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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 27, No. 4, October 1962

A NEW APPARATUS FOR SIMULTANEOUS DIFFERENTIAL THERMAL ANALYSIS AND GAS EVOLUTION ANALYSIS

A new apparatus is described which permits the simultaneous recording of the differential thermal analysis and gas evolution curves for a given sample from ambient to 900°. The sample is pyrolyzed in a dynamic helium gas atmosphere using a conventional DTA furnace and sample holder assembly. The evolved decomposition products are detected in the helium gas stream by means of a thermistor thermal conductivity cell. From a knowledge of the GE curve and an analysis of the decomposition products, a more accurate interpretation of the DTA curve can be made.

Wesley W. Wendlandt, *Anal. Chim. Acta*, 27 (1962) 309–314

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN STEEL BY NEUTRON ACTIVATION ANALYSIS

Sulphur and phosphorus in steel were determined by neutron activation analysis, being counted as ^{35}S and ^{32}P respectively. For steels with sulphur to phosphorus ratios larger than 10, it seems possible to determine both elements by counting ^{32}P, making use of a double irradiation technique at different fast to slow neutron fluxes.

P. Bouten and J. Hoste, *Anal. Chim. Acta*, 27 (1962) 315–319

DETERMINATION OF THE VALENCE DISTRIBUTION OF VANADIUM IN POLYOLEFIN CATALYSTS PREPARED FROM VANADIUM TRICHLORIDE

An electrochemical method has been developed for determining the relative amounts of V(II) and V(III) in polyolefin catalysts prepared using aluminum alkyls and vanadium trichloride. The catalyst, usually obtained as a slurry in *n*-heptane, is titrated potentiometrically with ceric sulfate using a platinum indicator electrode. Under proper experimental conditions, 2 breaks are obtained, corresponding to the reactions V(II) → V(III) + *e* and V(III) → V(IV) + *e*. Interferences from other components of the catalyst are negligible. The method is useful for the analysis of both laboratory catalysts and grab samples taken from pilot plant reactors.

J. E. Barney II, *Anal. Chim. Acta*, 27 (1962) 320–324

MERCURY DETERMINATION AT THE MICROGRAM LEVEL BY A REDUCTION-AERATION METHOD OF CONCENTRATION

At room temperature, reduction with tin(II) and aeration are suitable for quantitative separation of microgram quantities of mercury(II) from sulfuric and nitric acid solutions over wide ranges of concentrations. Mercury is concentrated during the separation, and is determined by a direct photometric dithizone procedure. This technique is applicable for 0.10 μg mercury per sample charge with a standard deviation for a single determination of 0.05 μg mercury in the 0 to 0.5 μg range.

Y. Kimura and V. L. Miller, *Anal. Chim. Acta*, 27 (1962) 325–331

RAPID COLORIMETRIC DETERMINATION OF MANGANESE IN WATERS CONTAINING IRON

A MODIFICATION OF THE FORMALDOXIME METHOD

A rapid photometric method with formaldoxime is described for the determination of small amounts of manganese in waters containing iron. The iron formaldoxime formed is decomposed by addition of EDTA and hydroxylamine after development of the manganese–formaldoxime color. Beer's law holds up to 3 mg Mn/l. Up to 25 mg iron(II) and (III) per l can be tolerated.

K. Goto, T. Komatsu and T. Furukawa, *Anal. Chim. Acta*, 27 (1962) 331–334

BIS-CYCLOHEXANONE-OXALYLDIHYDRAZONE AS A SPECTROPHOTOMETRIC REAGENT FOR COBALT AND NICKEL

Cobalt and nickel ions form yellow complexes with bis-cyclohexanone-oxalyldihydrazone in alkaline solutions. These complexes have maximum absorbances at 292 mμ and 330 mμ, respectively. The cobalt complex obeys Beer's law from 10^{-4} to $5 \cdot 10^{-3}$ mg cobalt per ml and the molar extinction coefficient is 6500. The nickel complex obeys Beer's law from 10^{-4} to $7 \cdot 10^{-3}$ mg nickel per ml and the molar extinction coefficient is 8750. Cobalt and copper or nickel and copper can be determined in presence of each other.

S. H. Omang and A. R. Selmer-Olsen, *Anal. Chim. Acta*, 27 (1962) 335–338

SELECTIVE SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH EDTA

A spectrophotometric determination of iron as its iron(III)-EDTA-H_2O_2-NH_3 complex is described; up to 10-fold amounts of metals that form EDTA complexes absorbing at the same wavelength do not interfere because hydrogen peroxide reacts with the iron(III)-EDTA complex but does not affect the EDTA complexes of copper(II), nickel(II), cobalt(III) and chromium(III).

B. C. Poeder, G. den Boef and C. E. M. Franswa, *Anal. Chim. Acta*, 27 (1962) 339–344

POLARIMETRIC DETERMINATION OF MALIC ACID, TARTARIC ACID, MANNITOL AND SORBITOL IN THE PRESENCE OF OTHER OPTICALLY ACTIVE COMPOUNDS

Optically active malic and tartaric acids, mannitol and sorbitol can be determined in the presence of other optically active compounds by measuring the difference in optical rotation of their solutions with and without molybdate. The optimal pH-values for the determinations have been established and procedures and standard curves are given.

W. J. Kirsten and S. K. Nilsson, *Anal. Chim. Acta*, 27 (1962) 345–350

AMPEROMETRIC TITRATION OF COPPER IN BRASS

A direct amperometric titration of copper is described; *o*-(*p*-tolylsulfonamido)aniline serves as titrant. The optimum conditions are discussed and the method is applied to the analysis of copper in brass alloys.

T. R. Williams and F. G. Burton, *Anal. Chim. Acta*, 27 (1962) 351–355

SEPARATION OF NIOBIUM AND TANTALUM WITH BENZO- AND PHENYLACETYLHYDROXAMIC ACIDS

Benzohydroxamic acid (I) or phenylacetylhydroxamic acid (II) is suggested for the quantitative separation of tantalum from niobium in an oxalate solution. The tantalum precipitate must be ignited for weighing; niobium is determined in the filtrate with another reagent. The pH range for complete separation is 4.0–6.4 for I and 4.5–6.2 for II. Single precipitation is satisfactory for Nb:Ta ratios of 18:1 to 1:20 for I, and 8:1 to 1:23 for II. Titanium, zirconium, tartrate, citrate and a large excess of oxalate interfere.

A. K. Majumdar and B. K. Pal, *Anal. Chim. Acta*, 27 (1962) 356–358

SEPARATION AND GRAVIMETRIC DETERMINATION OF THORIUM AND CERIUM(IV) WITH VANILLIN

Vanillin forms insoluble complexes with thorium and cerium(IV) at pH 4.0–6.2 and 2.5–7.0 respectively. Thorium and cerium can be determined gravimetrically and separated from each other as well as from uranium(VI) and typical trivalent rare earths. The precipitates obtained are ignited to the corresponding oxide and weighed; as little as 4.4 mg of ThO_2 and 4.9 mg of CeO_2 can be determined.

B. D. Jain and J. J. Singh, *Anal. Chim. Acta*, 27 (1962) 359–362

ANALYTICAL APPLICATIONS OF THE DETERMINATION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID

PART IV. DETERMINATION OF HYDROXYLAMINE

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L. Erdey, L. Koltai and G. Svehla, *Anal. Chim. Acta*, 27 (1962) 363–365

THE RAPID DETERMINATION OF TUNGSTEN AFTER REDUCTION WITH BISMUTH AMALGAM

A titrimetric determination of tungsten is described; it is based on reduction of tungsten to tungsten(V) by bismuth amalgam in concentrated hydrochloric acid solution and titration with ceric sulphate solution. The end-point can be detected potentiometrically or visually. The method may be extended to the determination of tungsten in a steel.

A. S. Witwit and R. J. Magee, *Anal. Chim. Acta*, 27 (1962) 366–370

IDENTIFICATION OF CERIUM IN THE PRESENCE OF OTHER RARE EARTHS

In the presence of other rare earths, cerium is best identified with redox indicators. *p*-Sulfanilic is a fairly specific indicator for cerium(IV), giving a red coloration with more than 6 p.p.m. *o*-Tolidine and diphenylamine sulfonate can identify smaller amounts of cerium(IV), but many oxidants interfere.

P. L. Sarma, *Anal. Chim. Acta*, 27 (1962) 370–372

MICROANALYSIS WITH THE AID OF ION EXCHANGERS

PART XXI. MODIFICATIONS OF THE RESIN SPOT TEST WITH HIGH MOLECULAR WEIGHT AMINES

The resin spot test is modified by the use of a high molecular weight amine, Amberlite LA-1, in carbon tetrachloride; 0.2 μg of cobalt(II) can be detected rapidly by shaking an acidic solution containing thiocyanate with a 5% amine solution. Amine-impregnated papers can also be used.

M. Fujimoto and Y. Nakatsukasa, *Anal. Chim. Acta*, 27 (1962) 373–376

DETERMINATION OF MONO-ALCOHOLS BY GAS CHROMATOGRAPHY

A gas chromatographic method is described for the determination of alcohols up to $C_{20}H_{41}OH$. The procedure is rapid and indicates the molecular weight distribution and the contents of straight-chain and branched-chain alcohols. A programmed temperature control with a silicone substrate was satisfactory. n-$C_{14}H_{29}OH$ and n-$C_{5}H_{11}OH$ were used as internal standards.

J.W. Robinson, *Anal. Chim. Acta*, 27 (1962) 377–380

THE MICROCHEMICAL INVESTIGATION OF SLIGHTLY RADIOACTIVE SOLUTIONS AND EFFLUENTS

(in German)

The ring-oven method and ring chronoautoradiography are shown to be suitable for the investigation of very dilute radioactive solutions. The limits of detection are of the order of nanocuries or less. A method for the concentration of large volumes of liquid on the ring oven is described.

H. Malissa and F. Loley, *Anal. Chim. Acta*, 27 (1962) 381–386

THE SEPARATION OF FLUORINE BY MICRO-DIFFUSION OF HYDROFLUORIC ACID

(Short Communication)

L. Greenland, *Anal. Chim. Acta*, 27 (1962) 386–389

THE RATE OF SOLVENT EXTRACTION OF SOME ZINC β-DIKETONE CHELATES

(Short Communication)

G. K. Schweitzer and J. R. Rimstidt, Jr., *Anal. Chim. Acta*, 27 (1962) 389–391

THE COMPLEX OF GALLIUM(III) WITH DIPHENYLTHIOCARBAZONE

(Short Communication)

T. B. Pierce and P. F. Peck, *Anal. Chim. Acta*, 27 (1962) 392–395

SOLVENT EXTRACTION OF LIGHT RARE EARTHS FROM SODIUM RARE EARTH SULPHATES

(Short Communication)

R. A. Edge, *Anal. Chim. Acta*, 27 (1962) 396–397

RADIOACTIVE TRACER STUDY OF THE REACTION BETWEEN CHROMIUM(VI) AND DIPHENYLCARBAZIDE

(Short Communication)

H. Sano, *Anal. Chim. Acta*, 27 (1962) 398–399

DIRECT-READING INSTRUMENT FOR AUTOMATIC COULOSTATIC ANALYSIS IN THE 10^{-5}–10^{-7} MOLE PER LITER RANGE

(Short Communication)

P. Delahay, *Anal. Chim. Acta*, 27 (1962) 400–401

THE SOLUBILITY OF SOME PYRROLIDINE CARBAMINATES IN ORGANIC SOLVENTS

(Short Communication, in German)

H. Malissa and S. Gomiščék, *Anal. Chim. Acta*, 27 (1962) 402–404

A NEW APPARATUS FOR SIMULTANEOUS DIFFERENTIAL THERMAL ANALYSIS AND GAS EVOLUTION ANALYSIS

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Department of Chemistry, Texas Technological College, Lubbock, Texas (U.S.A.)

(Received March 26th, 1962)

The technique of differential thermal analysis (DTA) was first proposed, in a rather crude manner, by LE CHATELIER in 1887[1]. Since its conception, DTA has been a useful tool in the fields of metallurgy, ceramics, geology, and chemistry. However, only in recent years has this technique been seriously applied to chemical problems. The reasons for this late acceptance in the field of chemistry are many. Perhaps the main reason for this has been the irreproducibility of the thermograms obtained from a known sample by various instruments. The curves obtained vary rather widely and are affected by such factors as furnace heating rate, sample particle size, furnace atmosphere, type of sample holder, etc.

Another problem has been the interpretation of the thermogram peaks. Generally, additional information is needed to supplement the DTA curve such as thermogravimetric analysis (TGA), X-ray diffraction, infrared absorption spectroscopy, visual phase examination, etc. With this supplemental data it is possible, in most cases, to interpret correctly the nature of the reaction or reactions which are responsible for the peak or peaks. However, due to environmental and instrumental effects, there are discrepancies between the DTA curve and, say, a TGA curve[2] which could lead to a completely false interpretation.

This problem has been attacked from the standpoint of analysis of the decomposition products, and a new apparatus is described which will lend itself to simplifying the interpretation of the DTA curve. An apparatus similar to the one discussed here has previously been described[3], but this apparatus was limited in use because of the use of a glass sample holder and also the presence of a large amount of a glass bead diluent in the sample chamber. The apparatus described herein will be designated as a DTA-GE (GE = gas evolution analysis) apparatus.

Basically, the instrument consists of a conventional DTA unit with provision for the detection and analysis of the evolved gaseous decomposition products. From 25 to 50 mg of sample, without the use of a supporting diluent for heat transfer purposes, are pyrolyzed in a dynamic helium gas atmosphere, under controlled furnace heating rates. The composition of the furnace gas stream is monitored by a thermistor thermal conductivity cell with provision for the collection of the gas samples in glass bulbs prior to their analysis. It is thus possible to record both the DTA and GE curves as a function of the furnace temperature. The composition of the gas samples can then be determined by conventional techniques such as mass spectrometry, gas chromatography, and infrared absorption spectroscopy. Since the sample is in a small Inconel crucible, it can be removed at any time and weighed. From this the composition of the residue can be ascertained or the contents can be subjected to X-ray diffraction, etc. By suitable calibration constants, the amount of gaseous decomposition product can also be obtained.

EXPERIMENTAL

Apparatus

The furnace and sample holder are shown in Fig. 1. The furnace consisted of a nickel tube, 2.40 cm in diameter by 15 cm long, to which was welded a flange to support the sample holder. The furnace heating element was wound directly on the outside of the tube which was first insulated with asbestos paper and then wound with 20 ft. of Nichrome resistance wire (1.05 ohms per ft.) giving a total resistance of about 23 ohms. The heater windings were covered with approximately a 1 cm thick layer of asbestos insulation. A fairly thin layer of asbestos insulation is preferable to a thick one in that there is a more even thermal gradient throughout the furnace chamber[4]. Also, the furnace will have a shorter cooling period between consecutive runs.

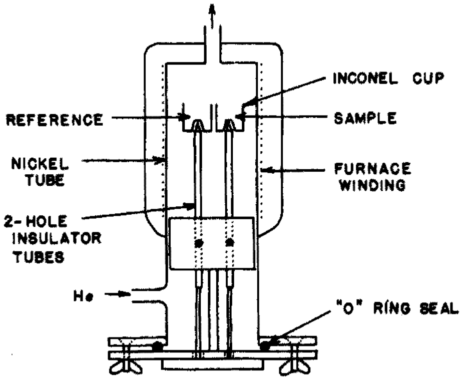

Fig. 1. Schematic illustration of DTA furnace and sample holder.

The thermocouples were made by spot-welding No. 26 gauge Chromel-Alumel wires together and then filing the resultant weld to give a smooth junction. The thermocouples were held in place in the sample holder by use of two-holed, 3.0 mm in diameter, ceramic insulator tubes and were brought out to an external connector through rubber gaskets at the base of the sample holder. To provide a gas-tight seal between the sample holder and the furnace assembly, a neoprene "O" ring of 3.50 cm diameter was employed.

The sample containers were small Inconel cups, 0.7 cm in diameter by 1.0 cm high, obtained from the Robert L. Stone Co., Austin, Texas. They had a capacity of 0.27 ml. The cups were seated on the insulator rods in such a manner that they made intimate contact with the thermocouple junctions. With this arrangement there was no contamination of the junctions with the sample or reference material.

The furnace power supply consisted of two variable voltage transformers, one of them driven by a small synchronous motor through a friction clutch[5]. By use of a suitable initial furnace input voltage, an approximately linear heating rate of 10 ± 1° per h was obtained. Slower or faster heating rates were obtained by varying the input voltages.

To aid in cooling the furnace between runs, a small squirrel-cage type blower was used. In this manner, the furnace could be cooled down from about 500° to ambient temperature in about 30 min.

The general arrangement of the apparatus is schematically illustrated in Fig. 2

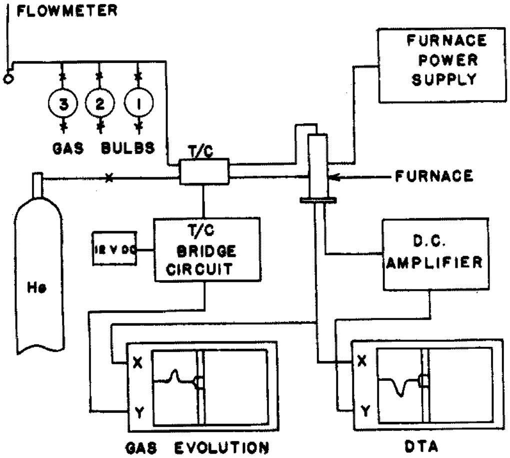

Fig. 2. Schematic illustration of DTA-GE apparatus.

The differential thermal analysis part of the apparatus consisted of a Leeds and Northrup Model 9835-B d.c. microvolt amplifier and a Houston Instruments Corp. X-Y recorder.

Detection of the gases in the helium gas stream was accomplished by the thermistor thermal conductivity cell, T/C. The stainless steel cell contained two matched 8000 ohm thermistors and was obtained from the F and M Scientific Corp., New Castle, Del. Normally, when evolved gases such as ammonia were involved, the T/C cell was operated at ambient temperatures. When used with water or other higher boiling liquids, the cell was operated at a temperature of 100° by means of a flexible heating tape wrapped around the cell. The temperature was controlled by varying the input voltage to the heating tape by means of a variable voltage transformer. If desired, a copper oxide catalytic combustion chamber previously described by ROGERS *et al.*[6] could be inserted between the furnace and detector cell. The cell bridge circuit was conventional in design and was powered by a Zener diode stabilized 12 volt d.c. supply, Model T-100, also obtained from the F and M Scientific Corp. The output from the bridge circuit was fed into the Y-axis of a Moseley Model 135R X-Y recorder. The X-axes of both recorders were connected to the reference thermocouple in the sample holder, through a 0° ice-water reference junction.

Procedure

The procedure for a DTA and GE run consisted of the following. Between 25 and

50 mg of the finely powdered sample was weighed out into the tared sample cup, an equivalent amount of freshly ignited alumina being placed in the reference cup. After loading, the sample holder assembly was inserted into the furnace chamber and locked in place by four bolts and wing-nuts. Helium was then allowed to flow through the system for 5 min at a flow-rate of 200 ml per min. After this initial flushing, the flow-rate was reduced to 100 ml per min and the initial bridge circuit and recorder adjustments made. Normally, the bridge was balanced with 9.5 mA of current flowing through each thermistor with the Y-axis attenuation of the recorder set at 10 mV per inch. The DTA d.c. amplifier was adjusted so that 100 μV of input gave a 1 mV deflection on the Y-axis of the 0–7 mV full scale recorder. After stabilization of the various system components for another 5 min, the furnace heating cycle was begun and the simultaneous DTA and GE curves recorded.

Through use of the appropriate stopcocks, gas samples could be collected at will in glass bulbs 1 through 3. Normally, gas samples were collected during the peak maxima since this corresponded to the maximum concentration of evolved gas in the helium gas stream. The composition of the gas mixtures collected in the glass bulbs was determined by use of a mass spectrometer or a gas chromatograph.

For semi-quantitative DTA or GE studies, the areas under the various peaks were integrated by connecting a Sargent Model SR recorder, equipped with a Disc Model 204 chart integrator, to the Y-axis of either X-Y recorder. In this manner, through use of appropriate calibration constants, the volume ratio of the gaseous decomposition products or the heat-of-reaction for the reaction could be obtained.

RESULTS AND DISCUSSION

The use of the apparatus is illustrated in Figs. 3 and 4. Fig. 3 shows the DTA and GE curves for $CuSO_4 \cdot 5H_2O$, under the heating rate and helium gas flow-rate as described. The maximum peak temperatures were in good agreement with REISMAN AND KAR-

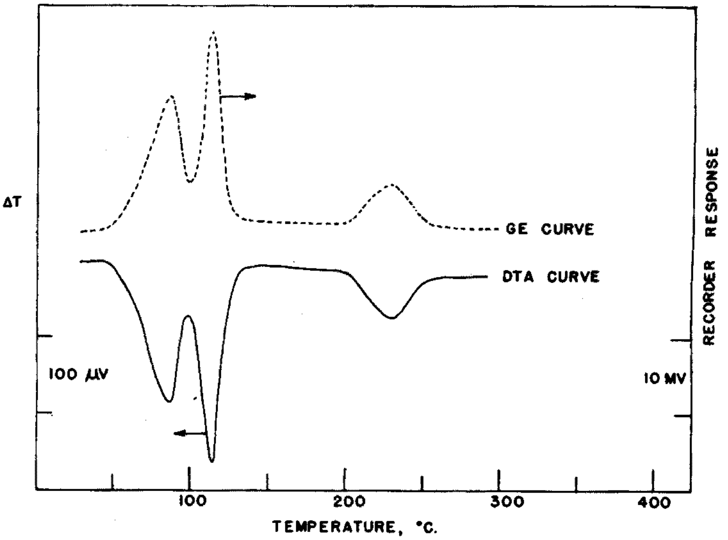

Fig. 3. DTA and GE curves of $CuSO_4 \cdot 5H_2O$ (35.7 mg of sample).

Lak[7] but slightly lower than those found by Borchardt and Daniels[8]. The origin of the various peaks has been established by the latter investigators as due to the following reactions:

$$\begin{aligned}
&85^\circ \text{ peak: } CuSO_4\cdot 5H_2O(s) \rightarrow CuSO_4\cdot 3H_2O(s) + 2H_2O(l)\\
&\qquad\qquad 2H_2O(l) \rightarrow 2H_2O(g) \text{ (from satd. soln.)}\\
&115^\circ \text{ peak: } CuSO_4\cdot 3H_2O(s) \rightarrow CuSO_4\cdot H_2O(s) + 2H_2O(g)\\
&230^\circ \text{ peak: } CuSO_4\cdot H_2O(s) \rightarrow CuSO_4(s) + H_2O(g)
\end{aligned}$$

The results obtained here are in agreement with the reactions as given above. From the GE curve it can be seen that each of the DTA peaks is matched by a corresponding GE peak showing that a volatile decomposition product was evolved. Analysis of the gas samples by a mass spectrometer showed that only water was evolved.

An even more interesting illustration of this apparatus is the thermogram for the thermal decomposition of Mohr's salt, $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$, as shown in Fig. 4.

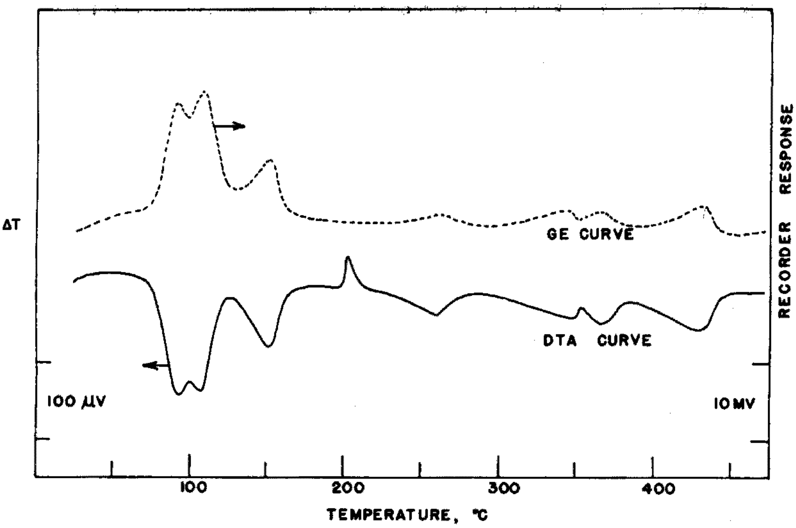

Fig. 4. DTA and GE curves of $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ (32.4 mg of sample).

The first three endothermic peaks at 92°, 108°, and 152°, respectively, are due to the transitions:

$$\begin{aligned}
&92^\circ \text{ peak: } Fe(NH_4)_2(SO_4)_2\cdot 6H_2O \rightarrow Fe(NH_4)_2(SO_4)_2\cdot 4H_2O + 2H_2O\\
&108^\circ \text{ peak: } Fe(NH_4)_2(SO_4)_2\cdot 4H_2O \rightarrow Fe(NH_4)_2(SO_4)_2\cdot 2H_2O + 2H_2O\\
&152^\circ \text{ peak: } Fe(NH_4)_2(SO_4)_2\cdot 2H_2O \rightarrow Fe(NH_4)_2(SO_4)_2 + 2H_2O
\end{aligned}$$

Weight-loss studies confirm the stoichiometry for the above reactions although there was no well-defined curve break for the transition from the hexahydrate to the tetrahydrate.

The next peak in the DTA curve was a small exothermic peak at a peak maximum temperature of 202°. It should be noted that the GE curve does not show a peak in this temperature range which would indicate that this peak was caused by a crystalline phase transition or a transition from an amorphous to a crystalline form. Further work is being carried out on this interesting transition. The other peaks in the curve were caused by the evolution of ammonium sulfate from the anhydrous $Fe(NH_4)_2(SO_4)_2$. However, due to the recorder setting, the maximum temperature attained by the furnace was not high enough to obtain the terminal decomposition product, Fe_2O_3.

From the above examples it is seen that this apparatus is inherently more useful than a single DTA apparatus. With a single 25 to 50 mg sample, the DTA and GE curves, the composition of the evolved gases, and the composition of the residue may be obtained. With this information available, it is far easier to interpret the nature of the reaction which caused the DTA curve peak. This apparatus has been in continuous operation in this Laboratory for over a year and has been extremely useful for the study of thermal decomposition processes in the temperature range from ambient to 900°.

ACKNOWLEDGEMENTS

The helpful assistance of Mr. WARNER KENDALL in construction of the instrument is gratefully acknowledged. This work was supported by the U.S. Atomic Energy Commission through Contract No. AT-(40-1)-2482.

SUMMARY

A new apparatus is described which permits the simultaneous recording of the differential thermal analysis and gas evolution curves for a given sample from ambient to 900°. The sample is pyrolyzed in a dynamic helium gas atmosphere using a conventional DTA furnace and sample holder assembly. The evolved decomposition products are detected in the helium gas stream by means of a thermistor thermal conductivity cell. From a knowledge of the GE curve and an analysis of the decomposition products, a more accurate interpretation of the DTA curve can be made.

RÉSUMÉ

Un nouvel appareil est décrit, permettant un enregistrement simultané des courbes d'analyse thermique différentielle et d'évolution de gaz. L'échantillon est pyrolysé dans une atmosphère d'hélium et les produits de décomposition sont décelés au moyen d'une cellule de conductibilité thermique thermistor.

ZUSAMMENFASSUNG

Beschreibung einer Apparatur zur gleichzeitigen Aufzeichnung der Kurven von Differential-Thermoanalysen und Gas-Bildung. Die Substanz wird in einem Heliumstrom pyrolysiert und die Zersetzungsprodukte in einer Wärmeleitfähigkeitszelle mit Thermistoren gemessen.

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THE DETER ATION OF SULPHUR AND PHOSPHORUS IN STEI NEUTRON ACTIVATION ANALYSIS

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(Received March 24th, 1962)

Neutron activation analysis of sulphur and phosphorus has already been investigated by various authors. GIBBONS AND SIMPSON[1] determined sulphur in chromium and arsenic using a double irradiation technique to correct for the phosphorus content; ALBERT *et al.*[2] and LEDDICOTTE[3] determined these elements in high purity aluminum, and HERR[4] used the technique for the determination of phosphorus in iron. The present work deals with the activation analysis of sulphur and phosphorus in steel where the method was applied in the concentration range of 0.01 to 1%. The procedure was tested successfully on a number of BCS standard steels.

NUCLEAR DATA AND INTERFERENCES

Reactor irradiation of sulphur gives rise to two long-living radioactive species, namely ^{35}S, a relatively weak β-emitter (energy: 0.167 MeV; half life: 87.1 days; activation cross section: 10.9 mb) and ^{32}P, also a pure β-emitter (energy: 1.71 MeV; half life: 14.3 days; activation cross section: 57 mb), the latter being due to the fast neutron flux. From these data it is apparent that, for relatively short irradiations, it is preferable to determine the sulphur content from the ^{32}P activity because this technique has a greater sensitivity and avoids the difficulties due to weak β-ray counting. When dealing with samples having a large P/S ratio, this method is, however, not sufficiently accurate as the reaction ^{32}S (n,p)^{32}P is swamped by the ^{31}P(n,γ)^{32}P reaction. For these samples the sulphur has to be determined from the ^{35}S activity. Interferences are then possible due to the ^{35}Cl(n,p)^{35}S reaction. This interference is, however, negligible in most cast irons and steels. The chlorine content of the samples was determined by activation analysis. After an irradiation for 15 min at a flux of $8 \cdot 10^{11}$n.cm^{-2}. sec.$^{-1}$, the chlorine was separated as silver chloride and the decay was followed as a function of time. Although the silver chloride was slightly contaminated with a short-life (period 15 min) and a long-life (period 2.6 h) species, the 38 min period of the ^{38}Cl could not be detected. It could be computed that, under the experimental conditions used, the chlorine content of the samples was below 0.1 p.p.m. Phosphorus was determined from the ^{32}P activity avoiding the interference of the ^{32}S(n,p)^{32}P reaction by irradiating the samples in the reflector of the reactor, where the fast neutron flux is negligible. Interference from the ^{35}Cl (n,α)^{32}P reaction is of course also negligible.

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Simultaneous determination of sulphur and phosphorus is feasible by the double irradiation technique at fast–slow neutron flux ratios as large as are available.

The specific activity of ^{32}P in a sample for irradiation sites (1) or (2) is given by

$$S^{32}{}_{P} = \alpha_{1(2)}\, c_P + \beta_{1(2)} c_S$$

where c_P and c_S represent the respective phosphorus and sulphur concentrations and $\alpha_{1(2)}$ and $\beta_{1(2)}$ the proportionality constants at irradiation sites 1 and 2.

It is apparent that c_P and c_S can easily be computed if α_1/β_1 and α_2/β_2 are sufficiently different.

These ratios were determined experimentally by irradiating samples of known content at different reactor sites and by using cadmium shielding to cut off the thermal neutron flux. Results are given in Table I.

TABLE I

DETERMINATION OF FLUX RATIOS BY IRRADIATION OF SAMPLES OF KNOWN CONTENT

Reactor site in BR-1	*flux ($n.cm^{-2} \cdot sec^{-1}$)*	*Cadmium*	α	β	α/β
Rabbit 1	2.10^{11}	none	680	0.9	710
2	8.10^{11}	none	1570	41.5	38
2	8.10^{11}	none	1630	38.8	42
3	8.10^{11}	none	487.3	13	37.5
3	8.10^{11}	110 mg/cm²	174	34.4	5.1
3	8.10^{11}	110 mg/cm²	328.6	67.7	4.9

TABLE II

SPECIFIC ^{59}Fe ACTIVITY IN BCS 232/1

Sample no.	*Fe 232/1*	*Specific activity of ^{59}Fe (counts/min/mg)*
1	standard	2632
2	standard	2764
3	standard	2773
4	standard	2795
5	samples	2785
6	samples	2686
7	samples	2710
8	samples	2719
9	samples	2639
10	samples	2690
11	samples	2728
12	samples	2637
		2688 ± 64 (2.3%)

From Table I it is apparent that the most favorable conditions for double irradiation are given by sites 1 and 3 using cadmium shielding in the latter. In this case sufficiently accurate results can be expected for S/P $\geqslant$ 10.

IRRADIATION TECHNIQUES

The BCS samples were available as fine turnings which could easily be pressed into pellets. Reference sulphur and (or) phosphorus samples were prepared by homogeneously mixing ammonium sulphate or ammonium dihydrogen phosphate into high purity iron carbonyl with a mechanical mixer. Samples and references were stacked alternately into an aluminum can using aluminum foils to avoid contamination. A separate experiment showed that the neutron flux is homogeneous throughout the can as is apparent from the ^{59}Fe specific activity (see Table II).

EXPERIMENTAL

Determination of sulphur as ^{35}S

1 g of the steel sample is accurately weighed and pressed into pellets (diam. 1/4 in.; thickness: 0.08 in.) at a pressure of 200,000 lb p.s.i. The standards are prepared by mixing a known amount (*ca.* 60 mg) of ammonium sulphate into high purity iron carbonyl with a mechanical mixer (Spec Mix) and are also pressed into pellets. Samples and standards are packed alternately into an aluminum can and irradiated during 6–48 h in BR-1 at a flux of $8 \cdot 10^{11}$ n.cm^{-2}. sec^{-1}. After irradiation the pellets are dissolved in concentrated nitric acid in the presence of a few drops of 6 *M* hydrochloric acid. A known amount (60 mg) of isotopic ammonium sulphate carrier is added to the unknown samples. The solutions are taken to dryness and redissolved in 200 ml of 6 *N* nitric acid. Iron is precipitated by bubbling gaseous ammonia through the solution and removed by filtration. The filtrate is slightly acidified with hydrochloric acid, 10 mg of iron is added and the precipitation process is repeated to secure complete scavenging of interfering activities. The filtrate is diluted to 100 ml, acidified with hydrochloric acid and the sulphate is precipitated by adding dropwise to the hot solution 10 ml of 0.1 *M* barium chloride. The precipitate is collected on a fine porosity filter paper, washed until free of chloride and incinerated at 600–800°. Approximately 80 mg of the barium sulphate precipitate is suspended in alcohol and transferred to a standard aluminum counting planchet. This quantity is greater than the infinite thickness for barium sulphate so that self-absorption corrections are unnecessary. After evaporation of the alcohol the barium sulphate is fixed with a dilute polymethacrylate solution and counted in a proportional flow counter using argon–methane gas. The sulphur content is then computed from the ratio of the activities of samples and standards, taking corrections into account for chemical yield.

A 12-h irradiation at a flux of $8 \cdot 10^{11}$ n. cm^{-2}, sec^{-1} gives rise to an activity of 2,300 counts/min/mg S. As the background of the flow counter is approximately 20 counts/min, 10^{-3}% represents the lower limit of the sulphur determination under these conditions.

Determination of sulphur and(or) phosphorus as ^{32}P

300 mg of the steel turnings are pressed into pellets (see above determination of sulphur) adding *ca.* 40 mg of ammonium dihydrogen phosphate to the standards. Separate standards containing 60 mg of ammonium sulphate are prepared if the double irradiation technique is used. Samples and standards are irradiated in an aluminum can in BR-1, site 1 for phosphorus determinations. Irradiation at sites 1

and 3, the latter with the 110 mg/cm^2 cadmium shielding, is used for simultaneous sulphur and phosphorus determinations. After the addition of 40 mg of ammonium dihydrogen phosphate isotopic carrier to the unknowns and to the sulphate standards, the samples are dissolved in 100 ml of 7 *N* nitric acid and taken to dryness on a hot plate. The residue is redissolved in 100 ml of water and 20 ml of 30% ammonium nitrate with 10 ml of 7 *N* nitric acid and heated to the boiling point. Fifteen ml of a hot 3% ammonium molybdate solution is added. The phosphomolybdate is digested for 15 min and filtered on a filter crucible. The precipitate is dissolved in 5 ml of 6 *N* ammonia. The phosphate is now precipitated with magnesia mixture, filtered and dissolved in 100 ml of 1 *N* nitric acid. The phosphate is again precipitated as phosphomolybdate, dried at 180° and weighed to determine the yield. The procedure ensures a highly satisfactory decontamination as appears from relative absorption curves *vs.* pure ^{32}P and from the half-life determinations. It also appears that the phosphomolybdate is easier to mount for beta counting than the magnesium phosphate. With an end-window GM-counter, 1 mg of phosphorus gives rise to an activity of 13,600 counts/min. The lower limit of the determination is consequently 0.001% for a 2-h irradiation at the stated flux.

TABLE III

ACTIVATION ANALYSIS OF SULPHUR AND PHOSPHORUS

Standard deviation on given contents were computed from the different results given in the certificates

BCS steel	*% S given*	*% S found*	*% P given*	*% P found*
No. 159/1 0.5% C steel 0.129% Si 1.05% Mn 0.06% Cr 0.02% Ni	0.045 ± 0.0018	0.0473 ± 0.0028(5)[a]	0.024 ± 0.0012	0.0244 ± 0.0025 (9)
No. 161/1 0.8% C steel 0.24% Si 0.1% Ni 0.3% Cr 1% Mn 0.16% Cu	0.050 ± 0.0014	0.0541 ± 0.0044 (7)	0.043 ± 0.001	0.0430 ± 0.0026 (9)
No. 152/1 1.11% Mn 0.08% Cr 0.22% Cu 0.18% Ni	0.259 ± 0.006 [b]	0.283 ± 0.02 (7) 0.27 ± 0.027 (5)[c]	0.020 0.023	0.0182 ± 0.0006 (6) 0.018 ± 0.002 (5)[c]
No. 232/1 0.1% C steel 1.22% Mn	0.114 ± 0.002[b] 0.116 ± 0.003[d]	0.124 ± 0.008 (8) 0.111 ± 0.005[c]	0.015	0.0148 ± 0.0006 (6)

[a] The figure in parentheses is the number of analyses done.
[b] By the standard gravimetric determination.
[c] The sulphur and the phosphorus are counted as ^{32}P by using the double irradiation technique.
[d] By the combustion method.

The above procedures were tested on a number of BCS steels and the results are summarized in Table III. It appears that in most cases the results of the activation analyses are within 10% of the values given in the certificates, the standard deviations also being well within acceptable limits.

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SUMMARY

Sulphur and phosphorus in steel were determined by neutron activation analysis, being counted as ^{35}S and ^{32}P respectively. For steels with sulphur to phosphorus ratios larger than 10, it seems possible to determine both elements by counting ^{32}P, making use of a double irradiation technique at different fast to slow neutron fluxes.

RÉSUMÉ

Le soufre et le phosphore dans l'acier ont été dosés par activation au moyen de neutrons, étant comptés respectivement comme ^{35}S et ^{32}P. Pour des aciers renfermant du soufre et du phosphore dans un rapport supérieur à 10, il paraît possible de doser ces deux éléments par comptage de ^{32}P, faisant usage d'une technique à double irradiation.

ZUSAMMENFASSUNG

Beschreibung einer radiometrischen Methode zur Bestimmung von Phosphur und Schwefel in Stählen. Nach Bestrahlung mit Neutronen werden die ^{35}S und ^{32}P Aktivitäten bestimmt. Durch Anwendung der Doppel-Bestrahlungstechnik können die beiden Elemente nebeneinander bestimmt werden.

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DETERMINATION OF THE VALENCE DISTRIBUTION OF VANADIUM IN POLYOLEFIN CATALYSTS PREPARED FROM VANADIUM TRICHLORIDE

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Organometallic catalyst systems are widely used for the low-pressure polymerization of olefins[1]. These catalysts may consist of mixtures of a metal alkyl and a transition metal halide, plus a third component to increase catalytic activity or stereospecificity. The nature of the interaction between the alkyl and the metal halide, especially between aluminum alkyls and titanium tetrachloride, has been a subject of controversy[2,3]. It is generally acknowledged that the alkyl reduces the transition metal halide to produce the active species by forming a complex in which the transition metal has been reduced[4,5], although the extent of the reduction is not usually established. Furthermore, at least 2 investigators claim that the valence of the transition metal can be related to catalytic activity[6,7]. Potentiometric and polarographic methods have been described for determining the valence distribution of titanium[4,8] and vanadium[7,9] in polyolefin catalysts.

This investigation is part of a program to relate the valence distribution of vanadium in polyolefin catalysts prepared from vanadium trichloride and aluminum alkyls to the activity of the catalyst. In these catalysts, the expected valences were vanadium(II) and (III). Oxidation states corresponding to vanadium(I) and vanadium(O) were not considered to be stable and were assumed not to be present in the catalyst.

Polarography, spectrophotometry, chromatography, and potentiometry were considered for the determination of vanadium(II) and (III) in these catalysts. The stepwise reduction of vanadium(IV) through vanadium(III) to vanadium(II) at the dropping mercury electrode has been thoroughly studied[10-13]; the reduction of vanadium(III) has been used to determine its amount in certain polyolefin catalysts[7]. Certain complexes of vanadium possess absorption spectra whose characteristics may depend on the valence states present[14]. Paper chromatography[15] has been used to separate penta- and tetravalent, and tetra- and trivalent, vanadium. Finally, extensive studies have been carried out on the stepwise oxidation and reduction of vanadium with many different oxidizing and reducing agents[16]. In particular, the oxidation of vanadium(II) to (III) and of vanadium(III) to (IV) by potassium permanganate with a platinum indicator electrode has been used to determine the amount of vanadium(II) and (III) in some polyolefin catalysts[7,9].

The catalyst to be analyzed is usually in the form of a slurry in a hydrocarbon solvent such as *n*-heptane. Upon treating this slurry with various aqueous solvents which will dissolve the catalyst, an emulsion often results because of the formation

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of organic alkoxides upon hydrolysis of the metal alkyl. Such a solution is not readily analyzed by optical methods, nor is it amenable to chromatographic separations. Furthermore, the presence of these high concentrations of alkoxides renders polarographic waves nonreproducible.

For these reasons, potentiometric methods were selected for further study. Because the vanadium is present in the catalyst as vanadium(II) and (III), the simplest approach is a stepwise oxidation of vanadium(II) to (III), and of vanadium(III) to (IV)[9] by direct titration with a suitable oxidizing agent. Again, the turbidity of the emulsion usually formed upon dissolution of the catalyst made the use of redox indicators difficult. Consequently, potentiometric titration with a platinum indicator electrode was selected. The choice of oxidizing agents was limited to those compounds that would quantitatively oxidize vanadium(III) to (IV) but would not oxidize the products of hydrolysis of the metal alkyls also present in the catalyst. In the catalytic systems analyzed in this study, potassium permanganate, used in earlier studies by CARRICK *et al.*[7,9], could not be used because it oxidized some hydrolysis products of the metal alkyls, so that high, variable blanks resulted. Ceric sulfate was selected as the oxidizing agent, as the best compromise between quantitative oxidation of vanadium and low blanks due to lack of oxidation of these hydrolysis products.

METHOD

In the method, the catalyst, usually in the form of a slurry in *n*-heptane or other hydrocarbon solvent, is dissolved in sulfuric acid, and the vanadium is titrated potentiometrically with ceric sulfate. Platinum foil indicator electrodes permit the detection of both the end-points.

A quantity of catalyst containing from 0.2–0.5 g of vanadium trichloride, protected by oxygen-free argon or nitrogen, is placed in a 125-ml Erlenmeyer flask, 100 ml of 4 *N* sulfuric acid, purged with oxygen-free argon or nitrogen to remove dissolved oxygen, is added, and the mixture is stirred magnetically until all the catalyst has dissolved. This solution is transferred with the argon or nitrogen to a 250-ml beaker fitted with a rubber stopper containing a platinum foil indicator electrode and a Leeds-Northrup Model 1199–31 reference electrode. The platinum foil electrode should have an area of about 1 cm^2; the Leeds & Northrup Model 1199–57 is satisfactory. Provision should also be made in the beaker for purging the sample continuously with the argon or nitrogen and for magnetic stirring. The sample is then titrated with standard 0.1 *N* ceric sulfate solution, to obtain breaks corresponding to the oxidation of V(II) to V(III) and of V(III) to V(IV). After the first end-point is passed, the solution should be heated to 70° before proceeding to the second end-point. The first end-point should occur at approximately 0.0 V *vs.* S.C.E., while the second end-point should occur at approximately +0.6 V *vs.* S.C.E. The exact e.m.f. at the end-point may depend on the manner in which the catalyst is dissolved, for some hydrolysis products of the metal alkyl may shift it slightly. From these 2 end-points, the percentages of vanadium(II) and vanadium(III) can readily be calculated without knowing the total amount of vanadium trichloride in the original sample.

DISCUSSION

The method was first tested by titrating, at 70°, solutions prepared by dissolving vanadium trichloride in purged 4 *N* sulfuric acid. In these samples, no vanadium(II) was present, and the only oxidation step observed was V(III)→V(IV). Results are shown in Table I. The amount of vanadium(III) found averaged 3.3% less than the vanadium taken (as VCl_3) because the vanadium trichloride was contaminated with tetrachloride. A more rigorous test of the method was provided by titrating solutions of vanadium(II) prepared by reducing solutions of vanadium pentoxide (prepared by igniting pure V_2O_5 at 500°, dissolving it in potassium hydroxide solution, and adjusting the pH to slightly acidic with sulfuric acid) on the Jones reductor[17]. Results are shown in Table II. Precision (percent standard deviation) and accuracy for vanadium(II) are ± 0.007 and ± 0.009; for vanadium(III), they are ± 0.016 and ± 0.010.

TABLE I

ANALYSIS OF VANADIUM TRICHLORIDE SOLUTIONS

Mequiv. V taken	*Mequiv. V(III) found*
0.550	0.532
0.519	0.504
0.260	0.252
0.189	0.182

TABLE II

ANALYSIS OF STANDARD SOLUTIONS OF VANADIUM FOR V(II) AND V(III)

Mequiv. V taken	*Mequiv. V found*	
	V(II)	*V(III)*
0.967	0.963	0.949
	0.987	0.965
	0.970	0.980
Ave	0.970	0.965

A series of catalysts prepared by treating vanadium trichloride with metal alkyls and additives were analyzed by this method. In preparing these catalysts, time, temp., and ratios of reactants were varied to obtain catalysts of different activity. Results of these studies are shown in Table III. All analyses have been normalized. As a part of this study, samples were prepared which contained all the ingredients in the recipe except the vanadium trichloride. In no case did any of these samples consume more than one drop of the ceric sulfate solution.

Although the method provides reasonably accurate results on these catalysts, it does possess certain limitations which may limit its usefulness. Immediately preceding the end-point, the e.m.f. of the system drifts to more positive readings, probably because the oxide film[18] on the platinum electrode catalyzes the reaction V(II)→ V(III) + *e*. After 15–60 min, the drifting ceases and e.m.f. readings become constant. This behavior is observed in the titration of both solutions of vanadium(II) prepared on the Jones reductor and solutions of catalysts, so that it cannot be attributed to the presence of hydrolysis products of the metal alkyl or other additives in the solution. This behavior is not observed following the V(II) - V(III) end-point. During a titration, it is convenient to stir the solution for about 15–30 min before taking e.m.f. readings just before the first end-point, even though some error may be introduced owing to oxidation of vanadium(II) to (III) by the platinum oxide layer. Titrations with standard vanadium(II) solutions have shown that this error is small, certainly less than 1%. The drifting phenomenon could probably be minimized by reducing the area of the electrodes by using platinum wire for the electrode, but these electrodes are easily coated with alkoxides formed during the hydrolysis of the catalyst, and they rapidly become insensitive. The electrodes of relatively large area become insensitive after 6–12 titrations. They may be cleaned by rinsing with acetone, water, and dilute nitric acid. Sometimes this treatment will not rejuvenate an electrode and it must be discarded. For this reason, relatively inexpensive homemade electrodes are preferred.

TABLE III

VALENCE DISTRIBUTION IN CATALYSTS PREPARED FROM VANADIUM TRICHLORIDE

Catalyst	*%V(II)*	*%V(III)*
A	2.7	97.3
B	9.9	90.1
C	54.0	46.0
D	55.6	44.4
E	65.2	34.8
F	67.3	32.7
G	74.6, 67.2	25.4, 32.8
H	79.4	20.6
I	81.5	18.5
J	84.2, 84.2	15.8, 15.8
K	88.8	11.2
L	90.4	9.6
M	91.6	8.4
N	92.2	7.8

The method is useful for the analysis of laboratory catalysts and for grab samples taken from pilot plant reactors. Small amounts of polymer present in pilot plant samples did not affect the reliability of the results significantly. This method most likely could be extended to the analysis of catalysts prepared from vanadium tetrachloride and metal alkyls. It should be useful whenever no other oxidizable metals are present in the catalyst, or if these metals are present in constant amounts.

SUMMARY

An electrochemical method has been developed for determining the relative amounts of V(II) and V(III) in polyolefin catalysts prepared using aluminum alkyls and vanadium trichloride. The catalyst, usually obtained as a slurry in *n*-heptane, is titrated potentiometrically with ceric sulfate using a platinum indicator electrode. Under proper experimental conditions, 2 breaks are obtained, corresponding to the reactions $V(II) \rightarrow V(III) + e$ and $V(III) \rightarrow V(IV) + e$. Interferences from other components of the catalyst are negligible. The method is useful for the analysis of both laboratory catalysts and grab samples taken from pilot plant reactors.

RÉSUMÉ

Une méthode électrochimique est décrite pour la détermination des teneurs relatives en vanadium(II) et vanadium(III) dans des catalyseurs polyoléfiniques. Elle s'effectue par titrage au moyen de cérium(IV), avec une électrode indicatrice de platine.

ZUSAMMENFASSUNG

Beschreibung einer elektrochemischen Methode zur Bestimmung der relativen Mengen von Vanadium-(II) und Vanadium-(III) in Vanadium-Polymerisationskatalysatoren. Sie beruht auf der potentiometrischen Titration met Cer-(IV)-lösung und einer Platin-Indikatorelektrode.

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MERCURY DETERMINATION AT THE MICROGRAM LEVEL BY A REDUCTION-AERATION METHOD OF CONCENTRATION*

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Mercury below one part per million in soil and grain samples is difficult or tedious to determine by available methods[1,2]. Materials low in mercury require large samples resulting in solutions of large volumes and high acidity; both interfere with accurate analysis. The residual finely divided particles in soil digests adsorb mercury(II) and must be centrifuged and filtered using a chloride wash solution[3].

In recent years, several analytical methods for mercury using the tin(II) reduction technique have appeared. BARTLETT AND MCNABB[4] successfully applied the reduction technique to a volumetric analysis of macro and semimicro quantities of mercury in organic and inorganic compounds. MILLER AND WACHTER[5] used the reduction technique combined with a steam distillation procedure to determine μg and submicrogram quantities of mercury in alloys. They demonstrated that up to 15 μg of mercury could easily be distilled from a dilute sulfuric acid medium. The MILLER AND WACHTER technique has been applied to biological materials[6,7]. Small quantities of mercury have been determined in dilute solutions of organic mercury compounds by a strong phosphoric acid–tin(II) reduction method in which mercury is carried from an electrically heated flask by a slow stream of carbon dioxide[8]. Very dilute solutions must first be concentrated by coprecipitation with ferric or cadmium sulfide.

The proposed method uses a concentrating aeration procedure at room temp. following digestion of the samples with sulfuric acid, hydrogen peroxide and potassium permanganate. Its chief advantages are elimination of filtration, applicability to mercury solutions in sulfuric acid to 22 N, nitric acid to 8 N, and nitric and sulfuric mixtures to 4 N and 8 N respectively, and ability to concentrate dilute mercury solutions during the process of mercury separation in order that the entire sample may be taken for analysis. Final analyses are made from solutions of constant composition and volume regardless of the original material and volume of the digest or solution.

EXPERIMENTAL

Reagents

Water. Use water redistilled from an all-pyrex distillation unit.

Hydrogen peroxide. 50% (Buffalo Electrochemical Co.).

Hydroxylammonium sulfate. 25%, dithizone-extracted.

Sodium chloride. ACS grade, 5 N, dithizone-extracted.

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Stannous chloride solution. Dissolve 70 g of 20 or 30 mesh ACS grade tin in 200 ml of concentrated hydrochloric acid.

Reducing solution A. Mix 250 ml of 5 *N* sodium chloride, 75 ml of 25% hydroxylammonium sulfate and 175 ml of water.

Reducing solution B. Mix 60 ml of 25% hydroxylammonium sulfate and 50 ml of 5 *N* sodium chloride. Dilute to 500 ml.

1.8 N sulfuric acid solution. Mix 100 ml of 18 *N* sulfuric acid, 750 ml of water, 5 ml of 25% hydroxylammonium sulfate and 10 ml of 5 *N* sodium chloride and dilute to 1 l.

Absorbing solution. Dilute 125 ml of 5% potassium permanganate to 1 l. Add 5 ml of 18 *N* sulfuric acid per 20 ml of diluted potassium permanganate just before use.

Chloroform. Shake USP chloroform with concentrated sulfuric acid, pour the chloroform layer into a bottle containing lime. Reshake, allow to settle, and decant the chloroform into a pyrex distillation flask. Filter the residue. Add 2 g of lime, 20 ml of ethanol and a boiling chip per 4 l and distil through a 25 × 100 mm column of loosely packed glass wool using an all-pyrex unit, into an amber bottle containing ethanol (refluxed and redistilled from sodium hydroxide) equivalent in volume to 0.5% of the chloroform to be distilled. Should the chloroform decompose on heating as sometimes happens with reprocessed chloroform, treat it with Darco G-60 activated powdered charcoal, filter through Whatman No. 2 filter paper using vacuum, and redistil.

Dithizone solution. Dilute a 1 mg/ml stock solution of dithizone (Eastman Kodak white label) as necessary with redistilled chloroform. Keep the stock solution refrigerated. Store the working solution at room temperature when used daily and standardize with each use. Protect from light.

Mercury standard. Dissolve 0.1354 g of ACS grade mercuric chloride per 100 ml of 1 *N* sulfuric acid. Dilute 1 ml of this stock solution and 4 ml of 5 *N* sodium chloride solution to 100 ml with water. The working solution (10 μg/ml) is stable for at least 14 days.

Potassium dichromate. ACS grade, 10 % or chromium equivalent in other salts.

Apparatus (Fig. 1)

A 250-ml conical boiling flask (available from Scientific Glass Apparatus Co., Bloomfield, N.J.) with 24/40 standard outer taper.

Agitator-aerator. With 24/40 standard inner taper to which a side arm with a 12/5 ball-joint has been sealed. The top is closed with a No. 2 or 3 polyethylene stopper through which a hole has been bored for an 8-mm pyrex tube.

Gas washing bottle stopper (Pyrex No. 31770). Tall-form with EC fritted cylinder and 12/5 ball and socket joints.

Absorber cylinder. A 29/42 inner standard taper is sealed 25 mm below the taper with a 32 × 200 pyrex test tube cut to 155 mm.

Capillary (air flow regulator). 50 × 0.5 mm I.D. capillary tubing.

Filter. 36 × 250 mm tubing stoppered on each end with rubber stoppers and packed with 50 mm of 8–14 mesh soda lime held by glass wool.

Method

For solutions of mercury(II) in sulfuric acid to 12 *N*, in nitric acid to 8 *N*, or in a mixture of nitric and sulfuric acids to 4 and 8 *N*, resp. proceed as under "aeration" using an aliquot or the entire sample. With sulfuric acid solutions greater than 12 *N* either dilute or use 100 ml of carbonate-phosphate solution[9] in a 250-ml absorber preceding the permanganate absorber.

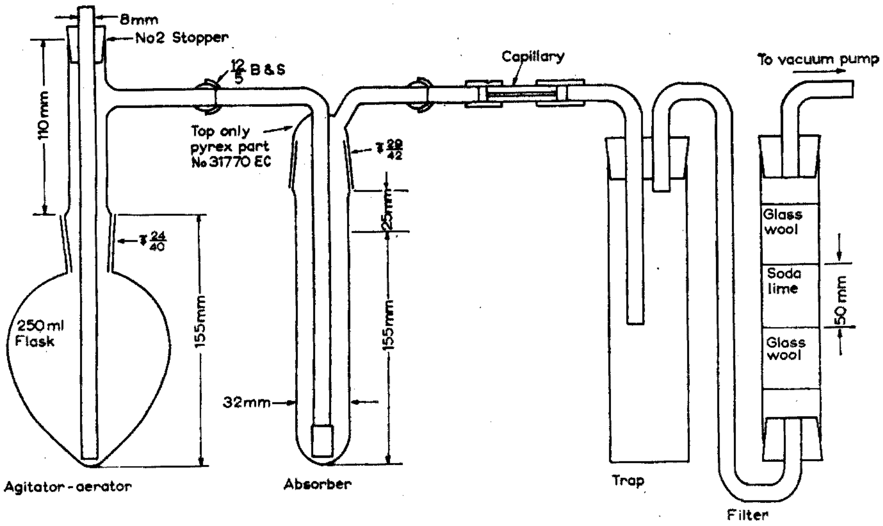

Fig. 1. Mercury reduction-aeration apparatus.

Digestion. For soil, turf and grain samples containing mercury(II), methylmercury, ethylmercury and phenylmercury compounds, weigh a 10-g sample of air-dried soil, 1 to 17% in organic matter and screened through a 32-mesh screen, a turf core 3/4 × 2 inches or a 5-g sample of grain into a conical flask. The amount of soil in samples of higher organic matter content is reduced somewhat for convenience of digestion. Add 1 ml of chromium solution in case of grains and highly organic soils. Attach the flask to a 300-mm West-type standard taper condenser. Add 20–30 ml of sulfuric acid through the condenser and mix vigorously. Place soil and turf samples on the steam bath with intermittent agitation for 30 min and cool to room temp. Add 50% hydrogen peroxide in 0.5-ml portions with vigorous mixing after each addition. Allow sufficient time for the peroxide to decompose after each addition. The decomposition of hydrogen peroxide being exothermic, the temp. will rise gradually to about 150°. When the danger of foaming subsides increase the amount of each addition to 1 ml. Continue the peroxide addition at a rate sufficient to keep the solution bubbling gently. When the temp. drops below the proper reaction temp., and 2 successive additions of peroxide fail to decompose, a microburner is used to raise the temp. No further additions of peroxide should be made until previous additions of peroxide have nearly decomposed. The addition of peroxide is discontinued after the solution turns blue green, or in the absence of chromium, light yellow, and residual peroxide is allowed to decompose with the use of low heat after the condenser has been washed down with water. When the decomposition of peroxide has apparently ceased, add 5% permanganate slowly to give a 5-ml excess while the temp. is maintained. The permanganate is added in 5-ml portions or less until the mixed color persists for 15 min. Cool the sample and add 20 ml of reducing solution A.

Aeration. Insert the agitator-aerator in the flask as shown in Fig. 1. The flask should be $^1/_2$–$^2/_3$ full. The absorber contains 25 ml of the absorption solution. The pressure to the right of the capillary is reduced to 23 in. of mercury. The air flow through the system should be about 80 l/h. For soil samples, adjust the intake tube as close to the bottom of the flask as possible to keep the particles in constant suspension. If aeration fails to begin in soil and turf digests after the vacuum is turned on, lift the agitator-aerator about 1 cm out of the flask and then replace. The process is repeated as necessary to start aeration. Continue aeration for 30 min after the addition of 5 ml of stannous chloride solution through the air inlet. Reduce the absorption solution with 5 ml of reducing solution B and transfer to a 50-ml volumetric flask. Allow the solution to stand for at least 2 h between reduction of the permanganate and analysis.

Determination. Transfer a suitable aliquot or the entire sample containing not more than 10 μg of mercury to a 125-ml cylindrical separatory funnel and dilute to 50 ml with the 1.8 *N* sulfuric acid solution. Add 3.5 ml of dithizone solution (containing 11 mg/l) and shake for 1 min. Transfer the chloroform phase to a clean 13 × 100 mm test tube, allowing any residual water to adhere to its walls. Then transfer to a 1-cm square cuvette and measure the excess of dithizone at 605 mμ. Read as soon as possible after shaking with the mercury solution. Aqueous mercury solutions may be allowed to stand in the separatory funnel. Work should be conducted in subdued light. Known amounts of mercury (0–10 μg) are run simultaneously with the samples. Blanks are subtracted where applicable.

As an alternative arrangement, a 1 × 5 cm rectangular cuvette may be used in conjunction with 11.5 ml of a dithizone solution containing 1.5 mg/l in the mercury range of 0–4 μg. The change in absorbance per μg of mercury is about 0.194 units as compared with the 0.125 units using the former arrangement.

DISCUSSION AND RESULTS

The reduction of mercury(II) in small concentrations by stannous chloride is apparently immediate without the application of heat; 95–97% of the mercury in a solution can be removed by aeration at room temp. with 7 l of air in a 6-min period

TABLE I

THE RECOVERY OF MERCURY FROM SULFURIC ACID SOLUTIONS AFTER VARYING PERIODS OF AERATION[a]

Time interval min	*Sulfuric acid solutions*[b]			
	Mercury recovered (100 μg original)			
	I	*II*	*III*	*IV*
0–5	97.30	98.00	95.40	96.30
5–10	1.84	1.16	2.42	2.92
10–15	0.28	0.24	0.28	0.62
15–20	0.00	0.12	0.08	0.00
20–40	0.00	0.14	—	0.00
40–50	0.00	—	—	—
Total recovered	99.4	99.7	98.2	99.8

[a] Air flow rate *ca.* 80 l/h.

[b] 150 ml 5 *N* H_2SO_4.

while 98–99% is removed by 14 l (Table I). In order to recover between 99 and 100 μg of mercury from a total of 101.7 μg present in 150 ml of unfiltered soil digest which is 5 *N* in sulfuric acid, aeration for about 20 min at a rate of 80 l/h was needed. Continued aeration for up to 60 min produced less than 1 μg of additional mercury. Silver ions, introduced as 100 mg of silver nitrate, are not reduced to the metallic state by tin(II) but interfere seriously as the chloride precipitate. Bromides at the 0.01 *M* concentration do not interfere. No reduction of mercury was observed in the presence of iodides at a similar concentration. The volume of the mercury solution apparently has no effect; 0.5 μg of mercury(II) can be recovered easily from as much as a liter of water.

TABLE II

RECOVERY OF ADDED MERCURY FROM VARIOUS CONCENTRATIONS OF SULFURIC, NITRIC, AND SULFURIC-NITRIC ACID MIXTURES BY THE REDUCTION-AERATION TECHNIQUE

Normality H_2SO_4	*Normality HNO_3*	*Hg recovered (μg)*	*Normality H_2SO_4*	*Normality HNO_3*	*Hg recovered (μg)*
0.6		101.[a]	6	3	5.17
12		100.[a]	6	4	5.07
17		99.0[a]	6	6	3.98
22		5.03	6	8	0.56
23		4.92	7	2	5.10
24		4.63	7	4	5.07
27		2.17	7	6	2.74
	8	0.02[b]	8	4	5.08
	8	5.08	9	1	5.16
	9	4.86	9	2	4.75
	10	4.32	9	4	4.17
	13	0.10			
5	3	5.03			
5	4	5.12			
5	5	4.63			
5	8	1.87			

[a] In these instances, 145 ml of solution containing 100 μg of mercury were analyzed. In the remaining cases 100 ml of solution containing 5 μg of mercury were used.

[b] No mercury was added.

Reduction at room temp. can be effected over wide ranges of sulfuric and nitric acid concentrations. Table II shows quantitative mercury recovery from sulfuric acid up to 22 *N*, nitric acid up to 8 *N*, and a nitric and sulfuric acid mixture up to 4 *N* and 8 *N* respectively. In 16 *N* sulfuric acid, hydrogen chloride evolution begins. Since chloride depresses the mercury-dithizone reaction, a carbonate-phosphate absorber was used ahead of the permanganate absorber for higher concentrations of sulfuric acid. In 27 *N* sulfuric acid there is almost total precipitation of tin(II) with only 40% mercury recovery. If the solution is diluted with water after precipitation of tin(II), the recovery of mercury increases to 97%.

Table III indicates that mercury in several forms can be digested and aerated from unfiltered soil, turf core and barley digests. The low values for mercury obtained from permanganate solutions reduced with hydroxylammonium salts in the absence of chloride has been noted previously[9]. The sodium chloride in the absorber and the digest reduction solutions is to preclude this possibility and to stabilize the solution during any standing period between aeration and analysis or digestion and aeration.

The colorimetric procedure used is discussed by SANDELL[2].

TABLE III

MERCURY RECOVERY

Sample	*Hg added (μg)*	*Total Hg found (μg)*	*Added Hg recovered (μg)*
		(Added as $HgCl_2$)	
10 g Puyallup sandy loam soil (air dried and screened, organic matter 6% air dry basis)	0.00	1.66	—
	0.56	2.17	0.51
	7.77	9.41	7.75
	111.0	111.1	110.1
		(Added as methylmercury chloride)	
	0.40	2.15	0.49
	4.00	5.55	3.89
		(Added as ethylmercury chloride)	
	0.38	2.08	0.41
	7.57	9.19	7.53
		(Added as $HgCl_2$)	
1.9 × 2.4 cm Turf cores (18 – 22 g as sampled)	0.00	1.35	—
	1.00	2.18	0.83
	5.00	6.46	5.11
	100.0	97.45	96.1
		(Added as $HgCl_2$)	
5 g Cracked whole barley	0.00	0.09	—
	0.20	0.40	0.31
	0.50	0.56	0.47
		(Added as methylmercury chloride)	
	0.16	0.21	0.12
	4.00	4.04	3.95
		(Added as $HgCl_2$)	
5 g Wheat (contaminated with seed grains)	0.00	0.18	—
	1.11	1.30	1.12
		(Added as $HgCl_2$)	
5 g Sucrose	0.00	0.00	—
	0.10	0.10	0.10
	0.50	0.47	0.47

For samples of 5 g of cracked whole barley, 10 g of soil, and 18–22 g of turf cores containing 5 μg of mercury or less, the standard deviations of a single determination were 0.12, 0.15, and 0.23 μg, resp., using 2-cm cylindrical optical cells. Using 1 × 5 cm rectangular cuvettes and 5-g samples of sucrose containing 0–0.5 μg of mercury the standard deviation of a single determination was 0.05 μg.

SUMMARY

At room temperature, reduction with tin(II) and aeration are suitable for quantitative separation of microgram quantities of mercury(II) from sulfuric and nitric acid solutions over wide ranges of concentrations Mercury is concentrated during the separation, and is determined by a direct photometric dithizone procedure. This technique is applicable for 0.10 μg mercury per sample charge with a standard deviation for a single determination of 0.05 μg mercury in the 0 to 0.5 μg range.

RÉSUMÉ

Une méthode de concentration (par réduction et aération) est décrite en vue du dosage photométrique de traces de mercure, au moyen de dithizone.

ZUSAMMENFASSUNG

Beschreibung einer photometrischen Methode zur Bestimmung von Quecksilber in Spurenmengen mit Dithizon. Die Abtrennung aus sauren Lösungen erfolgt nach Zusatz von Zinn-(II)-chlorid mit Hilfe eines Luftstromes.

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RAPID COLORIMETRIC DETERMINATION OF MANGANESE IN WATERS CONTAINING IRON

A MODIFICATION OF THE FORMALDOXIME METHOD

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The formaldoxime method[1–3] for manganese in water has advantages in both accuracy and simplicity over the standard permanganate prodecure[4], in which the removal of interferences such as chlorides and other reducing substances is time-consuming. A disadvantage of the formaldoxime method is that iron interferes by forming a colored complex with the reagent. Although several modifications have been described to minimize interference from iron[2,3] none is applicable to waters containing much iron.

It was found in the present investigation that the formaldoxime complex of iron is rapidly decomposed by addition of EDTA and hydroxylamine while the manganese formaldoxime is very stable under these conditions. If EDTA is added before the formaldoxime reagent, neither manganese nor iron forms colored complex with formaldoxime.

EXPERIMENTAL

Apparatus

A spectrophotometer with a glass prism and a barrier layer cell was used in preparing the absorption curves. For other work, a photoelectric colorimeter with a 480-mμ interference filter was used. Matched 1-cm cells were used.

Reagents

Formaldoxime reagent. Dissolve 8 g of hydroxylamine hydrochloride in 100 ml of distilled water. Add 4 ml of formaldehyde solution (37% w/w) and dilute to 200 ml with distilled water.

Standard manganese solution. Dissolve 143.8 mg of potassium permanganate in 50 ml of water. Add 2 ml of concentrated sulfuric acid. Add a 10% solution of sodium bisulfite dropwise until the color of permanganate disappears. Boil to expel excess of sulfur dioxide, cool, and dilute to 1 l. This solution contains 50 mg Mn^{2+}/l.

Iron(III) solution (500 mg Fe/l). Dissolve 863.4 mg of $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$ in water containing 0.5 ml of concentrated sulfuric acid and dilute to 200 ml.

Iron(II) solution (500 mg Fe/l). Dissolve 702.1 mg of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in water containing 1 ml of concentrated sulfuric acid and dilute to 200 ml.

All the chemicals used were guaranteed grade chemicals supplied by Kanto Chemicals Co.

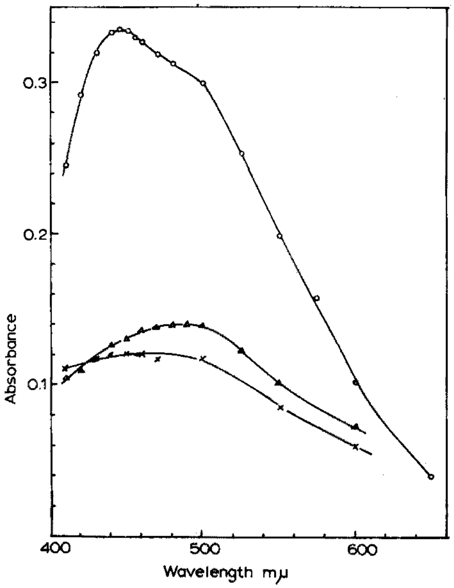

Fig. 1. Absorption curves of formaldoxime complexes. O—O—O Mn^{2+}, 1.82 mg/l; Δ—Δ—Δ Fe, 1.82 mg/l (added as Fe^{3+}); ×—×—× Fe, 1.77 mg/l (added as Fe^{2+}).

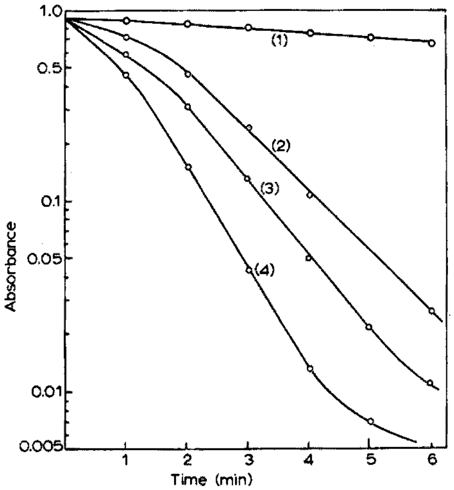

Fig. 2. Effect of hydroxylamine on the decolorization of formaldoxime. Fe^{3+}, 12.5 mg/l; temp. 16°. Volume of hydroxylamine added, (1) 0; (2) 1.0; (3) 1.5; (4) 2.0 ml.

Recommended procedure

To a 20-ml portion of water sample containing less than 3 mg/l of manganese, add 1 ml of formaldoxime reagent and 1 ml of 1 : 1 ammonia, stirring after each addition.

After at least 2 min, add 1 ml of *ca.* 0.1 *M* EDTA and 2 ml of 10% w/v hydroxylamine solution. When the iron formaldoxime has been decomposed (usually 10 min are required at ordinary temp.), measure the absorbance at a wavelength around 450 mμ.

DISCUSSION

Fig. 1 shows the absorption curves for the formaldoxime complexes of manganese and iron. The manganese–formaldoxime complex has an absorption maximum at about 450 mμ. Absorption curves for the iron–formaldoxime complex were obtained both with iron(III) and iron(II) and these curves were slightly different from each other. It is uncertain that the curves indicate the absorption curves of iron(III) and iron(II) formaldoxime respectively, because iron may undergo oxidation and reduction under the conditions of the measurement.

In order to determine the required volumes of hydroxylamine and EDTA solutions, the decolorization of iron formaldoxime prepared from iron(III) was studied by varying one component while keeping the other constant at the level given in the recommended procedure. Fig. 2 shows the effect of varying the concentration of hydroxylamine; at least 2 ml of 10% hydroxylamine are required for complete decomposition of iron formaldoxime within 10 min. The effects of various amounts of EDTA are shown in Table I; the quantity of 0.1 *M* EDTA added in excess of 0.5 ml has little effect on the rate of decomposition of the iron–formaldoxime complex.

TABLE I

EFFECT OF EDTA ON THE DECOLORIZATION OF IRON FORMALDOXIME

(16°; Fe^{3+} 12.5 mg/l)

Time (min)	*Absorbance at 480 mμ* EDTA *added*		
	0 ml	*0.5 ml*	*1.0 ml*
0	0.90	0.90	0.90
1	0.78	0.45	0.46
2	0.75	0.15	0.15
3	0.72	0.050	0.042
4	0.68	0.020	0.013
5	0.65	0.010	0.007
6	0.62	0.008	0.005
7	0.59	0.006	0.002
8		0.004	0.000

TABLE II

EFFECT OF IRON(II) AND (III) ON THE PROPOSED METHOD

(Mn^{2+} 2.5 mg/l)

Fe^{3+} added (mg/l)	*Absorbance*	*Fe^{2+} added (mg/l)*	*Absorbance*
0	0.357	0	0.357
12.5	0.353	12.5	0.350
25.0	0.350	25.0	0.355
37.5	0.350	37.5	0.360

Beer's law holds both at 480 (filter photometer) and at 450 mμ (prism photometer) over the range 0–3 mg of manganese per l.

From the results given in Table II, it is obvious that iron(III) and iron(II) in concentrations up to 25 mg/l have no effect on the determination.

SUMMARY

A rapid photometric method with formaldoxime is described for the determination of small amounts of manganese in waters containing iron. The iron formaldoxime formed is decomposed by addition of EDTA and hydroxylamine after development of the manganese–formaldoxime color. Beer's law holds up to 3 mg Mn/l. Up to 25 mg iron(II) or (III) per l can be tolerated.

RÉSUMÉ

Une méthode photométrique rapide est proposée pour le dosage de faibles quantités de manganèse, dans l'eau, en présence de fer. On utilise le formaldoxime comme réactif et on masque le fer au moyen d'EDTA et d'hydroxylamine.

ZUSAMMENFASSUNG

Beschreibung einer photometrischen Methode zur Bestimmung von geringen Mengen Mangan in eisenhaltigen Wässern mit Formaldoxim. Der störende Einfluss des Eisens wird durch Maskierung mit EDTA ausgeschaltet.

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BIS-CYCLOHEXANONE-OXALYLDIHYDRAZONE AS A SPECTROPHOTOMETRIC REAGENT FOR COBALT AND NICKEL

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Bis-cyclohexanone-oxalyldihydrazone forms a blue complex with copper ions and is used as a reagent for spectrophotometric analysis of this metal. It is highly selective for copper, which can be determined in presence of many other ions[1]. WETLESEN[2] claims, however, that large amounts of cobalt and nickel cause negative interference in this determination.

The present work was carried out in order to establish whether the negative interference is due to any complex formation between the reagent and cobalt or nickel ions, and probe the application of this reagent for the determination of ions other than copper.

EXPERIMENTAL

Apparatus

A Zeiss spectrophotometer, model PMQ II with 1.000 and 5.000 cm quartz cells was used for the determination of optical densities. A Beckman Zeromatic pH meter was used for pH measurements.

Reagents

All chemicals used were of reagent grade quality except for the bis-cyclohexanone-oxalyldihydrazone which was a product without specifications, obtained from Hopkin & Williams Ltd. Stock solutions of cobalt, nickel and copper were prepared by dissolving the appropriate amounts of $CoCl_2 \cdot 6\ H_2O$, $NiSO_4 \cdot 7\ H_2O$ and $CuSO_4 \cdot 5\ H_2O$ in water. The cobalt solution was standardized by titration with a standard EDTA solution, using murexide as indicator, the nickel solution was standardized by precipitation with dimethylglyoxime, and the copper solution was standardized by electrolysis. A 0.2% solution of bis-cyclohexanone-oxalyldihydrazone was prepared by dissolving 0.2 g reagent in 100 ml of 50% alcohol. An ammonia buffer of pH 9.5 was prepared by dissolving 54 g of ammonium chloride and 70 ml of ammonia (s.g. 0.9) in distilled water and diluting to 1 l.

Absorption curves

In alkaline solution the bis-cyclohexanone-oxalyldihydrazone forms yellow colours with cobalt and nickel ions and a blue colour with copper. The maximum absorbances

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are obtained at 292 mμ for cobalt, at 330 mμ for nickel and at 315 mμ and 600 mμ for copper. The absorption curves are given in Fig. 1.

The optical densities of all solutions were measured against reagent blanks prepared in the same way. The extinctions measured at 330 mμ and 600 mμ were constant for at least 30 min, but at 292 mμ they should be measured after 10 min. Moreover, it was found important to prepare the blank and the other solutions at the same time.

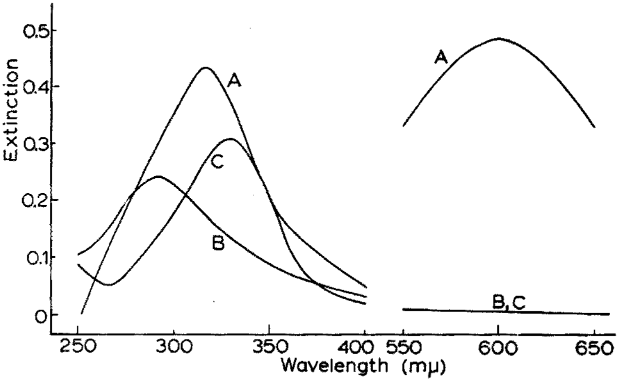

Fig. 1. Absorption curves of copper, cobalt and nickel complexes with bis-cyclohexanone-oxalyldihydrazone in ammonia buffer of pH 9.5 measured against a reagent blank. A 1.83 μg Cu per ml; B 2.18 μg Co per ml; C 2.06 μg Ni per ml.

Effect of pH

A number of solutions containing the same amounts of reagent and cobalt or nickel were prepared. The pH was varied by addition of ammonium chloride and ammonia. Above pH 9 the absorption was found to be nearly constant. The extinctions measured at 330 mμ are plotted against pH in Fig. 2. If the pH was adjusted with sodium hydroxide, the extinctions measured were less than those obtained with ammonia.

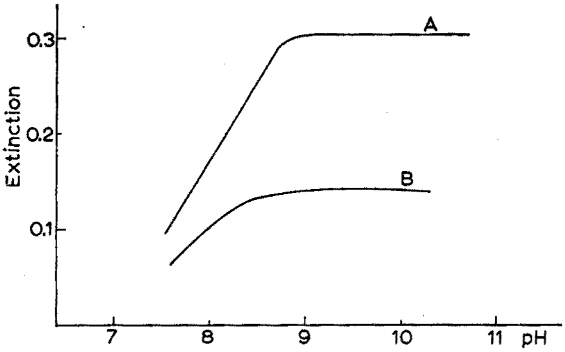

Fig. 2. Effect of pH on the absorption at 330 mμ of the nickel (A) and the cobalt (B) complex with bis-cyclohexanone-oxalyldihydrazone.

Beer's law

For the verification of Beer's law the optical densities were measured for a number of cobalt and nickel solutions. The solutions were prepared by addition of 10 ml of the bis-cyclohexanone-oxalyldihydrazone reagent and 10 ml of the ammonia buffer to different amounts of the standard cobalt or nickel solutions followed by dilution to 100 ml. The optical densities were measured at 292 mμ for the cobalt solutions and at 330 mμ for the nickel solutions.

The cobalt–bis-cyclohexanone-oxalyldihydrazone system was found to obey Beer's law in the concentration range 10^{-4} to $5 \cdot 10^{-3}$ mg of cobalt per ml. The molar extinction coefficient of the cobalt complex at 292 mμ is 6500.

The nickel complex obeys Beer's law in the concentration range 10^{-4} to $7 \cdot 10^{-3}$ mg of nickel per ml. The molar extinction coefficient at 330 mμ is 8750.

Determination of Cu, Co and Ni in presence of each other

The reaction between the reagent and mixtures of cobalt, nickel and copper was studied; 20 ml of the bis-cyclohexanone-oxalyldihydrazone reagent and 10 ml of the ammonia buffer were added to different amounts of the metal solutions and the mixture was diluted to 100 ml. The extinctions were measured against reagent blanks prepared at the same time, at 292 mμ, 330 mμ and 600 mμ. The results are given in Table I.

TABLE I

EXTINCTION DATA FOR MIXTURES OF Cu, Co AND Ni WITH BIS-CYCLOHEXANONE-OXALYLDIHYDRAZONE

Amounts (in μg) of metal added per ml	*Theoretical extinctions*			*Measured extinctions*		
	292 mμ	*330 mμ*	*600 mμ*	*292 mμ*	*330 mμ*	*600 mμ*
2.18 Co	0.240	0.128	—			
1.83 Cu	0.280	0.365	0.460	0.520	0.493	0.462
3.63 Co	0.400	0.213	—			
0.92 Cu	0.140	0.182	0.230	0.538	0.400	0.228
2.06 Ni	0.130	0.307	—			
1.83 Cu	0.280	0.365	0.460	0.398	0.671	0.460
3.09 Ni	0.195	0.462	—			
4.58 Cu	0.700	0.912	1.150	0.850	1.372	1.148
2.06 Ni	0.130	0.307	—			
2.18 Co	0.240	0.128	—	0.350	0.440	0
1.83 Cu	0.280	0.365	0.460			
2.06 Ni	0.130	0.307	—	0.528	0.753	0.455
1.45 Co	0.160	0.086	—			

DISCUSSION

The experimental work shows that cobalt and nickel ions form complexes with bis-cyclohexanone-oxalyldihydrazone in alkaline solution. This is why cobalt and nickel cause negative interference in the determination of copper as stated by WETLESEN[2].

Besides forming these complexes the reagent is slowly decomposed in alkaline solution[3] and after some time there is insufficient reagent present to form complexes with all the copper, cobalt and nickel in the solution. This negative interference may be avoided by adding enough reagent to complex all the copper, cobalt and nickel present and to allow for the destruction of the reagent. A 15-fold molar excess of reagent proved satisfactory in the present work.

Both the cobalt and the nickel complexes obey Beer's law. Thus it is possible to determine cobalt or nickel with this reagent. Measurements of the extinctions at 292 mμ and 330 mμ give the possibility of estimating cobalt and nickel in the presence of each other (see table I).

Neither the cobalt nor the nickel complex contributes to the optical density at 600 mμ where the blue copper complex has maximum absorbance. It is possible to correct for the absorption at 292 mμ and at 330 mμ caused by the copper complex and therefore one can determine both copper and cobalt or copper and nickel in presence of each other. A determination of copper, nickel and cobalt may be done in a mixture, but the determinations of cobalt and nickel are not very accurate.

Iron, manganese, chromium and lead gave precipitates with the reagent at pH 9.5. Zinc and arsenic did not interfere.

The advantage of this reagent compared with other reagents is that copper, cobalt and nickel can be determined in presence of each other with the same reagent and in the same solution. The complexes are easily prepared, and no extraction or any form of exchange–absorption is necessary so that an analysis can be made is a short time.

SUMMARY

Cobalt and nickel ions form yellow complexes with bis-cyclohexanone-oxalyldihydrazone in alkaline solutions. These complexes have maximum absorbances at 292 mμ and 330 mμ, respectively. The cobalt complex obeys Beer's law from 10^{-4} to $5 \cdot 10^{-3}$ mg cobalt per ml and the molar extinction coefficient is 6500. The nickel complex obeys Beer's law from 10^{-4} to $7 \cdot 10^{-3}$ mg nickel per ml and the molar extinction coefficient is 8750. Cobalt and copper or nickel and copper can be determined in presence of each other.

RÉSUMÉ

Le cobalt et le nickel réagissent avec la bis-cyclohexanone-oxalyldihydrazone, en donnant des complexes jaunes avec maxima d'absorption respectifs à 292 mμ et 330 mμ. Le cobalt et le nickel peuvent être ainsi dosés en présence de cuivre.

ZUSAMMENFASSUNG

Nickel und Kobalt bilden mit Bis-cyclohexanon-oxalyldihydrazon gelb gefärbte Komplexe, die sich zur spektrophotometrischen Bestimmung dieser Metalle, auch in Gegenwart von Kupfer, eignen. Die Absorptionsmaxima und die molaren Extinktionskoeffizienten werden angegeben.

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SELECTIVE SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH EDTA

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Chelating agents are principally used in quantitative inorganic analysis for titrimetric or spectrophotometric determinations and for masking. Spectrophotometric methods have advantages in selectivity over titrimetric procedures because only those metal ions that form chelates absorbing light at the selected wavelength interfere. However, many interferences may still occur and many physical and chemical methods for the separation of the interfering elements have been developed. Recently, some spectrophotometric determinations of metal ions with chelating agents have been described in which the separations of metal ions that would interfere with the determination under normal conditions are avoided. Such methods can be summarized as follows: two sample solutions of exactly the same composition are allowed to react with the chelating agent, and to one of the solutions is added a reagent which reacts with the required metal chelate but not with the metal chelates that normally interfere. The concentration of the required metal is then directly related to the difference in extinction, ΔE, of the two solutions by the equation

$$\Delta E = \Delta \varepsilon c d$$

where $\Delta \varepsilon$ is the difference in the molar extinction value of the two compounds of the element considered, c is the concentration and d is the cell length. This relation of course assumes the validity of Beer's law for these compounds. The necessary conditions for such determinations have been discussed[1] and will be briefly mentioned in the discussion below with reference to the present experimental results.

In the present paper a determination of iron in the presence of cobalt, chromium, copper and nickel is described. A preliminary note has already been published[1]. The determination is based on a spectrophotometric method developed by SCHNEIDER AND JANKO[2], in which the addition of hydrogen peroxide to an ammoniacal solution of the iron(III)–EDTA chelate results in the formation of a deep violet compound with maximum absorption at 515 mμ. This method has already been used to determine iron(III) after prior separation as iron(III) hydroxide[3]. A molecular extinction value of 520 was found for the violet complex at 515 mμ, with a Unicam SP 500 spectrophotometer[3].

However, it has been found unnecessary to separate iron(III) from the interfering EDTA chelates of cobalt, chromium, copper and nickel, which also absorb at a wavelength of 515 mμ. It is possible to determine the iron(III) from the difference between the extinctions at 515 mμ of two ammoniacal (pH 10–10.5) solutions, one of which contains hydrogen peroxide and the other does not. The molar extinction value of the iron(III)–EDTA chelate at 515 mμ in an ammonia–ammonium chloride buffer of pH 10 is about 20.

The EDTA chelates of nickel(II) and copper(II) are formed immediately on addition of EDTA to the solution. The extinction value of the nickel-EDTA complex is not affected by hydrogen peroxide. Therefore iron(III) can be determined in the presence of nickel(II) by taking 2 aliquots of the sample solution to be analysed, and adding EDTA and buffer solutions to both aliquots, but hydrogen peroxide only to one; the solutions are then diluted to the same volume. The extinction of the solution containing hydrogen peroxide is measured at 515 mμ against the other solution as reference. The iron concentration in the measuring flasks can then be calculated from

$$\Delta E = \Delta \varepsilon c d$$

where $\Delta\varepsilon$ is the difference between the molar extinction values of the violet iron(III)-H_2O_2-EDTA complex and the yellow iron(III)-EDTA complex at 515 mμ; $\Delta\varepsilon$ has been found to be about 500 (see above). The extent to which nickel(II) interferes when the extinction of the iron(III)-EDTA-H_2O_2 complex is measured against water, is evident from the fact that the molar extinction value of the nickel(II)-EDTA complex is 2.6 under the experimental conditions.

The molar extinction of the copper-EDTA complex under the experimental conditions is 0.6 when no hydrogen peroxide is present; hydrogen peroxide causes it to increase to 0.9. The difference $\Delta\varepsilon$ between these values is small, hence copper(II) will cause perceptible positive errors only when present in an amount more than the tenfold that of iron (see exp. 9 in Table I). When a 20-fold amount of copper(II) is present the error is about 1%.

Chromium(III) forms an EDTA complex very slowly at room temperature[4]. Heating for 30 min at a pH value of 3–4 is required for quantitative formation of the chelate. Moreover, at pH 10 the chromium(III)-EDTA chelate reacts slowly with hydrogen peroxide to form chromate and in some cases perchromate. This decomposition causes errors in the iron determination, because it is attended by a considerable change in the extinction at 515 mμ. When the chromium(III) content of the solution is small, the error is negligible, if the extinction is measured immediately after addition of hydrogen peroxide and dilution. The molar extinction value of the chromium(III)-EDTA chelate under the experimental conditions is about 65.

Another difficulty occurs when iron has to be determined in the presence of cobalt(II). As is obvious from the basis of this method, interfering metals must be present in exactly the same state in the solutions with and without hydrogen peroxide. However, cobalt(II) in presence of hydrogen peroxide and chelating agents such as EDTA tends to form cobalt(III), hence it is necessary to oxidise cobalt(II) to cobalt(III) before the two aliquots of the sample solution are taken. Nitrous acid or bromine in acid solution is the best reagent for the oxidation[5]; the absorption spectrum of the cobalt(III)-EDTA chelate is not affected by hydrogen peroxide at pH 10. In the present method, the acidic solution of cobalt(II) and iron(III) is heated with nitrous acid for 2 h. If chromium(III) is present, its EDTA chelate is formed during this time. When the oxidation is complete the analysis is continued in the usual way, depending on whether or not chromium(III) is present. The molar extinction value of the cobalt(III)-EDTA complex under the experimental conditions is about 260.

The composition of the violet complex formed by hydrogen peroxide with the iron(III)-EDTA complex in ammoniacal solution is not yet clear. We have proved that the presence of ammonia is essential for the development of the violet complex. In absence of ammonia, *e.g.* with a borax buffer, the increase in the extinction of the iron(III)-EDTA complex on addition of hydrogen peroxide is much smaller. The extinction at 515 mμ depends on the amounts of hydrogen peroxide and buffer added. When a large excess of these reagents is added, the effect is negligible for hydrogen peroxide but still measurable for the buffer. It is therefore necessary to add large excesses of hydrogen peroxide and buffer and to add the same amount of buffer as in the calibration experiments. The reproducibility under these conditions is very good. Investigations on the behaviour and the composition of the Fe(III)-EDTA-H_2O_2-NH_3 complex are in progress.

EXPERIMENTAL

Reagents and apparatus

All reagents were of analytical grade and metal-free water (prepared by ion exchange) was used. Buffer solution to give a final pH of 10 was prepared by dissolving 7 g of ammonium chloride and 57 ml of 25% ammonia in water and diluting to 100 ml. Interfering elements were added as chloride, nitrate or sulphate. A Unicam SP 500 spectrophotometer was used for all extinction measurements.

PROCEDURE

The slightly acidic sample solution may contain 0.2–5 mg of iron. Add EDTA in an amount twice that necessary to complex the metal ions present; addition of more than this may cause errors when cobalt is present. If cobalt(II) is present, oxidise it by adding 0.5 g of sodium nitrite and 1 ml of glacial acetic acid and heating for 2 h in a boiling water bath. If chromium(III) is present heat the sample solution containing EDTA for 30 min in a boiling water bath to ensure complete formation of the complex. This is not necessary when cobalt is present because the chromium(III)-EDTA complex is then formed during the oxidation of the cobalt(II).

Dilute the resulting solution to 25 ml in a measuring flask. Transfer two 10-ml aliquots to two other 25-ml measuring flasks. Add 10 ml of buffer solution to each flask. The pH of the solution should be between 10 and 10.5. Dilute one of the solutions to the mark and fill a cell of the spectrophotometer. Add 2 ml of 30% hydrogen peroxide to the other flask. Dilute to the mark immediately and measure the extinction of this solution against the first solution as reference.

Determine the iron content of the sample from a calibration curve obtained with the same amounts of the reagents.

Immediate measurement of the extinction is essential only when chromium is present but it is better always to measure as quickly as possible because oxygen bubbles may be formed from hydrogen peroxide after some time.

RESULTS

Table I shows some of the results obtained by this procedure. Only experiments in which large amounts of other elements were present are included. Determinations of iron in presence of similar amounts of other metals gave correct results without modification. The procedure was also applied to the analysis of some standard alloys. A quantity of the alloy corresponding to 0.4 mg of iron was dissolved in an appropriate acid or acid mixture and the excess of acid was removed by evaporation; any precipitate (*e.g.* of stannic oxide or silica) was removed by centrifugation. The resulting solution was treated as described above.

TABLE I

DETERMINATIONS OF IRON IN PRESENCE OF OTHER METALS

Number	*Other elements present, mg*							*Iron, mg*		*Error*
	Cr	*Co*	*Ni*	*Cu*	*Mn*	*Zn*	*Al*	*present*	*found*	*in %*
1	—	—	20	20	—	—	—	1.004	1.006	+0.2
2	1	—	—	—	—	—	—	1.004	0.999	—0.5
3	4	—	—	—	—	—	—	1.004	1.024	+2.0
4	—	1	—	—	—	—	—	1.004	1.002	—0.2
5a	—	10	—	—	—	—	—	1.004	0.957	—4.7
5b	—	10	—	—	—	—	—	1.004	1.001	—0.3
6a	—	15	—	—	—	—	—	1.004	0.900	—10
6b	—	15	—	—	—	—	—	1.004	0.979	—2.5
7	—	10	10	10	10	10	—	1.004	1.004	0
8	—	10	10	10	10	10	10	1.004	0.997	—0.7
9	—	—	20	20	—	—	—	0.401	0.417	+4.0
10	4	4	4	4	—	—	—	0.401	0.402	+0.2
11	4	4	20	8	—	—	—	0.401	0.406	+1.2
12	4	4	4	4	4	4	4	0.401	0.50	+25
13	4	—	4	4	4	4	4	0.401	0.408	+1.7
14	4	4	4	4	4	4	—	0.401	0.399	—0.5
15	4	4	4	4	4	—	4	0.401	0.48	+20
16	4	4	4	4	—	4	4	0.401	0.52	+30
17	4	4	4	4	4	4	4	0.401	0.405	+1.0
18	—	—	50	—	—	—	—	0.401	0.406	+1.2
19	4	—	—	—	—	—	—	0.200	0.202	+1.0
20	2	—	2	2	2	2	2	0.200	0.202	+1.0
21	1	1	1	1	1	1	1	0.200	0.195	—2.5
22	1	1	1	1	1	1	—	0.200	0.196	—2.0
23	—	—	40	—	—	—	—	0.050	0.054	+8.0
24	—	—	2	2	—	—	—	0.050	0.052	+4.0
25	0.5	0.5	1	1	1	1	1	0.050	0.050	0

The following results were obtained for standard alloys.

(*a*) N.B.S. 164, containing 2.52% Fe and about 64% Cu, 22% Zn, 6% Al, 5% Mn and 1% Sn. Two determinations gave values of 2.52% and 2.55% iron.

(*b*) B.C.S. 180/1, containing 0.82% Fe and about 67% Cu, 31% Ni and 1% Mn. Values of 0.85% and 0.85% iron were found.

(*c*) N.B.S. 85b, containing 0.24% Fe and about 93% Al, 4% Cu, 1.5% Mg, 0.6% Mn and 0.2% Cr. Values of 0.242% and 0.243% iron were found.

(*d*) B.C.S. 233, containing 51.15% Fe and about 24% Co, 11% Ni, 7% Al, 5% Cu and 0.8% Ti. A value of 51.3% iron was found.

Notes

(*1*) The time required for the determination of iron in presence of nickel, copper and other elements, not including chromium or cobalt, is not more than 10 min.

(*2*) The EDTA complexes of aluminium, zinc and manganese do not absorb light at 515 mμ, but these elements were included to prove that there were no secondary effects.

(*3*) Irrespective of the amount of iron present, the amount of chromium should not exceed 4 mg. Therefore only a few determinations of more than 0.4 mg of iron in presence of chromium are included in Table I. When relatively large amounts of chromium are present (1-4 mg), 1 ml instead of 2 ml of hydrogen peroxide is added, to avoid errors from decomposition of the chromium(III)-EDTA complex.

(*4*) When large amounts of cobalt are present, some difficulties may occur. The cobalt(III)-EDTA complex has a large molar extinction coefficient under the experimental conditions. With increasing amounts of cobalt it is therefore necessary to increase the slit width of the monochromator, which introduces scattering light. This is illustrated in Table I from experiments 5*a*, 5*b*, 6*a* and 6*b*. The experiments *a* were carried out with 4-cm cells, corresponding to $\Delta E = 0.580$ and experiments *b* were done with 1-cm cells, corresponding to $\Delta E = 0.145$. The slit widths in these four experiments were 0.6, 0.07, 1.4 and 0.1 mm resp. These and other results showed that iron could be determined with this particular instrument in presence of tenfold amounts of cobalt provided that the iron concentration and the cell length were such that ΔE lay between 0.1 and 0.2.

When very large amounts of other metals are present, difficulties may occur from decomposition of hydrogen peroxide which may cause oxygen evolution or, worse, incomplete oxidation of cobalt(II) (experiments 12, 15, 16); positive errors are found in both cases. When the oxidation of cobalt(II) is incomplete, after heating for 2 h with nitrous acid, it can be completed by allowing the solution to stand overnight; this was done in experiments 5, 6, 7, 8, 17.

(*5*) When small iron contents must be analysed, the best results are obtained by taking an amount of the sample corresponding to 0.2-0.4 mg of iron and measuring in a 4-cm cell. The concentration of the other elements is then as small as possible and the interferences mentioned in the previous notes are minimised.

(*6*) When errors of more than a few percent can be tolerated as little as 50 μg of iron, corresponding to $\Delta E = 0.035$ in a 4-cm cell, can be determined with reasonable accuracy (experiments 23, 24, 25).

(*7*) Iron(II), if present, is oxidised to the trivalent state as soon as EDTA is added, simply by shaking the solution in an air atmosphere.

DISCUSSION

The general principle of the iron determination described here should be applicable to other spectrophotometric determinations of metals in presence of interfering elements. In general, the most promising results can be expected when one of the molar extinction values involved in $\Delta\varepsilon$ is large and the other is small, as is the case with the present iron determination. To avoid large slit openings when other complexes present absorb considerably at the selected wavelength, the determinations should be carried out with such concentrations of the required element that ΔE is between 0.1 and 0.2.

ACKNOWLEDGEMENT

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SUMMARY

A spectrophotometric determination of iron as its iron(III)-EDTA-H_2O_2-NH_3 complex is described; up to 10-fold amounts of metals that form EDTA complexes absorbing at the same wavelength do not interfere because hydrogen peroxide reacts with the iron(III)-EDTA complex but does not affect the EDTA complexes of copper(II), nickel(II), cobalt(III) and chromium(III).

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique du fer(III) au moyen d'EDTA sans qu'il soit nécessaire de séparer le nickel, le chrome, le cobalt et le cuivre.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Eisen-(III) mit Hilfe von EDTA ohne Abtrennung von Nickel, Chrom, Kobalt und Kupfer.

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POLARIMETRIC DETERMINATION OF MALIC ACID, TARTARIC ACID, MANNITOL AND SORBITOL IN THE PRESENCE OF OTHER OPTICALLY ACTIVE COMPOUNDS

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It has been known for a long time[1] that certain compounds such as tartaric, malic and mandelic acids, mannitol, sorbitol, arabitol, etc. form complexes with molybdic acid which have optical rotations different from those of the compounds alone. These complexes have been thoroughly investigated by many authors and several attempts have been made to use the complex formation for the quantitative polarimetric determination of one or more of the mentioned organic compounds[2-10].

Methods for the determination of malic and tartaric acids, mannitol and sorbitol in the presence of other optically active compounds were needed in this laboratory. After studies of the literature and a few experiments it appeared that the most favourable conditions for analytical procedures had not yet been sufficiently elucidated and the investigations reported below were therefore carried out.

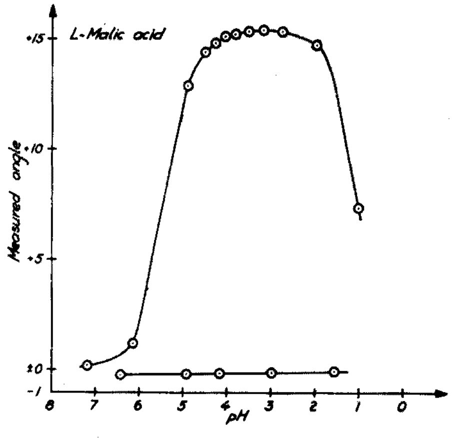

Fig. 1. Optical rotation of *l*-malic acid-molybdate (upper curve) and of *l*-malic acid alone (lower curve) at different acidities.

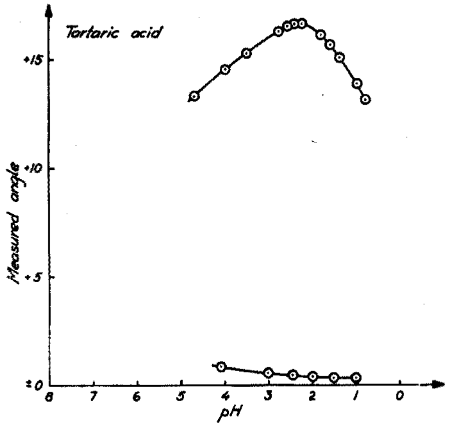

Fig. 2. Optical rotation of tartaric acid-molybdate (upper curve) and of tartaric acid alone (lower curve) at different acidities.

Figs. 1–4 show the optical rotations of some of the mentioned compounds at different acidities with and without an excess of molybdate. It can be seen that the rotations of the solutions without molybdate vary very little with changes of the acidity in the investigated range. The curves of rotation of the molybdate-containing solutions show well developed maxima.

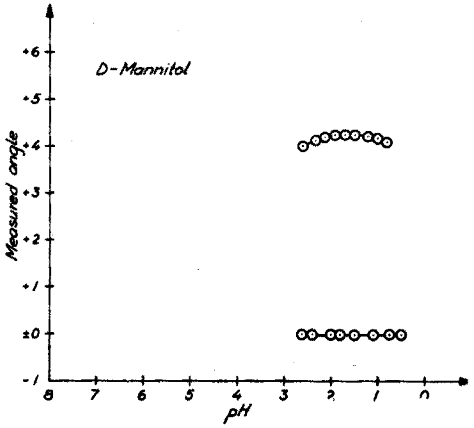

Fig. 3. Optical rotation of mannitol-molybdate (upper curve) and of mannitol alone (lower curve) at different acidities.

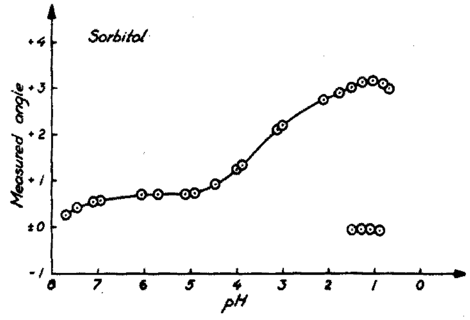

Fig. 4. Optical rotation of sorbitol-molybdate (upper curve) and of sorbitol alone (lower curve) at different acidities.

Standard curves of the compounds to be determined are given in Figs. 5–8. The curves show the differences in rotation obtained with and without molybdate at the acidity of the maxima from Figs. 1–4. The standard curves are straight lines. They have rather sharp breaks at the points where the amount of molybdate used becomes insufficient.

A small amount of sodium nitrite was added to every solution in order to prevent the reduction of molybdate.

A number of measurements were made in the presence of compounds which could

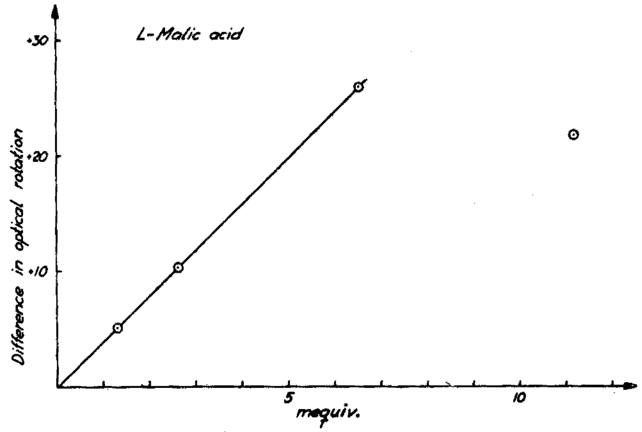

Fig. 5. Standard curve of malic acid.

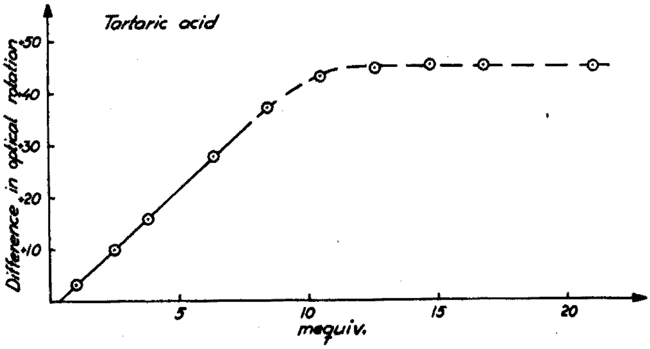

Fig. 6. Standard curve of tartaric acid.

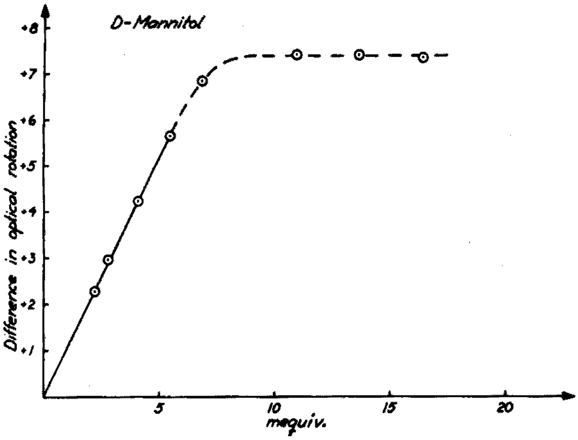

Fig. 7. Standard curve of mannitol.

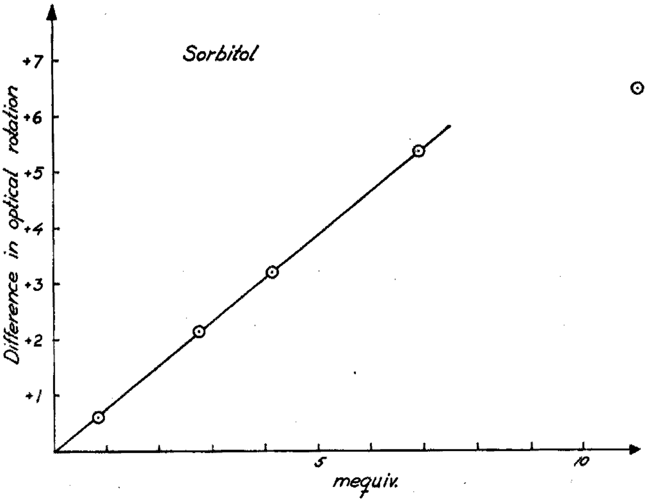

Fig. 8. Standard curve of sorbitol.

be suspected to interfere. The results given in Tables I and II show that reasonable amounts of fructose, galactose, glucose, lactose, mannose, sorbose and dextran do not interfere appreciably with the determination of sorbitol and tartrate. There is no reason to suspect that they would interfere in the determination of the other compounds.

TABLE I

TESTS FOR INTERFERENCE

The tested compound was added to two 50-ml measuring flasks with 750 mg of sorbitol. All was dissolved in water. 1 ml of aqueous 2.5% solution of sodium nitrite was added to each flask and to one of the flasks 20 ml of 17.4% sodium molybdate was added. Water was added to 45 ml and pH was adjusted to 1.2 in both flasks. The volume was made up to the mark and the optical rotation measured in 2-dm cuvettes.

Tested compound	*Read angle of rotation*		*Difference between angles*	*Recovery of sorbitol (%)*
	with molybdate	*without molybdate*		
—	3.14	359.92	3.22	
—	3.14	359.94	3.20	
0.40 g dextran	6.10	2.93	3.17	98.8
0.40 g fructose	1.70	358.53	3.17	98.8
0.40 g galactose	4.42	1.20	3.22	100.3
0.40 g glucose	3.90	0.70	3.20	99.7
0.40 g lactose	4.00	0.78	3.22	100.3
0.40 g mannose	3.46	0.16	3.30	102.8
0.40 g sorbose	2.46	359.32	3.14	97.8
0.40 g fructose + 0.40 g glucose	2.50	359.30	3.20	99.7

TABLE II

TESTS FOR INTERFERENCE

Procedure as in Table I, except that sodium tartrate, $Na_2C_4H_4O_6 \cdot 2\,H_2O$ was used instead of sorbitol and pH adjusted to 2.35.

Tested compound	*Read angle of rotation*		*Difference between angles*	*Recovery of tartrate (%)*
	with molybdate	*without molybdate*		
—	16.02	0.41	15.61	
—	15.98	0.43	15.55	
0.40 g dextran	19.15	3.38	15.77	101.2
0.40 g fructose	14.75	359.01	15.74	101.0
0.40 g galactose	17.59	1.68	15.91	102.1
0.40 g glucose	16.69	1.16	15.53	99.7
0.40 g lactose	16.91	1.27	15.64	100.4
0.40 g mannose	16.49	0.63	15.86	101.8
0.40 g sorbose	15.68	359.74	15.94	102.3

EXPERIMENTAL

Reagents

Sodium molybdate. 17.4 g of $Na_2MoO_4 \cdot 2\,H_2O$ are dissolved in water and diluted to 100 ml.

Sodium nitrite. 2.5 g are dissolved in water and diluted to 100 ml.

Procedure

Equal amounts of the sample are introduced into two 50-ml measuring flasks and 1 ml of sodium nitrite solution is added to each flask. 20 ml of sodium molybdate solution are added to one of the flasks and the contents of both flasks are diluted to about 45 ml. By means of a pH-meter, their acidity is adjusted with concentrated hydrochloric acid to the acidity which is optimal for the compound to be determined *i.e.* the pH values of the maxima of the curves in Figs. 1–4.

The solutions are diluted to volume and their optical rotations are measured. The content of the compound to be determined is then calculated from the difference in rotation of the 2 flasks using a standard curve or a factor.

The following compounds were used for the results shown in Figs. 1–4:

Sodium tartrate. 12.036 g of $Na_2C_4H_4O_6 \cdot 2\,H_2O$(C.P., moisture content including crystal water 15.57%; J. T. Baker, Phillipsburg, N.J., U.S.A., lot 72045) were dissolved in water and diluted to 200 ml.

l-Malic acid. 7.014 g of $HOOC.CHOHCH_2.COOH$ (C.P., moisture content 1.48%; Pfanstiehl Lab. Inc., Waukegan, Ill., U.S.A.) were dissolved in water and diluted to 200 ml.

d-Mannitol. 10.000 g of *d*-mannitol (0170–15 C.P., moisture content 0.00%; Difco, Detroit, Mich., U.S.A.) were dissolved in water and diluted to 200 ml.

d-Sorbitol. 12.500 g of *d*-sorbitol (C.P., moisture content 0.49%; Pfanstiehl Lab. Inc.) were dissolved in water and diluted to 250 ml.

15 ml of these solutions were pipetted into 50-ml measuring flasks and treated according to the procedure given above with the exception that different pairs of flasks containing the same organic compound were adjusted to different acidities. The rotations were read in 20-cm tubes at 20° using sodium light. They are directly given in the diagrams.

For the results shown in Figs. 5–8, different volumes of the solutions of malic and tartaric acids, mannitol and sorbitol were pipetted and treated according to the procedure given above. The pH values used were 3.20 for malic acid, 2.35 for tartaric acid, 1.75 for mannitol, and 1.20 for sorbitol. Measurements were made in 20-cm tubes at 20° in sodium light.

The results shown in Tables I and II were obtained with the following compounds:

Dextran (Dextran 1072, Pharmacia, Uppsala, Sweden; average molecular weight 72000),

Levulose (D(—)Levulose, C.P. Special, Pfanstiehl Lab. Inc., Waukegan, Ill., U.S.A.),

Galactose (D(+)Galactose, Puriss., Merck, Darmstadt, Germany),

Glucose, Dextrose (Crystal, $C_6H_{12}O_6 \cdot H_2O$, J.T. Baker, Phillipsburg, N.J., U.S.A., lot 2944),

Lactose, D-Mannose (for bacteriological use, Pfanstiehl Lab. Inc., Waukegan, Ill., U.S.A.),

Sorbose (Dr. F. Jonas Co., New York, U.S.A.).

15 ml of the solutions given under Figs. 1–4 were pipetted into pairs of 50-ml measuring flasks along with solutions of the compounds to be tested for interference. They were then analyzed according to the analytical method given above.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. Adolf Berggren for interest and valuable suggestions and to AB Pharmacia, Uppsala, for generous support of the work.

SUMMARY

Optically active malic and tartaric acids, mannitol and sorbitol can be determined in the presence of other optically active compounds by measuring the difference in optical rotation of their solutions with and without molybdate. The optimal pH-values for the determinations have been established and procedures and standard curves are given.

RÉSUMÉ

Les auteurs ont mis au point une méthode de dosage polarimétrique pour les acides malique, tartarique, le mannitol et le sorbitol, en présence d'autres substances optiquement actives.

ZUSAMMENFASSUNG

Beschreibung einer polarimetrischen Methode zur Bestimmung von Aepfelsäure, Weinsäure, Mannitol und Sorbitol neben anderen optisch aktiven Substanzen.

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AMPEROMETRIC TITRATION OF COPPER IN BRASS

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Several methods for the amperometric determination of copper have been reported in the literature. KALVODA AND ZÝKA[1] reported a procedure using potassium ferrocyanide which was applicable to the relatively concentrated solutions of 10^{-1}–10^{-3} M copper. LIBERTI AND DE CESARIS[2] titrated copper(I) with potassium thiocyanate in the concentration range of 10^{-2}–10^{-3} M with 1% accuracy. KOLTHOFF AND LANGER[3] titrated copper amperometrically with α-benzoinoxime (cupron) but the solubility of the precipitate and the interferences limit the applicability of the method. The relative instability of cupferron makes this reagent suggested by KOLTHOFF AND LIBERTI[4] less desirable for amperometric titrations. Several other methods[5–9] suggested for the amperometric determination of copper are of general interest in this field. KHADEEV AND ZHDANOV[10] have determined copper in brass by titrating copper(I) with potassium thiocyanate using a rotating platinum electrode.

BILLMAN *et al.*[11] have reported the gravimetric determination of copper with *o*-(*p*-tolylsulfonamido)aniline. The determination of copper in brass by this method did not require any prior separation. The extension of this procedure to the amperometric determination discussed in this paper reduced the time for a given analysis without sacrifice in accuracy. A single determination requires a maximum of 25 min.

The cathodic polarographic wave of copper in tartrate media, using a dropping mercury electrode, is well defined. The titrant, *o*-(*p*-tolylsulfonamido)aniline, which quantitatively precipitates copper in tartrate media, is not electroactive in this supporting electrolyte. These facts form the basis for the direct titration of copper with *o*-(*p*-tolylsulfonamido)aniline (henceforth called T-sulfonamidine). The method described is simple and rapid, and is relatively free from interferences; large amounts of such metals as cadmium, zinc, and lead can be tolerated. The procedure has been satisfactorily applied to the direct determination of copper in a number of brass samples containing a wide variety of elements.

EXPERIMENTAL

Apparatus

The titrations were carried out in 180-ml Berzelius beakers using a Sargent-Heyrovsky polarograph, Model XII. A dropping mercury indicating electrode and a saturated calomel electrode, separated by a sintered glass plug were used for all titrations. pH measurements were made with a Beckman "Zeromatic" pH meter.

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* This work is taken in part from the senior independent study of Frederick G. Burton.

Chemicals and reagents

The T-sulfonamidine was obtained from General Chemical Consultants, Memphis, Tenn. A standard solution was prepared by dissolving 1.25 g of reagent in 200 ml of ethanol and 50 ml of water. The alcohol content should be 80% by volume to prevent precipitation of the T-sulfonamidine. The solution was stored in a brown bottle to prevent possible decomposition in daylight. It was standardized amperometrically against a copper sulfate pentahydrate solution in 0.2 *M* sodium tartrate buffer of pH 7–8.5. After the first 4 days, the titer of this solution did not change significantly over a four-week period (Table I). This 4% drop in the titer during the first 4 days, followed by a long period of stability, was reproducible and may be due to oxidation of the amine group by impurities in the solution.

TABLE I

STABILITY OF *o*-(*p*-TOLYLSULFONAMIDO)ANILINE SOLUTION

Time, days	*mg Cu/ml T-sulfonamidine*	*Dev. from mean titer, %*
0	2.04[a]	3.78
1	2.03	4.25
2	2.06	2.83
3	2.07[a]	2.36
4	2.10[a]	0.94
7	2.14	0.94
10	2.14	0.94
15	2.12	0.00
26	2.14	0.94
38	2.12	0.00
mean for days 4–38	2.12	

Average of two determinations. The others are single determinations.

A standard copper solution was prepared by dissolving 0.7 g of electrolytic copper in a minimum quantity of concentrated nitric acid, heating to destroy the excess acid, and diluting to 1 l with tartrate buffer. The T-sulfonamidine used for the brass analysis was standardized with this solution. All other chemicals were of reagent or C.P. grade, and used without further purification.

Amperometric titration procedure

The sample size should be adjusted so that the copper concentration is at least 0.1 m*M*. Volumes of 25–70 ml were suitable. Add sufficient sodium tartrate to make the test solution about 0.20 *M* in sodium tartrate and adjust the pH to about 7.5 with sodium hydroxide. Deaerate the solution with nitrogen for 2 min and adjust the drop time of the dropping mercury electrode to 3 sec. Apply a potential of —0.8 V to the dropping mercury electrode and adjust the galvanometer sensitivity to the value that gives the largest scale deflection for the titration. Gelatin should not be used to suppress the maximum since the copper chelate does not then precipitate quantitatively.

Add small volumes of titrant from a 10-ml buret in approximately 0.5-ml increments. A period of 0.5–3 min, usually 1 min, after each addition of titrant is required for the current to become constant. The extrapolation method was used to obtain the end-point from the plotted data.

Determination of copper in brass

Dissolve a weighed sample of brass in concentrated nitric acid. Heat the solution to remove the excess acid and remove meta-stannic acid by filtration through Whatman No. 2 paper. Dilute the solution to 1 l and take an aliquot containing 5–20 mg of copper. Dilute it to 50 ml with 0.2 M sodium tartrate and adjust the pH to 7.5 with 0.1 M sodium hydroxide. Titrate with T-sulfonamidine as previously described.

DISCUSSION

In order to determine the scope of application of this method, factors such as pH, copper concentration, and interfering ions were investigated. The current–potential curve of copper(II) in tartrate media showed a single wave with a slight maximum; the half-wave potential was −0.35 V *vs.* the saturated calomel electrode. The titrant, T-sulfonamidine, showed no reduction wave from 0 to −1.8 V *vs.* S.C.E. Stoichiometric addition of T-sulfonamidine to a copper solution eliminated its reduction wave. A potential of −0.8 V *vs.* the S.C.E. was chosen for the amperometric titration.

BILLMAN *et al.*[11] suggested a pH range of 6.2–8.5 for gravimetric work but their work was not concerned with the minute solubility of the precipitate. The present titration procedure gives similar results at pH values between 7.0 and 8.5 (Table II). The high result obtained below pH 7 may be due to the increased solubility of the precipitate in acidic media.

TABLE II

EFFECT OF pH ON TITRATION OF COPPER WITH T-SULFONAMIDINE[a]

pH	*Volume of T-sulfonamidine (ml)*	*Titer*	*Dev. from mean titer (%)*
6.6	3.48	1.82	9.05
7.1	3.16	2.01	0.0
7.5	3.16	2.01	0.0
8.0	3.15	2.02	0.5
8.5	3.17	2.00	0.5
9.2	2.95	2.16	7.15
mean of values (pH 7.1–8.5)		2.01	

[a] Each sample contained 3.18 mg of Cu diluted to 50 ml with 0.2 M sodium tartrate solution; the pH was adjusted with sodium hydroxide.

The optimum copper concentration was established by titrating copper(II) solutions of varying concentrations (Table III). Since at low concentrations the current comes to equilibrium very slowly, it is not feasible to titrate samples with copper contents lower than $1 \cdot 10^{-4}$ M. Volume corrections were required for titrations using more than 3 ml of titrant. A typical titration curve is shown in Fig. 1. The effect of the volume corrections may be seen from this graph.

Analytical applicability

The success of BILLMAN *et al.*[11] in the gravimetric determination of copper in brass suggested the extension of the titrimetric procedure to this alloy. Preliminary studies indicated that the presence of equal concentrations of cadmium, iron(III),

TABLE III

TITRATION OF COPPER WITH T-SULFONAMIDINE

$CuSO_4$(mM)	*T-Sulfonamidine required (mM)*[a] *Experimental*[b]	*Theoretical*	*% error*
0.1223	0.2452	0.2445	0.29
0.0612	0.1226	0.1223	0.25
0.036	0.0561	0.0612	8.33
0.00612	0.0127	0.0122	4.1[c]

[a] One mole of copper requires two moles of reagent.
[b] Average of 3 values.
[c] At this concentration the reagent was diluted ten-fold.

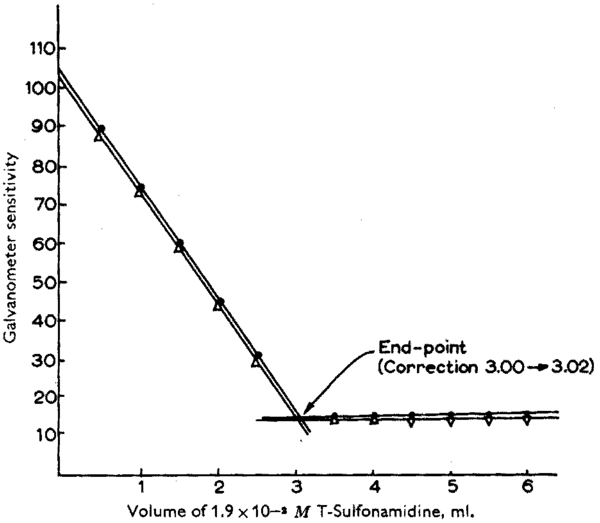

Fig. 1. Typical titration curve for amperometric titration of copper with T-sulfonamidine. Solution: 10 ml 0.005 M $CuSO_4 \cdot 5H_2O$, 40 ml 0.2 M sodium tartrate. Observed —△—△—△—; with volume corrections —●—●—●—.

lead, or zinc did not interfere with the copper determination. Cadmium and zinc did not interfere at concentrations ten times that of copper. The accuracy that was obtained indicated the possibility of a wide range of applications for this titration procedure.

The determination of copper in brass was studied. A series of brass samples containing many other elements was chosen. Table IV shows the constitution of the samples taken. The results of the amperometric titration of the copper in the brass samples with T-sulfonamidine are summarized in the bottom line of Table IV. It can be seen that the experimental values are in close agreement with the analyzed results of alloys in spite of the presence of many foreign ions.

SUMMARY

A direct amperometric titration of copper is described; *o*-(*p*-tolylsulfonamido)aniline serves as titrant. The optimum conditions are discussed and the method is applied to the analysis of copper in brass alloys.

TABLE IV

ANALYSIS OF VARIOUS SAMPLES IN WHICH COPPER WAS DETERMINED

(Values given as percentages)

Constituents	*Thorn Smith # 30*	*Thorn Smith # 54*	*NBS # 37E*	*NBS # 63C*
Cu present	59.30	84.04	69.61	80.48
Zn	37.81	1.452	27.85	0.093
Pb	0.1	8.590	1.00	9.35
Sn	Trace	5.737	1.00	9.03
Sb	—	—	—	0.52
Ni	Trace	—	0.53	0.32
P	—	—	—	0.145
S	—	—	—	0.060
As	—	—	—	0.023
Fe	1.22	—	0.004	0.0013
Al	1.15	—	—	—
Mn	0.35	—	—	—
Cu found	59.09	83.64	69.68[a]	80.54[a]

[a] Average of 3 determinations.

RÉSUMÉ

Une méthode ampérométrique est décrite pour le dosage du cuivre au moyen d'*o*-(*p*-tolylsulfonamido) aniline, pouvant être appliquée à l'analyse de cet élément dans les bronzes.

ZUSAMMENFASSUNG

Beschreibung einer amperometrischen Methode zur Bestimmung von Kupfer durch Titration mit *o*-(*p*-Tolylsulfonamido)-anilin.

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SEPARATION OF NIOBIUM AND TANTALUM WITH BENZO- AND PHENYLACETYLHYDROXAMIC ACIDS

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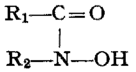
Since 1866, many attempts have been made to separate niobium and tantalum from each other but none of the methods proposed is rapid, precise and accurate from the analytical point of view. Solvent extraction and ion exchange are little better than precipitation in this respect. In recent publications[1–4], it has been shown that organic reagents capable of forming five-membered rings with oxygen as coordinating units are highly suitable for the determination of niobium and tantalum in presence of other common ions, and for their separation from each other and from titanium and zirconium. The reagents described are of the type



$$\begin{array}{l} R_1\text{—}C{=}O \\ \quad\;\;| \\ R_2\text{—}N\text{—}OH \end{array}$$

where R_1 = (OH)C_6H_4, C_6H_5, $C_6H_5CH{=}CH$, or C_9H_6N

and R_2 = C_6H_5, or H.

With changes in the electron density on the oxygen atom of the $C{=}O$ group and in the acidic character of the N—OH group, the reagents differ in their reactions as precipitants. N-Cinnamoyl-N-phenylhydroxylamine, N-cinnamoylhydroxamic acid[2], and quinaldinohydroxamic acid[3] completely precipitate both niobium and tantalum, but salicylhydroxamic acid[4], with its solubilising OH group, precipitates the elements only partially from tartrate, oxalate and citrate solutions, and not at all from hydrogen peroxide medium. N-Benzoyl-N-phenylhydroxylamine[1] allows a clear separation of highly pure niobium and tantalum from each other, even at ratios of 1 : 100 and 100 : 1, at pH 3.5–6.5 within 45 min. For gravimetric determinations, the niobium complex, which is stable up to 229°, can be weighed directly, but the tantalum complex recovered from the filtrate by acidification must be ignited to the oxide.

Benzohydroxamic and phenylacetylhydroxamic acids are ineffective in presence of tartrate and citrate, but precipitate tantalum from oxalate solution if it is made ammoniacal, digested for 30–40 min on a boiling water-bath and then adjusted to an acidic pH (4–6.4 for benzo- and 4.5–6.2 for phenylacetylhydroxamic acid). The former reagent, however, requires addition of about 1 g of ammonium chloride for complete formation and coagulation of the tantalum precipitate. The tantalum precipitates are of indefinite composition and must be ignited to the pentoxide for final weighing; the niobium in the filtrate can be recovered with quinaldinohydroxamic acid or N-benzoyl-N-phenylhydroxylamine.

With benzohydroxamic acid, a single precipitation gives complete separation for Nb : Ta ratios of up to 18 : 1; reprecipitation extends the range further. When tantalum is in excess, a single precipitation suffices even for Nb : Ta ratios of 1 : 20.

A single precipitation with phenylacetylhydroxamic acid is satisfactory only for Nb : Ta ratios of up to 8 : 1. Higher ratios necessitate reprecipitation. With tantalum in excess, single precipitation is quite accurate even for Nb : Ta ratios of 1 : 23. When the concentration of niobium is about twice that of tantalum, the pH for the separation can be extended up to 8.0; for higher concentrations of niobium reprecipitation is needed at this pH.

It seems likely that benzo- and phenylacetylhydroxamic acids, like tannic acid, form adsorption compounds with the hydrolytic products of tantalum, whereas niobium, which forms a more stable oxalate complex, remains in solution.

EXPERIMENTAL

The chemicals used were all of analytical reagent quality.

Standard solutions of niobium and tantalum were prepared by fusing the specpure pentoxides (Johnson, Matthey & Co.) with a ten-fold amount of potassium bisulphate, and extracting the clear cooled melt with a solution containing 5% (w/v) oxalic acid and 5% (v/v) sulphuric acid (s.g. 1.8). The niobium and tantalum contents of the solutions were determined by the N-benzoyl-N-phenylhydroxylamine method[1].

Benzohydroxamic acid (I) and phenylacetylhydroxamic acid (II) were prepared according to the method of BLATT[5]; an aqueous 2% solution of each was used.

For the wash solution, a solution of 0.5 g of ammonium chloride and 0.2 g of reagent per 100 ml was adjusted to pH 5–6 with ammonium acetate.

pH measurements were made with a Cambridge pH meter.

Procedures

An aliquot of the standard tantalum solution containing a ratio of oxalate to Ta_2O_5 of not more than 90 : 1 was diluted to 100 ml with water and mixed with about 10 ml of reagent (I) solution. The solution was made ammoniacal and digested on a boiling water-bath for 30–40 min. About 1 g of ammonium chloride was added and the solution was acidified with acetic acid; it was then allowed to cool to room temperature and the pH was adjusted with either dilute acetic acid or ammonia. The precipitate was filtered, washed with the wash solution till free from sulphate, dried and ignited to the pentoxide.

With phenylacetylhydroxamic acid, the procedure was exactly the same; in this case addition of ammonium chloride is less essential.

TABLE I

SEPARATION OF Nb AND Ta WITH BENZOHYDROXAMIC ACID

pH	*Ta_2O_5 taken (mg)*	*Ta_2O_5 found (mg)*	*Nb_2O_5 taken (mg)*	*Nb_2O_5 found (mg)*
4:0	16.2	16.2	11.6	11.7
4·5	5.06	5·1	93·0	93·0
5·5	81.0	80.8	3·9	4.0
5.8	5.0	7.6[a] 4.8[b]	108.8	106.2[a] 2.4[b] } 108.6
6.4	10.0	9.8	15.6	15.6

[a] = single precipitation; [b] = double precipitation.

TABLE II

SEPARATION OF Nb AND Ta WITH PHENYLACETYLHYDROXAMIC ACID

pH	*Ta_2O_5 taken (mg)*	*Ta_2O_5 found (mg)*	*Nb_2O_5 taken (mg*	*Nb_2O_5 found (mg)*
4.5	7.6	7.6	4.4	4.6
5.5	5.8	7.0[a] 5.8[b]	54.6	54.6
5.5	5.8	6.0	44.0	43.8
6.0	48.0	47.8	2.2	2.2
6.2	6.0	6.0	18.0	17.8
7.0	6.0	11.2[a] 5.8[b]	36.0	30.6[a] 5.2[b] } 35.8
8.0	6.0	6.6[a] 6.0[b]	18.0	17.8
8.0	6.0	6.0	13.8	13.8

[a] = single precipitation; [b] = double precipitation.

For reagent I, the optimum pH range was 4.0–6.4, and for reagent II, the range was 4.5–6.2.

For the separation of niobium and tantalum, the oxalate ion concentration should be not more than 90 times the amount of the mixed oxides. Tantalum was precipitated, washed and ignited as described above. In the filtrate and washings, niobium was determined either with quinaldinohydroxamic acid[3] or with N-benzoyl-N-phenylhydroxylamine[1]. Results are given in Tables I and II.

Titanium, zirconium, citrate and tartrate interfere seriously and must be absent. A large excess of oxalate tends to keep tantalum in solution.

SUMMARY

Benzohydroxamic acid (I) or phenylacetylhydroxamic acid (II) is suggested for the quantitative separation of tantalum from niobium in an oxalate solution. The tantalum precipitate must be ignited for weighing; niobium is determined in the filtrate with another reagent. The pH range for complete separation is 4.0–6.4 for I and 4.5–6.2 for II. Single precipitation is satisfactory for Nb:Ta ratios of 18:1 to 1:20 for I, and 8:1 to 1:23 for II. Titanium, zirconium, tartrate, citrate and a large excess of oxalate interfere.

RÉSUMÉ

L'acide benzohydroxamique et l'acide phénylacétylhydroxamique sont proposés pour la séparation du tantale d'avec le niobium en solution oxalique. Le tantale pourra ensuite être dosé par calcination du précipité obtenu et pesée de son oxyde Ta_2O_5. Quant au niobium, il sera dosé dans le filtrat à l'aide d'un autre réactif[1].

ZUSAMMENFASSUNG

Als Reagenzien zur Trennung von Tantal und Niob werden Benzhydroxamsäure und Phenylacetylhydroxamsäure vorgeschlagen. Mit Tantal entsteht eine Fällung, die abgetrennt und zu Ta_2O_5 verascht wird. Im Filtrat wird Niob mit einem anderen geeigneten Reagenz gefällt.

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SEPARATION AND GRAVIMETRIC DETERMINATION OF THORIUM AND CERIUM(IV) WITH VANILLIN

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The importance of thorium as nuclear reactor fuel has necessitated the development of methods for its purification and determination. The analytical chemistry of thorium is complicated owing to the close similarities between its compounds and those of uranium, zirconium and rare earths, which makes the separation of thorium difficult[1]. BEAMISH AND McBRYDE[2] and recently VERMA *et al.*[3] have reviewed the analytical chemistry of thorium. So far no suitable reagent for the complete separation of thorium, cerium(IV) and uranium from one another and their determination has been reported.

None of the reagents[4-7] which have been reported for the gravimetric determination of cerium(IV) can be conveniently used for its separation from uranium, thorium and trivalent rare earths. The gravimetric iodate method[8] is generally used for cerium(IV) and thorium and their separation from trivalent rare earths, but thorium cannot be separated from cerium(IV) in this way. BHAT AND JAIN[9] have recently used 3-acetyl-4-hydroxycoumarin for the gravimetric determination of cerium(IV) and its separation from trivalent rare earths.

In the present paper, a method is described in which 4-hydroxy-3-methoxybenzaldehyde (vanillin) is used to separate thorium and cerium(IV) from each other and from large quantities of uranium(VI) and other trivalent rare earths, as well as for the gravimetric determination of thorium and cerium(IV).

Vanillin has previously been used[10] to detect iron(III), chlorine and hydrochloric acid. ROSENTHALER[11], during his studies on the reaction of cerium(IV) ammonium nitrate with aldehydes, reported the formation of a bright brown precipitate. The chelate-forming reaction of vanillin with molybdenum(VI), tungsten(VI), vanadium(V), tin(IV) and bismuth(III) has been studied by HELMEKOSKI[12] and the reaction with titanium(IV) in non-aqueous medium has been investigated by SOMMER[13].

When an aqueous solution of vanillin is added to an aqueous solution of thorium salt at pH 4.0, an insoluble white thorium–vanillin complex is immediately formed. This complex is soluble in alcohol. With cerium(IV) solutions at pH 2.5 an insoluble reddish brown cerium(IV)–vanillin complex is formed. With uranyl salts the reagent forms at pH 4.0–7.5 a stable orange water-soluble complex which may be studied spectrophotometrically. Thorium and cerium(IV) are quantitatively precipitated at pH 4.0–6.2 and 2.5–7.0 respectively; as little as 4.4 mg of ThO_2 and 4.9 mg of CeO_2 can be determined.

EXPERIMENTAL

Reagents and equipment

An aqueous 1.0% solution of vanillin (E. Merck) was used as precipitant.

Gadolinium nitrate and yttrium nitrate were prepared from Gd_2O_3 (Johnson Matthey R.E. 454 grade) and Yt_2O_3 (Johnson Matthey R.E. 112 grade) respectively. Other metal salts used were either B.D.H. (AnalaR) or E. Merck (Pro Analysi) quality.

Dilute hydrochloric acid, ammonium acetate and ammonium hydroxide were used for adjustment of pH.

The pH measurements were made with a Beckman pH meter Model H 2, using a suitable glass electrode.

Determination of thorium with vanillin

To approximately 100 ml of thorium nitrate solution (containing about 15 mg of thorium dioxide) at pH 4.5–6.0, 20 ml of a 1% aqueous solution of vanillin was added slowly with constant stirring. The white flocculent thorium complex obtained was digested on a water bath for 15 min, cooled, filtered through Whatman No. 40 filter paper, washed with water, dried and ignited to thorium dioxide. Recoveries of 4.4–28.8 mg of thorium dioxide by this method agreed exactly with recoveries by the oxinate method.

The effect of pH on the precipitation of thorium complex was studied using dilute ammonium acetate and ammonium hydroxide solution for pH values higher than 3.5, and dilute hydrochloric acid solution for lower pH values. Precipitation of the thorium–vanillin complex was quantitative between pH 4.0 and 6.2.

Determination of thorium in presence of uranium(VI) and rare earths

Since uranium(VI) salts produce a stable water-soluble orange complex, the procedure for the determination of thorium in presence of varying amounts of uranium(VI) salt was the same as for thorium alone. 14.4 mg of thorium dioxide was quantitatively recovered in presence of 10–200 mg of U_3O_8.

The reagent does not form any insoluble complex with lanthanum, cerium(III), gadolinium and yttrium up to pH 6.0. Thorium was determined in the presence of varying amounts of these ions between pH 4.5 and 6.0. The precipitated thorium complex was thoroughly washed with dilute reagent solution before the final ignition. 14.4 mg of thorium dioxide was quantitatively recovered in presence of 20–200 mg of lanthanum, cerium(III), gadolinium or yttrium oxide and in presence of 20-mg amounts of each of these oxides together.

Determination of cerium(IV) with vanillin

To about 100 ml of an aqueous solution of cerium(IV) ammonium nitrate solution (containing about 20 mg of cerium dioxide) adjusted to pH 2.5–7.0, about 25 ml of an aqueous 1% solution of vanillin was slowly added with constant stirring. The reddish brown cerium(IV)–vanillin complex was digested on a water bath for about 20 min and subsequently cooled; it was then filtered through a Whatman No. 42 filter paper, washed, dried and ignited to cerium dioxide. Recoveries of 4.9–19.7 mg of cerium(IV) oxide by this method agreed exactly with recoveries by the oxinate method.

The formation of the cerium(IV) complex with vanillin was investigated at pH 1.0–7.5, using dilute solutions of ammonium acetate and ammonium hydroxide for pH values higher than 2.0, and dilute hydrochloric acid for lower pH values. Cerium(IV) formed an orange-red complex with this reagent at pH 1.0–7.5, but the precipitation was only quantitative between pH 2.5 and 7.0.

Separation and determination of cerium(IV) and thorium

Vanillin precipitates thorium at pH 4.0–6.2, while cerium(IV) is quantitatively precipitated even at pH 2.5. Accordingly the metals can be separated by a simple pH adjustment.

To a solution at pH 2.5–3.0, containing cerium dioxide and thorium dioxide in ratios of 1 : 10 to 10 : 1, a large excess of an aqueous 1% solution of vanillin was added with constant stirring; cerium(IV) was thus precipitated completely. The precipitate was digested and filtered as described above; it was then washed thoroughly with a dilute aqueous solution of the reagent, ignited to the oxide and weighed. The thorium in the filtrate was then precipitated as the thorium–vanillin complex by raising the pH of the solution to 4.0–6.0. The precipitate was treated as described above for pure thorium solutions. The results obtained are shown in Table I.

TABLE I

SEPARATION AND DETERMINATION OF CERIUM(IV) AND THORIUM

Wt. of CeO_2 taken (mg)	*Wt. of ThO_2 added (mg)*	*Wt. of CeO_2 found (mg)*	*Wt. of ThO_2 found (mg)*
19.7	14.4	19.7	14.4
19.7	36.0	19.7	36.0
9.8	72.0	9.7	72.0
9.8	154.0	9.8	154.0
19.7	7.2	19.7	7.2
98.5	14.4	98.5	14.4
197.0	14.4	197.0	14.4

Determination of cerium(IV) in presence of uranium(VI), lanthanum, gadolinium and yttrium

Since vanillin forms no insoluble complexes with uranium(VI) or with trivalent rare earths, cerium(IV) could be determined without modification of the method described for cerium alone. 9.8–19.7 mg of cerium(IV) oxide was quantitatively recovered in presence of 20–200 mg of U_3O_8. Lanthanum, gadolinium and yttrium were taken as typical trivalent rare earths; cerium(IV) was precipitated at pH 3.0–6.0 in presence of varying amounts of their nitrates. 19.7 mg of cerium(IV) oxide was quantitatively recovered in presence of 20–200 mg of lanthanum, gadolinium or yttrium oxide, and in presence of 20-mg amounts of each of these oxides together.

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SUMMARY

Vanillin forms insoluble complexes with thorium and cerium(IV) at pH 4.0–6.2 and 2.5–7.0 respectively. Thorium and cerium can be determined gravimetrically and separated from each other as well as from uranium(VI) and typical trivalent rare earths. The precipitates obtained are ignited to the corresponding oxide and weighed; as little as 4.4 mg of ThO_2 and 4.9 mg of CeO_2 can be determined.

RÉSUMÉ

Une méthode est proposée pour le dosage gravimétrique du thorium et du cérium(IV) au moyen de vanilline. Ces deux éléments peuvent être séparés l'un de l'autre en faisant varier le pH. Ils peuvent être séparés aussi d'avec l'uranium(VI) et les terres rares. Les précipités obtenus sont calcinés et pesés sous forme d'oxydes.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur gravimetrischen Bestimmung von Thorium und Cer-(IV) mit Vanillin. Durch Einhalten bestimmter pH-Werte können die beiden Elemente nacheinander gefällt und von Uran-(VI) und den seltenen Erden getrennt werden. Die erhaltenen Niederschläge werden verascht und als Oxyde gewogen.

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ANALYTICAL APPLICATIONS OF THE DETERMINATION OF HEXACYANOFERRATE(III) WITH ASCORBIC ACID

PART IV. DETERMINATION OF HYDROXYLAMINE

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Several methods are known for the determination of hydroxylamine. In acid-base methods, hydroxylamine can be titrated with acids in the presence of methyl orange[1] while the acid content of hydroxylamine salts can be titrated with alkalies with phenolphthalein indicator[2]. However, it is generally advisable to use redox methods, because hydroxylamine is commonly used as a reducing agent. Among such procedures may be mentioned titrations with permanganate[3], bromate[4] and bromine chloride[5], all of which require a complicated procedure or apparatus. It is interesting to note that hydroxylamine cannot be determined iodimetrically.

Hydroxylamine can also be oxidized with hexacyanoferrate(III). RAY AND SEN[6] established that the reaction in alkaline medium yields nitrogen, ammonia and dinitrogen oxide. The ratio of the products depends on the pH, temperature and concentration of hydroxylamine. SANT[7] was the first to determine the experimental conditions under which the reaction proceeds stoichiometrically; both cerimetric[7] and iodometric[8] methods of completion were applied to this reaction. We have confirmed that hydroxylamine reacts with hexacyanoferrate(III) in slightly alkaline solution; the reaction results in the formation of nitrogen:

$$2NH_2OH + 2Fe(CN)_6^{3-} + 2OH^- \rightarrow N_2 + 2Fe(CN)_6^{4-} + 4H_2O$$

The reaction is stoichiometric only if hexacyanoferrate(III) is present in excess, therefore care must be taken to add hydroxylamine to hexacyanoferrate(III) and not the reverse. Favourable pH values can be obtained with boric acid–borax buffer. The reaction is rather slow; with 0.1 N solutions it requires about 20 min for completion. The solution should not be heated, because other reactions may then occur. The equivalent weight of hydroxylamine is the same as its molecular weight.

The rapidity, simplicity and accuracy of the determination of hexacyanoferrate(III) with ascorbic acid[9] suggested the use of the reaction for the determination of hydroxylamine. Hexacyanoferrate(III) can be titrated directly with ascorbic acid in a solution buffered with potassium hydrogen carbonate, in the presence of 2,6-dichlorophenolindophenol indicator. The colour of the solution is green at the start, and gradually turns blue during the titration. At the end-point the colour disappears.

EXPERIMENTAL

Reagents

0.1 N Potassium hexacyanoferrate(III) standard solution. 32.925 g of analytically pure (Merck) $K_3Fe(CN)_6$ was dissolved in water and diluted to 1 l.

0.1 N Ascorbic acid standard solution. 8.9 g of commercial ascorbic acid was dissolved in glass-distilled water and diluted to 1 l. The solution was standardized against 0.1 *N* potassium hexacyanoferrate[9].

Hydroxylamine solution. An approximately 0.1 *M* solution was prepared from commercial hydroxylamine hydrochloride. For standardization an iron(III) sulphate-permanganate method[3] was used.

Boric acid – borax buffer: 80 g of $Na_2B_4O_7 \cdot 10H_2O$ and 40 g H_3BO_3 were dissolved in water and diluted to 1 l.

2,6-Dichlorophenolindophenol indicator

A 0.1% aqueous solution was prepared. The solution is stable for 3 weeks. The indicator can be stored for a longer time, if analytically pure 2,6-dichlorophenolindophenol and sodium chloride (1 :500) are ground thoroughly; this solid mixture is also satisfactory as an indicator.

Procedure

Two titrations are required, one to standardize the ascorbic acid and the other for the actual determination.

(*1*) To 30.00 ml of standard 0.1 *N* potassium hexacyanoferrate(III), add 1–2 g of solid potassium hydrogen carbonate and 1 ml of the indicator solution (or 0.5 g of the solid mixture). Titrate the green solution with 0.1 *N* ascorbic acid till colourless (A ml).

(*2*) To 30.00 ml of standard 0.1 *N* potassium hexacyanoferrate(III), add 40 ml of buffer solution, and then add the unknown sample solution containing 30–150 mg of hydroxylamine hydrochloride. Mix the solution and allow to stand for 30 min. Acidify slightly with hydrochloric acid and neutralize the excess of acid with 1–2 g of potassium hydrogen carbonate. Add 1 ml of the indicator solution (or 0.5 g of the solid mixture) and titrate with the ascorbic acid solution until colourless. If B ml of ascorbic acid is consumed, the amount of 0.1 *N* ascorbic acid (V ml) equivalent to the hydroxylamine present is calculated from the following equation: $V = (A-B)f$ ml, where f is the factor of the ascorbic acid solution. 1 ml of 0.1 *N* ascorbic acid is equivalent to 6.950 mg $NH_2OH \cdot HCl$ or 3.303 mg NH_2OH.

Some results of hydroxylamine determinations are summarized in Table I. The standard deviation calculated from 12 parallel determinations, was found to be ± 0.17 mg (0.24%), while the standard deviation of the mean of these determinations was 0.05 mg (0.07%).

TABLE I

$NH_2OH \cdot HCl$ taken (mg)	*$NH_2OH \cdot HCl$ found (mg)*	*Error (mg)*	
		maximum	*minimum*
35.93	36.20 (3 results)	+0.41	+0.13
71.85	71.80 (12 results)	−0.34	±0.00
107.78	108.08 (3 results)	+0.42	+0.14
143.70	144.20 (3 results)	+0.64	+0.38

SUMMARY

Hydroxylamine can be determined by reaction with an excess of standard potassium hexacyanoferrate(III) solution at pH 8–10. After 30 min the excess is titrated with ascorbic acid solution in the presence of 2,6-dichlorophenolindophenol indicator.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'hydroxylamine au moyen de ferricyanure de potassium. Après 30 min on titre le réactif en excès par une solution étalon d'acide ascorbique, en présence de 2,6-dichlorophénolindophénol comme indicateur.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Hydroxylamin mit Hilfe von Kaliumferricyanid, dessen Ueberschuss mit einer Lösung von Ascorbinsäure in Gegenwart von 2,6-Dichlorophenolindophenol als Indikator titriert wird.

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THE RAPID DETERMINATION OF TUNGSTEN AFTER REDUCTION WITH BISMUTH AMALGAM

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Tungsten is most commonly determined gravimetrically as tungsten oxide, after preliminary separation and purification of the impure oxide, but many procedures have been suggested for the titrimetric determination. A number of these methods involve the reduction of tungsten to a lower valency state followed by re-oxidation with a standard solution of an oxidising agent. The first to attempt the determination of tungsten by an oxidation-reduction procedure was PFORDTEN[1] who reduced tungsten-(VI) to the quadrivalent state with zinc and back-titrated with permanganate. SOMEYA[2] used the same oxidant but reduced the tungsten present in hydrochloric acid either to tungsten(III) with lead amalgam, or to tungsten(V) with bismuth amalgam. HOLT AND GRAY[3] also used lead amalgam but carried out the reduction in a special reduction vessel under an atmosphere of carbon dioxide and titrated tungsten-(III) with potassium dichromate. Reduction of tungsten to lower valencies was achieved by GEYER AND HENZE[4] using zinc powder and a cadmium reductor, while LUKE[5] has recently published a method in which the reduction is achieved by first boiling the hydrochloric acid solution with granulated lead, and then passing the solution through a lead reductor. The reduced tungsten is collected in an iron(III) solution, and the iron(II) produced is finally titrated with potassium dichromate.

None of these procedures is, however, entirely satisfactory. Some are complicated and time-consuming; others require the use of a column reductor. In the course of investigations with tungsten, molybdenum, chromium and vanadium, it became necessary to develop a rapid and simple method for the determination of tungsten. A study was made of the use of bismuth amalgam as a reducing agent. The results of this study are presented in following pages.

EXPERIMENTAL

Apparatus and chemicals

All of the following reagents were prepared from reagents of analytical grade purity. Bismuth amalgam was prepared by dissolving 3 g of bismuth metal in 100 g of mercury. Standard tungstate solution was prepared by dissolving 5.00 g of sodium tungstate in 250 ml of water. Aliquots of this solution were carefully evaporated on a hot plate until the salt began to separate out. The residue was dissolved in a minimum amount of water (a few drops), followed by 60 ml of concentrated hydrochloric acid. The precipitated WO_3 formed was dissolved either by shaking or by heating.

A glass reduction apparatus similar to that described by NAKAZONO[6] was used. It consisted of a separating funnel fitted with a side-arm through which nitrogen or carbon dioxide could be admitted and a closed bulb of 20 ml capacity was attached to the outlet stem to act as the amalgam collector.

The titration vessel consisted of a 250-ml beaker covered with a rubber bung through which there were 5 openings, which held respectively a nitrogen gas inlet and outlet, the tip of a burette, a platinum indicating electrode, and the salt bridge side-arm of a standard calomel electrode.

Preliminary investigations

In earlier work in this laboratory, bismuth amalgam was found to be very useful as a reductant for other transition metals[7]. As far as tungsten is concerned, however, an extensive use has not been made of this reductant. One reference alone, that of SOMEYA[2], notes its application in this direction. The work of SOMEYA was carried out in 1925 and little detail is given of the value of bismuth amalgam as a reductant for tungsten. It has one advantage over other reductants of a similar type, *e.g.* zinc and cadmium amalgams, in that tungsten is reduced to the pentavalent state. Zinc and cadmium amalgams are somewhat too reactive to be used conventionally while lead amalgam at elevated temperatures yields the trivalent state.

It was felt that bismuth amalgam was worthy of further investigation and, in view of the lack of information of its effect on tungsten, investigations were carried which led successfully to the development of a standard procedure.

PROCEDURE

The acid tungstate solution was transferred to the reduction vessel in which 100 g of bismuth amalgam had previously been placed, the flask was washed twice with 10-ml portions of concentrated hydrochloric acid, and the washings were transferred to the reduction vessel. Nitrogen gas was introduced for 3 min to remove air from the system.

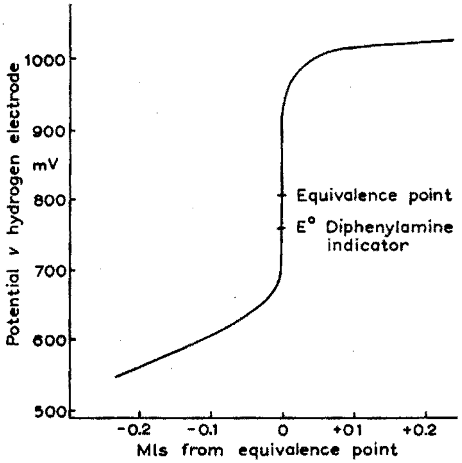

Fig. 1. Potential jump at equivalence point in titration of pentavalent tungsten with 0.1 *N* ceric sulphate solution in presence of 8 *N* hydrochloric acid

The tungsten solution was then shaken with the amalgam for 3 min, the colour of the solution becoming blue owing to the formation of tungsten(V). The amalgam was separated from the solution by opening the lower cock of the reduction vessel, the amalgam replacing the water originally present in the lower container. During this displacement process the amalgam is washed by the water, thus minimising any loss of tungsten solution.

The reduced solution was then transferred quickly to the titration vessel which had been previously filled with an inert atmosphere. The solution was titrated with $0.1\ N$ ceric sulphate solution, the potential changes being plotted during the course of the titration. The end-point was determined from the resultant graph as shown in Fig. 1.

The series of titrations were repeated using diphenylamine as visual indicator.

The method proved to be satisfactory for sodium tungstate solution. It was decided, therefore, to apply it to the determination of tungsten in a steel.

Application to steel analysis

The tungsten in a standard alloy steel was isolated as crude tungstic oxide by the well known procedure[8] in which the bulk of the tungsten is precipitated from a hydrochloric acid solution by oxidation with concentrated nitric acid. The last traces are precipitated by the addition of cinchonine hydrochloride solution. The tungstic oxide is filtered off and washed, first with dilute cinchonine solution, and finally with hot water.

In one series of tests the crude precipitate was ignited in a platinum crucible at about 700°. The residue was fused with sodium carbonate, cooled, the melt taken up with water, and the tungsten content determined by the procedure outlined for the standard tungsten solutions. In a second series of tests, the precipitate was dissolved from the filter paper with normal sodium hydroxide and this alkaline tungstate solution was neutralised and treated as previously described.

RESULTS

The results obtained in the titration of standard tungsten solutions by the potentiometric end-point detection and with diphenylamine as visual indicator are recorded in Table I.

TABLE I

Potentiometric titration			*Visual titration*		
mg used	*mg found*	*% error*	*mg used*	*mg found*	*% error*
200	198.30	—0.85	200	198.26	—0.87
180	179.32	—0.37	180	179.24	—0.42
160	158.17	—1.14	160	158.15	—1.15
150	148.20	—1.20	150	148.19	—1.18
140	139.57	—0.30	140	139.47	—0.37
100	98.60	—1.40	100	98.17	—1.83
80	79.07	—1.16	80	79.12	—1.10
60	58.92	—1.80	60	58.88	—1.90
50	49.57	—0.86	50	49.56	—0.88
40	39.56	—1.10	40	39.65	—0.85
20	19.53	—2.35	20	19.51	—2.45
Standard deviation from true value		1.31			1.33

The steel was obtained from the Bureau of Analysed Samples Ltd. with a certified 5.66% W. The results obtained from the titration of ignited tungstic oxide precipitates were of the order of 5.8% but when the initial precipitate was merely dissolved off the filter paper by strong alkali, the results were higher, being around 6.4% W. The high values were traced to the interfering effect of co-precipitated molybdenum.

DISCUSSION

Table I shows that the titration procedure gives a consistently low tungsten result. A study of the results indicates that the error (expressed as standard deviation from the true value) is 1.3% of tungsten present. This indicates a recovery of 98.7% which is similar to the 99% recovery claimed by LUKE[5] who used a two-stage reduction process involving lead granules and a lead reductor. From Fig. 1 it can be seen that diphenylamine is a very suitable indicator for this titration; this is confirmed by the similarity of the results obtained by means of the two methods of end-point detection. The hydrochloric acid present in very high concentration during the titration forms a chloro complex with the tungsten and allows the satisfactory use of diphenylamine as indicator. The technique for reduction is comparatively simple and reasonably fast. With the visual indicator readily available, the method has much to commend it.

One limitation, however, is the low tungsten recovery. Losses can result from incomplete reduction, loss of solution, partial oxidation by trapped air during the transfer of the reduced solution to the titration vessel or the presence of small amounts of oxygen in the gas used to give an inert atmosphere. The magnitude of the tungsten loss (expressed as percentage) is fairly consistent, so that this limitation can be minimised by standardising the ceric sulphate against standard tungsten solution treated as above. A more important limitation is the effect of other reducible species. Many elements are reduced to lower valencies by bismuth amalgam and the influence of even traces of impurities is shown by the results obtained in the analysis of alloy steels.

It is well known that molybdenum readily co-precipitates with tungsten when it is isolated as the insoluble oxide. Even precipitation from homogeneous solution as described by DAMS AND HOSTE[9] does not overcome this problem. Molybdenum is reduced to the trivalent state by bismuth amalgam so that oxidation involves a three electron change. Small amounts of molybdenum accompanying the tungsten thus consume appreciable amounts of titrant and are responsible for the major errors obtained in the alloy steel analysis.

The completely satisfactory application of this redox titration technique to alloy steel analysis requires an efficient preliminary separation of the tungsten from other reducible elements, particularly molybdenum. Classical procedures such as the precipitation of molybdenum as sulphide from a tartrate solution containing tungsten and molybdenum are available, but alternative procedures are desirable. A satisfactory separation of tungstate, molybdate, vanadate and chromate has been achieved by paper chromatography[10].

SUMMARY

A titrimetric determination of tungsten is described; it is based on reduction of tungsten to tungsten(V) by bismuth amalgam in concentrated hydrochloric acid solution and titration with ceric sulphate solution. The end-point can be detected potentiometrically or visually. The method may be extended to the determination of tungsten in a steel.

RÉSUMÉ

Une méthode est décrite pour le dosage volumétrique du tungstène, par réduction au moyen d'amalgame de bismuth et titrage avec une solution du sulfate de cérium(IV). Le point final est décelé à l'aide d'un indicateur coloré ou par potentiométrie. Cette méthode peut être appliquée au dosage de tungstène dans un acier.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Wolfram durch Reduktion mit Wismutamalgam und Titration mit Cer-(IV)-lösung. Die Bestimmung des Endpunktes kann mit einem Indikator oder potentiometrisch erfolgen.

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IDENTIFICATION OF CERIUM IN THE PRESENCE OF OTHER RARE EARTHS

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Many colorimetric reagents[1] such as gallic acid, pyrogallol, quinalizarin, tannin, brucine and others have been used for the identification of cerium. Generally, they are not very selective. Being a strong oxidant, cerium(IV) has also been identified with redox indicators[2].

Some rare earths exist in only one oxidation state, and others in more than one. In aqueous solutions it is easier to change the oxidation state of cerium than that of other rare earths. Cerium, praseodymium and terbium exist in tri- and tetravalent states, but praseodymium and terbium exhibit their tetravalent state only in solids made by the dry methods[3]. With the exception of cerium(III), trivalent rare earth ions resist oxidation in aqueous solutions. Divalent rare earth ions decompose water producing their trivalent ions and hydrogen. Therefore, in aqueous solutions all rare earths, except cerium, are normally tripositive. This suggested that, in the presence of other rare earths, cerium is best identified with the redox indicators. A search was made in this work for a suitable indicator.

EXPERIMENTAL

Reagents

o-Tolidine. A saturated solution of *o*-tolidine in water.

Sulfanilic acid. A saturated solution of aniline *p*-sulfonic acid in water.

Diphenylamine sulfonate. A barium diphenylamine sulfonate solution prepared by dissolving 0.32 g of the salt in 100 ml of water. Barium was precipitated with 0.5 g of sodium sulfate, and the solution was filtered through a fine quantitative filter paper.

Ferroin. 1,10-Phenanthroline ferrous sulfate complex diluted to 0.0001 *M*.

Cerium(IV) solution. *N*/10 Ceric sulfate solution (Fisher Scientific Company) was suitably diluted with sulfuric acid. All the solutions were made approximately 2 *N* in sulfuric acid.

RESULTS

The reactions were studied in test tubes by the dropwise addition of the reactants from medicine droppers which were previously calibrated in drops per ml. Because cerium(IV) precipitates from a solution above pH 2.7, tests were made in an approximately *N* sulfuric acid medium. The concentrations of cerium, or of an interfering ion, were calculated from its quantity and from the total volume of solutions in the test medium. Results are shown in Table I.

Lanthanum, thorium, zirconium, hydrogen peroxide (3%) and less than 30,000 p.p.m. of nitrate do not interfere with any of these indicators. *p*-Sulfanilic acid, used by MONTIGME[4] for identifying cerium, is a fairly specific indicator for cerium(IV). Spot testing allows identification of 1 μg of cerium(IV). Iron(III) and many other oxidants do not interfere. Table II shows the concentrations above which certain oxidants give the same color reactions with the indicators and, thus, interfere with the identification.

TABLE I

REACTION BETWEEN CERIUM(IV) AND SOME REDOX INDICATORS

indicator	*color change*	*identification limit, µg*	*concentration limit, p.p.m.*
o-Tolidine	Colorless to yellow	0.4	0.6
Sulfanilic acid	Colorless to red	4	6
Diphenylamine sulfonate	Colorless to green	1	3
Ferroin	Red to colorless	2	9

Reactions between these indicators and other rare earths were studied by using 99.9% pure rare earth oxides obtained from American Potash and Chemical Corp-

TABLE II

MINIMUM INTERFERING CONCENTRATION OF OXIDANTS, p.p.m.

indicator	*persulfate*	*nitrate*	*bromate*	*vanadate*	*iodate*	*chlorate*
o-Tolidine	0.01**	30,000	10	3	10	2,000
Sulfanilic acid	*	*	40	*	*	*
Diphenylamine sulfonate	100**	*	0.1	0.01	1	200
Ferroin	*	70,000	600	*	*	*

* Under the experimental conditions no color appeared within 10 min

** Only a faint color appeared at this and higher concentrations

oration. Except for praseodymium (Pr_6O_{11}) and terbium (Tb_4O_7), all the oxides were in R_2O_3 form. Solutions were made by dissolving the oxides in 6 *N* sulfuric acid. Samarium, europium and ytterbium, which can exist in di- and trivalent states, did not react with the indicators. The solutions of praseodymium and terbium were heated with cobaltic oxide for possible oxidation, but no reaction was observed with the indicators. Under similar treatment, cerium(III) was oxidized to cerium(IV), which reacted with the indicators. Promethium was not available for this investigation. Other rare earths and yttrium also gave no color reactions.

ACKNOWLEDGEMENT

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SUMMARY

In the presence of other rare earths, cerium is best identified with redox indicators. *p*-Sulfanilic acid is a fairly specific indicator for cerium(IV), giving a red coloration with more than 6 p.p.m. *o*-Tolidine and diphenylamine sulfonate can identify smaller amounts of cerium(IV), but many oxidants interfere.

RÉSUMÉ

Une réaction est proposée pour l'identification du cérium (sous forme de cérium(IV)), en présence d'autres terres rares, au moyen d'indicateurs redox. L'acide *p*-sulfanilique est recommandé.

ZUSAMMENFASSUNG

Zum Nachweis von Cerium neben anderen seltenen Erden kann Sulfanilsäure als Reagenz verwendet werden.

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MICROANALYSIS WITH THE AID OF ION EXCHANGERS*

PART XXI[1]. MODIFICATIONS OF THE RESIN SPOT TEST WITH HIGH MOLECULAR WEIGHT AMINES

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The microchemical applications of high molecular weight amines (HMWA),** so-called liquid anion exchangers, have been investigated as reaction media for micro detection of ions, in an attempt to improve and extend the range of resin spot tests; such tests have been extensively developed in the past decade by FUJIMOTO[2,3]. The essential merits of the resin spot test are the efficient concentration of traces of ions in the small space of an ion exchanger particle[4] and the easy elimination of interfering substances with a charge opposite to that of the counter-ion of the resin. However, the resin spot test has a practical drawback because of the slow attainment of maximum sensitivity. As reaction media for micro tests, HMWA (or their solutions in some immiscible solvent) are superior to cross-linked ion-exchange resins and to the usual inert immiscible solvents because of the rapid attainment of the distribution equilibria and because of their applicability to the extraction of strong electrolyte systems. Interesting results would therefore be expected when HMWA are applied in microdetection, similarly to the resin spot tests.

As a typical example for colour reactions, the cobalt(II)-thiocyanate system was examined; tests involving this sensitive blue coloration on a resin or in an immiscible solvent have been examined previously[3,5]. When the system is shaken with a carbon tetrachloride solution of a HMWA, Amberlite LA-1 (N-dodecyltrialkylamine), the colourless or pale yellow organic phase becomes blue or greenish blue; the colour is very similar to that obtained with strongly basic anion-exchange resins or with an immiscible solvent*** and permits the sensitive detection of cobalt(II). Similar observations

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* Since various materials with ion-exchange abilities other than resins can be applied by the same principles as those in the resin spot test, the general title of the series has been revised.

** The name "HMWA" was used here, since it is not yet clear whether the extraction of ions by these amines is true ion exchange or not.

*** Preliminary experiments showed that a 5% carbon tetrachloride solution of previously conditioned commercial Amberlite LA-1 absorbs strongly at wave lengths below 500 mμ (vide infra), but has no appreciable absorption in the region 550–750 mμ. The blue solution of cobalt(II)-thiocyanate complex in the same phase shows an absorption maximum at 625 mμ and a characteristic shoulder at about 590 mμ, both of which are very similar to the absorption curve of the same system in an immiscible solvent (*e.g.* isoamyl alcohol-ethyl ether) or in the strongly basic anion-exchange resin phase[3,5,6]. Further details will be reported elsewhere.

have been reported by ZIEGLER *et al.*[7] who employed association of complex anions with tri-*n*-butyl ammonium cation followed by extraction with iso-amyl alcohol, for the detection and colorimetric determination of cobalt(II).

The use of a new ion-exchange paper, which is easily prepared by simple impregnation of filter paper with HMWA, is also proposed. SANSONI[8] also already reported the use of specially prepared ion-exchange papers for the detection of cobalt(III) with thiocyanate.

EXPERIMENTAL

Reagents

All chemicals were of reagent grade.

HMWA: Amberlite LA-1 was chosen as the HMWA. A 10% (v/v) stock solution was prepared by dissolving a commercial specimen of Amberlite LA-1 (vide infra) in carbon tetrachloride. The solution was purified and conditioned by washing successively with 0.3 *F* nitric acid, deionized water, 0.1 *F* aqueous sodium hydroxide, to convert to the hydroxide form, and finally with 0.1 *F* hydrochloric acid to reconvert to the chloride form. Immediately before the experiment the solution of the purified HMWA was again thoroughly shaken with 0.1 *F* hydrochloric acid.

Stock solution of cobalt(II): This was prepared by dissolving cobalt(II) chloride in 0.01 *F* hydrochloric acid; a series of standard solutions was prepared by diluting this solution with 0.01 *F* hydrochloric acid.

2 *F* Ammonium thiocyanate: The solution was passed through a column of an anion-exchange resin in the thiocyanate form to remove traces of iron(III)[3,5].

Other reagents: Hydrochloric acid, nitric acid and carbon tetrachloride were redistilled.

Dropping pipettes. These were adjusted to deliver a drop of 0.04 ± 0.002 ml of deionized water.

MICRO DETECTION OF COBALT(II) WITH THIOCYANATE BY SHAKING WITH HMWA

Procedure

In a micro test tube (5 mm × 50 mm) mix a drop of the slightly acidic test solution with a drop of 2 *F* ammonium thiocyanate. Shake the mixture vigorously with a drop of the carbon tetrachloride solution of the HMWA, and observe the green or sky blue colour of the organic phase; the colour appears at once in the presence of cobalt(II).

Results

Increasing the concentration of the HMWA in the organic phase enhances the sensitivity of the test; the limits of identification are 1, 0.5, 0.2 and 0.2 μg of cobalt(II) with 1, 2, 5 and 10% carbon tetrachloride solutions of Amberlite LA-1, respectively. With solutions stronger than 10%, the brownish colour of the commercial HMWA in the organic phase interferes slightly with the detection, hence a 5% solution was adopted. However, the coloured impurities in Amberlite LA-1 can easily be removed by a single distillation under reduced pressure; the distillate from a brown crude specimen at 185–200° at 2–3 mm Hg pressure is only pale yellow. Data on the purification of HMWA will be reported in detail elsewhere.

The effects of foreign substances are summarized in Table I.

TABLE I

EFFECT OF FOREIGN SUBSTANCES

Foreign ion	*Added compound*	*Colour of the organic phase*[a,b]	*Amount of foreign ion (μg)*	*Amount of detectable cobalt(II) (μg)*	*Limiting proportion*	*Remark*
Ti(IV)	$TiOSO_4$	Or	85	0.7	$1:1.3\cdot10^2$	(*c*)
		cl	100	0.4	$1:2.5\cdot10^2$	(*d*)
V(V)	NH_4VO_3	cl(Ye)	720	0.2	$1:3.6\cdot10^2$	(*d*)
Cr(III)	$KCr(SO_4)_2$	pl Ye	530	0.7	$1:8\cdot10^2$	(*e*)
Mn(II)	$MnSO_4$	cl	1600	0.4	$1:4\cdot10^3$	
Fe(III)	$FeCl_3$	pl Ye ~ Ye(Re)	130	0.7	$1:2\cdot10^2$	(*d*)
Ni(II)	$NiCl_2$	pl Ye	1600	0.4	$1:4\cdot10^3$	(*e*)
Cu(II)	$CuSO_4$	cl ~ pl Ye(dk Br)	130	0.7	$1:2\cdot10^2$	(*f*)
Zn(II)	$ZnSO_4$	cl	1600	0.4	$1:4\cdot10^3$	(*g*)
Cd(II)	$CdSO_4$	cl	1600	0.4	$1:4\cdot10^3$	
Hg(II)	$Hg(NO_3)_2$	cl	1600	0.4	$1:4\cdot10^3$	(*h*)
Mo(VI)	Na_2MoO_4	cl(Or)	530	0.7	$1:8\cdot10^2$	(*d*)
W(VI)	Na_2WO_4	cl	400	1	$1:4\cdot10^2$	
		cl	530	0.7	$1:8\cdot10^2$	(*i*)
Pb(II)	$Pb(NO_3)_2$	cl	1600	0.4	$1:4\cdot10^3$	
Sn(IV)	$SnCl_4$	cl	270	0.7	$1:4\cdot10^2$	
Sb(III)	$SbCl_3$	cl	320	0.4	$1:8\cdot10^2$	
Bi(III)	$Bi(NO_3)_3$	cl	1300	0.3	$1:4\cdot10^3$	(*j*)
Al(III)	$Al(NO_3)_3$	cl	1000	1	$1:1\cdot10^3$	(*c*), (*d*)
HPO_4^{2-}	Na_2HPO_4	cl	1100	0.7	$1:1.6\cdot10^3$	
$C_2O_4^{2-}$	$(NH_4)_2C_2O_4$	cl	320	0.4	$1:8\cdot10^2$	
$C_4H_4O_6^{2-}$	Rochelle salt	cl	1600	0.4	$1:4\cdot10^3$	
$C_6H_5O_7^{3-}$	Ammonium citrate	cl	1600	0.4	$1:4\cdot10^3$	

(*a*) The coloration by the foreign compound only. Colour code [1,2]: cl, colourless; dk, dark; pl pale; Br, brown; Or, orange; Re, red; Ye, yellow.

(*b*) In parentheses are shown the colours of the organic phase when KF is omitted (*cf.* Remark (*d*)).

(*c*) Values obtained by comparison with a blank test.

(*d*) A drop of 10% KF was added to prevent interference from iron(III).

(*e*) If the blueish colour in the organic phase is masked by coloured compounds in the aqueous phase, the latter is removed and the organic phase is washed with a few drops of distilled water.

(*f*) Traces of solid KI and $Na_2S_2O_3$ were added to mask copper(II).

(*g*) Zinc(II) was previously separated by passing the test solution containing 4 *F* HCl through a microcolumn of a strongly basic anion-exchange resin(RCl)[1], and eluting cobalt(II) with 4 *F* HCl[9].

(*h*) Mercury(II) was precipitated with a few grains of NH_4SCN.

(*i*) The sample solution was evaporated to dryness on a water bath with a drop of concentrated hydrochloric acid before the test.

(*j*) A few drops of aqueous ammonia were added and the supernatant solution was tested.

PREPARATION AND MICROCHEMICAL APPLICATIONS OF HMWA PAPER

To prepare the HMWA paper, a strip of quantitative filter paper was treated with dilute nitric acid to remove traces of impurities, washed with deionized water and dried at room temperature. The paper was immersed in a 10% carbon tetrachloride solution of Amberlite LA-1 in the chloride form. After a few h, the paper was dried in air, cut into pieces of 3 × 3 mm (LA-1 paper), and kept in the dark in a well-stoppered bottle.

This paper was used in a modification of the resin spot test for cobalt(II) as follows. On a white spot plate, a drop of the slightly acidic test solution was mixed with a drop of 2 *F* ammonium thiocyanate and a small piece of the LA-1 paper. In the presence of cobalt(II) a sky blue colour appeared at the edge of the paper and gradually covered the whole.

The limit of identification was found to be 0.2 μg cobalt(II) per 0.04 ml ($1:2\cdot10^5$) after 10 min; this is the same value as that found in the above-mentioned test with HMWA or in the resin spot test after 1 h. The wide utility of HMWA papers as reaction media for micro tests is thus clear.

ACKNOWLEDGEMENT

The authors express their gratitude to Nippon Organo Shokai, Ltd., Tokyo, Japan, for the supply of Amberlite LA-1.

SUMMARY

The resin spot test is modified by the use of a high molecular weight amine, Amberlite LA-1, in carbon tetrachloride; 0.2 μg of cobalt(II) can be detected rapidly by shaking an acidic solution containing thiocyanate with a 5% amine solution. Amine-impregnated papers can also be used.

RÉSUMÉ

Les auteurs proposent une réaction sensible permettant de déceler facilement 0.2 μg de cobalt, en utilisant le thiocyanate d'ammonium comme réactif, et une amine à poids moléculaire élevé, l'amberlite LA-1, en solution dans le tétrachlorure de carbone. Cette réaction peut se faire sur un papier imprégné d'amberlite LA-1.

ZUSAMMENFASSUNG

Beschreibung einer Modifikation der Tüpfelproben mit Austauscherharzen durch Verwendung hochmolekularer Amine (Amberlit LA-1). Als Beispiel wird der Nachweis von Kobalt mit Thiocyanat beschrieben. Der Nachweis kann auch papierchromatographisch erfolgen.

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DETERMINATION OF MONO-ALCOHOLS BY GAS CHROMATOGRAPHY

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The determination of alcohol by wet chemical procedures is made difficult by the fact that the alcoholic OH group is not very reactive; of the physical methods, infrared spectroscopy has been used extensively. However, with both chemical and infrared methods, only the total alcohol content is determined. This gives little information on the range of molecular weights in the sample. This is often important in mixtures of alcohols. Further, unless the alcohol is substituted in the α-position, these procedures do not indicate the type of alcohol present.

The determination of alcohols by gas chromatography, however, provides a rapid procedure which indicates molecular weight distribution and the straight chain and branched chain alcohol content. This is particularly important in detergent manufacture. The degree of branching controls bacterial disposal of detergents. Since these are frequently made from aliphatic alcohols, the *n*-alcohol content is an important property of the product.

EXPERIMENTAL

The procedure was developed for alcohols up to and including $C_{20}H_{41}OH$. Of these, a number of the higher molecular weight alcohols are solids and would normally have a very long retention time. This can be overcome by using an apparatus with programmed temperature. In this case an F and M Model 500 apparatus was found to be satisfactory.

Column

A silicone substrate proved satisfactory. This material was chosen because it was able to withstand temperatures up to 300°. For lower molecular weight alcohols ($<C_{13}$) a 3-m column was used; for $C_{13}H_{27}OH$ and higher alcohols a 1-m column was used. This was necessary to reduce the retention time to a reasonable period (30 min). This was not only convenient for reducing the time required for analysis but was necessary to minimize the tendency of the sample to crack to lower molecular weight components in the column. At best, this causes a broadening of the band, at worst a completely erroneous trace. With long retention times this is a constant source of error.

Under the experimental conditions described, such decomposition was not observed. A further check was made by trapping the material leaving the column and identifying by infrared analysis[1]. This confirmed the presence of alcohols at the expected retention time.

Column life. Silica bled from the column causing an increasing baseline as the temperature increased. This was particularly so during the first few weeks of use. However, with further use, the degree of bleeding decreased to a satisfactory level for routine analysis. Of course, it was necessary to correct for this effect on the apparent area of the peaks.

Internal standard

The most accurate quantitative analyses were obtained using an internal standard. n-$C_{14}H_{29}OH$ (10–15%) was used with samples containing $C_{13}H_{27}OH$ and/or lower molecular weight alcohols. For higher molecular weight alcohols, n-$C_5H_{11}OH$ (30–40%) was used. This acted as a solvent for the sample. If the internal standard was a higher alcohol, or was present in lower percentages, there was a tendency for the higher molecular weight alcohol in the solution to solidify. This caused unrepresentative sampling, poor transfer to the injection port and generally erratic results.

CONDITIONS

The conditions for running samples are summarized below:

Column	Silicone E-301
Programmed temp. range	50–300°
Inlet temperature	275°
Heating rate	7.9°/min
Detector temperature	275°
Carrier gas	Helium

Sample	*Column length*	*Carrier gas flow*	*Internal standard*
C_{13}-C_{20} Alcohol	1 m	55 ml/min	30–40% n-C_5OH
C_5-C_{13} Alcohol	3 m	35 ml/min	10–15% n-$C_{14}OH$

For higher molecular weight alcohols, it was necessary to melt the sample by heating n hot water. Sufficient n-$C_5H_{11}OH$ (30–40%) was then added to prevent partial crystallization of the sample. The quantity added was determined by weighing into a capped vial or other suitable container. The quantity required to maintain solution increased with the molecular weight of the alcohol. With the highest molecular weight alcohols it was also necessary to warm the injection syringe and needle

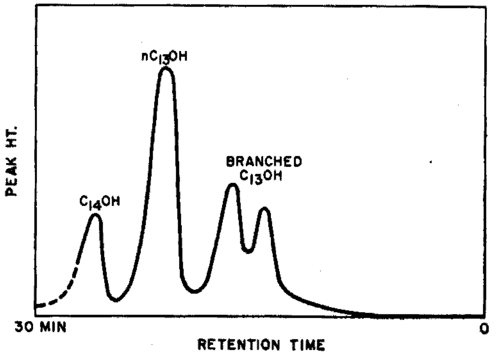

Fig. 1. Trace of C_{13} alcohols plus n-$C_{14}OH$ internal standard.

to prevent solidification of the sample and consequent enrichment of the solvent. Typical traces are shown in Figs. 1 and 2.

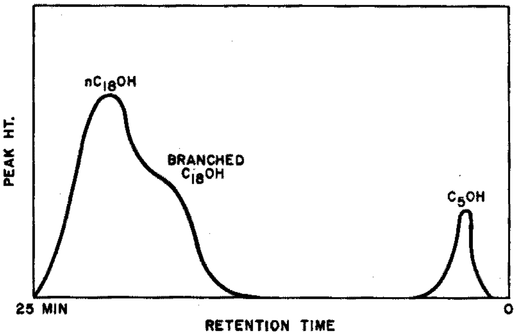

Fig. 2. Trace of C_{18} alcohol plus C_5OH internal standard.

RETENTION TIMES AND RESPONSE FACTORS (PEAK AREA/UNIT WEIGHT)

The retention times and response factors for normal alcohols were determined by making synthetic blends of pure alcohols and the relevant internal standard. The results are shown in Fig. 3.

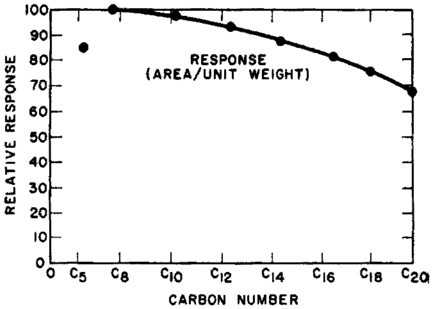

Fig. 3. Response factors for *n*-alcohols. Note: response for C_5OH was for *n*-C_5OH peak only. Area contributed by C_5OH isomers and impurities was not included.

The retention time of straight chain alcohols was a useful guide for identification purposes. However, with branched alcohols a shorter retention time was obtained for the same carbon number. It was noted that the retention time was sensitive to column temperature, particularly with the higher alcohols. Since the rate of heating varied slightly between instruments no attempt has been made to record the retention times observed. It is best to obtain this information on the equipment to be used for analysis. Further, the response factors of straight chain and branched alcohols were slightly different. This made it preferable to determine both retention time and response factor from distillation cuts of a typical sample since the type and degree of branching would be similar in both cases. However, when this is not possible, synthetic blends can be used for calibration purposes.

CALCULATIONS

The response factor was determined by adding the required amount of internal standard to a distillation cut of the sample or to a synthetic blend. This cut should be composed predominantly of the material causing the relevant peak. The factor was calculated as follows.

Component	*Area*	*Blank*	%	*Expected area if factor = 1*	*True area*	*Response factor*
C_5OH (internal standard)	5.2	0.1	30 (weighed)	5.1	5.1	1
Peak 3 (alcohol)	10.4	0.2	70 (by diff.)	$\frac{5.1 \times 70}{30} = 11.9$	10.2	$\frac{11.9}{10.2} = 1.13$

When the distillation cut gives the main peak and small quantities of spurious peaks, the best estimate of the factor is obtained by measuring the total area contributed by the distillation material.

A typical analytical calculation is given below.

Component	*Total area*	*Blank*	*True area*	*Factor*	*Effective area*	*% in blend*	*% in original sample*
C_5OH	6.2	0.1	6.1	1	6.1	34 (by weight)	
Alcohol peak	9.6	0.2	9.4	1.13	10.6	$34 \times \frac{10.6}{6.1} = 59$	$\frac{59 \times 100}{(100 - 34)} = 89$

The precision of this procedure was within 3%. Also, there was reasonable agreement with distillation data. It was observed, however, from the analysis of distillation cuts that alcohols distilled over with lighter materials and some lighter materials came over with the alcohols. This probably leads to a compensation of errors in the distillation data.

In routine operation the procedure was satisfactory provided that adequate care was taken in blending the internal standard and injecting into the column.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Mr. G. BYARS for his numerous suggestions on this problem and to Humble Oil and Refining Company for permission to publish.

SUMMARY

A gas chromatographic method is described for the determination of alcohols up to $C_{20}H_{41}OH$. The procedure is rapid and indicates the molecular weight distribution and the contents of straight-chain and branched-chain alcohols. A programmed temperature control with a silicone substrate was satisfactory. n-$C_{14}H_{29}OH$ and n-$C_5H_{11}OH$ were used as internal standards.

RÉSUMÉ

Une méthode par chromatographie gazeuse est décrite pour le dosage des alcools (jusqu'à $C_{20}H_{41}OH$). Ce procédé est rapide. On utilise comme étalon interne n-$C_{14}H_{29}OH$ et n-$C_5H_{11}OH$.

ZUSAMMENFASSUNG

Beschreibung einer gaschromatographischen Methode zur Bestimmung der Alkohole bis $C_{20}H_{41}OH$. Das Verfahren erlaubt Rückschlüsse auf die Molekulargewichtsverteilung sowie auf den Gehalt an geradkettigen und verzweigten Molekülen.

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ZUR MIKROCHEMISCHEN UNTERSUCHUNG SCHWACH RADIOAKTIVER LÖSUNGEN UND ABWÄSSER

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Vor der Beseitigung radioaktiver Abwässer ist es nicht nur wichtig die Gesamtaktivität kennzulernen, sondern es gilt auch die Frage zu beantworten, von welchen Radionukliden diese herrührt. Handelt es sich um kurzlebige Nuklide, so kann man diese in einem entsprechenden Vorfluter oder in Sammeltanks abklingen lassen; nötigenfalls müssen andere Wege beschritten werden. Weiters möchte man auch die Konzentration dieser Nuklide wissen, da die höchstzulässige Konzentration der Radionuklide nicht nur von der Strahlungsintensität, sondern vielmehr von der Gefährlichkeit der speziellen Nuklide abhängig ist.

Die erlaubten Höchstkonzentrationen radioaktiver Isotope liegen im Bereich von 10^{-12} bis 10^{-15} g im ml[1], daher müssen alle Analysenmethoden den geringen Mengen vorhandener Nuklide angepasst sein. Daraus ersieht man die Schwierigkeiten bei Analysen, in diesen Bereichen noch quantitative Aussagen zu machen.

Es ist das Ziel dieser Arbeit, einige Grundlagen für eine möglichst einfache analytische Arbeitsmethode zu schaffen, (wobei von vornherein auf aufwendige und teure Apparaturen verzichtet wurde) die den Nachweis, die Trennung und wenn möglich auch die spezifische Bestimmung einzelner radioaktiver Isotope durchzuführen gestattet.

Die WEISZ'sche Ringofentechnik[2], ein sehr empfindliches, semiquantitatives Bestimmungsverfahren in der Mikrochemie, ist auch zum Nachweis radioaktiven Materials geeignet[3].

Um die bereits vorhandenen Angaben und Erfahrungen für die speziellen Zwecke der Abwasseranalyse wirksam einbauen zu können, waren noch grundlegende Studien zur Frage der Erfassungsgrenzen mit der Ringofenmethode, sowohl für aktives als auch inaktives Material notwendig.

Bei der Bestimmung schwach radioaktiver Wässer geht jeder Analysenmethode, je nach deren Erfassungsgrenze, eine mehr oder minder hohe Anreicherung des zu bestimmenden Nuklids voraus[4-9]. Mit Ionenaustauschern und anschliessender selektiver Elution lässt sich sogar eine gewisse Trennung der angereicherten Ionen in Gruppen durchführen.

Bei den Fällungsverfahren werden Trägersubstanzen zugesetzt, um eine praktisch quantitative Fällung des Radionuklids zu erzielen, oder man erzeugt einen grossoberflächigen Niederschlag, der die in geringen Mengen vorhandenen Stoffe dann quantitativ mitreisst[10–12].

Daneben könnte man noch alle die Methoden aufzählen, die die Chemiker und Physiker zur Bestimmung von kleinsten Mengen eines Stoffes ausgearbeitet haben, wie Extraktion, Gammaspektroskopie, Spektrophotometrie, Mikrotitrationen mit und ohne elektrischer Endpunktsanzeige, Röntgenfluoreszenzanalyse, Flammenphotometrie und polarographische Methoden.

Analyse radioaktiver Lösungen mit dem Ringofen nach H. Weisz

Als tüpfelanalytische Methode besitzt die WEISZ'sche Ringofentechnik den Vorteil, dass die Konzentration der Ionen im Kreisring grösser ist, als im ursprünglichen Tüpfelfleck. Mit Hilfe einer Farbreaktion wird das gesuchte Ion im Ring in eine gefärbte Verbindung übergeführt und die Konzentration durch Vergleich mit Standardringen ermittelt[13].

Voraussetzung für das Studium der Erfassungsgrenzen einzelner Ionen ist, dass man Mikrotropfen in gleichbleibender und bekannter Grösse aufbringen kann. Die von WEISZ[14] empfohlene Mikropipette besteht aus einer 10-mm langen, dickwandigen Kapillare, die an einem Ende konisch zugeschliffen ist und an einem Glasstab befestigt ist. Sie füllt sich beim Berühren der Flüssigkeitsoberfläche von selbst und wird durch Aufsetzen auf Filterpapier leergesaugt. Die Messung des Volumens unserer Mikropipette ergab ein Volumen von 5.9 μl ± 0.16 μl. Die Messwerte zeigten eine Schwankung von ± 3%. Dies ist für unsere Zwecke hinreichend genau.

Die Frage, ob die am Ringofen erreichbare Erfassungsgrenze zur Bestimmung radioaktiver Isotope genügen würde, wurde am Beispiel des Kobaltnachweises mit α-Nitroso-β-Naphtol untersucht und dabei gefunden, dass noch $12 \cdot 10^{-9}$ g Kobalt ($50 \cdot 10^{-9}$ g auf der Tüpfelplatte) erfassbar sind.

Würde nun diese Nachweisgrenze zur Bestimmung des radioaktiven Kobalt-60 in Abwässer genügen?

Das Zerfallsgesetz für radioaktive Elemente sagt aus, dass die Abnahme der Teilchen mit der Zeit proportional der Anzahl der vorhandenen Teilchen ist.

$$-\frac{dN}{dt} = \lambda N; \quad \lambda = \frac{\ln 2}{\tau}$$

N = Anzahl der Teilchen; t = Zeit; λ = Zerfallskonstante; τ = Halbwertszeit.

Für ein bestimmtes Isotop gilt dann:

$$\frac{\text{Zerfälle}}{\text{sec}} = \frac{2.3 \cdot \log 2}{\tau} \cdot \frac{g}{AG} \cdot N_L$$

g = Menge des Isotops in Gramm; AG = Atomgewicht des Isotops; N_L = LOSCHMIDT'sche Zahl.

Auf Kobalt-60 angewendet ergibt das: Die Nachweisgrenze für Kobalt mach der Ringofenmethode liegt bei $12 \cdot 10^{-9}$ g Kobalt; dies entspricht $5.15 \cdot 10^{-5}$ Zerfällen pro Sekunde, das sind 13.9 μC.

Es sind also für den Nachweis eines Abwassers mit der zulässigen Höchstkonzentration 27.8 l Abwasser für die Bestimmung aufzuarbeiten.

Man müsste aber dann noch eine Aktivitätsmessung vornehmen, um zu sehen, wieviel von dem nachgewiesenen Kobalt eigentlich radioaktiv ist. Diese Methode ist also unzweckmässig. Da aber eine Aktivitätsmessung sowieso unerlässlich ist und diese Messung viel empfindlicher ist als ein tüpfelkolorimetrischer Nachweis, so genügt es, wenn man gleich weniger Wasser zur Untersuchung nimmt. Dieses wird auf irgendeine Weise vorkonzentriert; sei es durch Anreicherung der gelösten Ionen mit Hilfe eines Ionenaustauschharzes oder durch Eindampfen des Wassers.

Im Eluat oder Konzentrat kann man nun nach Zugabe von Trägersubstanzen für die in Frage kommenden radioaktiven Nuklide einen Trennungsgang am Ringofen durchführen.

Semiquantitative Autoradiographie mit Hilfe des Ringofens

WEISZ UND SCOTT[3] zeigten, dass ein empfindlicher, qualitativer Nachweis radioaktiver Substanzen auf autoradiographischem Wege mit Hilfe des Ringofens ausgeführt werden kann. Das Rundfilter mit der in der Ringzone konzentrierten Probe wird eine genügend lange Zeit auf einen Röntgenfilm gelegt. Nach dem Entwickeln erscheint die autoradiographische Abbildung als scharfer dunkler Ring. Eine quantitative Bestimmung liesse sich durch Vergleich der Intensität mit Standardringen durchführen. Einen besseren Weg wiesen WEISZ UND OTTENDORFER[15], bei dem man nicht nur die Menge pro Flächeneinheit, sondern auch noch die Zeit als frei wählbare Variable einbeziehen kann. Die Schwärzung einer lichtempfindlichen Schicht hängt von folgenden Grössen ab:

$$\frac{\text{Menge der radioaktiven Substanz}}{\text{Fläche}} \cdot \text{Zeit}$$

Die als Reziprozitätsgesetz in der Radiometrie bekannte Beziehung besagt, dass dieselbe Schwärzung erzielt wird, wenn man Proben geringerer Aktivität lange Zeit oder Proben stärkerer Aktivität kurze Zeit einwirken lässt.

Wird nun das Filter mit dem abzubildenden Ring entlang einem Radius aufgeschnitten, mit Röntgenfilm in Kontakt gebracht und von der Schnittstelle beginnend allmählich vom Röntgenfilm abgehoben und dadurch die Exposition beendet, so erhält man ein Autoradiogramm mit zunehmender Schwärzung.

Die Auswertung erfolgt durch Vergleich von Probenring-Chronoautoradiogrammen und Standardring-Chronoautoradiogrammen durch Verdrehen und Feststellen der Stufendifferenz[15]. Die Expositionszeiten zweier aufeinanderfolgender Stufen unterscheiden sich um den Faktor $k = \sqrt[8]{2} = 1.0905$; 8 Stufen ergeben daher eine Verdopplung der Expositionszeit $((\sqrt[8]{2})^8 = 2)$.

Bestimmung der Erfassungsgrenzen einiger radioaktiver Isotope mit Hilfe der Ringchronoautoradiographie

Es wurde für folgende radioaktive Ionen die autoradiometrischen Erfassungsgrenzen bestimmt:

Isotop	*im Ring fixiert als*
Kobalt-60	Sulfid
Ruthenium-106	Sulfid
Cäsium-137	Platinhexachlorid
Strontium-90	Karbonat
Cer-144	Phosphat

Die Aktivität der Versuchslösungen war auf ± 10% bekannt. Jeder Lösung wurde 0.1 bis 0.2 mg/ml Träger zugesetzt. Die Herstellung der Ringe geschah auf die übliche Weise[2].

Bei Ruthenium-106 musste allerdings vor dem Waschen mit 0.1 N Salzsäure ein Tropfen Salpetersäure aufgebracht werden, da im Tüpfelfleck eine teilweise Reduktion zum Rutheniummetall eintrat.

Durch entsprechendes Verdünnen wurden Lösungen hergestellt, die bei der genannten Arbeitsweise Chronoautoradiogramme lieferten, die im Bereich der kürzeren Belichtungszeiten überhaupt keine sichtbare Schwärzung mehr aufwiesen. Die Berechnung der Erfassungsgrenzen setzt die Tatsache voraus, dass bei dem hier verwendeten Kodak Röntgenfilm *Kodirex* (entwickelt wurde mit dem Kodakentwickler DX-80) der Schwarzschildexponent eins ist, dass also das Reziprozitätsgesetz bis zu kleinsten Aktivitäten und langen Belichtungszeiten gültig ist[16].

Für die Auswertbarkeit ist eine genügende Anzahl von Stufen notwendig, um den Vergleich des Probenring-Chronoautoradiogramms mit dem Standardring mit ausreichender Genauigkeit durchführen zu können.

Ist nun bei einem Standardring-Chronoautoradiogramm die erste schwärzungsmässig sichtbare Stufe die Stufe n und nimmt man an, dass für eine quantitative Auswertung ein Schwärzungsverlauf über 8 Stufen notwendig ist, so ist die erfassbare Mindestmenge aus der Expositionszeit, die der Stufe 8 entspricht zu errechnen. Man berechnet also für die Stufe $n + 8$ die Belichtungszeit:

$$T = t_{(n+8)} = t \cdot 1.0905^{(n+8)-1}$$

t = Zeit bis zum ersten Impuls = Belichtungszeit der ersten Stufe in Minuten; $1.0905 = \sqrt[8]{2}$ = Stufenfaktor.

Aus dem Reziprozitätsgesetz lässt sich nun die Aktivität errechnen, die bei einer Laufzeit für eine Umdrehung des Autoradiogrammes von 6 Stunden die gleiche Schwärzung hervorruft wie die in dem obigen Standardring-Chronoautoradiogramm verwendete Menge in der Zeit T.

$$C \cdot 360 = C_r \cdot T_{(\mathrm{min})}$$

C = Erfassungsgrenze bei einer sechsstündigen Autoradiographie in Curie; C_r = Aktivität des Ringes in Curie.

Für einige radioaktive Isotope wurden so die Erfassungsgrenzen für eine sechsstündige Laufzeit der Chronoautoradiographie bestimmt. Tabelle I zeigt die erhaltenen Werte.

In der letzten Spalte sind die Mengen an Abwasser angegeben, die für die Bestimmung aufzuarbeiten sind, wenn man das in der gerade noch erlaubten Höchstkonzentration vorliegende Nuklid erfassen will.

TABELLE I

Isotop	*erfassbare Aktivität in nC (= 10^{-9}C)*	*erfassbare Menge in 10^{-12} g*	*benötigte Abwassermenge in ml*
Kobalt-60	0.38	3.29	0.76
Ruthenium-106	2.25	6.55	22.50
Cäsium-137	1.08	4.05	5.40
Strontium-90	0.66	1.63	660.00
Cer-144	1.80	1.39	18.00

Die Anreicherung grösserer Flüssigkeitensmengen am Ringofen

Um Mengen von Millilitern am Ringofen aufzubringen wurden verschiedene Methoden versucht. Als brauchbar hat sich folgende Methode erwiesen. Die auf zwei bis drei Milliliter vorkonzentrierte Flüssigkeit befindet sich in dem Spitzröhrchen 2 der Abb. 1. Es wird mit der Gummiballpumpe 3 ein gelinder Überdruck erzeugt, der die Kapillare 6 mit Flüssigkeit füllt. Dann wird der Hahn des Tropftrichters 4 geöffnet, so dass das Wasser die Möglichkeit hat aus dem Tropftrichter abzutropfen. Das Filter saugt aus der Kapillare gerade so viel Flüssigkeit, als im Ring verdampft; dabei tropft aus dem Tropftrichter das Wasser nach. Reisst durch Eindringen einer Luftblase in die Kapillare vom Filter her der Flüssigkeitstransport ab, so wird durch den Überdruck, der dann durch die abtropfende Flüssigkeit entsteht, gleich wieder der Kontakt der Flüssigkeit mit dem Filter hergestellt.

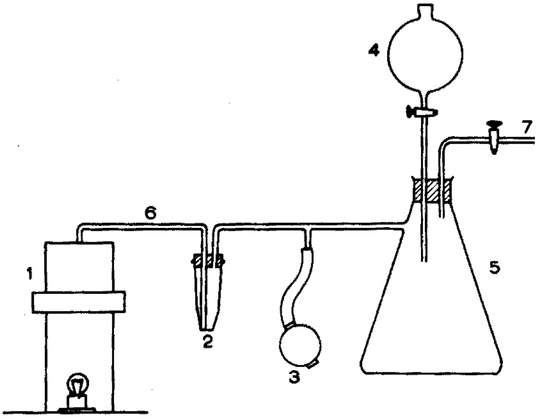

Abb. 1. Anreicherungsverfahren. 1. Ringofen, 2. Spitzröhrchen nach Gorbach, 3. Gummiballpumpe, 4. Tropftrichter, 5. Saugflasche, 6. Kapillarrohr, 7. Entlüftungshahn.

Mit dieser Methode lassen sich Flüssigkeiten mit verschiedenem spezifischen Gewicht, wie organische und wässrige Lösungen gleich gut anreichern.

Das vorkonzentrierte Abwasser wird mit Trägersubstanz versetzt und am Ring angereichert. Durch spezifische Fällungsreaktionen führt man eine Fixierung des gesuchten Stoffes herbei. Anschliessend wird autoradiographiert.

ZUSAMMENFASSUNG

Es wird die Brauchbarkeit des Ringofens und der Ringchronoautoradiographie zur Untersuchung sehr verdünnter radioaktiver Lösungen aufgezeigt, und die damit erreichbaren Erfassungsgrenzen angegeben; sie sind in der Grössenordnung von Nanocurie und darunter. Ein Anreicherungsverfahren für grössere Flüssigkeitsmengen am Ringofen wird beschrieben.

SUMMARY

The ring-oven method and ring chronoautoradiography are shown to be suitable for the investigation of very dilute radioactive solutions. The limits of detection are of the order of nanocuries or less. A method for the concentration of large volumes of liquid on the ring oven is described.

RÉSUMÉ

La méthode du four annulaire et la chronoautoradiographie circulaire peuvent être utilisées pour

les recherches utilisant des solutions radioactives très diluées. Les limites de détection sont de l'ordre du nanocurie ou moins. Une méthode est décrite pour la concentration de grands volumes de solution.

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Short Communications

The separation of fluorine by micro-diffusion of hydrofluoric acid

The separation of fluorine by micro-diffusion of hydrofluoric acid in polythene bottles has been described by SINGER AND ARMSTRONG[1]. More recently HALL[2] has described an improvement of this technique which permits the relatively simple separation of as little as 1 μg of fluorine. The major disadvantage to this method of separation has been the relatively long time required (20 h) for complete recovery. The present work describes an attempt to decrease the diffusion time by the use of small polythene cells modelled after the standard Conway type.

Apparatus and reagents

Figure 1 shows the dimensions of the diffusion cell. This is easily turned on a lathe from polythene rod. A cover for the cell is cut from 1/8" sheet polythene.

Dowex "High Vacuum" silicone grease is used to seal the lid to the cell. Other sealants were investigated, but this gave the best results.

All determinations reported in this paper used the colorimetric procedure of MEGREGIAN[3] after appropriate scaling down of volume.

Procedure

The procedure given here is one evolved after numerous preliminary experiments. All of the work reported here used this method unless stated otherwise.

The upper surface of the diffusion cell is smeared with the grease fixative. 0.3 ml of 10 N sodium hydroxide is pipetted into the central compartment and 0.5 ml of the sample solution into the outer compartment. Aqueous solutions do not wet polythene, and the sample solution thus forms a drop occupying no more than 1/3 of the surface of the cell. The lid is then placed on the cell leaving just enough room for insertion of a pipette tip opposite the sample drop; 0.5 ml of concentrated sulphuric acid (A.R. grade) is rapidly run into the outer compartment and the lid is immediately sealed shut. This operation must be done quickly (a pipette with the tip cut off is convenient since the volume of acid is not critical) as the acid does wet polythene and will thus flow around the cell and react with the sample. With a little practice, however, this operation can be easily accomplished with no danger of losing fluoride from the cell, thus making the freezing of the sample solution[1] unnecessary. After being closed, the cell is rotated to mix the acid and sample solution, and incubated at 60° in a laboratory oven for a minimum of 4 h. After incubation, the centre compartment and washings are transferred with a hypodermic syringe to a 10-ml volumetric flask and diluted to volume. The fluoride is then determined colorimetrically by the zirconium eriochrome cyanine R system as described by MEGREGIAN[3]. For the determination of 1–10 μg of fluoride, it has been found convenient to scale this procedure down so that 1.0 ml of the zirconium reagent and 1.0 ml of the colour reagent is added to the 10.0 ml fluoride sample.

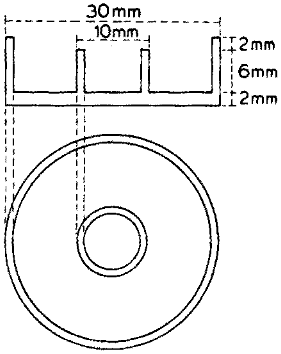

Fig. 1. Micro-diffusion cell cut from polythene rod.

It is preferable to run samples in duplicate and to include standards with each batch of samples. This is no hardship since individual sample handling time is no more than 10 min for the entire procedure and, by stacking the cells on top of each other, 30–60 cells can be operated concurrently.

RESULTS AND DISCUSSION

Early attempts to liberate hydrofluoric acid with perchloric acid as recommended by SINGER AND ARMSTRONG[1] and HALL[2] led to low recoveries of fluorine. Other acids were therefore investigated as possible liberating agents with the results shown in Table I. It is not clear why perchloric acid should give low results; phosphoric acid gives high results possibly because of some carry-over of the acid. Sulphuric acid gave good results and was used in all further experiments. In a brief letter, FRERE[4] also reports the use of sulphuric acid as a liberating agent. The results obtained in the

TABLE I

COMPARISON OF LIBERATING ACIDS

μg F taken	*μg F found*		
	$HClO_4$	*H_2SO_4*	*H_3PO_4*
2	1.4	2.2	3.1
4	2.9	3.9	4.6
6	4.9	6.0	6.9
8	7.2	7.5	8.6
10	8.0	10.4	8.5

1.0 ml of acid added to 0.5 ml aqueous NaF solution.

present work demonstrated that fluorine can be adequately separated from at least moderate amounts of the common interferences, phosphate and sulphate, by this technique.

The amount of sulphuric acid added to the cell is not critical. Standard curves derived from adding 1.0 and 0.5 ml of sulphuric acid are indistinguishable. The 0.5 ml volume was chosen for addition because it can be added faster, thus decreasing the possibility of loss of hydrofluoric acid through the opening, and because the diffusion rate is slightly faster.

Temperature does not affect the diffusion rate as much as might be expected; this is probably due to the fact that ambient temperature does not truly reflect cell temperature because of the heat liberated when the sulphuric acid is mixed with the sample. Several experiments extending to 20 h at room temperature yielded incomplete recovery of fluoride in spite of the rapid initial diffusion rate. FRERE[4] has apparently been successful in liberating hydrofluoric acid at room temperature, but he gives no details of his experimental procedure.

Fig. 2 demonstrates that under the recommended conditions, fluorine is completely transferred to the centre compartment of the cell within 4 h. If desired, the cells can be incubated overnight or even over a week-end without ill-effect. If the cells are incubated for a sufficient length of time, it will be found that the centre compartment has evaporated to dryness. This effect does not result in loss of fluorine and can be safely ignored.

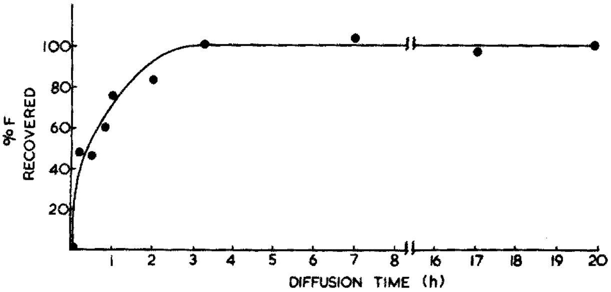

Fig. 2. Recovery rate of 8.0 μg F liberated as HF by 0.5 ml concentrated H_2SO_4.

The reproducibility of this separation and determination of fluoride was estimated

TABLE II

PRECISION OF MICRO-DIFFUSION OF HF

µg F found		*% Deviation*	
Individual	*Mean*	*Individual*	*Mean*
5.4, 6.0	5.7	−10, 0.0	−5
6.2, 5.8	6.0	+3, −3	0
6.0, 6.3	6.15	0, +5	+2.5
5.8, 5.5	5.65	−3, −8	−5.5
5.9, 5.7	5.8	−2, −5	−3.5
6.0, 6.4	6.2	0, +7	+3.5
6.1, 6.1	6.1	+2, +2	+2.0

Duplicate samples containing 6.0 µg F. Each pair was included in a different experiment, thus these results represent the precision obtained over a period of several months.

by including a pair of 6 µg F standards in seven different experiments (Table II). Of many standard curves constructed over several months, no point has deviated by more than 10% from the resultant line. Although insufficient samples have been analysed to allow a meaningful statistical analysis, it is apparent that samples run in duplicate should not deviate by more than 5% from the true value. Precision appears to improve in the range 10–20 µg F, but little work has been done at these concentrations.

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The rate of solvent extraction of some zinc β-diketone chelates

Little detailed attention has been given to the rates of the solvent extraction of metal chelates. Some few authors have related the rates of particular extractions to pH, reagent type, reagent concentration, non-aqueous solvent type, and metal ion concentration[1]. Apparently the rate of achievement of equilibrium depends upon the rate of formation of the extractable species and the rate of transfer of this species from the aqueous phase into the organic phase. The slower of the two processes will be rate-determining in any particular system. In the present study the extraction of zinc from an aqueous phase into a chloroform phase containing several β-diketone chelating reagents has been examined.

Samples consisting of 40 ml of chloroform-saturated water, 0.1 *M* in sodium perchlorate, and 40 ml of water-saturated chloroform containing 0.1, 0.01, or 0.001 *M* chelating reagent were equilibrated at 30°, at a predetermined constantly-maintained pH, and at a stirring rate which was fast enough that an increase would not increase the subsequently measured rates of zinc extraction. Then enough zinc perchlorate solution (about 100 μl) labelled with ^{65}Zn was introduced to give an aqueous zinc concentration of $10^{-5.7}$ *M*. Samples of 150 μl were taken from each phase at several time intervals after stopping the stirrer and timer simultaneously. These samples were placed in small vials and counted in a well-type scintiliation counter.

Plots of the logarithm of the total zinc concentration in the aqueous phase against time in min gave straight lines in all determinations. The first three columns of Tables I and II present a summary of the kinetic data. The concentration of the ion of the chelating reagent in the aqueous phase, [AcAc$^-$] or [R$^-$] has been calculated from the relation $[R^-] = [HR]_0/P_rK_r\,[H^+]$ where $[HR]_0$ is the concentration of the chelating reagent in the organic phase, $[H^+]$ is the hydrogen ion concentration in the aqueous phase, P_r is the partition coefficient of the chelating reagent, and K_r is the association constant of the chelating reagent. These values are available in the literature[2]. By assuming very rapid establishment of chemical equilibria and by utilizing association constants available in the literature[3], the concentrations of various species in the acetylacetone systems may be estimated. These appear in Table I. Proper constants were not available for the other two chelating reagents. At high pH values more than one hydroxo complex had to be assumed in order to give proper mass balance.

TABLE I

SUMMARY OF EXTRACTION RATE DATA FOR THE ZINC-ACETYLACETONE SYSTEM

$[HR]_0$[a]	pH	Slope[b]	$[AcAc^-]$	$[Zn^{2+}]$	$[ZnOH^+]$	$[Zn(OH)_3^-]$	$[Zn(OH)_4^{2-}]$	$[ZnAcAc^+]$	$[Zn(AcAc)_2]$
0.1	6.0	0	$10^{-5.2}$	$10^{-6.00}$	$10^{-9.60}$			$10^{-6.10}$	$10^{-7.38}$
0.1	7.0	−0.38	$10^{-4.2}$	$10^{-6.78}$	$10^{-9.38}$			$10^{-5.88}$	$10^{-6.16}$
0.1	8.0	−0.90	$10^{-3.2}$	$10^{-8.35}$	$10^{-9.95}$			$10^{-6.45}$	$10^{-5.73}$
0.1	9.0	−0.90	$10^{-2.2}$	$10^{-10.28}$	$10^{-10.88}$			$10^{-7.38}$	$10^{-5.66}$
0.1	10.0	−0.73	$10^{-1.2}$	$10^{-12.48}$	$10^{-12.08}$	$10^{-6.08}$	$10^{-9.08}$	$10^{-8.58}$	$10^{-5.86}$
0.01	8.0	−0.19	$10^{-4.2}$	$10^{-6.78}$	$10^{-8.38}$			$10^{-5.88}$	$10^{-6.16}$
0.01	9.0	−0.75	$10^{-3.2}$	$10^{-8.35}$	$10^{-9.95}$			$10^{-6.45}$	$10^{-5.73}$
0.01	10.0	−1.00	$10^{-2.2}$	$10^{-10.28}$	$10^{-9.88}$			$10^{-7.38}$	$10^{-5.66}$
0.01	11.0	−0.28	$10^{-1.2}$	$10^{-12.30}$	$10^{-10.90}$	$10^{-6.90}$	$10^{-8.90}$	$10^{-8.40}$	$10^{-5.70}$
0.001	9.0	−0.20	$10^{-4.2}$	$10^{-6.78}$	$10^{-7.38}$			$10^{-6.48}$	$10^{-6.16}$
0.001	10.0	−0.26	$10^{-3.2}$	$10^{-8.36}$	$10^{-7.96}$			$10^{-6.46}$	$10^{-5.75}$
0.001	11.0	0	$10^{-2.2}$	$10^{-11.13}$	$10^{-9.93}$	$10^{-5.73}$	$10^{-7.73}$	$10^{-8.23}$	$10^{-6.51}$
0.001	12.0	0	$10^{-1.2}$	$10^{-14.08}$	$10^{-11.68}$	$10^{-5.71}$	$10^{-6.64}$	$10^{-9.18}$	$10^{-7.46}$

[a] All concentrations are in moles/l.

[b] Slope of the line obtained by plotting log (zinc × 10^7) in aqueous phase *vs.* elapsed time.

TABLE II

SUMMARY OF EXTRACTION DATA FOR THE ZINC-BENZOYLACETONE AND ZINC-DIBENZOYLMETHANE SYSTEMS

System: benzoylacetone				*System: dibenzoylmethane*			
$[HR]_0$[a]	*pH*	*Slope*[b]	$[R^-]$	$[HR]_0$[a]	*pH*	*Slope*[b]	$[R^-]$
0.1	7.1	−1.00	$10^{-6.3}$	0.1	6.5	−0.06	$10^{-9.0}$
0.1	8.0	−1.35	$10^{-5.4}$	0.1	7.0	−0.80	$10^{-8.5}$
0.1	9.0	−1.40	$10^{-4.4}$	0.1	8.0	−0.78	$10^{-7.5}$
0.1	10.0	−1.60	$10^{-3.4}$	0.1	9.0	−0.94	$10^{-6.5}$
0.01	8.1	−0.30	$10^{-6.3}$	0.01	7.5	−0.23	$10^{-9.0}$
0.01	9.0	−0.48	$10^{-5.4}$	0.01	8.0	−0.75	$10^{-8.5}$
0.01	10.0	−3.1	$10^{-4.4}$	0.01	9.0	−2.50	$10^{-7.5}$
0.01	11.0	−0.65	$10^{-3.4}$	0.01	10.0	−1.30	$10^{-6.5}$
0.001	9.1	−0.75	$10^{-6.3}$	0.001	8.5	−0.03	$10^{-9.0}$
0.001	10.0	−1.00	$10^{-5.4}$	0.001	9.0	−0.42	$10^{-8.5}$
0.001	11.0	−0.35	$10^{-4.4}$	0.001	10.0	−0.30	$10^{-7.5}$
0.001	12.0	0	$10^{-3.4}$	0.001	11.0	−0.15	$10^{-6.5}$

[a] All concentrations are in moles/l.

[b] Slope of the line obtained by plotting log (zinc × 10^7) in aqueous phase *vs.* elapsed time.

The straight-line character of the plots indicates that the extraction behaves as first order with respect to the total zinc concentration in the aqueous phase. If one assumes the simple zinc ion to be directly involved in the extraction, then an increase in zinc ion concentration should increase the extraction rate. This is not the case. Similar observations apply to $[ZnOH^+]$ and $[ZnAcAc^+]$. Further, no correlation between pH or chelating reagent concentration and the rates is apparent. However, increases in $[Zn(AcAc)_2]$ result in increased rates. This suggests that the rate of extraction is controlled by the rate of transfer of the neutral chelate from the aqueous phase into the organic phase. This rate of transfer would depend upon the metal chelate concentration in the aqueous phase. The amount of metal chelate in the aqueous phase is a function of the total zinc concentration and this explains the first order relationship with respect to total zinc. By analogy, the other two systems (benzoylacetone and dibenzoylmethane) probably may be explained similarly to the acetylacetone one. It is concluded that the rate of extraction in these systems is probably controlled by the rate of transfer of the neutral species from the aqueous to the organic phase.

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The complex of gallium(III) with diphenylthiocarbazone

The reaction of diphenylthiocarbazone (dithizone) with a number of metals to form highly coloured inner complexes is well known, and the development of schemes involving the use of masking agents and the control of pH to provide more selective reaction between these elements and the chelating agent, has led to the extensive use of dithizone as a reagent for the solvent extraction and the colorimetric determination of metals[1]. Although much time has been devoted to characterising the behaviour of familiar dithizonates under conditions of specialised practical interest, it has recently become apparent that certain elements, formerly considered to be outside that group in the centre of the periodic table which form dithizonates, do in fact form complexes with the reagent[2,3].

Of the group IIIb elements, indium(III) and thallium(I) form complexes with dithizone, but thallium(III) oxidises the reagent[4]. Gallium(III) is generally considered not to form a dithizonate, no positive evidence for the existence of the complex having been obtained, but it has been reported that a violet coloration may result when a mixture of gallium and dithizone are carefully heated in a dry test tube[4]. Before analytical determination, indium(III) has been extracted from an aqueous phase by dithizone which has been retained with an organic solvent on a solid support[5], and gallium may be removed from aqueous solution by this type of column[6], a violet band being formed. Similarities in the behaviour of dithizone in the liquid-liquid and liquid-solid systems suggested that gallium might also be extracted from an aqueous phase by dithizone in organic solution, and investigations have been carried out to confirm this with gallium-72 as tracer.

EXPERIMENTAL

Reagents

Commercially available dithizone (Hopkin and Williams Ltd.) was dissolved in carbon tetrachloride, extracted into dilute aqueous ammonia solution, and the aqueous phase washed with fresh organic solvent. After acidifying with hydrochloric acid, the precipitated dithizone was dissolved in carbon tetrachloride, and its purity assessed by measurement of the ratios of the optical absorbancy at the absorption maxima of 620 mμ and 450 mμ and the minimum of 510 mμ. Purification by extraction was repeated, if necessary, until satisfactory values were obtained. The concentration of the dithizone solution was calculated from the absorbancy at 620 mμ of a diluted sample, assuming an extinction coefficient[7] of 34.6×10^3, and checked by titration with a standard mercury solution.

Before use, laboratory-distilled water was passed through a mixed-bed deioniser, and then distilled in all-pyrex glassware to remove any traces of organic matter that may have been eluted from the ion-exchanger. Aqueous phases were prepared from either 0.1 M sodium perchlorate-perchloric acid, or from 0.1 M sodium acetate-acetic acid, and these were allowed to stand over solutions of dithizone in carbon tetrachloride to remove any trace metals that might be present.

Irradiated "Specpure" gallium was dissolved in a mixture of sulphuric and perchloric acids, and the radiochemical purity of the element checked by γ-ray spectrometry and by half-life determinations.

Procedure

Batch extractions were carried out by placing 20 ml of aqueous phase in a shaking tube, together with 20 ml of a solution of dithizone in carbon tetrachloride, each phase having been pre-saturated with the other. The active gallium was then added in 0.005 ml of solution, and the tubes and their contents were shaken for 1 h; a longer shaking time did not alter the value of the distribution ratio of the metal between the two phases. After equilibration, the phases were separated by centrifugation, and the activity of 2 ml of each phase was γ-counted using a well-type scintillation counter and associated equipment, corrections for decay of the gallium being applied where necessary. A separate series of experiment, not reported here, indicated that no attenuation of count occurred when the gallium was extracted into the non-aqueous phase, and that the radioactivity of the aqueous and organic phases could be directly compared to obtain a value of the distribution ratio of the metal between the two phases.

The acidity of the aqueous phase was measured by means of a glass electrode used in conjunction with a Morton Electrode System and a Cambridge pH meter.

Initially equilibration was carried out in Pyrex shaking tubes but it was found that a considerable proportion of the tracer gallium added was adsorbed on to the glass. Although the same distribution ratio was obtained at equilibrium when the quantity of metal in the system was increased, *i.e.* when a smaller proportion of the tracer was adsorbed, extractions were eventually carried out in polythene tubes, in which the extent of absorption was decreased considerably.

The molar ratio of metal to dithizone present in the system was always less than 0.1%.

Batch extraction experiments carried out with pure carbon tetrachloride instead of the dithizone solution, showed that no gallium was extracted into the non-aqueous phase in the absence of dithizone.

RESULTS AND DISCUSSION

Preliminary experiments showed that gallium could be extracted into a strong dithizone solution at low acidities, but since this extraction did not occur when pure carbon tetrachloride was used as the non-aqueous phase, the formation of a complex of gallium with dithizone was indicated. Plots of the log of the distribution ratio (log q) against the pH and against the log of the reagent concentration in the non-aqueous phase (log $[\mathrm{HDZ}]_0$) were obtained and these gave slopes of 2.7 and 3.0 respectively, which indicates that a 1:3 complex is formed between gallium and dithizone.

Because the solubility of metal dithizonates and dithizone in aqueous acid solution is normally low it is usual to calculate a composite equilibrium constant K' for metal dithizone equilibria[1], referring to concentrations of reagent and complex in the organic, rather than the aqueous phase. Thus

$$K' = \frac{[\mathrm{GaDZ_3}]_0[\mathrm{H^+}]^3}{[\mathrm{Ga^{3+}}][\mathrm{HDZ}]_0^3}$$

where square brackets represent concentrations which are used in place of activities, and the subscript o refers to species present in the non-aqueous phase. Values for K' for gallium dithizonate, calculated on the assumption that $[GaDZ_3]_o/[Ga^{3+}] = q$, are given in Table I, extractions being carried out from a 0.1 M perchlorate phase.

TABLE I

EQUILIBRIUM CONSTANT FOR THE REACTION BETWEEN GALLIUM AND A SOLUTION OF DITHIZONE IN CARBON TETRACHLORIDE

q	$10^3[HDZ]_o$	$10^4[H^+]$	$10^2K'$	q	$10^4[HDZ]_o$	$10^4[H^+]$	$10^2K'$
76.7	1.21	0.87	2.86	0.0739	2.73	2.82	8.14
8.25	1.21	1.78	2.62	0.497	6.03	2.82	5.08
4.186	1.21	2.29	2.84	1.257	8.39	2.82	4.76
1.574	1.21	3.71	4.56	2.91	9.63	2.82	7.30
0.310	1.21	6.92	5.79	5.26	13.1	2.82	5.18
0.118	1.21	8.71	4.40	4.76	11.9	2.82	6.30

Average value for $K' = 4.99 \pm 1.73 \cdot 10^{-2}$

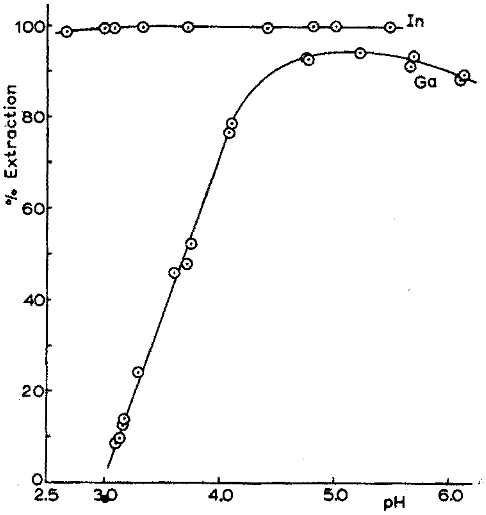

Fig. 1. The extraction of gallium and indium from a 0.1 M acetate phase by a solution of dithizone in carbon tetrachloride.

The extraction of gallium by a strong (10^{-3} M) solution of dithizone in carbon tetrachloride from a 0.1 M acetic acid-sodium acetate buffer was also investigated in order to assess the behaviour of the complex at higher pH values than was possible with an aqueous perchlorate phase. The results are shown in Fig. 1 together with values for the extraction of indium under similar conditions. The value for K' quoted in Table I compares with a figure of $6.9 \cdot 10^4$ which has already been reported for the reaction between indium, in an acetate phase, and dithizone dissolved in carbon tetrachloride[1], thus giving a value for the separation factor β, where $\beta = K'_{InDz_3}/K'_{GaDz_3}$ of $\sim 10^6$. Although the K' values for indium dithizonate are given with reference to an acetate rather than a perchlorate phase, clearly the separation of indium from gallium by dithizone extraction should present no problem.

It has been pointed out[8] that the elements forming dithizonates most readily are those for which the halide stability increases in the order $F^- \ll Cl^- < Br^- < I^-$, that is to say class (b) metals according to a recent classification[9]. If the value for K' reported in Table I is compared with similar constants for other dithizonates of the type MDZ_3[1], assuming that the partition coefficients for the metal complexes are similar, it would appear that gallium dithizonate is a rather weak complex. This is to be expected since gallium(III) is considered to be of class (a) character, showing a greater tendency to combine with oxygen rather than with sulphur donors, and as such would not be expected to form strong complexes with dithizone.

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Solvent extraction of light rare earths from sodium rare earth sulphates

Sodium sulphate precipitation of the light (cerium group) rare earths as double sodium sulphates is used in mineral analysis[1,2] for separating the light earths from the heavy yttrium group.

Solution of sodium rare earth sulphates in ammonium acetate solution, followed by oxalate precipitation of the rare earths*, has been suggested[2,3] as an alternative to sodium hydroxide metathesis for extracting these elements from the double sodium sulphates. When this procedure was applied to a sodium rare earth sulphate of known light rare earth content, recoveries of 90–92% were obtained. The recovery of rare earths was rendered incomplete by the solubilising effect of acetate and ammonium ions on the rare earth oxalates[3]. Since it has been reported[4,5] that the light rare earths are extracted from nitrate salt solutions of low acidity by tri-*n*-butyl phosphate (TBP), the possibility of improving rare earth recovery by TBP extraction from an ammonium acetate solution containing a high concentration of nitrate ion was investigated.

Cerium(III) showed a maximum distribution coefficient** ($D = 2$) when a solution of pH 0.1 containing 0.2 g of sodium rare earth sulphate***, 2.0 g of ammonium acetate, 4.0 g of ammonium nitrate and 2.0 ml of concentrated nitric acid (S.G. 1.42) per 10 ml, was extracted for 3 min with an equal volume of undiluted TBP. The TBP was previously equilibrated with 6 N ammonium nitrate solution adjusted to pH 0.1 with acetic acid. Cerium(III) distribution coefficients were measured using cerium-144 ($T_{\frac{1}{2}} = 290$ d) tracer.

Extraction of the above solution with 3 separate portions of undiluted, pre-equilibrated TBP at an aqueous-organic phase ratio of 1 : 1 yielded essentially quantitative extraction of cerium(III). Cerium was stripped quantitatively from the TBP with 5 equal-volume portions of water. Contact periods of 3 min were employed throughout.

The procedure developed for the TBP extraction of light rare earths from sodium rare earth sulphates dissolved in ammonium acetate was as follows. Ammonium acetate (10 g) and 10 ml of distilled water were added to 1 g of sodium rare earth sulphate in a 200-ml beaker. The contents of the beaker were heated for 5 min at 80°, the mixture being stirred continuously with a glass rod, and 20 g of ammonium nitrate was dissolved in the warm solution. When cool, the resultant solution was adjusted to pH 0.1 with concentrated nitric acid (S.G. 1.42, 10 ml) using a pH meter, and then diluted to 50 ml with distilled water. The aqueous solution thus prepared

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* The rare earths contained in double sodium sulphates consist largely of Ce, La and Nd, together with smaller amounts of Pr, Sm and Gd.

** Distribution coefficient, $D = \dfrac{\text{concn. of element in TBP phase}}{\text{concn. of element in aqueous phase}}$.

*** 20.0% Ce_2O_3; 9.6% La_2O_3; 9.5% Nd_2O_3; 2.2% Pr_6O_{11}; 1.3% Sm_2O_3 and 0.7% Gd_2O_3.

was transferred to a 250-ml separating funnel and extracted with 3 × 50 ml portions of undiluted TBP pre-equilibrated with 6 N ammonium nitrate solution adjusted to pH 0.1 with acetic acid. A shaking time of 3 min was employed for each extraction.

The TBP extracts were combined in a 500-ml separating funnel and the rare earths were stripped from the TBP by shaking it with 5 × 150 ml portions of water. A contact time of 3 min was employed for each extraction. The aqueous extracts were combined in a 1-l beaker and carefully evaporated to *ca.* 50 ml. The rare earths were precipitated as oxalates under the conditions recommended by BROADHEAD AND HEADY[6] for minimising rare earth oxalate losses. The rare earth oxalates were finally dried and ignited at 900° in a muffle furnace.

Recoveries of 99.3 and 99.8% (average, 99.6%) were obtained when the sodium rare earth sulphate used in the cerium(III) distribution coefficient measurements (see above) was carried through the procedure.

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Radioactive tracer study of the reaction between chromium(VI) and diphenylcarbazide

The reaction between diphenylcarbazide and chromium(VI) has long been used for the colorimetry of chromium,[1] but little is known of the nature of the colored species. A survey of the literature reveals many inconsistent and contradictory statements[2].

In the present work, a radioactive tracer technique was employed to clarify the ambiguous behavior of chromium in the extraction of the colored species. A stoichiometric study and magnetic susceptibility measurements were also carried out. A radioactive tracer, ^{51}Cr(VI), was prepared by neutron irradiation of potassium chromate in the JRR-1 reactor.* In the tests, 2 ml of 5 N sulfuric acid and 15 ml of saturated sodium chloride solution were added to the chromate-^{51}Cr solution, and an appropriate volume of an ethanolic solution of diphenylcarbazide was added. After being diluted to 25 ml with water, the solution was shaken with 25 ml of an organic solvent, such as iso-amyl alcohol, benzene, chloroform, for 30 sec. The radioactivity and the absorbance at 540 mμ of the aqueous and organic phases were measured in a well-type scintillation counter and a spectrophotometer, respectively. The distribution ratios obtained are shown in Table I. It is worth mentioning that in the iso-amyl alcohol extraction the distribution ratio of ^{51}Cr reaches unity in the presence of excess of diphenylcarbazide; this means that half the chromium is never extracted from the aqueous phase even when the red-purple color has been completely extracted into the organic phase, although diphenylcarbazide has been recommended as a reagent for the separation of chromium.[3]

TABLE I

DISTRIBUTION RATIO

Organic solvent	*Molar ratio Cr : Carbazide*	*Distribution ratio of*	
		Colored species	*Chromium-51*
Benzene	1 : 10.4	0.10	0.052
	1 : 0	—	0.010
Chloroform	1 : 10.4	0.77	0.35
	1 : 0	—	0.000
iso-Amyl alcohol	1 : 10.4	450	0.96
	1 : 3.97	300	1.09
	1 : 2.02	250	1.16
	1 : 1.04	400	0.93
	1 : 0.84	300	1.44
	1 : 0.42	1000	1.46
	1 : 0.17	1000	1.51
	1 : 0.10	1000	1.95
	1 : 0.052	1000	2.12
	1 : 0	—	2.63

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* The ^{51}Cr(III) species produced by the Szilard-Chalmers effect was removed, and the ^{51}Cr(VI) species was used as a tracer.

The ratio of reagent to chromium in the colored compound was studied. The chromate–^{51}Cr solution was mixed with diphenylcarbazide in 0.4 N sulfuric acid medium, the resulting colored solution was poured onto a cation-exchange column, and the column was washed with 0.4 N sulfuric acid, water and ethanol in that order. The resin loaded with the colored material was then mixed with a saturated sodium chloride solution and shaken with iso-amyl alcohol or chloroform for about 1 h. The deeply colored organic phase was evaporated in a vacuum desiccator. After repeated recrystallization from iso-amyl alcohol or chloroform medium, deep violet crystals were obtained. The content of chromium was determined radiochemically, whereas the contents of carbon and nitrogen were determined by the conventional methods. The ratios of N_4 to Cr and of C_{13} to Cr were found to be 2.1_4 and 2.4_1, respectively, for the crystals obtained from iso-amyl alcohol. The ratio of N_4 to Cr was 2.0_1 for the crystals obtained from chloroform. The results suggest that the colored species contains chromium and reagent in the ratio of 1:2. The molar ratio method, however, indicates that three moles of reagent react with two moles of chromium(VI). This ratio agrees with those reported by the other investigators.

Bose[2] performed a magnetic susceptibility study and concluded that chromium was present in the chromium(II) state, but the measurement was carried out in aqueous medium, where both the extractable and unextractable chromium species were present. In the present study, the magnetic susceptibility was determined in the isoamyl alcohol phase containing the colored species extracted from the aqueous phase. The observed molar susceptibility was 3.8_7 Bohr magneton, which is close to the value of chromium(III) state. It seems probable that the following reaction occurs in the system:

$$2CrO_4^{2-} + 3H_2(RH) + 8H^+ \rightarrow [Cr^{III}R_2]^+ + Cr_{aq}^{3+} + RH + 8H_2O\,,$$

where $H_2(RH)$ and RH represent carbazide and carbazone respectively, the ion associated complex, $[Cr^{III}R_2]^+Cl^-$, is the extractable colored species, and Cr_{aq}^{3+} is the unextractable aquo complex species. Further work on this and related systems (*e.g.* chromium(III)-dithizonate) is in progress, and detailed results will be reported elsewhere.

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Direct-reading instrument for automatic coulostatic analysis in the 10^{-5} - 10^{-7} mole per liter range

A method is described for direct-reading coulostatic analysis. The method involves a principle which, to the writer's knowledge, has not been applied in electroanalytical chemistry, namely sampling and storage of voltage readings for a non-repetitive, continuously varying voltage across an electrochemical cell. The instrument based on this principle involves only simple circuitry and allows rapid coulostatic analysis in the $10^{-5}-10^{-7}$ mol.l^{-1} range. Application appears feasible for any substance which can be analyzed by classical polarography or voltammetry with a solid electrode.

Fundamentals of coulostatic analysis were recently discussed in papers from this Laboratory[1,2]. The method is based on the determination of the potential-time variations of an electrode, at open circuit, upon charging with a known quantity of electricity. The latter is selected to bring the potential from the foot of the current-potential curve for the analyzed substance to the diffusion current range. The change of potential ΔE after charging was derived for various electrodes and conditions of electrolysis[1,2]. For example, $|\Delta E|$ increases linearly with $t^{\frac{1}{2}}$ when mass transfer is controlled by semi-infinite linear diffusion, and the slope of the ΔE versus $t^{\frac{1}{2}}$ line is proportional to the concentration of the substance being reduced or oxidized. Theory shows that the method is of practical value in the $10^{-5}-10^{-7}$ mol. l^{-1} range. This conclusion was confirmed by a detailed experimental study[3] now in progress.

Potential-time curves can easily be recorded by the method previously described[2] but an automatic instrument with direct read-out of ΔE's for preselected values of t seems desirable. The schematic circuit of such an instrument, which is now under development in this laboratory, is shown in Fig. 1. The instrument includes: (a) the polarization circuit of potentiometer P_2 with which the potential of the working electrode is set at the foot of the current-potential curve for the analyzed substance

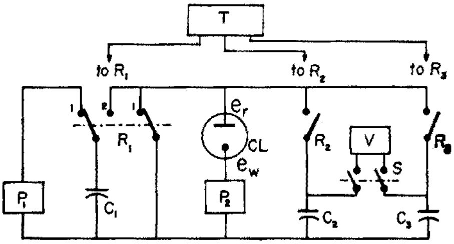

Fig. 1. Schematic diagram of instrument.

P_1, P_2 Potentiometers
C_1 Capacitor (*e.g.*, 0.05 microfarad)
C_2, C_3 Low leakage capacitors (*e.g.*, 0.01 to 0.05 microfarad)
R_1, R_2, R_3 Relays
V Voltage read-out instrument with high input resistance, *e.g.*, 10^{12} ohms
T Timing device
CL Electrolytic cell
e_r Reference electrode
e_w Working electrode such as hanging mercury drop, platinum electrode, etc.

for the prevailing electrolysis conditions; (b) the "coulostat" (P_1 and C_1) by which a known quantity of electricity is supplied to the cell; (c) a circuit for sampling and read-out of the cell voltage (V, C_2, C_3).

The sequences of operations is as follows:

(a) Relay R_1 is in position 1 and switch S is open; C_1 is charged at the voltage set on P_1 (*e.g.* 10–20 v), and e_w is set at the proper potential by means of P_2. (b) Relay R_1 switches to position 2, and C_1 discharges across the cell; a short time (*e.g.* a few millisec) afterwards, R_2 closes and opens immediately so that C_2 is charged at the cell voltage corresponding essentially to $t = 0$ provided that C_2 is very small in comparison with the double layer capacity (*e.g.* 1 microfarad for the hanging mercury drop). (c) After a given time t (*e.g.* 0.1 to 1 sec), which is set on the timing device T, relay R_3 closes and opens immediately; C_3 is thus charged at the cell voltage corresponding to time t. (d) Switch S is closed and the variation of potential ΔE of the working electrode from time $t = 0$ to time t is read directly on meter V. The latter must have a sufficient high input resistance (*e.g.* ,10^{12} ohms) to render leakage of the charges on C_2 and C_3 negligible. A pH-meter of the direct reading potentiometer types is adequate since ΔE is easily of the order 0.05 to 0.2 v. The measurement proper is about as rapid as a pH determination, and the time-consuming operation is oxygen removal from the solution. The variation ΔE is determined for the analyzed substance and for the blank, and the unknown concentration is computed from the difference of the ΔE's.

Two or even a larger number of substances can be determined by one of the two methods previously outlined[1,2]. (a) The ΔE's are determined separately for the successive plateaus in the current-potential curve, and the concentrations are computed, after correction for the blank, from the differences in the ΔE's at a given t. (b) A multiple charging unit is used which charges successively the working electrode to potentials in the plateaus of the more easily reducible (oxidizable), the next substance, etc; voltages are stored in capacitors and are read-out by the method of Fig. 1. The first method can be applied with the instrument of Fig. 1 without modification and may be adequate in most instances.

It is believed that this instrument should make coulostatic analysis convenient for routine analysis.

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Über die Löslichkeit einiger Pyrrolidinkarbaminate in organischen Lösungsmitteln

Obwohl die Extrahierbarkeit[1–5] der Metallkarbaminate weitgehend von ihrer Löslichkeit in den betreffenden organischen Lösungsmitteln abhängig ist, wurde letzteres jedoch verhältnismäßig wenig Aufmerksamkeit geschenkt und nur selten gehen diesbezüglich Angaben über Schätzungen hinaus. Šedivec und Flek[6] haben die Löslichkeit einiger Metall-Diäthyldithiokarbaminate quantitativ bestimmt.

Nachfolgend werden über die Löslichkeit dreier, als Fällungsmittel dienender Karbaminate sowie der Pyrrolidinkarbaminatmetallverbindungen berichtet.

EXPERIMENTELLES

Vorerst wurde die Löslichkeit des Natriumdiäthyldithiokarbaminates sowie des Ammonium- und Natriumpyrrolidindithiokarbaminates in reinem Wasser und in einigen organischen Lösungsmitteln bestimmt. Zu diesem Zweck wurde jeweils 100 ml der bei 20° gesättigten Lösungen zur Trocknung eingedampft und der bei 105° gewonnene Trockenrückstand gewichtsmäßig ermittelt. In keinem Fall konnte beim Trockenrückstand eine Zersetzung beobachtet werden. Die erhaltenen Resultate sind in Tabelle I zusammnegefaßt und geben die Menge in g an.

TABELLE I

LÖSLICHKEIT VON DISUBSTITUIERTEN DITHIOKARBAMINATEN IN WASSER UND EINIGEN ORGANISCHEN LÖSUNGSMITTELN

(g Karbaminat/100 ml Lösungsmittel bei 20°)

	Wasser	*Chloroform*	*Tetrachlorkohlenstoff*	*Toluol*	*Äethylazetat*	*Pyridin*
Na-diäthylkarbaminat	35.06	0.03	0.006	0.095	1.08	7.08
Na-pyrrolidinkarbaminat	27.49	Sp.	0.003	0.09	0.04	7.56
NH_4-pyrrolidinkarbaminat	18.91	0.38	0.12	0.20	0.11	1.75

Aus dieser Tabelle kann unschwer ersehen werden, daß sich die reinen Fällungsmitteln außer in Wasser noch in Pyridin relativ gut lösen. Interessant ist auch, daß das Ammoniumpyrrolidindithiokarbaminat in Wasser und Pyridin schlechter löslicher als das entsprechende Natriumsalz, aber in organischen Lösungsmitteln durchwegs besser löslich ist.

Zur Bestimmung der Löslichkeit der Metallkarbaminatverbindungen wurde im allgemeinen wie folgt vorgegangen:

die entsprechende Pyrrolidinkarbaminate wurden durch Fällen aus, so weit als möglich, neutralen Lösungen des entsprechenden Metallsalzes mit jeweils einer 5 %igen wässrigen Karbaminatlösung gebildet. Nachdem die abfiltrierten Niederschläge mit Wasser gut ausgewaschen und vorsichtig getrocknet wurden, wurde zu einer kleinen Menge in einer Eprouvette 10 ml des zur Untersuchung gelangenden organischen Lösungsmittels hinzugefügt und gut geschüttelt. Um eine gesättigte

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Lösung sicher herzustellen wurde nach dem Schütteln noch ein kleiner Überschuß an Metallkarbaminatlösung hinzugefügt und ungefähr 20 St. lang bei 20° im Thermostaten gelassen. Nach dieser Zeit wurde von der organischen Phase 5 ml abpipettiert, das Lösungsmittel vorsichtig abgedampft und der Rückstand ausgewogen. Diese Arbeitsweise wurde in Anlehnung an die Methodik nach ŠEDIVEC UND FLEK verwendet, um vergleichbare Resultate zu erhalten. Die verwendeten Lösungsmittel von p.A. Qualität, wurden keiner Reinigung unterzogen. Die erhaltenen Resultate sind in Tabelle II zusammengestellt.

TABELLE II

LÖSLICHKEIT VON METALL-PYRROLIDINKARBAMINATE IN EIGENEN ORGANISCHEN LÖSUNGSMITTELN

(g Chelates/100 ml des Lösungsmittels bei 20°)

Lösungsmittel / *Pyrrolidinkarbaminat des*	*Chloroform*	*Tetrachlorkohlenstoff*	*Toluol*	*Äthylazetat*	*Pyridin*
Eisens	14.49	0.23	1.89	0.20	2.45
Kobalts	0.39	3.64	2.18	0.41	11.13
Nickels	0.09	0.02	0.07	0.13	0.17
Vanadins	5.55	0.15	0.36	0.14	2.85
Kupfers	0.32	0.01	0.11	0.04	1.44
Zinks	0.70	0.04	0.28	0.04	0.89
Kadmiums	0.02	Spuren	0.05	0.31	1.03
Antimons	5.28	0.06	0.63	0.07	6.41
Wismuts	26.37	0.06	0.55	0.16	1.99
Zinns	1.77	0.19	0.15	0.04	0.39
Bleis	0.03	0.02	0.09	0.04	0.39

TABELLE III

Element	*Chloroform*		*Tetrachlorkohlenstoff*		*Benzol*	*Toluol*	*Äthylazetat*		*Pyridin*	
	D	P	D	P	D	P	D	P	D	P
Fe	5.80	14.49	1.0	0.23	3.8	1.89	0.4	0.20	7.8	2.45
Co	7.50	0.39	0.4	3.64	3.0	2.18	0.3	0.41	3.5	11.13
Ni	2.80	0.09	0.1	0.02	0.3	0.07	0.1	0.13	1.1	0.17
V	—	5.55	—	0.15	—	0.36	—	0.14	—	2.85
Cu	3.3	0.32	0.2	0.01	0.5	0.11	0.1	0.04	7.2	1.44
Zn	11.8	0.70	0.6	0.04	2.3	0.28	0.6	0.04	21.5	0.89
Cd	2.0	0.02	Spuren	Spuren	Spuren	0.05	Spuren	0.31	29.5	1.03
Sb	56.9	5.28	4.4	0.06	33.8	0.63	1.2	0.07	50.2	6.41
Bi	14.4	26.37	0.2	0.06	2.8	0.55	0.1	0.16	27.5	1.99
Sn	17.0	1.77	0.1	0.19	1.1	0.15	Spuren	0.04	5.5	3.23
Pb	6.6	0.03	0.2	0.02	1.1	0.09	0.1	0.04	9.4	0.39

P = Pyrrolidindithiokarbaminat
D = Diäthyldithiokarbaminat

FOLGERUNGEN

Für die Untersuchungen der Metallpyrrolidinkarbaminate sind Chloroform und Pyridin hinsichtlich der Löslichkeit der einzelnen Verbindungen mit Abstand die besten Lösungsmittel. Lediglich das Kobaltkarbaminat löst sich besser in Tetrachlorkohlenstoff und Toluol als in Chloroform und das an und für sich nicht sehr lösliche Nickelpyrrolidinkarbaminat, soweit es nach der Fällung wieder in Lösung gebracht werden soll, löst sich in Äthylacetat fast ebenso gut wie in Pyridin, bedeutend schlechter aber in Chloroform, Tetrachlorkohlenstoff und Toluol.

Gleiches gilt auch für das Kadmiumsalz.

Tabelle III gibt eine Gegenüberstellung der Löslichkeiten der Diäthyldithiokarbaminate nach den Angaben von ŠEDIVEC UND FLEK mit den entsprechenden Pyrrolidinverbindungen.

Besonders auffällig ist, daß im allgemeinen die Pyrrolidinmetallkarbaminate in organischen Lösungsmitteln schlechter löslich sind, als die Diäthylverbindungen. Dies mag auch im Zusammenhang damit stehen, daß die Pyrrolidindithiokarbaminate bei der Extraktion aus sauren Lösungen[5] beständiger sind.

Aus Tabelle III ist weiters zu ersehen, dass das Wismutpyrrolidinkarbaminat in Chloroform besser löslich ist als das entsprechende Diäthylsalz. In Tetrachlorkohlenstoff hingegen ist das Kobalt- und Zinnsalz des Pyrrolidinkarbaminates besser löslich als die entsprechenden Diäthyldithiokarbaminate. In Äthylacetat und Pyridin hingegen ist lediglich das Kobaltsalz des Pyrrolidinkarbaminates wesentlich besser löslich als das entsprechende Diäthyldithiokarbaminat.

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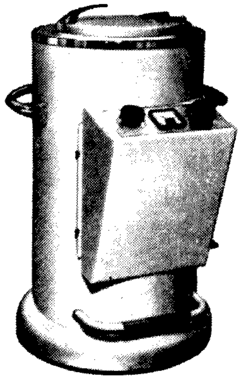

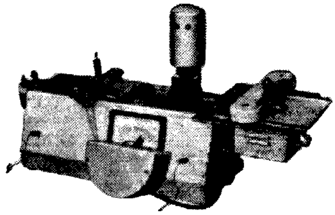

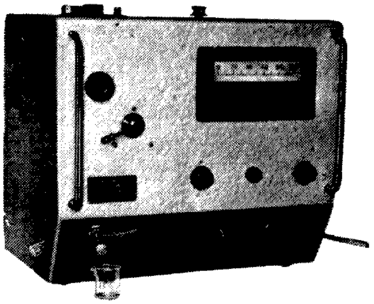

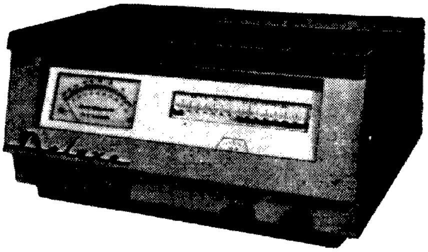

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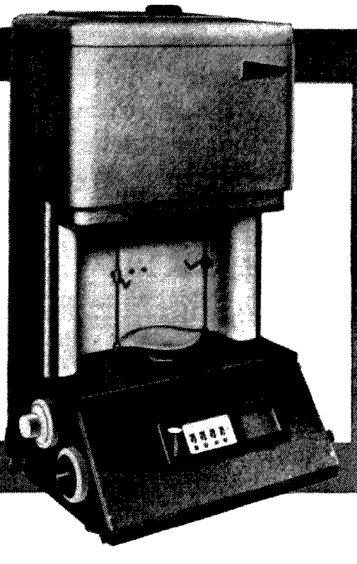

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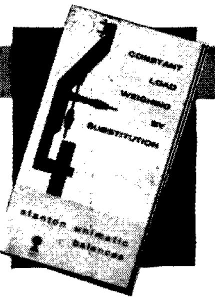

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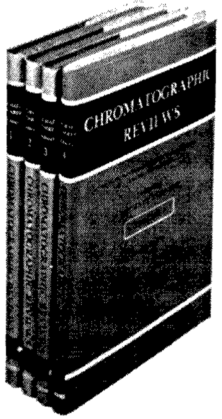

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