium concentration [I], if [M] is computed from eqn. (10) and eqns. (5), (6) and (7) are used for substitution. Thus:

$$E = \varepsilon_{01}[I] + (C_I - [I]) \frac{\varepsilon_{1(n-2)}K_{n-2} + \varepsilon_{1(n-1)}K_{n-1}[I] + \varepsilon_{1n}K_n[I]^2}{(n-2)K_{n-2} + (n-1)K_{n-1}[I] + nK_n[I]^2} \tag{12}$$

By introducing $[I] = C_I\alpha$, any of the previous equations can be written as a function of α.

If the equilibrium concentration of [I] is then expressed as a function of the equivalent fraction a, the exact theoretical shape of the photometric titration curve is obtained.

DERIVATION OF FUNCTION $a = f(\alpha)$

General expression

The function $[I] = f(a)$ which is necessary for substitution into eqn. (12), would result in an algebraic function of the degree $2n + 1$. It is more convenient, therefore, to solve its inverse function $a = f(I)$, which can also be readily broken down to partial additive functions reflecting the specific effects of the equilibrium considered. The contributions of the individual ionic species to the value of this function can be seen when both conditions for analytical concentrations C_Y and C_M (eqns. (8) and (9)) are combined. Hence we obtain:

$$a = 1 - \frac{1}{C_M}\Big([M] + [MI_{(n-2)}] + [MI_{(n-1)}] + [MI_n]\Big) + \frac{[Y]}{C_M} = 1 - {}^{n}_{n-2}T + {}^{n}_{n-2}U \tag{13}$$

As indicated in eqn. (13), the function $a = f(I)$ can be taken as composed of additive functions ${}^{u}_{n-2}T$ and ${}^{n}_{n-2}U$; ${}^{n}_{n-2}T$ represents the fraction of the total metal concentration, C_M, which is present as free metal ion M and as complexes with the indicator, while ${}^{n}_{n-2}U$ represents the ratio of the uncomplexed EDTA to C_M. Both expressions are functions of α and will be discussed in detail below. By subsequent substitutions from the fundamental set of equations and by substituting $[\mathrm{I}] = C_I\alpha$, the general expression for $a = \mathrm{f}(\alpha)$ is obtained:

$$\begin{aligned} a = 1 - \left\{\frac{C_I}{nC_M}(1-\alpha)\left[1 + \frac{n(C_I\alpha)^{(2-n)} + K_{n-1}C_I\alpha + 2\,K_{n-2}}{nK_nC_I^2\alpha^2 + (n-1)K_{n-1}C_I\alpha + (n-2)K_{n-2}}\right] + \frac{1}{C_MK_{MY}}\right\} + \\ + \frac{K_{n-2}}{K_{MY}}(C_I\alpha)^{(n-2)}\left[\frac{n-2}{C_I(1-\alpha)} - \frac{1}{C_M}\right] + \\ + \frac{K_{n-1}}{K_{MY}}(C_I\alpha)^{(n-1)}\left[\frac{n-1}{C_I(1-\alpha)} - \frac{1}{C_M}\right] + \\ + \frac{K_n}{K_{MY}}(C_I\alpha)^n\left[\frac{n}{C_I(1-\alpha)} - \frac{1}{C_M}\right] \end{aligned} \qquad (14)$$

In some cases formation of lower steps can be neglected and eqn. (14) will be correspondingly simplified by putting $K_{n-2} = 0$ or $K_{n-1} = 0$. For $n = 1$, eqn. (14) yields the expression derived in previous contributions[4,7].

Discussion of the function U

By comparing eqns. (13) and (14), it can be seen that the function ${}^{n}_{n-2}U$ consists of partial functions U_n, U_{n-1}, etc., each pertaining to a particular step of the complex formation and being denominated by the ratio of its stability constant to the stability constant K_{MY}. Hence from eqn. (14) we obtain:

$$\begin{aligned} {}^{n}_{n-2}U = U_{n-2} + U_{n-1} + U_n = \frac{K_{n-2}}{K_{MY}}(C_I\alpha)^{(n-2)}\left[\frac{n-2}{C_I(1-\alpha)} - \frac{1}{C_M}\right] + \\ + \frac{K_{n-1}}{K_{MY}}(C_I\alpha)^{(n-1)}\left[\frac{n-1}{C_I(1-\alpha)} - \frac{1}{C_M}\right] + \frac{K_n}{K_{MY}}(C_I\alpha)^n\left[\frac{n}{C_I(1-\alpha)} - \frac{1}{C_M}\right] \end{aligned} \qquad (15)$$

It is also evident that the form of each partial function U_{n-i} is not affected by any changes in the other components of the system. For a step $n - i$, where i is equal to 0, 1 or 2, the corresponding partial function U_{n-i} can be written as follows:

$$\begin{aligned} U_{n-i} = \frac{K_{n-i}}{K_{MY}}C_I^{(n-i-1)}\alpha^{(n-i)}\left[\frac{n-i}{1-\alpha} - \frac{C_I}{C_M}\right] = \\ = \frac{K_{n-i}}{K_{MY}}C_I^{(n-i-1)}\cdot\left[u(\alpha)_{n-i} - \frac{C_I}{C_M}\alpha^{(n-i)}\right] \end{aligned} \qquad (16)$$

where the auxiliary function $u(\alpha)_{n-i}$ is not influenced by parameters other than $n-i$. The function U_{n-i} can be evaluated easily by means of the plot of $\log u(\alpha)_{n-i}$ and $\log \alpha^{(n-i)}$ for varied values of α (ref. 6).

The negative expression $(C_I/C_M)\alpha^{(n-i)}$ approaches a constant value with increasing α and can be neglected for the first approximation of U_{n-i}. The numerical degree of the expression U_{n-i} depends on the value of the ratio $K_{n-i}C_I^{(n-i-1)}/K_{MY}$, which is also responsible for the contribution of the function U_{n-i} to the overall value of a.

The influence of the function ${}^{\,n}_{n-i}U$ on the shape of the $a = \mathrm{f}(\alpha)$ curve can be visualized in Fig 1, where curve 3 is plotted for various values of K_{MY}. If the value of the ratio $K_{n-i}C_{I}^{(n-i-1)}/K_{MY}$ is smaller than 10^{-4}, the function U_{n-i} has practically no influence on the general shape of the curve before the end-point, and it causes only a small bend in the vicinity of the end-point. If this ratio is greater than 10^{-4}, the bend becomes more pronounced and extended. The indicator colour change would be rather poor for a visual titration under such conditions. The evaluation of photometric titration curves is feasible even in such cases, but it might become somewhat emprical and even uncertain (*cf.* curves d and e).

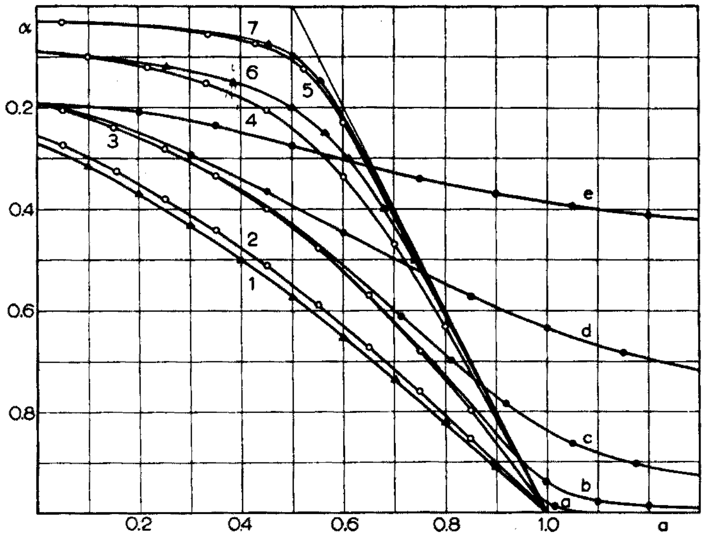

Fig. 1. Effect of the equilibrium of step complexes MI and MI_2 and of the competition with MY (for $C_I = 10^{-5}$, $C_M = 10^{-5}$). The systems involve the following species: ▲ the overall complex MI_n, ○ MI and MI_2, ● MI, MI_2 and MY. For $K_1 = 10^6$, $K_2 = 0$ (curve 1), 10^{10} (curve 2), 10^{11} (curve 3), 10^{12} (curve 4), 10^{13} (curve 5). For $K_1 = 0$, $K_2 = 10^{12}$ (curve 6), 10^{13} (curve 7). For $K_1 = 10^6$ and $K_2 = 10^{11}$, $K_{MY} = 10^{10}$ (curve a), 10^9 (curve b), 10^8 (curve c), 10^7 (curve d), 10^6 (curve e).

In most practical compleximetric titrations, the ratio is very small: $K_{n-i}C_{I}^{(n-i-1)}/K_{MY} \ll 1$. Then the contributions of ${}^{\,n}_{n-2}U$ to the value of a can be neglected in a certain portion of the titration curve before the end-point region. The conditions for such a simplification can be derived from the following assumptions. If δ_a is the permissible error in a, the overall function ${}^{\,n}_{n-2}U$ can be neglected in any portion of the curve where its values are smaller than δ_a. Analogously, from eqn. (15) after neglecting the negative expressions, we obtain:

$$\delta_a \leqslant \frac{K_{n-2}}{K_{MY}} C_{I}^{(n-3)} u(\alpha)_{n-2} + \frac{K_{n-1}}{K_{MY}} C_{I}^{(n-2)} u(\alpha)_{n-1} + \frac{K_n}{K_{MY}} C_{I}^{(n-1)} u(\alpha)_n \qquad (17)$$

After the end-point has been passed, the concentration of free EDTA ions, [Y], cannot be neglected and the functions U must be taken into account.

Discussion of the function T

For a three-step complex equilibrium the function ${}_{n-2}^{\ n}T$, which is represented by the negative expression in eqn. (14), may be written in the following form:

$$a = 1 - \frac{C_I(1-\alpha)}{nC_M} - \frac{C_I(1-\alpha)}{nC_M} \frac{n(C_I\alpha)^{(2-n)} + K_{n-1}C_I\alpha + 2K_{n-2}}{nK_nC_I^2\alpha^2 + (n-1)K_{n-1}C_I\alpha + (n-2)K_{n-2}} - \frac{1}{K_{MY}C_M} =$$

$$= 1 - t_s - t_h - \frac{1}{K_{MY}C_M} \qquad (18)$$

The negative expression $1/(C_MK_{MY})$ is usually very small and may be neglected.

The first expression t_s represents a straight line, which is obtained when K_n is very high. This limiting curve of the whole family of curves is approached more or less closely, especially at the end-point portion of the curve. It also indicates the steepest possible slope of the curve, C_I/nC_M. If the straight line t_s can be extrapolated from the end-point portion of the curve the total number of addends n can be easily calculated. It is not without interest that the expression t_s itself is not affected by the number of steps in the equilibrium system of complexes. This can be seen in Fig. 2 where the t_s function might be plotted for 3 values of n, each one belonging to the appropriate family of complexes. The curves 8 and 9 coincide in a considerable portion with the t_s function for $n = 3$. The decreasing stability of the last step is marked by a decline of the curve from its t_s function and if the stability of the last step is low, the extrapolation of the straight line might become uncertain (*cf.* also Fig. 4).

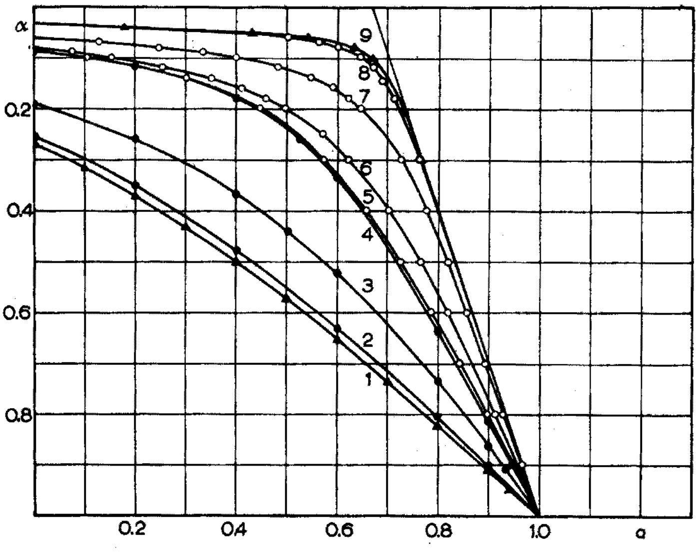

Fig. 2. Effect of the step equilibrium and the stability constants involved (for $C_I = 10^{-5}$, $C_M = 10^{-5}$). The systems involve the following steps: ▲ the overall complex MI_n, ● MI and MI_2, ○ MI, MI_2 and MI_3. For $K_1 = 10^6$, $K_2 = 0$ (curve 1), 10^{10} (curve 2), 10^{11} (curve 3), 10^{12} (curve 4). For $K_1 = 10^6$ and $K_2 = 10^{12}$, $K_3 = 10^{16}$ (curve 5), 10^{17} (curve 6), 10^{18} (curve 7), 10^{19} (curve 8). For curve 9, $K_3 = 10^{19}$.

The second function t_h expresses the effect of the dissociation of the indicator complex system. The values of $t = t_h/t_s$ depend on all the parameters that influence the equilibrium and this function is responsible for the general shape of the $a = f(\alpha)$ curve, whenever the contributions of ${}_{n-2}^{\;n}U$ become negligible.

The calculated shapes of the curves $a = f(\alpha)$ for systems of two and three indicator step complexes can be seen in Figs. 1 and 2. The formation of a higher step is marked by the appearance of a more pronounced bend in the curve and by a decrease in the initial values. With an increasing stability of the higher step, the first part of the curve becomes flatter and after the bend the end-point portion is steeper. Only when the stability of one of the complexes is much greater than that of the other steps, does the shape of the curve begin to resemble the case of only one overall complex formation; this can be seen from comparison of the curves 1 and 2, 5 and 7 in Fig. 1 and curves 4 and 5, 8 and 9 in Fig. 2.

To summarize, the equilibrium system is reflected markedly in function t, which determines specifically the curvature of the titration curve in the first place. On the other hand, fitting of the titration curves provides a useful method for determining the number of the steps involved and all the corresponding equilibrium constants. This aspect of the theory of photometric titration curves will be worked out in another publication.

Effect of the indicator and metal concentrations

The indicator concentration C_I affects the shape of the simplified function $a = 1 - T$ in two ways, as can be deduced from eqn. (18). First, the slope of the linear functions t_s is changed and, secondly, the equilibrium is shifted in favour of the formation of the last step of the system of indicator complexes; this can also be seen from the expression for the non-linear function t_h in eqn. (18). Both effects are demonstrated

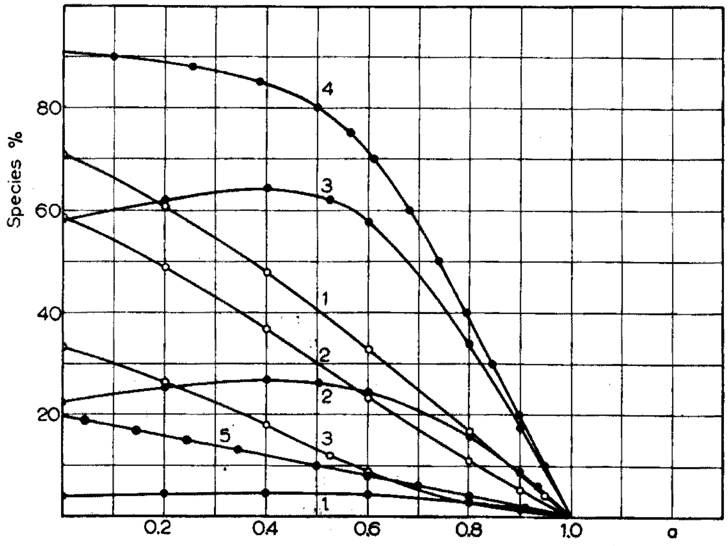

Fig. 3. Effect of the stability of the complex MI_2 on curves for $[MI] = f(a)$ and $[MI_2] = f(a)$ (for $C_I = 10^{-5}$, $C_M = 10^{-5}$, $K_1 = 10^6$). ○ $[MI]/C_I = f(a)$, ● $2[MI_2]/C_I = f(a)$. Values of K_2: (1) 10^{10}, (2) 10^{11}, (3) 10^{12}. (4) $K_1 = 0$, $K_2 = 10^{12}$. (5) $K_1 = 10^6$, $K_2 = 10^{12}$, $C_I = 10^{-4}$.

in Fig. 3 by curve 5, which shows a practically linear decomposition of the complex MI_2, the concentration being increased ten times. The concentration of the lower step MI is practically negligible in this case. In this way the portion of the microtitration curve suitable for end-point extrapolation can be extended by adding a certain excess of the indicator. On the other hand, a low concentration of the indicator helps to achieve a shorter and more pronounced colour change, which is preferable in the case of visual titrations and might also be useful with some automatic titrators which utilize photometric indication.

The metal concentration C_M affects mainly the slope of the t_s functions in $\alpha = f(a)$ plots. The shape of the titration curves $E = f(v_t)$ for various C_M values remains unaffected[6], because from the definition of a, $v_t = (aVC_M)/M$. Thus a change of C_M results only in a shift of the consumption of titrant at the end-point, if the molarity M of the standard EDTA solution remains unchanged.

FUNCTIONS $[MI_{(n-i)}] = f(\alpha)$

Since the expression for the function $a = f(\alpha)$ has now been derived and interpreted, it is more convenient to express the equilibrium concentrations of the other complex ions as functions of α. The function $[MI_{(n-i)}] = f(\alpha)$ may be written from eqn. (12) as:

$$[MI_{(n-i)}] = \frac{K_{n-i}(C_I\alpha)^{(2-i)}}{nK_nC_I^2\alpha^2 + (n-1)K_{n-i}C_I\alpha + (n-2)K_{n-2}} (1-\alpha)C_I \qquad (19)$$

The shape of these functions for i equal to 0, 1 and 2 can be seen in Figs. 3 and 4 in the form of $(n-i)$ $[MI_{(n-i)}]/C_I = f(a)$. The function $[MI_n] = f(a)$ exhibits a maximum while the function $[MI_{(n-1)}]$ has an S-form with a point of inflection at the position of the maximum of the higher complex. The function $[MI_{(n-2)}]$ has also an S-shape.

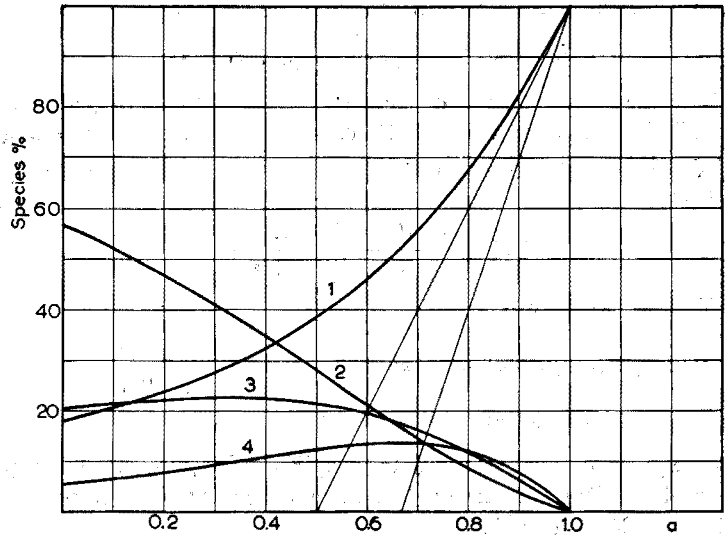

Fig. 4. Distribution of the indicator into its ionic species during titration (for $C_I = 10^{-5}$, $C_M = 10^{-5}$, $K_1 = 10^6$, $K_2 = 10^{11}$, $K_3 = 10^{16}$). (1) $\alpha = f(a)$, (2) $[MI]/C_I = f(a)$, (3) $2[MI_2]/C_I = f(a)$, (4) $3[MI_3]/C_I = f(a)$.

The position of the maximum of the function $[MI_n] = f(a)$ on the abscissa depends on the values of all the parameters involved; this can be shown by solving the condition for the existence of the maximum, $d[MI_n]/da = 0$.

The photometric titration curve, which is expressed by the general eqn. (11) includes the influence of all light-absorbing species involved in the indicator complex equilibrium. The extent of their individual contributions to the measured overall value of absorbance depends largely on the molar absorptivities of the ions at the wavelength used. If the wavelength settings are changed in a certain direction, it is practically always possible to find a region where one particular ion absorbs more than the others. In such a case, the shape of the photometric titration curve will approach the shape of the function $[I] = f(a)$ for $\varepsilon_{01} > \varepsilon_{1(n-i)}$ or any of the functions $[MI_{(n-i)}] = f(a)$, if $\varepsilon_{1(n-i)}$ is greater than the other molar absorptivities. It is also interesting to inspect the portions of the curves in Fig. 4 just before the point of equivalence. While the curve MI_n is convex, the curve $MI_{(n-2)}$ is concave in this region. Photometric titrations with such a convex or concave portion before the end-point, according to the wavelength used, have been obtained in the cases of bismuth and lead when xylenol orange is used as indicator[1]; a system of step-wise formation is found for both metals[3].

EFFECT OF MOLAR ABSORPTIVITIES ON THE SHAPE OF THE TITRATION CURVE

As has been shown, the formation of a higher step in the step-wise equilibrium results in a distortion of the titration curve and a convex or concave portion before the end-point is observed. Experimentally, it has been found[1] that the same portion of the titration curve becomes linear at a certain narrow wavelength region and may, therefore, be advantageous for the exact evaluation of the end-point.

Let us examine the influence of the molar absorptivities on the linearity of the curve for the simplified case of a step equilibrium of two complexes $MI_{(n-1)}$ and MI_n.

The equation for the photometric titration curve may then be written as follows:

$$E = \varepsilon_{01}[I] + \varepsilon_{1(n-1)}[MI_{(n-1)}] + \varepsilon_{1n}[MI_n] \qquad (20)$$

Supposing that the concentration of free EDTA ions can be neglected in eqn. (8), then the equilibrium concentration of [M] can be expressed by combining eqns. (8), (9) and (10) (putting $[Y] = [MI_{(n-2)}] = 0$) as a function of [I] and of the equivalent fraction a; thus:

$$[M] = \frac{nC_M(1-a) - C_I - [I]}{K_{n-1}[I]^{(n-1)} + n} \qquad (21)$$

Hence for $[MI_{(n-1)}]$ we obtain

$$[MI_{(n-1)}] = (nC_M(1-a) - C_I + [I])\,\frac{K_{n-1}[I]^{(n-1)}}{K_{n-1}[I]^{(n-1)} + n} = (nC_M(1-a) - C_I + [I])[1 - \psi(I)] \qquad (22)$$

The negative expression in eqn. (22), $\psi(I) = n/(K_{n-1}[I]^{(n-1)} + n)$, will approach zero in the portion of the titration curve before the end-point; this corresponds to neglecting concentration [M] in eqn. (9).

Let us suppose further, that the function $[I] = f(a)$ may be written in the form:

$$[I] = f(a) = C_I - \varphi(a) \qquad (23)$$

where $\varphi(a)$ is a continuous function and its values are greater than zero within the studied interval of the equivalent fraction $a < 0, 1 - >$. The function $\varphi(a)$ can be equal to zero only for $a = 1$, *i.e.* at the point of equivalence.

Substituting for $[MI_n]$ from eqn. (10) and for $[MI_{(n-1)}]$ from eqn. (22) and then for [I] from eqn. (23), we obtain

$$E = \varepsilon_{01}C_I + [n\varepsilon_{1(n-1)} - (n - 1)\varepsilon_{1n}]C_M(1 - a) - [\varepsilon_{01} + \varepsilon_{1(n-1)} - \varepsilon_{1n}]\varphi(a) -$$

$$- \left[\varepsilon_{1(n-1)} - \frac{n-1}{n}\varepsilon_{1n}\right]\left[nC_M(1 - a) - \varphi(a)\right]\psi(I) \qquad (24)$$

When the function $\psi(I)$ approaches zero in the portion of the curve before the equivalence point, the photometric titration curve will have a linear shape only if the individual molar absorptivities satisfy the condition:

$$\varepsilon_{1n} = \varepsilon_{01} + \varepsilon_{1(n-1)} \qquad (25)$$

This linear portion of the titration curve is limited to the range where the function $\psi(I)$ becomes negligible, of course. Thus the linear portion of the curve may be extended by suppressing the dissociation of the complexes involved, *e.g.* by adding a higher concentration of the indicator. If the step-wise equilibrium involves complexes other than the last two, the photometric titration curve will show a non-linear shape at any wavelength in the region of their light absorption.

Since a step-wise equilibrium system of the indicator–metal complexes only has been considered, the results obtained in previous sections are also fully applicable for the titration of a coloured ligand with a metal salt. Thus, the condition for a linear titration curve expressed by eqn. (25) can be used in choosing a suitable wavelength for the spectrophotometric determination of a metal salt with a reagent forming two-step complexes.

DISCUSSION

The relationship between the shape of a titration curve and the reliability and accuracy of the end-point evaluation is a very important practical aspect of the theory of photometric titrations. In particular, the following points should be considered.

(*1*) The extent of the competitive equilibrium of the step-wise system of the metal–indicator complexes and the metal complexan, which results in a rounding off at the end-point and is also shown by the relative values of the function ${}_{n-2}^{\ n}U$ (see eqns. (14) and (15)). If the dissociation of MY is pronounced, the end-point evaluation may become uncertain. Empirical corrections should be applied for the evaluated end-points in these cases, otherwise positive errors may arise.

(*2*) The feasibility of linear end-point extrapolation, which is influenced mainly by two factors: (*a*) the steepness of the titration curve before the end-point, and (*b*) the extent of the curve which may serve for the extrapolation.

(*a*) The maximum attainable steepness of the titration curve is characterized by the linear function t_s, which represents a portion of a limiting curve of the whole family of titration curves. The position of this straight line is not influenced by changes in the step-wise equilibrium of the complexes.

(*b*) The step-wise equilibrium is marked by convex or concave shapes of the curves before the end-point according to the wavelength used (see p. 560). Exact evaluation of the end-point may become inaccurate in such cases. If a system containing only the last two step-complexes prevails in this region of the indicator colour change, it is possible to find a wavelength at which the condition expressed in eqn. (25) is valid. The titration curve will then have a linear shape in the portion decisive for the end-point extrapolation. This result of the theory confirms previous experimental observations[1]. In all the theoretical derivations presented, the validity of Lambert–Beer's law is assumed, *i.e.* the use of monochromatic light of sufficient purity is supposed. Many instruments for photometric titrations are designed, however, with colour filters. In such cases, the fine differences in the shapes of titration curves for narrow wavelength bands may disappear and escape observation owing to the broad light bands used. In some cases, it has been found that the shapes of the curves are then closer to the linear course than when instruments with effective monochromators are used.

Increased concentrations of the metallochromic indicator added shift the equilibrium in favour of a higher step, and the linear portion of the curve before the end-point is thus extended. From this point of view, it is convenient to use a larger amount of indicator than in common visual titrations (up to about $2 \cdot 10^{-5}$ M of indicator). This result is in apparent disagreement with the theoretical requirements for visual titrations. In these titrations the sharpness of the colour change is stressed more than its course.

The theory of photometric titrations has also elucidated the specific influence of the equilibrium system on the shape of the titration curve. The effect of the function ${}^{n}_{n-2}U$ has already been mentioned; this is shown in the extent of the bend in the vicinity of the end-point. In many practical cases, this effect is negligible, which is shown by expression 17. The step-wise complex formation becomes evident from comparison of titration curves at various wavelengths. Although the general shape of the curve remains practically unaffected by the choice of wavelength in the case of a single complex[6], the step-wise equilibrium is marked by substantial changes in the shapes of the curves, depending on prevailing absorption of a certain indicator form. The curvature of the $\alpha = f(a)$ function is specifically characterized by function t(see p. 558). By means of such a system of titration curves, it is possible to obtain valuable information, at first approximation, about the complex equilibrium of an indicator colour change.

SUMMARY

The theory of photometric titrations is developed to cover a step-wise system of indicator complexes, the simultaneous presence of the last three steps being considered. A general expression for the dependence of the equivalent fraction on the fraction of the free indicator form is derived. This allows: (*1*) easy calculation of the theoretical shapes of curves for different values of all parameters involved; (*2*) critical consideration of the specific effect of these parameters on the shape of the curve. Noticeable dissociation of the metal complexan due to the competitive equilibrium is shown in more or less pronounced rounding-off at the end-point; in extreme cases the accuracy of the end-point evaluation may be decreased. Increased indicator concentrations help to extend the portion of the curve suitable for linear extrapolation of the end-point, because the step-wise equilibrium is thus shifted in favour of the last step. It is shown that the step-wise equilibrium is reflected by changes in the shape of the titration curves at different wavelengths. If only the last two step-complexes prevail before the end-point, it is possible to find a wavelength at which this portion of the curve has a linear course suitable for accurate end-point evaluation.

RÉSUMÉ

Les auteurs ont effectué une étude sur les microtitrages photométriques, au moyen d'indicateurs métallochromiques. Une expression générale est donnée sur le rapport de la fraction équivalente et de la fraction d'indicateur libre. Ceci permet: (*1*) une interprétation facile des formes des courbes, pour différentes valeurs comprenant tous les paramètres. (*2*) une considération critique de l'effet spécifique de ces paramètres sur la forme de la courbe.

ZUSAMMENFASSUNG

Für die photometrische Titration mit Komplexonen wird eine Theorie entwickelt, die die stufenweise Bildung von Indikatorkomplexen umfasst und die gleichzeitige Anwesenheit der letzten 3 Stufen berücksichtigt. Bezeichnet man mit a das Verhältnis von Gesamtkonzentration des Komplexbilderns zur Gesamtkonzentration des Indikators und mit α das Verhältnis der Gleichgewichtskonzentration des Indikators zu seiner Gesamtkonzentration, so lässt sich für $a = \mathrm{f}(\alpha)$ ein allgemeiner Ausdruck ableiten, der eine einfache Berechnung der theoretischen Kurvenform für verschiedene Parameter ermöglicht. Eine kritische Betrachtung der charakteristischen Einflüsse dieser Parameter auf die Form der Kurven führt zu folgenden Ergebnissen: (*1*) Eine bemerkenswerte Dissoziation der Metallkomplexe, die dem Konkurrenzgleichgewicht zuzuschreiben ist, zeigt sich in einer mehr oder weniger ausgeprägten Abrundung der Kurven am Endpunkt. In extremen Fällen kann die Genauigkeit der Endpunktsbestimmung dadurch verringert werden. (*2*) Steigende Indikatorkonzentrationen ermöglichen eine Verlängerung des Teiles der Kurve, der zur linearen Extrapolation des Endpunktes dient. Dadurch kann man die Genauigkeit der Endpunktsbestimmung verbessern. (*3*) Liegen mehrere Indikatorkomplexe gleichzeitig vor, so ändert sich die Form der Titrationskurven, wenn man bei unterschiedlichen Wellenlängen misst. Wenn vor dem Endpunkt nur die letzten 2 Stufen vorherrschen, ist es möglich, für die Messung eine Wellenlänge zu finden, bei der die Kurve in der Nähe des Endpunktes einen linearen Verlauf nimmt und so eine genaue Endpunktsbestimmung ermöglicht.

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THE ISOLATION OF CAESIUM-137 FROM LIQUID RADIOACTIVE FALL-OUT

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(Received June 10th, 1963)

The individual determination of important radioisotopes in liquid fall-out offers substantial advantages over the determination of total fall-out radioactivity[1]. One of the radio-nuclides, whose concentration is determined most frequently, is long-lived caesium-137. The aim of the present work was to develop a suitable procedure for the concentration and isolation of caesium-137 from liquid fall-out in such a way that relatively few and simple chemical operations would allow the preparation of caesium-137 for measurement by means of a multi-channel gamma-spectrometer.

To concentrate caesium from large volumes of water, the method of coprecipitation of caesium by Prussian blue[2] was used. The method has a number of advantages: the reagents employed are cheap and readily available and the method is sufficiently rapid with a relatively high efficiency. Moreover, it is possible to separate caesium from any potassium ions present, which under the experimental conditions employed, are practically not coprecipitated[2]. Other advantages are that a suitable subsequent chemical isolation of caesium is possible and that a sufficient amount of literature data concerning the sorption mechanism is available[2-4]. For further isolation of caesium, extraction of caesium picrylaminate by nitrobenzene[5] was chosen because of its simplicity and selectivity. To develop the whole procedure for the concentration and isolation of caesium it was necessary to extend the available data on both methods, to study their amalgamation, and to verify the efficiency, selectivity and reproducibility of the final procedure.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. The nitrobezene solution of sodium dipicrylaminate (0.1 *M*) was prepared by extraction with nitrobenzene of an aqueous solution of commercial dipicrylaminate (HDPA), and addition of an equivalent amount of sodium carbonate and 1 *M* sodium nitrate to increase the extraction yields. Aqueous solutions of 0.5 *M* iron(III) chloride in 1 *N* hydrochloric acid and 0.5 *M* sodium hexacyanoferrate(II) were standardized by the usual methods, the strength of the dipicrylaminate solution was determined by titrating the excess amount of acid in the aqueous phase after extraction with nitrobenzene solution. Inactive caesium chloride was labelled with radioactive caesium-137, added in the form of the chloride. To determine the selectivity of the method, a mixture of fission products was used, formed by irradiation of U_3O_8 in a nuclear reactor for a period of 24 h by a flux of $1.5 \cdot 10^{13}$ n/sec/cm^2. The uranium oxide was dissolved in aqua regia, and the solution thus formed was added to the fall-out sample.

Apparatus

Radiometric measurements were performed by means of a Geiger-Müller tube of the window-type, connected to a decadic reductor of conventional type. All necessary corrections were made. Gamma-spectra were measured by means of a 200-channel Type-SAI 332 analyser (Intertechnique Co., France).

Preliminary tests

In the coprecipitation of caesium ions by Prussian blue, ferrocyanide solution was always added first to the solution containing the caesium salt (10 mg Cs/l); then with agitation by a glass propeller, an excess of about 15% of the iron(III) chloride solution was added. In the preliminary experiments, small volumes of the precipitate were separated by centrifuging; when large volumes were used, the clear solution was poured onto a paper filter and the remaining suspension was centrifuged.

For the extraction, both phases were agitated by a propeller-type stirrer for a period of 5 min and then separated by centrifugation.

Samples for activity measurements were prepared by evaporating appropriate amounts of the aqueous or nitrobenzene phase on circular aluminium dishes. When the yield of caesium ion sorption by Prussian blue from a large volume of solution was determined, the precipitate was dissolved in an EDTA solution of pH 10, the solution was made up to a given volume and an aliquot of this solution was evaporated.

RESULTS AND DISCUSSION

The conditions for the maximum coprecipitation of caesium ions with Prussian blue (pH 0–2, efficient agitation and correct order of addition of reagents) had been established previously[2,3]. In the present work, it was necessary to determine the minimum amount of precipitate necessary and the coprecipitation yield when large solution volumes were used. The results are given in Fig. 1. It can be seen that an amount of 150 mg of Prussian blue was sufficient for 1 l of initial solution. The lower yields obtained with larger volumes may be explained on the basis of lower agitation efficiency, and partly by a certain loss of caesium on glass and possibly also on the paper filter.

In order to allow the use of the caesium dipicrylaminate extraction in the subsequent procedure, the dissolution of Prussian blue in a saturated EDTA solution (*ca.* 0.25 *M*) was tested at pH 10 and elevated temperature, a red-brown solution being formed. At lower pH values the EDTA solution dissolved the precipitate incompletely, and at higher pH values iron(III) hydroxide was precipitated. By means of the colour change from blue to red-brown, it was found that 1 g of Prussian blue dissolved in 25 ml of the EDTA solution, *i.e.* the molar ratio of iron to EDTA was *ca.* 1 : 1. Dissolution of Prussian blue by other reagents, which form an acid solution, would either render impossible or at least greatly hinder the following extraction of the caesium salt by nitrobenzene. Figure 2 shows that caesium could be effectively extracted from an EDTA solution of Prussian blue by dipicrylaminate in nitrobenzene. At an insufficient EDTA concentration, the yield of the caesium extraction was substantially lower; this was evidently caused by the presence of colloidal particles of Prussian blue containing occluded caesium ions. This explanation is in agreement with the fact that the molar ratio of Fe:EDTA at which the extraction became practically quantitative, was identical with the molar ratio at which the colour of the solution changed from blue to red-brown. This also made it possible to control the solution visually before extraction.

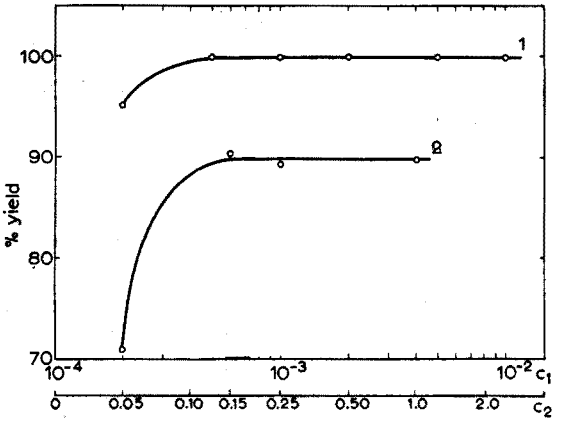

Fig. 1. Percentage yield of the coprecipitation of caesium ions with Prussian blue in relation to the amount of sorbent (c). c_1 = concentration of $Fe(CN)_6^{4-}$ in moles/l; c_2 = g of Prussian blue/l. Curve 1, Aqueous phase before precipitation = 5 ml; curve 2, Aqueous phase before precipitation = 500 ml.

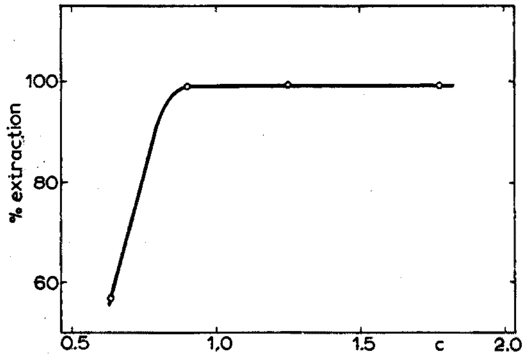

Fig. 2. Percentage extraction of caesium from a solution of Prussian blue in EDTA. c = molar ratio EDTA: Fe; solution volume = 2 ml aqueous phase and 2 ml organic phase; Prussian blue concentration = $2.7 \cdot 10^{-3}$ moles/l.

TABLE I

PERCENTAGE RECOVERY OF Cs BY EXTRACTION

Extraction period (min)	*Recovery (%)*
1	99.7
5	99.7
10	99.8
15	99.7
20	99.8
30	99.7

Table I shows that as little as 1 min was sufficient time for attainment of extraction equilibrium; however, the extraction was prolonged in all experiments to 5 min.

In further tests, the amount of organic phase necessary to obtain a sufficiently high extraction yield in the extraction of caesium from a solution of Prussian blue in EDTA was examined. This dependence is illustrated in Fig. 3.

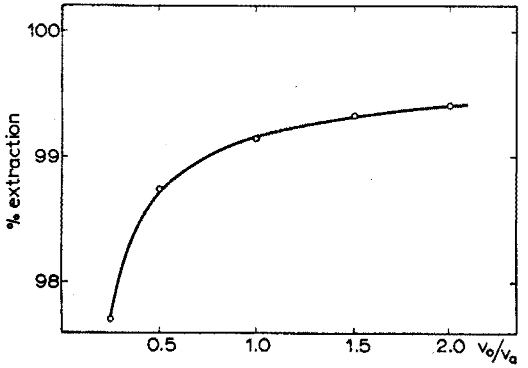

Fig. 3. Percentage extraction of caesium from a solution of Prussian blue in EDTA, in relation to the phase ratio (v_o/v_a). Prussian blue concentration $2.7 \cdot 10^{-3}$ moles/l; molar ratio EDTA : Fe = 1.2 : 1.

RECOMMENDED PROCEDURE

The following procedure is proposed for the isolation of caesium-137 from liquid radioactive fall-out.

Add 5 mg of the carrier and 0.8 ml of 0.5 *M* sodium hexacyanoferrate(II) to a water sample with a volume of 500 ml. Form a precipitate of Prussian blue by adding a 10% excess of 0.5 *M* iron(III) chloride solution in 1 *M* hydrochloric acid dropwise during 1 min. Agitate the solution vigorously during these additions. After agitating for 1–2 min, leave the precipitate to sediment.

Filter off the supernatant solution through a paper filter, and then centrifuge. Dissolve the precipitate, including the slight amount retained on the filter, in 8 ml of a warm 0.25 *M* EDTA solution at pH 10: complete the dissolution on a water bath. Extract caesium from this solution with two 2.5-ml portions of 0.1 *M* sodium dipicrylaminate in nitrobenzene, shaking for 5 min with each portion. Wash the organic phase twice with EDTA solution: first with 2 ml of a 0.12 *M* EDTA solution at pH 10, and then with 2 ml of a 0.02 *M* EDTA solution at the same pH value, washing for 2 min each time, with vigorous agitation. Back-extract caesium with three 1-ml portions of 1 *N* nitric acid, and then evaporate the solution on a counting dish.

Eight parallel tests were carried out by the above procedure in order to determine the reproducibility of the method and its yield. A value of 89.3 ± 0.4% was obtained for the yield, the mean square error of one determination being ± 1.3%. Figure 1 shows that the decisive portion of the loss is due to the concentration of caesium by means of Prussian blue.

The selectivity of this method was verified, using a natural mixture of fission products eight months old[6]. The amount of cerium in the resulting preparation was decreased by means of the above procedure to less than 3% of the initial value, and the amount of zirconium was decreased to less than 0.4% of the initial value; this result is quite satisfactory when the activity of the final sample is evaluated by means of a gamma-spectrometer. Other isotopes did not show their presence on the gamma-spectrometer in any discernible amounts.

If it were necessary to measure the resulting activity without spectrometer, it would be suitable finally to remove sodium salts and possible residues of interfering radioisotopes, by one of the methods used in the isolation of radio-caesium (*e.g.*, precipitation in the form of the iodobismuthate[7]).

The authors wish to thank Mr. P. SELUCKÝ for his valuable technical assistance.

Addendum

While this work was in progress, several reports were published, which demonstrated the usefulness of nickel[8-10], magnesium[11], copper[9] and zinc[9] ferrocyanides for isolation of caesium-137 from low-activity natural solutions.

SUMMARY

A method is suggested for the isolation of caesium-137 from liquid radioactive fall-out, suitable for the treatment of up to 1 l of water in one batch. Caesium is coprecipitated with Prussian blue and dissolution of the precipitate in a saturated EDTA solution at pH 10, is followed by extraction of caesium as its dipicrylaminate, by nitrobenzene.

RÉSUMÉ

Une méthode est proposée pour isoler le césium-137 de retombées radioactives liquides, permettant de traiter jusqu'à 1 litre à la fois. Le césium est coprécipité avec le bleu de Prusse. Le précipité est ensuite dissous dans une solution saturée d'EDTA au pH 10. Puis on effectue l'extraction du césium sous forme de dipicrylaminate, dans le nitrobenzène.

ZUSAMMENFASSUNG

Zur Abtrennung von Cäsium-137 aus flüssigen, radioaktiven Niederschlägen wird eine Methode empfohlen, mit der sich bis zu 1 l Wasser in einem Arbeitsgang aufarbeiten lässt. Das Cäsium wird durch Berlinerblau mitgefällt, der Niederschlag abgetrennt und in gesättigter EDTA-Lösung mit dem pH-Wert 10 aufgelöst. Das Cäsium wird dann als Dipikrylaminat mit Nitrobenzol extrahiert.

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SOLVENT EXTRACTION OF CHROMIUM(VI) WITH TRIBENZYLAMINE

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(Received June 18th, 1963)

In the present paper, a solvent extraction method for chromium based on the formation of addition compounds of chromic acid with tribenzylamine is described. A simple and selective separation of chromium(VI) is possible, and spectrophotometric determinations may be performed on the extracted phase.

It is known from the literature that concentrated solutions of tribenzylamine in chloroform (5–8%) are able to extract such elements as Zn[1], Nb, Ta[2], Pu and Po[3] from acid solutions. Similarly, chromium(VI) forms an extractable species, and quantitative separation may be readily performed. Although some other elements, including Fe(III), Co, Cu, Ga and Cd, are extracted to important extents when high acid and/or tribenzylamine concentrations are applied, a selective and still complete separation of chromium is possible by operating under more dilute conditions. Chromic

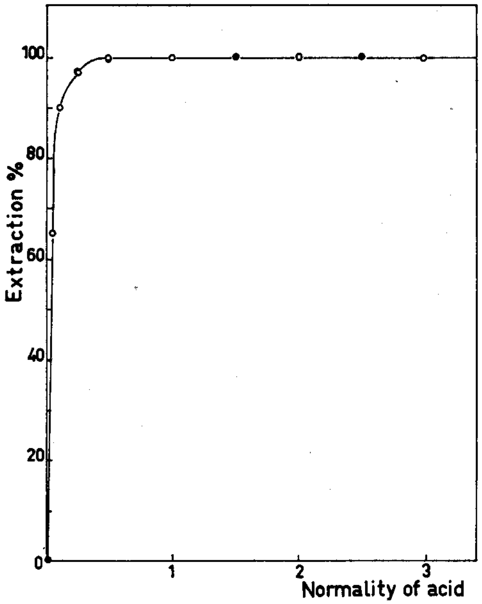

Fig. 1. Influence of acidity on chromium extraction (1% tribenzylamine in $CHCl_3$, double extraction, 1 : 1 volume ratio).

acid can be quantitatively extracted from hydrochloric or sulphuric acid solutions down to 0.1 *N*, with diluted solutions of tribenzylamine in chloroform.

Figure 1 shows the influence of acidity and Fig. 2 the influence of tribenzylamine concentration on chromium(VI) extraction. Partial extractions were observed from nitric, acetic and citric acid solutions, whereas from phosphoric acid solution the extraction was negligible. Quantitative back-extractions of chromium(VI) into dilute alkaline solutions are readily performed.

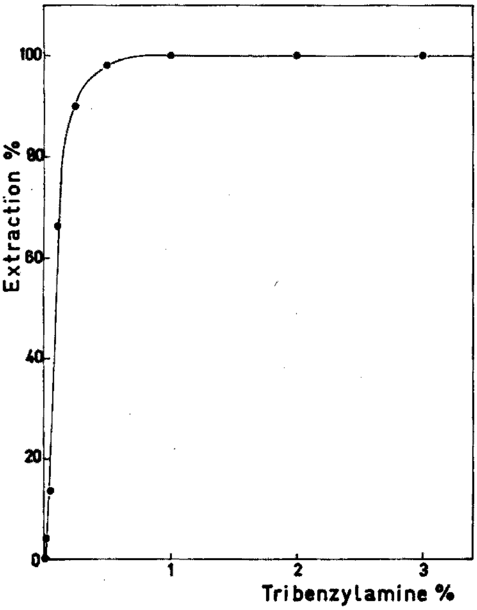

Fig. 2. Influence of tribenzylamine concentration on chromium extraction (from 1 *N* HCl, double extraction, 1 : 1 volume ratio).

The selectivity of the chromium(VI) extraction was tested, for 1 *N* hydrochloric acid–1% tribenzylamine conditions, by using radioactive tracers: quantitative extraction was found for chromium(VI) (100%), Au (100%), Sb (>90%), Hg (>95%), whereas negligible extraction occurred for Co, Ni, Ga, Cd, Zn, Mo(VI) (1–0.5%) and Cr(III), Fe(III), Cu, Mn, As(V), V(V), U(VI), Ce(IV), Sc, rare earths, and alkaline earths (< 0.5).

A direct spectrophotometric determination of chromium in the extracted phase is possible: the absorption curve shows the typical shape of the dichromate curve (λ_{max} at 355 and 458 mμ)[4].

The acidity of the aqueous solution (0.25–3 *N* HCl) and the tribenzylamine concentration (0.1–5%) do not affect the measurements, within 0.3%. Among the above-mentioned elements, the only serious interference is gold, for the other elements are either not extracted or colorless. The direct determination on the chloroform phase may be carried out for the chromium concentration range 2–30 p.p.m. at 355 mμ and 15–300 p.p.m. at 458 mμ. Since chromium(VI) is quantitatively stripped in an alkaline solution, chromate spectrophotometry[5] can also be performed.

EXTRACTION AND SPECTROPHOTOMETRIC PROCEDURE

Solutions (about 50 ml) containing 1–300 p.p.m. of chromium(VI) are acidified to give an approximately 1 *N* hydrochloric acid solution and are shaken in a separatory funnel with two successive 5-ml portions of a 1% chloroform solution of tribenzylamine (analytical-grade, recrystallized from ethanol and free from any solvent residues). The combined chloroform extracts are diluted to 25 ml, and the absorbance is measured at 355 or 458 mμ. Anhydrous sodium sulphate is used to dry the organic extracts.

APPLICATION TO CHROMIUM ACTIVATION ANALYSIS

The tribenzylamine method was applied to neutron activation analysis of chromium traces in different materials: refined aluminium, crude oil, crude asphalt and commercial polyphenyl.

Since most of the activities originating from in-pile irradiations are not extracted, it is possible to use this method for single-step chromium separations (Fig. 3).

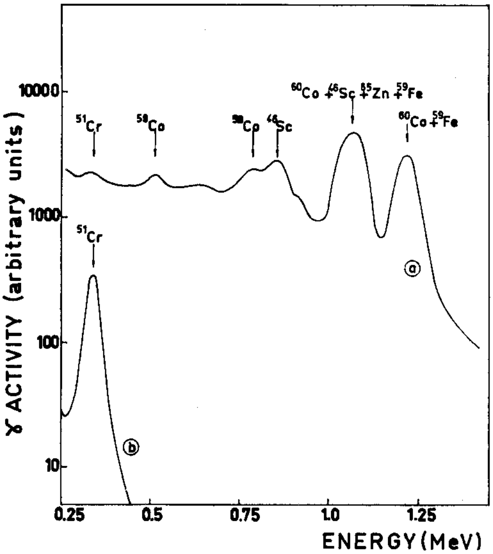

Fig. 3. Separation of ^{51}Cr activity (γ-spectrum taken with a 200-channel pulse analyser, NaI(Tl) 3″ × 3″ crystal). (a) γ-spectrum of the untreated sample; (b) γ-spectrum of the extracted phase.

TABLE I

ANALYTICAL RESULTS FOR CHROMIUM IN ALUMINIUM ALLOYS

Sample	*Cr concentration (%)*		
	Radioactivation and tribenzylamine extraction	*Spectrophotometry*	
		Tribenzylamine extraction	*Diphenylcarbazide method*
1	0.110 ± 0.004	0.107 ± 0.002	0.105 ± 0.001
2	0.076 ± 0.002	0.079 ± 0.005	0.079 ± 0.002
3	0.046 ± 0.002	—	0.045 ± 0.000

Tests on aluminium alloys (0.1–0.05% Cr and Co, 0.2–0.1% Fe and Zn, 0.5–0.3% Ni, 0.1% Sc) have shown that results which are precise to within 5% may be easily obtained (see Table I); the radiochemical purity of the extracted phase is good (see Fig. 3) and 70–98% chemical recoveries are generally found.

Procedure

Weighed samples (0.2–1 g) are irradiated in sealed quartz vials together with standard Al–Cr alloys in water pool reactor Avogadro RS1, for 50–200 h at thermal fluxes of $5 \cdot 10^{12}$–$4 \cdot 10^{13}$ neutrons/cm²/sec. After a 10-day cooling time, the samples are transferred and chemically treated: chromium(III) carrier is added (20 mg), and the aluminium samples are dissolved in sodum hydroxide, oxidized with potassium permanganate and acidified with hydrochloric acid, whereas the organic substances are fused with an oxidizing alkaline flux and then leached with hydrochloric acid.

The extraction is carried out with tribenzylamine as described above; γ-spectrometry measurements and spectrophotometric determination of chemical yields are made directly on the extracted phases or on aqueous solutions after an alkaline stripping.

Results

Analytical results are reported in Table II. The data are averaged over 2–3 independent determinations; the spread is within 12% for aluminium, and 20% for organic substances.

TABLE II

ANALYTICAL RESULTS FOR NEUTRON ACTIVATION DETERMINATIONS OF CHROMIUM TRACES IN VARIOUS MATERIALS

Materials	*Cr concentration (p.p.m.)*
Refined Al	0.072
Oil A	0.045
B	0.15
Asphalt A	3.6
B	1.3
C	3.1
D	0.54
Polyphenyl A	0.11
B	0.13

SUMMARY

The use of tribenzylamine as an extracting agent is recommended for a simple and selective separation of chromium(VI). Interferences from foreign elements were investigated by means of radioactive tracers and spectrophotometric techniques. The method is applied to neutron activation analysis of chromium traces in various materials.

RÉSUMÉ

Les auteurs recommandent la tribenzylamine comme réactif d'extraction pour une séparation simple et sélective du chrome(VI). L'influence d'ions étrangers a été examinée au moyen de traceurs radioactifs et de techniques spectrophotométriques. La méthode est appliquée à l'analyse, par activation au moyen de neutrons, de traces de chrome dans diverses substances.

ZUSAMMENFASSUNG

Zur einfachen und selektiven Abtrennung von Chrom(VI) wird die Extraktion mit Tribenzylamin in Chloroform aus 1 *N* Salzsäure vorgeschlagen. Der Einfluss zahlreicher anderer Elemente wurde untersucht. Mit dieser Methode wurden Spuren Chrom, die in verschiedenen Materialien mit Neutronen aktiviert worden waren, abgetrennt.

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TETRAPHENYLPHOSPHONIUM CHLORIDE AS A REAGENT FOR THE DETERMINATION OF VANADIUM(V) (DECAVANADATE)

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(Received June 18th, 1963)

In a study[1] of the analytical application of tetraphenylphosphonium chloride, it was found that besides other anions, vanadium(V) can also precipitate with this reagent. In earlier work[2] it was established that of the different vanadium(V) anions only decavanadate reacts with the tetraphenylphosphonium cation; the precipitate formed has the composition $[(C_6H_5)_4P]_3H_3V_{10}O_{28}$. It is very slightly soluble in water but completely soluble in ethylene chloride and in amines.

This paper describes a new method for the determination of vanadium(V) or decavanadate, based on this reaction.

EXPERIMENTAL

Reagents and apparatus

Tetraphenylphosphonium chloride (TPP). Prepared and purified as reported by WILLARD *et al.*[3]. Solutions in water (about 0.1 *M*) were used.

Ethylene chloride. The commercial solvent was purified by drying with calcium chloride and distillation.

Buffer solution pH 3.8. Prepared by mixing 50 ml of 1 *N* sodium acetate solution with 43 ml of 1 *N* hydrochloric acid solution and making up to 250 ml with water.

A Zeiss-Jena spectrophotometer with 1-cm quartz cells was used for the absorbance measurements.

General procedure

Sodium vanadate solution (0.5–5 ml of 10^{-2}–10^{-3} *M*) was adjusted to the desired pH with hydrochloric acid solution and shaken in a 30-ml separating funnel with 1 ml of TPP solution for 1 min. Then, ethylene chloride was added to give a water–organic phase ratio of 1 : 1 and the mixture was again shaken for 1–2 min. The layers were allowed to settle for about 5 min. The yellow-coloured organic layer was drained into a 25-ml volumetric flask. The same extraction was repeated once again. The absorbance was measured against a reagent blank.

Effect of pH

The solvent extraction behaviour of the vanadium(V)–TPP system was studied over the pH range 2 to 8. Fig. 1 shows the plot of percentage extraction of TPP–decavanadate by ethylene chloride as a function of pH. Extraction is at a maximum and is essentially complete in the pH range 2.8–4.2.

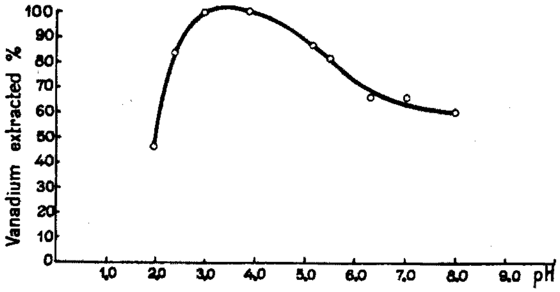

Fig. 1. Extraction of TPP–decavanadate with ethylene chloride as a function of pH.

Absorption curve

The absorption spectrum of a solution of TPP–decavanadate (vanadium = $6.15 \cdot 10^{-4}$ *M*) extracted as above at pH 3.8 and measured against the solvent is shown in Fig. 2. The curve shows maximum absorption at 275 mμ, after which the absorbance

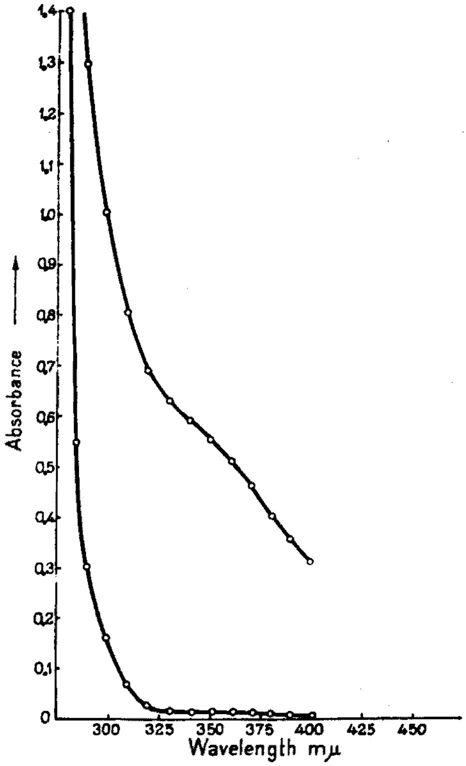

Fig. 2. (right) Absorption spectrum of TPP–decavanadate in ethylene chloride *vs.* ethylene chloride. V = $6.15 \cdot 10^{-4}$ *M*; TTP = 0.1 *M* ; pH = 3.8. (left) Reagent extracted in ethylene chloride *vs.* ethylene chloride. TTP = $1.57 \cdot 10^{-3}$ *M*; pH = 3.8.

gradually drops. The reagent blank also shows strong absorption at 275 mµ and becomes relatively negligible from 325 mµ onwards. All absorbance measurements were therefore carried out at 350 mµ and 400 mµ.

Calibration curve

The absorbances of different amounts of vanadium(V) extracted at pH 3.8 were measured against a reagent blank at 350 mµ and at 400 mµ. The results given in Table I show that at both 350 mµ and 400 mµ, Beer's law is followed over a concentration range of 4 to 60 µg of vanadium per ml. The equation of the calibration curve calculated[4] from this data according to the formula

TABLE I

DATA FOR BEER'S LAW

Vanadium taken		*Absorbance (E)*	
Total µg	*µg/ml*	*At 350 mµ*	*At 400 mµ*
98.05	3.92	0.071	0.043
196.1	7.84	0.139	0.079
392.2	15.69	0.271	0.160
784.4	31.38	0.571	0.330
980.5	39.22	0.713	0.407
1176.6	47.06	0.868	0.504
1568.8	62.75	1.138	0.667

$$y = A_0 + A_1 x$$

where y = amount of vanadium (µg/ml) and x = absorbance (E) measured under standard conditions,

$$A_0 = \frac{\sum_{i=1}^{n_1} x_i^2 \sum_{i=1}^{n_1} y_i - \sum_{i=1}^{n_1} x_i \sum_{i=1}^{n_1} x_i y_i}{n_1 \sum_{i=1}^{n_1} x_i^2 - \left(\sum_{i=1}^{n_1} x_i\right)^2}$$

and

$$A_1 = \frac{n_1 \sum_{i=1}^{n_1} x_i y_i - \sum_{i=1}^{n_1} x_i \sum_{i=1}^{n_1} y_i}{n_1 \sum_{i=1}^{n_1} x_i^2 - \left(\sum_{i=1}^{n_1} x_i\right)^2}$$

is at 350 mµ : $y = 0.31 + 54.55x$ (1), and at 400 mµ : $y = 0.39 + 93.66x$ (2).

Reagent concentration

The concentration of reagent (TPP) was varied from 0.02 to 0.3 M, other factors being kept constant. A satisfactory reagent concentration proved to be 0.1 M.

Recommended procedure

To an aqueous solution containing *ca.* 20 mg of vanadium, add hydrochloric acid and then buffer solution pH 3.8 (in a ratio of 10% by volume). Dilute to 100 ml in a volumetric flask. Transfer 0.5–5 ml of this solution to a 30-ml separatory funnel, add 1 ml of 0.1 *M* TPP solution and shake for 1 min. Then add ethylene chloride in a ratio of aqueous phase to organic phase of 1 : 1 and again shake for 1–2 min. Allow the two layers to settle for 5 min and then transfer the organic layer through a dry filter paper into a 25 ml volumetric flask. Repeat the extraction once again and dilute to 25 ml with ethylene chloride. Then measure the absorbance at 350 mμ or 400 mμ against a reagent blank. Calculate the vanadium concentration using an equation based on the calibration data.

The proposed method is simple and rapid and at the same time shows a satisfactory reproducibility and accuracy (Table II).

TABLE II

REPRODUCIBILITY OF METHOD AT 350 mμ AND 400 mμ

Vanadium present		*Measurement at 350 mμ*			*Measurement at 400 mμ*		
Total μg	*μg/ml*	*Absorbance (E)*	*V found (μg/ml)*	*Error (%)*	*Absorbance (E)*	*V found (μg/ml)*	*Error (%)*
392.2	15.69	0.278	15.47	−1.40	0.160	15.38	−1.97
		0.277	15.42	−1.72	0.154	14.81	−5.54
		0.271	15.09	−3.82			
784.4	31.38	0.578	31.84	+1.46	0.332	31.48	+0.32
		0.568	31.29	−0.28	0.330	31.30	−0.25
		0.573	31.57	+0.61	0.327	31.02	−1.15
		0.571	31.46	+0.25	0.337	31.95	+1.81

Effect of diverse foreign ions

The ions (12 to 8000 μg) shown in Table III were examined for interference. Upto 40–8000 μg of Ti, Co, Cu, Al and Zn could be tolerated, but iron(III) interferes.

SUMMARY

The extraction and spectrophotometric determination of vanadium(V) (decavanadate) by means of tetraphenylphosphonium chloride (TPP) is described. The yellow TPP–decavanadate solution in ethylene chloride obeys Beer's law at 350 mμ and at 400 mμ over the range 4–60 μg of vanadium (V) per ml. At pH 3.8 a single extraction with 0.1 *M* aqueous TPP solution and ethylene chloride is satisfactory. Zn, Al, Cu, Co and Ti do not interfere.

RÉSUMÉ

Une méthode est décrite pour l'extraction et le dosage spectrophotométrique du vanadium au moyen du chlorure de tétraphénylphosphonium. La coloration jaune de décavanadate de tétraphénylphosphonium dans le chlorure d'éthylène obéit à la loi de Beer entre 4 et 60 μg V/ml (à 350 et 400 mμ). Au pH 3.8, avec une solution de tétraphénylphosphonium 0.1 *M* et du chlorure d'éthylène, une seule extraction est suffisante. Zn, Al, Cu, Co et Ti ne gênent pas.

ZUSAMMENFASSUNG

Es wird die Extraktion und spektralphotometrisphe Bestimmung vom Vanadin(V) *bzw.* vom Dekavanadatanion mit Tetraphenylphosphoniumchlorid (TPP) beschrieben. Die gelbe TPP–De-

TABLE III

EFFECT OF DIVERSE IONS

Other elements present (μg)						*V present*		*Measurement at 350 mμ*			*Measurement at 400 mμ*		
Co	*Cu*	*Zn*	*Al*	*Fe*	*Ti*	*Total μg*	*μg/ml*	*Absorbance (E)*	*V found (μg/ml)*	*Error (%)*	*Absorbance (E)*	*V found (μg/ml)*	*Error (%)*
58.9	—	—	—	—	—	784.4	31.38	0.568	31.29	−0.28	0.327	31.02	−1.15
2300	—	—	—	—	—			0.568	31.29	−0.28	0.327	31.02	−1.15
—	126	—	—	—	—			0.578	31.84	+1.46	0.328	31.11	−0.86
—	750	—	—	—	—			0.583	32.11	+2.33	0.330	31.30	−0.25
—	—	8000	—	—	—			0.578	31.84	+1.46	0.332	31.48	+0.32
—	—	—	593	—	—			0.573	31.57	+0.61	0.332	31.48	+0.32
—	—	—	5400	—	—			0.548	30.20	−3.76	0.316	29.99	−4.42
—	—	—	—	20	—			0.548	30.20	−3.76	0.326	30.92	−1.46
—	—	—	—	50	—			0.558	30.75	−2.01	0.313	29.71	−5.32
—	—	—	—	—	12			0.588	32.38	+3.18	0.328	31.11	−0.86
—	—	—	—	—	12			0.583	32.11	+2.33	0.337	31.95	+1.81
—	—	—	—	—	32			0.578	31.84	+1.46	0.327	31.02	−1.15
100	100	—	1000	50	—			0.543	29.93	−4.62	0.307	29.14	−7.13
2300	750	8000	—	—	32			0.582	32.06	+2.13	0.336	31.86	+1.52
2300	750	8000	—	—	32			0.588	32.38	+3.18	0.326	30.92	−1.46
2300	750	8000	4300	—	32			0.583	32.11	+2.33	0.330	31.30	−0.25

kavanadatlösung in Äthylenchlorid folgt dem Beerschen Gesetz bei 350 mμ und 400 mμ bei Gehalten von 4 bis 60 μg V/ml.

Beim pH 3.8 ist die Extraktion mit 0.1 *M* wässriger Lösung von TPP und Äthylenchlorid befriedigend. Zn, Al, Cu, Co und Ti stören nicht.

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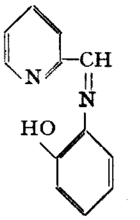
Short Communications

Detection of α-amino- and α-halogeno-fatty acids by spot tests

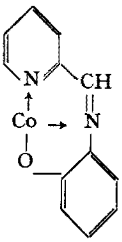
Elsewhere[1] a test for *o*-aminophenol (and its differentiation from the isomers) has been described, which is based on the fact that when an aqueous solution of pyridine-(2)-aldehyde containing cobaltous chloride is added to *o*-aminophenol, a red coloration is formed. In this color reaction a condensation of the amine with the aldehyde takes place. The Schiff base (I) thus produced forms a complex univalent cation (II) which contains the tervalent metal (through autoxidation). In this cation, as shown by III, the formation of 2 five-membered chelate rings causes coloration as well as resistance to diluted acids.



I ($C_{12}H_{10}NO$)

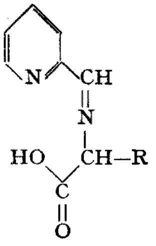
$[Co(C_{12}H_9NO)_2]^+$

II

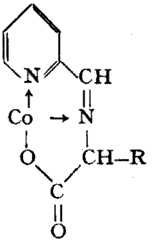


III

In accordance with the concept of group action[2] in analytical reactions of organic compounds, it could be expected that Schiff bases of α-amino-fatty acids with pyridine-(2)-aldehyde, to which the structure IV has to be ascribed, should behave towards cobalt(II) in a way analogous to Schiff base I. This is caused by the fact that on salification of the carboxyl group by cobalt, and its coordination to two nitrogen atoms, chelate rings are formed which, as shown by V, are completely analogous to chelate ring III.



IV



V

Experiments have shown that this expectation has been fulfilled. When a pyridine-(2)-aldehyde solution containing cobalt is mixed with α-amino acids (in quantities of about 100 μg) and pyridine is added, blue to blue-violet solutions are formed upon heating (the only exception being 2-amino-isobutyric acid, which gives a yellow color in all concentrations). The addition of pyridine is required because α-amino acids are inner-complex ammonium salts. The amino group necessary for the condensation with pyridine aldehyde is made available by addition of pyridine, whereby pyridine salts are formed.

The easy formation of a compound from chelate ring V renders the detection of α-amino acids possible (Procedure 1).

It is well-known that α-halogeno-fatty acids, when treated with ammonia, are converted to the respective α-amino-fatty acids. This transformation may be easily realized by dry heating α-halogeno-fatty acids or their salts with ammonium carbonate, which acts as ammonia donor:

$$\mathrm{RCH{\cdot}HalCOOH} + 3\ \mathrm{NH_3} \rightarrow \mathrm{RCH(NH_2)COONH_4} + \mathrm{NH_4Cl}$$

$$\mathrm{RCH{\cdot}HalCOONa} + 2\ \mathrm{NH_3} \rightarrow \mathrm{RCH(NH_2)COONa} + \mathrm{NH_4Cl}$$

By this treatment and subsequent application of the tests for amino acids a new test for halogeno-fatty acids is obtained (Procedure 2).

Procedure 1 (Detection of α-amino-fatty acids)

In a micro test tube, 1 drop of the test solution is mixed with 1 drop each of the reagent and of pyridine; the mixture is heated for 1–3 min in a water bath and then allowed to cool. If the quantity of amino acid is greater than about 50 µg, a blue or violet coloration appears. With smaller quantities, upwards from about 10 µg, especially near the limit of identification, the color is red, orange or yellow.

The following quantities could be detected:

3 µg cystine
3 µg cysteine
2.5 µg methionine
5 µg α-alanine
2 µg lysine

1 µg glycine
3 µg tyrosine
1 µg L-leucine
5 µg aspartic acid
5 µg asparagine

Positive responses were also obtained with mono-iodo-L-tyrosine, valine, citroline, arginine, ornithine, phenylalanine, tryptophane and 2-amino-*n*-octoic acid.

Reagent. 5 drops of a 0.5% aqueous solution of pyridine-2-aldehyde are mixed with 1 drop of 0.1 *M* cobalt nitrate (the reagent keeps about 1 week).

Through the above procedure, the isomeric α- and β-alanine can be differentiated, as only the former is an α-amino-fatty acid.

Procedure 2 (Detection of α-halogeno-fatty acids)

In a micro test tube a small quantity of the solid sample or one drop of its alcoholic solution is mixed with a few cg of ammonium carbonate and, if necessary, evaporated to dryness. Subsequently, the test tube is immersed as deeply as possible into a glycerol bath heated to 120°. The heating should be continued so long as no residue remains in a parallel test performed with an approximately equal quantity of ammonium carbonate. The further treatment is carried out as given in *Procedure 1*.

The following quantities could be detected:

10 µg monochloroacetic acid
10 µg monoiodoacetic acid
10 µg α-monochloropropionic acid
10 µg α-monobromo-isovaleric acid

15 µg α-monobromobutyric acid
20 µg α-monobromohexoic acid
25 µg α-momobromooctoic acid
30 µg α-monobromodecoic acid

We are grateful to the Conseilho National de Pesquisas (Rio de Janeiro) and the Department of Inorganic and Analytical Chemistry of the Hebrew University for material support.

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(Received July 15th, 1963)

Intensification of colour reactions between copper ions and polyamines by montmorillonite

The cationic complexes formed between copper(II) and amines are coloured characteristically. As shown in earlier papers [1,2], montmorillonite extracts copper amine complexes from aqueous solutions by ion exchange and itself becomes coloured by these complexes. It is thus possible to accumulate these complexes in the clay in visible form, even if present in solution in quantities below normal detectability.

A comparative study has been made of the minimum quantities of copper amine complexes visible in aqueous solutions as against those which can be detected by sorption by Wyoming bentonite (montmorillonite). At the same time, the interference of complexes of other metal ions or hydroxides formed simultaneously was investigated. In this series a number of polyamines were used as ligands, *viz.* ethylenediamine (*en*), 1,2-propylenediamine (1,2-*pn*), 1,3-propylenediamine (1,3-*pn*), pentamethylenediamine (*pen*), diethylenetriamine (*dien*), triethylenetetramine (*trien*) and tetraethylenepentamine (*tepa*).

The quantity of clay employed had to be as small as possible in order to achieve maximum colouring, and large enough to be conveniently visible. For two drops of solution, 1–1.5 mg of clay is sufficient; with 20 ml of solution, 5–8 mg of clay were used.

(1) *Minimum of copper required for colouring montmorillonite in the presence of a surplus of amine*

One drop of a 0.1 *M* amine solution and one drop of a very dilute copper nitrate solution were mixed, 1–1.5 mg of clay was added, and the mixture shaken. This

TABLE I

MINIMUM QUANTITIES OF COPPER AND AMINE REQUIRED FOR COLOURING MONTMORILLONITE

Amine	*Complex*	*Colour of complex*	*In the presence of montmorillonite*								*Soln.only*
			Surplus of amine				*Surplus of Cu*				*Surplus of amine*
			2 drops	*in 20 ml*			*2 drops*	*in 20 ml*			*Limiting concn. of complex* $\cdot 10^{-5}$ *M*
			μg Cu^{2+}	μg Cu^{2+}	*Diln. limit* $\cdot 10^{-5}$	*Complex concn.* $\cdot 10^{-5} M$	μg *amine*	μg *amine*	*Diln. limit* $\cdot 10^{-5}$	*Complex concn.* $\cdot 10^{-5} M$	
en	$[\mathrm{Cu\ en_2}]^{2+}$	Mauve	3	37.5	1:5.6	3	12.5	96	1:2.5	4	200
1,2-pn	$[\mathrm{Cu\ pn_2}]^{2+}$	Mauve	3	37.5	1:5.6	3	15.0	177	1:1.2	6	200
1,3-pn	$[\mathrm{Cu\ pn_2}]^{2+}$	Mauve	1	25	1:8.4	2	15.0	177	1:1.2	6	190
pen	$[\mathrm{Cu\ pen_2}]^{2+}$	Light blue	10	12.5	1:1.7	10	—	320	1:0.6	8	220
dien	$[\mathrm{Cu\ dien}]^{2+}$	Blue	1	37.5	1:5.6	3	5	120	1:1.7	6	140
trien	$[\mathrm{Cu\ trien}]^{2+}$	Mauve	3	37.5	1:5.6	3	3	106	1:2.0	4	160
tepa	$[\mathrm{Cu\ tepa}]^{2+}$	Blue	1	37.5	1:5.6	3	5	152	1:1.4	4	170

procedure was repeated with copper solutions of decreasing concentration until the clay could not be coloured any more. Centrifugation was occasionally necessary in order to precipitate the clay.

Experiments were also carried out in 20 ml of 0.0025 *M* solutions of amine using 5–8 mg of clay. Under these conditions, the solutions themselves remained uncoloured. Feigl's dilution limit was determined for the sorbate.

(2) *Minimum of amine required for colouring montmorillonite in the presence of a surplus of copper*

Experiments similar to those described above were carried out using a fixed concentration of copper, varying the amounts of amine. In the two-drop volume, the *pen* solution gave no results, and for *en*, 1,2-*pn* and 1,3-*pn*, a 0.0005 *M* copper solution, and for *dien*, *trien* and *tepa* a 0.001 *M* solution was employed. Again, the experiments were extended to 20-ml volumes using a 0.001 *M* solution of copper nitrate and 5–8 mg of clay.

In all cases, in (*1*) and (*2*), parallel experiments were carried out to establish the minimum quantity of complex required to colour a clay-free solution, for purposes of comparison.

All results are shown in Table I.

Interference of other ions

As there are many other ions which form either coloured complexes or hydroxides, their interference in the above test had to be investigated. 0.5 *M* solutions of such ions were added in drops to the reaction mixtures. The results obtained are shown in Table II.

TABLE II

IONS INTERFERING WITH THE DETECTION OF COPPER(II)

Amine	*Solution with montmorillonite present*	*Solution without montmorillonite*
en	Hg^+, Fe^{3+}, Cr^{3+} (in strong concns.), Co^{2+}, Mn^{2+}	Hg^+, Pb^{2+}, Bi^{3+}, As^{5+}, As^{3+}, Sb^{3+} Sb^{5+}, Sn^{2+}, Al^{3+}, Cr^{3+}, Ni^{2+}, Co^{2+} Mn^{2+}, Fe^{3+}
1,2-*pn*	As above	As above
1,3-*pn*	Hg^+, Co^{2+}, Mn^{2+} (in strong concns.)	As above
pen	Hg^+, Cr^{3+}, Co^{2+}	Hg^+, Pb^{2+}, Bi^{3+}, Cd^{2+}, Sb^{3+}, Sb^{5+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}
dien	Hg^+, Fe^{3+} (in strong concns.), Cr^{3+}, Co^{2+}, Mn^{2+}	Hg^+, Bi^{3+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Ni^{2+}, Co^{2+} Mn^{2+}
trien	As above, Cr^{3+} only in strong concentrations	As above
tepa	Hg^+, Co^{2+}	As above, except Mn^{2+}

Conclusions

By absorbing copper in the form of amine complexes on to montmorillonite, they can be detected even in greatly diluted solutions in the presence of many other ions. Mercury(I) interferes by blackening the clay through forming finely divided metal, and cobalt(II) gives itself strongly coloured amine complexes which are absorbed by the clay. Nickel(II) forms coloured complexes but does not colour the clay noticeably. Cations like Al^{3+} and Pb^{2+}, which form white precipitates, do not interfere, whilst Fe^{3+} does. However, as 1,3-*pn*, *pen*, *trien* and *tepa* adsorbates with clay coagulate easily and precipitate faster than iron hydroxide, the coloured copper amine clay sorbate can easily be distinguished by means of these amines. The use of a centrifuge speeds up the formation of a distinct compact clay layer. Chromium(III) forms a green precipitate which interferes in small quantities with *pen* only; otherwise it behaves like iron(III), and settles more slowly than the clay sorbate. With *tepa*, there is no interference either by manganese(II), which at the pH of other amine solutions oxidizes to Mn^{3+} and Mn^{4+}, or by Cr^{3+}, even in large quantities.

These experiments show the possibility of accumulating coloured metal complexes in clay, enabling their detection even in quantities where their colour could not be distinguished otherwise in aqueous solution.

The authors wish to thank Prof. F. FEIGL for useful discussions on this paper.

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Received July 25th, 1963

Simple vapor sorption method for determination of water in liquids

Although numerous methods have been developed for the determination of water and other vapors or gases by sorption on solids, it is frequently supposed that the apparatus required for sorption measurements is too complex for ordinary laboratory use. A simple method is described here for the determination of water by sorption on a desiccant, using a modified McBain[1] sorption balance.

The apparatus is sketched in Fig. 1. A helical silica spring (100 mg total capacity; sensitivity, approximately 0.65 mm/mg — obtained from Worden Laboratory, Houston, Texas) is suspended from the glass hook, *A*, attached to the inside of the standard taper cap, *B*. Approximately 30 mg of desiccant are contained in the aluminum foil bucket, *C*.

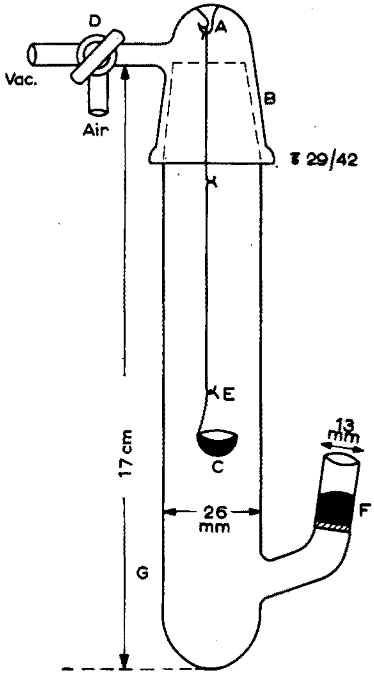

Fig. 1. Sorption balance.

To operate the apparatus, the system is first evacuated through the three-way vacuum stopcock, *D*. By means of a cathetometer, the blackened tip of the hook, *E*, is observed until it remains stationary, and its height is recorded. With the stopcock closed, a liquid sample is introduced through the valve, *F*, using a graduated pipet. The valve consists of a medium-porosity sintered glass disc covered with mercury to a depth of about 1 cm. When the tip of the pipet is brought into contact with the disc, liquid is drawn through. (The use of a valve of this sort to introduce measured volumes of a liquid into an evacuated system is described by CHRISTIAN, AFFSPRUNG AND LIN[2].) When the weight of the sample in the bucket has become constant, its final height is recorded, and the weight of the sorbed water is calculated from the difference between the final and initial heights. In practice it is found that the height varies linearly with sample weight over a considerable range of weights.

If the liquid contains volatile components other than water, it is necessary to ensure that these are not sorbed onto the desiccant. In the case of the analysis of benzene solutions, it has been noted that at the end of a run some benzene may remain sorbed or condensed on the desiccant (magnesium perchlorate). However, by simply placing an ice bath around the lower end of the tube, *G*, the benzene is removed in a few minutes, while the water remains sorbed.

Table I gives the results of 3 sorption balance determinations of water in a stock solution of water in benzene. For comparison, the same solution was titrated with Karl Fischer reagent, using the Beckman KF-3 Aquameter. The cathetometer used in the sorption balance determinations appeared to limit the precision of the method. Objects of known weight could be weighed to within about 0.08 mg, which is an error consistent with the discrepancies between concentration values obtained by the two methods.

TABLE I

COMPARISON OF SORPTION BALANCE AND BECKMAN KF-3 AQUAMETER DATA

Method	*Sample volume (ml)*	*Water found (mg)*	*Concentration found (M)*
Sorption balance	9.20	3.63	0.0219
Sorption balance	9.22	3.50	0.0211
Sorption balance	9.22	3.53	0.0213
Aquameter	25.00	9.44	0.0210
Aquameter	25.00	9.46	0.0210

The rapidity with which water is removed from liquid solutions by sorption from the vapor phase is surprising. Benzene solutions of water ranging in molarity from 0.01 to 0.04 have been analyzed with an apparatus having the dimensions shown in Fig. 1. The half-life for removal of water from these solutions is of the order of 30 min, indicating that water is quantitatively removed in approximately 5 h. A discussion has been given previously of the factors which determine the rate of drying of liquid samples by means of a non-contiguous desiccant[3].

The primary advantages of the present method for determining water are its simplicity and the low cost of the apparatus. The only relatively expensive item is the cathetometer, which may be set up for use with several sorption balances simultaneously. Alternately, a simple reading telescope with calibrated reticle may be used in place of the more expensive cathetometer.

This work was supported by a research grant from the United States Department of the Interior, Office of Saline Water. The authors wish to thank Mr. JAMES R. JOHNSON of this laboratory for performing the Karl Fischer titrations.

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(Received July 8th, 1963)

Book Reviews

G. CHARLOT ET B. TRÉMILLON, *Les Réactions Chimiques dans les Solvants et les Sels Fondus (Monographies de Chimie Minérale)*, Gauthier-Villars Editeur, Paris, 1963. 602 pages. Cartonné 94 F ($ 20).

Cet ouvrage important est un complément des livres du Professeur Charlot. On y retrouve sa "patte", sa technique, sa facon très personnelle d'amener le sujet par une chaine de raisonnements, par une suite de déductions logiques. Ce vaste chapitre qui intéresse aussi bien la chimie minérale que la chimie organique est traité dans toute son ampleur. La bibliographie y est très importante puisqu'elle comporte plus de 5000 références; elle s'arrête en 1961 et permet au lecteur de retrouver à peu près sans peine tout ce qui est écrit dans ce domaine.

Il est certain que ce livre prendra une très grande importance: les réactions en milieu non aqueux sont appelées à un développement considérable.

Dans une courte introduction les auteurs présentent leur ouvrage qui comprend l'étude des réactions des acides et des bases, des systèmes oxydo-réducteurs et des complexes dans les solvants inertes, actifs et ionisants.

Le premier chapitre traite des réactions acide–base en milieu peu dissocié. Des échelles d'acidité et de basicité et des couples acide–base permettent de se rendre compte immédiatement des réactions possibles. Il est montré comment on peut étudier ces dernières par voie expérimentale: spectrophotométrie, conductimétrie, potentiométrie.

Le chapitre II, identique au premier, étudie les solvants dissociants et donne une échelle générale d'acidité, la relation entre les constantes d'équilibre dans divers solvants à l'aide des coefficients de partage et le problème des mélanges de solvants. Une table donne les pK_{H_2O} de plus de 400 couples acide–base.

Le chapitre III a pour objet les complexes avec les mêmes rubriques que les précédents et le chapitre IV traite des réactions d'oxydo-réduction.

Enfin le dernier chapitre de cette première partie s'intitule "Solubilité et produit de solubilité".

La deuxième partie est entièrement consacrée aux propriétés chimiques dans les divers solvants: hydrocarbures et dérivés halogénés, acides, bases, alcools et phénols, amides, dérivés nitrés, nitriles et cétones, anhydrides, éthers et esters, solvants variés, halogénures et enfin le dernier chapitre s'intitule "Solvants fondus ionisés" (chlorures, bromures et iodures alcalins, chlorures alcalino-terreux, chlorure de magnésium, chlorure et bromure d'argent, chlorures de thallium, de cadmium, de plomb, de zinc, de bismuth, de cérium, etc...

Enfin un index alphabétique des composés organiques, de même qu'une table des différents solvants décrits terminent ce remarquable ouvrage que nous nous faisons un plaisir de recommander aux lecteurs de ce journal. D. MONNIER (Genève)

R. BERTHON, *Représentation des Equilibres de Solubilités et Utilisation des Diagrammes, Monographies de Chimie Minérale)*, Gauthier-Villars Editeur, Paris, 1963. 272 pages. Cartonné 38 F ($ 8).

Il vient de paraître, dans la collection des monographies de Chimie Minérale éditées par les soins de la maison d'édition Gauthier-Villars, un ouvrage écrit d'une manière claire par M. ROBERT BERTHON et intitulé *Représentation des équilibres de solubilités et utilisation des diagrammes*. Cet ouvrage est destiné aux étudiants avancés dans leur étude de chimie minérale, mais la lecture attentive de ce livre sera surtout d'une grande utilité pour les chercheurs en chimie minérale qui se penchent tout particulièrement sur les problèmes de séparation des substances minérales pures à partir des solutions des minéraux de composition très complexe par la voie de cristallisation isotherme.

L'ouvrage est partagé en deux parties.

(1) La première traite d'une manière logique des différents modes de représentation dans un espace à deux et trois dimensions d'un système en équilibre dont chaque état particulier est convenablement défini par la connaissance des valeurs numériques des variables de position et d'action. Une part importante de cette première partie de l'ouvrage est consacrée aux systèmes isothermes. De nombreux exemples, bien connus des chimistes, sont utilisés afin d'illustrer plusieurs chapitres de cette première partie.

(2) Quant à la deuxième partie de l'ouvrage, elle est exclusivement consacrée à la recherche des règles clairement énoncées par l'auteur relatives à la cristallisation par évaporation isotherme et suivies des diagrammes de solubilités se rapportant à de nombreux exemples de chimie minérale.

On ne saurait trop recommander la lecture de ce livre dont le but est de familiariser le lecteur d'une maniére très sûre à l'emploi des méthodes des diagrammes utilisées dans les procédés de séparation chimique dans la recherche et surtout dans l'industrie.

D. MONNIER (Genève)

M. P. SOUCHAY, *Polyanions et polycations (Monographies de Chimie Minérale)*, Gauthier-Villars Editeur, Paris, 1963. 248 pages. Cartonné 42 F ($ 9).

L'existence des ions condensés est connue depuis déjà fort longtemps, mais ce n'est guère que depuis Gibbs que cet important chapitre de la chimie minérale a pris son essor, et depuis 1930 seulement on en a effectué l'étude théorique.

Dans un premier chapitre l'auteur situe le sujet et donne les définitions: polyanion, polycation, détermination de l'état des systèmes en solution, réactions d'élimination et de solvolisation (hydrolyse, alcoolyse, ammonolyse). L'exposé est clair et bien ordonné.

Le second chapitre traite des isopolyanions. Il donne quelques exemples, les conditions d'équilibre et les acides correspondants. Remarquons en passant que certaines lettres ne sont pas définies et que l'indication des charges des ions en chiffre romains ne nous semble pas très indiquée.

Les méthodes d'étude des polyanions en solution telles que l'absorption lumineuse — la polarographie, la cryoscopie, et celles basées sur la diffusion la dialyse, l'ultracentrifugation et la potentiométrie — font l'objet du chapitre IV.

Le chapitre V (méthodes d'étude à l'état solide et structure des polyanions) comprend les méthodes générales d'étude à l'état solide, les types ne comportant pas d'octaèdres, ceux en comportant, et des considérations sur la structure cristalline.

Le chapitre VI (composés apparentés aux polyanions) comprend les peroxyanions et substances analogues, les dérivés provenant de la substitution des atomes d'oxygène, les dérivés provenant de la substitution de l'élément caractéristique par un autre élément chez les polyanions, et les dérivés de réduction.

Le chapitre VII traite des polyanions phosphoriques, le chapitre VIII de l'étude des polycations en solution, et le chapitre IX de l'étude des sels basiques à l'état solide.

Une bibliographie assez restreinte (299 références) mais judicieusement choisie, termine cet ouvrage dont la lecture est fort instructive pour le chimiste analyste car les méthodes d'investigation et de recherches de structure sont décrites de façon très claire et très suggestive.

D. JANJIC (Genève)

I. P. ALIMARIN AND M. N. PETRIKOVA, *Anorganische Ultramikroanalyse*, translated into German by Dipl.-Chem. K. URBAN, Veb. Deutscher Verlag der Wissenschaften, Berlin, 1962. 169 S. Kld. DM 27.—.

With this book the authors have brought together in a single volume, published information on ultramicroanalysis and their own recent work on this subject. Originally the techniques of chemical analysis under the microscope, by using micromanipulators, with sample sizes of 10^{-6}–10^{-12} g and volumes of 10^{-3}–10^{-6} ml were only applied in biochemistry in the examination of single living cells, but Benedetti-Pichler carried them into the field of inorganic qualitative and quantitative analysis. With the apparatus and techniques described in great detail in their book, *Microtechnique of Inorganic Analysis*, H. M. EL-BADRY AND C. L. WILSON were able to make considerable progress in the development of this new trend. Considering the figures copied from their publications, the authors have paid full attention to the work of these pioneers. The aim of their own investigations was the further development of ultramicroanalysis by introducing the methods of instrumental analysis. Their work resulted in techniques of chromatographic separation in small volumes, of electrochemical methods of separation and determination, and of physicochemical determination of the end-points in titrations. All techniques, based on conventional as well as on instrumental methods, are described with great care and in great detail so that the book is a real guide for the analyst whose work has to be performed on ultramicroscale as, for instance, in investigating high radioactive materials.

J. W. L. VAN LIGTEN (Delft)

Microchemical Techniques, Proceedings of the 1961 International Symposium, Pennsylvania State University, Edited by NICOLAS D. CHERONIS, Microchemical Journal Symposium Series Vol. II, Interscience Publishers, New York, 1962. xviii + 1181 pp., price 300/–.

This volume contains the complete proceedings of the 1961 Pennsylvania State University Symposium on Microchemical Techniques, organised by the Metropolitan Microchemical Society of New York, and sponsored by IUPAC. The text is divided into eleven parts. The introductory Part I contains welcoming addresses and accounts of microchemistry in Austria and in the United States. This is followed by the texts of the four plenary lectures delivered by VAN SLYKE, SAWICKI, BELCHER and CHERONIS. Part III deals with microscopical techniques, the texts and discussions of ten lectures being given. Part IV and V cover the techniques of inorganic (7 lectures) and organic (17 lectures) elemental analysis. Part VI contains 8 lectures on the techniques of general organic and functional group analysis; Part VII 8 lectures on chromatographic techniques. Part VIII covers titrimetric, polarographic, electrochemical and radiochemical techniques (19 lectures); Part IX microchemical implements and techniques for the determination of molecular weight and physical properties (13 lectures). Part X deals with micro and semimicro methods in teaching (6 lectures), and the concluding Part XI reports 5 round-table discussions held during the Symposium. Author and subject indexes are included.

In a volume of this size and content, it is impossible to comment on individual contributions. The complete volume has some merit, although it is difficult to equate the cost with the value of the content. In recent years it has become obvious that authors of papers at Symposia of this kind tend to review work already published, and even to present material which few self-respecting journals would accept for publication. This is caused partly by the iniquitous system in which attendance grants are given only to intending lecturers, and partly by the reluctance of research workers to present good original work owing to the generally excessive time required to process and publish volumes of symposia proceedings. Both these factors have contributed to making the present volume less important to the majority of possible readers.

The publishers of such proceedings should seriously consider their overall value as a contribution to the literature of microchemistry — which is already sadly overburdened with irrelevancies and frivolities.

In conclusion it should be recorded that this last editorial task of the late Dr. Cheronis has been accomplished with his accustomed high efficiency and competence. It is unfortunate that much of the contents of the volume do not approach the same standard.

WILLIAM I. STEPHEN (Birmingham)

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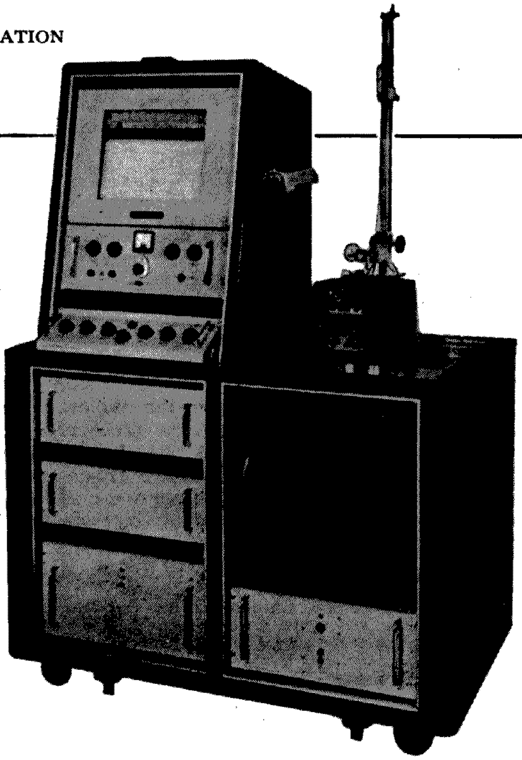

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