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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 28, No. 5, May 1963

THE DETERMINATION OF URANIUM AND THORIUM IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

A neutron activation method is described for the determination of thorium and uranium in rocks at the microgram and submicrogram levels. Radiochemical separations are carried out using the alpha-active nuclides protactinium-231 and neptunium-237 as tracers. The method is applied to the standard granite G1 and the standard diabase W1.

J. W. Morgan and J. F. Lovering, *Anal. Chim. Acta*, 28 (1963) 405–417

LEWIS ACID-BASE TITRATIONS EMPLOYING MEGACYCLE-FREQUENCY OSCILLATORS

III. PREPARATION, ISOLATION AND CHARACTERIZATION OF SOME ADDUCTS PREDICTED FROM TITRATION CURVES

Adducts of stannic chloride with thirteen oxygen bases, isolated as solids from benzene or heptane solution, were characterized by analysis and melting point behavior; several of these are new compounds. Diethyl ether, *n*-dibutyl ether and tetrahydrofuran form AB_2 adducts; *p*-dioxane, in conformity with its being a diacid base, forms only a 1 : 1 species. Methyl, ethyl, *n*-propyl and *n*-butyl alcohols form simple AB_2 adducts at room temperature which on recrystallization from boiling solvent give $SnCl_3(OR)ROH$; iso-propyl alcohol gives only the AB_2 adduct; *tert.*-butyl alcohol only forms $SnCl_3 \cdot OC_4H_9$ (steric hindrance probably prevents formation of the AB_2 adduct). Water gives a AB_4 or AB_5 adduct.

Adducts of aluminum chloride with three nitrogen bases were similarly prepared from acetonitrile solution. Pyridine forms a 1 : 1 species. Acetonitrile itself forms a AB_2 species. Piperidine forms a AB_3 species. The latter two adducts support the view that $AlCl_3$ can form other than 1 : 1 adducts with nitrogen bases.

E. T. Hitchcock and P. J. Elving, *Anal. Chim. Acta*, 28 (1963) 417–425

PARTITION CHROMATOGRAPHY ON ION-EXCHANGE RESINS

SEPARATION OF SUGARS

Factors affecting the chromatographic separation of sugars in ethanol–water solutions by means of anion-exchange resins in the sulfate form have been studied. When proper conditions are chosen a satisfactory separation of mono-, di-, tri-, tetra-, and pentasaccharides from one another can be achieved. In some cases it is possible to separate sugars of similar molecular weight.

O. Samuelson and B. Swenson, *Anal. Chim. Acta*, 28 (1963) 426–432

ETHYLENEGLYCOL-BIS(AMINOETHYL)TETRAACETIC ACID IN THE AMPEROMETRIC TITRATION OF CADMIUM IN THE PRESENCE OF ZINC

Cadmium can be titrated amperometrically with EGTA in the presence of zinc: three modifications of the titration are described. The diffusion current of cadmium may be used to follow the titration at −0.90 or −0.70 V *vs.* the S.C.E. in ammoniacal or acetate-buffered medium respectively. The titration may also be performed in ammoniacal solution at −0.30 V *vs.* the S.C.E., using copper as the amperometric indicator. The influence of iron, aluminium, magnesium, alkaline earths and lead was studied. Ascorbic acid could be used to mask iron and as an effective remover of oxygen. Under appropriate conditions cadmium could be titrated in the presence of 500-fold amounts of zinc. The titration error is approximately 0.002–0.003 ml of a 0.1 *M* titrant solution.

H. Flaschka and R. Speights, *Anal. Chim. Acta*, 28 (1963) 433–440

POLAROGRAPHY OF THE FRUCTOSE–BORATE SYSTEM

The polarographic characteristics of the fructose wave in the presence and absence of borate ions were studied. The borate ions form a complex with fructose in a manner very similar to that formed with the simple polyhydroxy alcohols, such as mannitol. The polarographic data indicate that the predominant complex is a 1 : 1 addition. The equilibrium constant for this complex was calculated at 30°.

W. B. Swann, W. M. McNabb and J. F. Hazel, *Anal. Chim. Acta*, 28 (1963) 441–449

THE DIRECT FLAME PHOTOMETRIC DETERMINATION OF STRONTIUM : CALCIUM RATIOS IN THE ASH OF HUMAN BONES AND TEETH

Samples of bone or tooth ash are dissolved in hydrochloric acid and the strontium : calcium ratio is determined directly by flame photometry using an oxygen–propane flame, surrounded by a mantle of oxygen in order to eliminate the suppressing effect of phosphate. The effective concentration range is 20–1000 p.p.m. of strontium with respect to calcium and the standard deviation, which remains constant over this range, is 10 p.p.m. of strontium with respect to calcium.

M. S. W. Webb and M. L. Wordingham, *Anal. Chim. Acta*, 28 (1963) 450–456

ATOMIC ABSORPTION STUDIES USING A HOLLOW-CATHODE TUBE AS AN ABSORPTION SOURCE

When hollow-cathode tubes are used as the emission source and as the absorption source, atomic absorption studies reveal microgram quantities of several elements; sodium, magnesium, calcium, beryllium, and silicon were detected in the discharge of the absorption tube. Conventional, independent circulating systems and d.c. power supplies were used with each tube, along with other readily available equipment. An analytical curve plotted for sodium over the range 0–100 μg, obeys Beer's law. Lithium and magnesium suppress the sodium absorption values, thus careful standardization is necessary. The average percent deviation from the mean for a number of sodium samples analyzed was ± 8.0%.

J. A. GOLEB AND J. K. BRODY, *Anal. Chim. Acta*, 28 (1963) 457–466

A SEMIQUANTITATIVE ESTIMATION OF RADIO-ISOTOPES BY THE RING-OVEN TECHNIQUE

(in German)

A method for the semiquantitative autoradiographic determination of radio-isotopes by β-ray measurement is proposed. The techniques of ring-oven spot colorimetry are applied in a modified form and no special exposure device is needed. The occurrence of a fading effect and its avoidance are discussed.

H. WEISZ UND D. KLOCKOW, *Anal. Chim. Acta*, 28 (1963) 467–471

TOTAL LUMINESCENCE OF ORGANIC MOLECULES OF PETROCHEMICAL INTEREST

PART I. NAPHTHALENE, PHENANTHRENE AND 1,2,4,5-TETRAMETHYLBENZENE

Total emission, phosphoroscopically resolved emission, excitation and mean lifetime in the excited triplet state were measured for three organic molecules of petrochemical interest in EPA rigid glass at 77°K. Fluorescence was also measured at room temperature in *n*-heptane. Methods for the determination of these three molecules in individual solutions are presented and compared with known methods by absorption spectroscopy. An attempt was made to quantify a blend of the three components by luminescence techniques.

S. P. McGLYNN, B. T. NEELY AND C. NEELY, *Anal. Chim. Acta*, 28 (1963) 472–479

A STUDY OF THE FERROCYANIDE–FERRICYANIDE SYSTEM WITH APPLICATION TO THE DETERMINATION OF ZINC BY NULL-POINT POTENTIOMETRY

The effect of pH and potassium ion concentration on the potential of the ferricyanide–ferrocyanide system and the stability of solutions of ferricyanide and ferrocyanide were studied. An equation relating the potential of the system to pH and potassium ion concentration was derived and agreed well with experimental data. The proper experimental conditions for applying the very rapid, accurate and sensitive precision null-point potentiometric technique to the determination of zinc were then chosen. Zinc in the concentration range of 1–100 p.p.m. was determined with good accuracy within 10 min; as little as 5 μg of zinc can be determined. The stability of solutions, the type of precipitate, the rate of attainment of equilibrium, the accuracy and reproducibility, and the effect of cationic interferences were studied.

J. D. Winefordner and G. A. Davison, *Anal. Chim. Acta*, 28 (1963) 480–494

THE DETECTION OF TITANIUM WITH HYDROXYPHENYLBENZYL KETONES

(Short Communication)

S. D. Paul and M. S. Krishnan, *Anal. Chim. Acta*, 28 (1963) 494–496

OBSERVATIONS ON THE FLUORESCENCE OF SOME TETRACYANOETHYLENE COMPLEXES

(Short Communication)

R. E. Wyant, E. J. Poziomek and R. H. Poirier, *Anal. Chim. Acta*, 28 (1963) 496–498

THE DETERMINATION OF URANIUM AND THORIUM IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

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(Received October 20th, 1962)

The technique of neutron activation analysis has been applied to the determination of traces of many elements in a large number of different materials. The advantages of high sensitivity and comparative freedom from contamination problems made neutron activation analysis an obvious choice when it became necessary to determine uranium and thorium at the microgram and submicrogram level in rocks of considerable geochemical importance. Uranium has been determined in rocks and meteorites by many workers by this method[1-19], and several procedures for thorium have also been reported[2,9,20-24]. In the present work, it was desirable for both uranium and thorium analyses to be carried out on the same sample, because of economy and because of possible sample inhomogeneity, and several analytical procedures were combined to this end. The method was applied to the standard granite G1 and the standard diabase W1.

Nuclear data

Table I lists the relevant nuclear data for the nuclides produced by slow neutron irradiation of the naturally occurring isotopic mixture of uranium and thorium.

TABLE I

NUCLEAR DATA FOR URANIUM AND THORIUM

Target	*Abundance in natural element (%)*	*Isotopic activation cross-section (barns)*	*Product of neutron irradiation*	*Half-life*
^{232}Th	100	7.33	^{233}Th	22.4 min
			^{233}Pa	27.0 days
^{235}U	0.714	582	fission products	
^{238}U	99.3	2.74	^{239}U	23.5 min
			^{239}Np	2.36 days

Several uranium determinations have been based on the fission of uranium-235 by neutron bombardment. The fission product barium-140 was selected by SMALES[4] as being the most suitable for radiochemical assay, because it has a high fission yield and is not produced by neutron capture by any non-fissile naturally occurring nuclide. Barium-140 can be positively detected in the presence of other radioactive barium nuclides by determination of its radioactive daughter product lanthanum-140. KONIG AND WANKE[17] found it convenient to extract fission product xenon from irradiated samples, using a glass vacuum system, which was also employed for potassium–argon dating work.

The inherent sensitivity of the fission-product methods is not as high as those based on the ^{238}U (n,γ) reaction because the natural isotopic abundance of uranium-235 is low and the magnitude of the fission yield is only about 6% even for fission product nuclides near the fission-yield peaks at mass numbers 90 and 140.

The short half-life of uranium-239 makes it inconvenient to base determinations on this nuclide; however, the daughter product neptunium-239 is sufficiently long lived to survive the protracted separations necessary to obtain it in a radiochemically pure form.

JENKINS[20] has employed thorium-233 to determine thorium by neutron activation analysis, using a rapid chromatographic separation. The short half-life of this nuclide, however, precludes its use when very rigorous separations are required; its daughter product protactinium-233 is then more suitable.

EXPERIMENTAL

Preparation of samples for irradiation

Silica ampoules were made from 3 to 4 mm internal diameter tubing, cleaned overnight in aqua regia and rinsed several times with demineralized water. Excess of water was removed by centrifuging and the ampoules were dried in an oven at 110° for several hours. Samples of 0.1 to 0.2 g of the ground rock were weighed into the ampoules, which were then sealed.

Preparation of standards for irradiation

Standard solutions were prepared from analytical grade uranyl nitrate and thorium nitrate. The uranyl salt was standardized gravimetrically by the preparation of stoichiometric U_3O_8 following the method of PETIT AND KIENBERGER[25]. The uranyl nitrate, nominally $UO_2(NO_3)_2 \cdot 6H_2O$, was found to contain 47.31% of uranium. Thorium nitrate was standardized by titration with an EDTA solution, previously standardized against metallic zinc, using Xylenol Orange as indicator[26]. The thorium salt, nominally $Th(NO_3)_4 \cdot 4H_2O$, was found to contain 40.22% thorium.

The solutions were made up and diluted by weight to give a final concentration of uranium or thorium of about 100 μg/g of solution.

Standards were prepared for irradiation by spiking spectrographically pure silica with known weights of standard solution. About 20 mg of silica was weighed into a clean dry silica ampoule, and a similar weight of standard solution was added and weighed accurately. The ampoule was then centrifuged to ensure that any liquid adhering to the wall of the ampoule was brought into contact with the silica. The silica was extremely absorbent and took up the solution readily. The standards were dried overnight at 80° and then for several hours at 110°. The ampoules were then sealed.

Two batches of spectrographically pure silica were analysed for uranium and thorium by neutron activation. Batch *A* consisted of 2 g of silica obtained from a used bottle. Batch *B* was 10 g of silica obtained in a new unopened bottle. The results are shown in Table II.

Batch *B* was used for the preparation of standards in subsequent determinations; the thorium and uranium present in the silica was then less than 0.1% of the amount added.

TABLE II

URANIUM AND THORIUM CONTENTS OF TWO BATCHES OF SPECTROGRAPHICALLY PURE SILICA

Batch	*Uranium* 10^{-8} *g/g*	*Thorium* 10^{-8} *g/g*
A (used bottle)	3.4	31
	0.8	41
B (new bottle)	0.26	4.2
	0.23	0.9

Irradiation

Samples and standards were irradiated together in the medium flux position in HIFAR, in a flux of $6 \cdot 10^{12}$ neutrons/cm^2/sec. The duration of irradiation was one week for samples of G1 and two weeks for samples of W1.

Dissolution

After irradiation, samples were weighed into zirconium crucibles and known amounts of the alpha-emitting nuclides protactinium-231 and neptunium-237 were added as tracers. The samples were then fused with sodium peroxide. Standards were dissolved in hydrofluoric acid after the addition of tracers.

Outline of radiochemical procedure

The initial separation of protactinium from a sodium peroxide melt was achieved by BATE *et al.*[24] by reacting the melt with water and adding ammonium chloride to ensure complete precipitation of silica and scavenging of protactinium; the precipitate of mixed hydroxides and silica was then separated by centrifuging. Protactinium was quantitatively coprecipitated. This procedure was investigated and it was found that neptunium was also coprecipitated under similar conditions. However, recoveries of neptunium and protactinium at later stages in the separation were improved by omitting the addition of ammonium chloride. The subsequent treatment of the precipitate by fuming with hydrofluoric acid and perchloric acid described by BATE *et al.* was adopted to ensure radiochemical equilibration of tracer and sample activities.

A procedure for the separation of neptunium and protactinium by anion exchange from hydrochloric acid was in use in the laboratory for the determination of protactinium-233[27] and was adapted to the present work. In addition to separating these two elements from each other, most of the extraneous activity in the sample was removed by this procedure. Separation from thorium, uranium and plutonium was also achieved. This was highly desirable as the radiochemical purity of the alpha tracer activity recovered was important in the determination of the radiochemical yields.

The extraction of neptunium(VI) into methyl isobutyl ketone (MIBK) from an acid-deficient salting-out solution of aluminium nitrate containing tetrapropyl ammonium nitrate has been described by MAECK *et al.*[28], and this procedure was chosen for the further decontamination of neptunium after the anion-exchange separation.

It was found convenient to concentrate neptunium(IV) from the column eluate by coprecipitation with lanthanum fluoride, which was then easily redissolved in the aluminium nitrate salting solution. The neptunium can be stripped from the MIBK into a reducing (ferrous chloride) solution from which it can be again coprecipitated with lanthanum fluoride or extracted into a xylene solution of 2-thenoyltrifluoroacetone (TTA). Initially, sources were prepared by the evaporation of the MIBK extract on to a stainless steel counting disc, but it was later found that better sources were obtained by evaporation of the TTA–xylene solution. The use of ethylenediamine as a spreading agent was tried with the sources prepared from TTA–xylene, but was found to make little, if any, improvement on the quality of the sources.

The protactinium eluted from the column was contaminated with iron; niobium was another known contaminant. The separation of protactinium from iron and fission products by extraction into di-isobutyl carbinol (DIBC) from hydrochloric acid has been reported by MOORE AND REYNOLDS[29]. Iron was reduced with stannous chloride and oxalic acid was added as a complexing agent for other activities. This procedure was investigated and found suitable. A second extraction of protactinium was included using MIBK, from which it was stripped into dilute hydrochloric acid. As with neptunium, protactinium was finally extracted into TTA–xylene from which the counting source was prepared.

Measurement of radioactivity

The beta-activity of the sources was determined using an end-window beta counter (2" diam.). The sources were usually placed one cm from the end window to get good counting efficiency. The sources prepared on the stainless steel discs were weightless and therefore no corrections were necessary for self-absorption and self-scattering.

The alpha-activity was measured using a 2π proportional flow counter using argon as counting gas. In order to ensure that only alpha particles were counted and that the contribution to the counting rate by "beta pile-up" when using highly active beta sources, was insignificant, short amplifier time constants were used and the operating high voltage was selected to be well below the beta-counting threshold. This was checked periodically using a low protactinium-231 source containing a high activity of protactinium-233.

It was found that when counting was done close to the end window, there was a significant contribution from the alpha-emitting tracers. In the case of protactinium-231 the apparent beta to alpha ratio was constant, but with neptunium-237 it increased with time owing to the growth of the beta-active protactinium daughter. An empirical growth curve was plotted and used to correct the beta count rate of neptunium.

Investigation of radiochemical purity

The radiochemical purity of the activity in the sources was checked where possible by construction of decay curves, determination of beta absorption in aluminium and examination of the gamma spectra. Decay curves were plotted from data obtained using the beta counter mentioned above. The absorption of the beta-activity in aluminium was investigated using an automatic sample changer. Gamma spectra were initially plotted using a 5" × 4" thallium-activated sodium iodide crystal connected to a 256-channel analyser; later, it was found more convenient to use a smaller 1" × 1½" sodium iodide crystal which had rather better resolution and a much lower background in the low-energy range where the principal gamma radiation of neptunium-239 and protactinium-233 occurs. The half-life of protactinium was considered too long to be followed routinely and was not generally plotted.

The energy of the alpha-activity was checked by alpha spectrometry using a gridded ionization chamber connected to a slow Wilkinson 100-channel pulse-height analyser. The resolution, though excellent with platinum trays, was only fair when stainless steel discs were used, but it was sufficiently good to verify the identity of the alpha-activity and to indicate the absence of major contaminants.

METHOD

Preparation of anion-exchange columns

Prepare the anion-exchange columns by slurrying 1 g of Deacidite FF (SRA 71, 100–200 mesh, 7–9% cross-linked) into a polythene tube, 6 mm internal diameter, drawn down to about 2 mm internal diameter at the lower end, the resin being retained by a small plug of cotton wool. Wash the column with 10 ml of demineralized water followed by 10 ml of 8 *M* hydrochloric acid.

Preparation of tracers

(*a*) *Neptunium-237.* Purify the neptunium-237 tracer immediately before use. Take 0.1 ml of a solution containing $5 \cdot 10^4$ alpha counts per min per ml of neptunium-237, add 1 ml of 5 *M* hydroxylamine hydrochloride solution, 1 ml of 0.1 *M* ferric chloride solution and 8 ml of 10 *M* hydrochloric acid. Mix well and warm for 10 min. Cool and load on to the prepared anion-exchange column. Wash through with 5 ml of 8 *M* hydrochloric acid. Elute with 10 ml of 5.9 *M* hydrochloric acid and make up to 50 ml with 8 *M* hydrochloric acid. Note the time of elution.

(*b*) *Protactinium-231.* Take 1 ml of a solution containing about $5 \cdot 10^4$ alpha counts per min per ml of protactinium-231 and make up to 10 ml, 8 *M* in hydrochloric acid. Load on to a prepared anion-exchange column and wash through with a further 5 ml of 8 *M* hydrochloric acid. Elute with 10 ml of 3.8 *M* hydrochloric acid and make up to 50 ml in 8 *M* hydrochloric acid. Take 5 ml of this stock solution and dilute to 50 ml in 8 *M* hydrochloric acid for use.

Preliminary treatment of samples

Weigh 0.1 to 0.2 g of the ground rock samples into clean dry marked silica ampoules and seal the tubes. Irradiate together with standards for a suitable period, usually one to two weeks. Leave for about 24 h in order to allow the shorter-lived activities to decay. Open the sample ampoules and transfer each to a clean weighed zirconium crucible, and reweigh.

Add 1 ml each of neptunium-237 and protactinium-231 tracer solutions. Evaporate to dryness under a lamp and cool. Add 2–4 g of analytical reagent sodium peroxide and heat gently in a gas flame until the peroxide melts. Heat to a dull heat and swirl gently for about 5 min to aid mixing of sample and tracers. After cooling, wash the outside of the zirconium crucible with demineralized water, transfer the crucible to a 250-ml beaker containing 100 ml of demineralized water and cover with a watch glass. When the reaction has finished, remove the crucible from the solution with clean platinum-tipped tongs and wash the outside of the crucible carefully into the beaker. Wash the crucible out with 3 ml of concentrated hydrochloric acid, warming to assist dissolution of any residue, add 10 ml of demineralized water to the contents of the crucible and transfer the solution to the beaker. Wash the beaker out with a further 10 ml of water and add this to the solution in the beaker. Stir the solution to aid mixing and allow to stand for 10 min. Centrifuge the solution in 30-ml batches in a polypropylene centrifuge tube and discard the supernatant liquid. Wash the precipitate with water, centrifuge and discard the washings. Dissolve the precipitate in dilute hydrochloric acid and transfer to a clean platinum dish. Add 5 ml of 40% hydrofluoric acid and evaporate to dryness under a heat lamp. Allow to cool, add 5 ml of 40% hydrofluoric acid and 5 ml of 72% perchloric acid and again take to dryness. Cool, add a further 5 ml of perchloric acid and take to dryness once more. After cooling, dissolve the residue in the dish in 15 ml of 2 M hydrochloric acid, warming gently if necessary, and transfer the solution to a polypropylene centrifuge tube. Wash the platinum dish with 5 ml of 2 M hydrochloric acid and transfer this also to the centrifuge tube.

Add sufficient 5 M sodium hydroxide solution to precipitate the insoluble hydroxides and allow to stand for 10 min. Centrifuge and discard the supernatant liquid, wash the precipitate with demineralized water, centrifuge again and discard the washings. Redissolve the precipitate in 10 ml of 10 M hydrochloric acid and return to the platinum dish. Wash the tube out with 5 ml of demineralized water and add to the solution in the dish. Take to dryness. Dissolve the residue in 1 ml of 5 M hydroxylamine hydrochloride solution and 1 ml of demineralized water, warming slightly if necessary. Add 8 ml of 10 M hydrochloric acid. If a precipitate forms on addition of the acid, remove by centrifuging.

Load the 8 M hydrochloric acid solution of the sample on to a prepared anion-exchange column and allow to pass through under gravity. Redissolve any precipitate in the dish or centrifuge tube in 1 ml of demineralized water, add 4 ml of 10 M hydrochloric acid, centrifuge if necessary and put the resulting solution on to the anion-exchange column. Elute the neptunium from the column with 10 ml of 5.9 M hydrochloric acid, and note the time in order to calculate the growth of protactinium-233 from neptunium-237 while in contact with the protactinium-231 tracer.

Elute protactinium from the column with 10 ml of 3.8 M hydrochloric acid, and collect in a receiver containing 5 ml of 10 M hydrochloric acid.

Procedure for neptunium

Collect the 5.9 M hydrochloric acid eluate from the anion-exchange column in a clean polypropylene centrifuge tube. Add 1 ml of zirconium hold-back carrier solution (containing 5 mg of Zr^{4+} per ml), 1 ml of 5 M hydroxylamine hydrochloride solution, 0.5 ml of lanthanum carrier solution (containing 20 mg of La^{3+} per ml), and mix well. Add 3 ml of 40% hydrofluoric acid solution and stir for 10 min. Centrifuge to compact the lanthanum fluoride precipitate. Add 0.5 ml of lanthanum carrier solution and stir gently for 10 min, endeavouring to leave the centrifuged precipitate undisturbed. Centrifuge and discard the supernatant liquid. Wash the precipitate in 5 ml of a wash solution containing 1 M nitric acid and 1 N hydrofluoric acid, stirring vigorously to break up the precipitate. Spin in a centrifuge and discard the supernate.

Prepare a salting-out solution by dissolving 1050 g of aluminium nitrate nonahydrate in water to give 800 ml of solution, warming gently to give a clear solution. Add 135 ml of concentrated (14.8 N) ammonia and stir well until the solution clears. Cool below 50° and add 50 ml of 10% tetrapropyl ammonium hydroxide solution. Make up to 1 litre with demineralized water.

Add 6 ml of salting-out solution to the tube containing the precipitate and centrifuge. (Owing to the high density of the salting-out solution, centrifuging breaks up the lanthanum fluoride precipitate and assists dissolution.) Stir for 10 min to dissolve the precipitate completely. Add 0.1 ml of 0.25 *M* potassium permanganate solution to oxidize neptunium to the hexavalent state. Extract for 3 min with 3 ml of MIBK. Separate the organic and aqueous phases by spinning in a centrifuge, and transfer the MIBK to a clean polypropylene centrifuge tube. Add 4 ml of a reducing solution containing 0.25 *M* ferrous chloride, 0.5 *M* hydroxylamine hydrochloride and 1 *M* hydrochloric acid and stir for 10 min. (The reducing solution should be made up fresh daily.) Centrifuge, remove the MIBK layer and discard. To the aqueous layer, add 2 ml of 10 *M* hydrochloric acid, 4 ml of demineralized water, 1 ml of 5 *M* hydroxylamine hydrochloride solution, 1 ml of zirconium hold-back carrier and 0.5 ml of lanthanum carrier. Mix well. Add 3 ml of 40% hydrofluoric acid and stir for 10 min. Spin in a centrifuge, then add 0.5 ml of lanthanum carrier and stir for 10 min. Centrifuge and discard the supernate. Wash the precipitate with 5 ml of a solution containing 1 *M* nitric acid and 1 *N* hydrofluoric acid, spin in a centrifuge and discard the washings.

Redissolve the lanthanum fluoride precipitate in 6 ml of the salting-out solution, oxidize the neptunium by the addition of 0.1 ml of 0.25 *M* potassium permanganate solution, and extract for 3 min with 3 ml of MIBK. Separate the phases in a centrifuge and transfer the organic layer to a clean glass centrifuge tube. Note the time for the zero point of the growth of protactinium-233. Strip the MIBK with 4 ml of the abovementioned reducing solution, stirring gently to avoid atmospheric oxidation of the iron(II). Spin in a centrifuge and transfer the aqueous layer to a clean glass centrifuge tube containing 3 ml of a 0.5 *M* solution of TTA in xylene. Stir carefully for 10 min, avoiding atmospheric oxidation of the iron(II) as far as possible. Centrifuge and discard the aqueous phase.

Procedure for protactinium

Collect the 3.8 *M* hydrochloric acid eluate from the anion-exchange column in a clean polypropylene tube containing 5 ml of 10 *M* hydrochloric acid. Stopper the tube and retain until the neptunium separations are complete. Add 1.4 g of stannous chloride and 0.6 g of oxalic acid and stir well until dissolved. Add 5 ml of DIBC, previously equilibrated with 6 *M* hydrochloric acid, and stir for 10 min. Spin in a centrifuge and transfer the organic phase to a clean polypropylene centrifuge tube. Add a further 3 ml of DIBC to the aqueous phase and extract for 10 min. Separate the phases in a centrifuge and add the organic phase to the first DIBC extract. Wash the combined organic phases three times with 5 ml of a solution containing 6 *M* hydrochloric acid and 4% oxalic acid, discarding the washings each time.

Add 4 ml of 1 *N* sulphuric acid and stir for 10 min. Centrifuge and transfer the aqueous phase to a clean polypropylene centrifuge tube. Add 6 ml of 10 *M* hydrochloric acid and mix well. Extract for several minutes with 5 ml of MIBK, previously equilibrated with 6 *M* hydrochloric acid. Spin in a centrifuge and discard the aqueous phase. Strip the MIBK with 3 ml of 2 *M* hydrochloric acid, separate the phases in a centrifuge and transfer the hydrochloric acid to a clean polypropylene tube containing 3 ml of 0.5 *M* TTA solution in xylene. Strip the MIBK with a further 2 ml of 2 *M* hydrochloric acid and combine the two aqueous phases. Extract for 10 min, centrifuge and carefully remove all the aqueous phase.

Preliminary treatment of standards

Prepare standard solutions of uranium and thorium containing about 100 μg of the element per g of solution. Weigh about 20 mg of spectrographically pure silica into a clean dry marked silica ampoule. Carefully add a similar weight of standard solution, reweigh and centrifuge. Dry overnight in an oven at 80°, increase the temperature to about 110° and leave for several hours more. Seal the ampoules.

After irradiation it is advisable to leave the standards unopened until the processing of the samples is well advanced, in order to avoid any possibility of cross-contamination. Tap the silica down into the bottom of the ampoule, then carefully crack open the tube, allowing any pressure release to take place before separating the two pieces. Empty the contents of the tube into a clean platinum dish. Wash the ampoules out at least ten times with 8 *M* hydrochloric acid, using a transfer pipette. Pipette 25 ml of the appropriate tracer solution accurately into the dish, add 5 ml of 40% hydrofluoric acid and take to dryness under a lamp. Add 5 ml of 40% hydrofluoric acid and 5 ml of 72% perchloric acid and fume down again. Add 5 ml of 72% perchloric acid and take to dryness.

Add 1 ml of 0.1 *M* ferric chloride solution and 15 ml of 2 *M* hydrochloric acid, warm gently to assist dissolution of the residue and transfer to a 40-ml polypropylene centrifuge tube. Wash the platinum dish with 5 ml of 2 *M* hydrochloric acid and add to the contents of the centrifuge tube. Add 5 *M* sodium hydroxide solution to precipitate ferric hydroxide and allow to stand for 10 min.

Spin in a centrifuge and discard the supernate. Wash the precipitate with water, centrifuge and discard the washings. Dissolve the precipitate in a few ml of hydrochloric acid and make up to 50 ml in 8 *M* hydrochloric acid.

Take suitable aliquots of the uranium standards and make up to 10 ml, 5.9 *M* in hydrochloric acid. Process by the same method as the neptunium fraction of the samples from the anion-exchange procedures.

Take suitable aliquots of the thorium standards and make up to 15 ml in 6 *M* hydrochloric acid. Treat in the same manner as the protactinium eluate from the anion-exchange separation on the samples.

Source preparation

Clean a 1"-diam. stainless steel counting disc in acetone, and heat on a 1" length of 1" diameter aluminium tubing standing on a hot plate. Adjust the temperature so that the organic solution evaporates steadily without spraying or charring. Carefully transfer the final TTA–xylene solution to the counting disc drop by drop. When the solution has all evaporated, burn off the organic residue in a gas flame. Allow the disc to cool before counting.

Recoveries in the range between 10% to 40% are usual for neptunium. In the case of protactinium the yields are lower, normally between 5% and 30%.

Counting of samples and standards

Determine the beta-activity with an end-window beta counter; collect at least 10^4 counts in order to obtain good counting statistics.

Determine the alpha-activity in a 2π proportional flow counter, collecting at least $2.5 \cdot 10^3$ counts.

Calculations

(*a*) *Uranium from neptunium-239 activity.* Correct the beta count rate of neptunium for dead-time losses and the background count rate. Divide the neptunium count rate by the fractional recovery and then subtract the contribution from the neptunium-237 tracer and the growth of its daughter protactinium-233 since the end of the separation. The resulting count rate is then corrected for decay (half-life of ^{237}Np = 2.36 days [30]). Then

$$\text{mass of uranium in sample} = \frac{\text{mass of uranium in standard} \cdot \text{corrected } ^{239}\text{Np activity in sample}}{\text{corrected } ^{239}\text{Np activity in standard}}$$

(*b*) *Thorium from protactinium-233 activity.* Correct the beta count rate of protactinium for dead-time losses and background count rate. Correct the alpha count rate for background and calculate the radiochemical yield. Divide the corrected beta count rate by the fractional yield and subtract the contribution from the protactinium-231 tracer. Correct the resulting count rate for decay (half-life of ^{233}Pa = 27.0 days[31]). Make a correction for the protactinium-233 contamination introduced by the neptunium-237 tracer between the time of purification of this tracer and the time of separation of the neptunium and protactinium fractions on the anion-exchange column.

Then

$$\text{mass of thorium in sample} = \frac{\text{mass of thorium in standard} \cdot \text{corrected } ^{233}\text{Pa activity in sample}}{\text{corrected } ^{233}\text{Pa activity in standard}}$$

RESULTS AND DISCUSSION

The results obtained for the standard granite G1 and the standard diabase W1 are listed in Table III. Also listed are values quoted in a recent compilation of data on G1 and W1 by FLEISCHER AND STEVENS[32], together with the results for uranium obtained by HAMILTON[18] by neutron activation.

The uranium results obtained for G1 are in reasonable agreement with the other neutron activation figures quoted, but are considerably lower than the values obtained by other methods. The thorium results for the granite are also about 20% lower than the values obtained by other methods.

Agreement with other values for uranium in W1 is quite good except in the case of the neutron activation figure given by HAMAGUCHI. This figure is a single value obtained using the low-flux reactor JRR-1; no details were given but it is suspected that the level of uranium in W1 is at the limit of the method used, which may account for the discrepancy.

The results obtained for thorium in the standard diabase are in excellent agreement with those obtained by other workers.

Possible interferences

The production of protactinium-233 and neptunium-239 by mechanisms other than the (n,γ) reaction is possible and the probability of interference from these sour-

TABLE III

VALUES FOR URANIUM AND THORIUM IN G1 AND W1

	G1(p.p.m.)		*W1(p.p.m.)*		*Method*	*Reference*
Uranium	3.7		0.52		various	AHRENS AND FLEISCHER (1960)
	4.2		0.6		fluorimetric	GRIMALDI (1961)
	3.46		0.54		neutron activation	DAS AND MEINKE (1960)
	2.7		0.28		neutron activation	HAMAGUCHI *et al.* (1961)
	3.93		0.49		gamma-ray spectroscopy	ADAMS (1961)
	3.55		0.53		neutron activation	HAMILTON (1959)
	3.10 ± 0.08	3.1	0.562 ± 0.013	0.55	present work[a]	
	3.12 ± 0.07		0.542 ± 0.014			
Thorium	52		2.4		various	AHRENS AND FLEISCHER (1960)
	52		2.3		chemical	GRIMALDI (1960)
	51		2.3		gamma-ray spectroscopy	ADAMS (1961)
	41.6 ± 1.0	42	2.08 ± 0.03	2.2	present work[a]	
	42.5 ± 1.0		2.24 ± 0.06			

[a] The error quoted is the standard deviation based on the counting data.

ces must be considered. In addition, a more serious interference could occur by the formation of the alpha-emitters protactinium-231 and neptunium-237 during neutron irradiation. If significant activities of these nuclides were produced, the chemical recoveries determined by alpha counting would be higher than the true yield, resulting in incorrect values for thorium and uranium. Some of the reactions which might cause interference are listed in Table IV.

The uranium isotopes of mass number 233 and 236 do not exist in nature so that direct interferences from these nuclides is not possible. Second order reactions can be postulated following the formation of these nuclides during neutron irradiation, but the small amounts produced in a short irradiation period combined with the low probability of fast neutron reactions taking place in a predominantly thermal flux make interferende from this source unlikely.

TABLE IV

POSSIBLE NUCLEAR REACTIONS CAUSING INTERFERENCES

Target	*Abundance in natural element (%)*	*Nuclear reaction*	*Product of nuclear reaction*
^{232}Th	100	$(n, 2n)$	$^{231}Th \xrightarrow{\beta^-} {}^{231}Pa$
^{233}U	—	(n, p)	^{233}Pa
^{235}U	0.714	$(n,\gamma)\ {}^{236}U\ (n,\gamma)$	$^{237}Np \xrightarrow{\alpha} {}^{233}Pa$
^{236}U	—	(n, α)	$^{233}Th \xrightarrow{\beta} {}^{233}Pa$
^{238}U	99.3	$(n, 2n)$	$^{237}Np \xrightarrow{\alpha} {}^{233}Pa$
^{239}Pu	—	(n, p)	^{239}Np

Plutonium-239 has been reported to exist in nature[33] to the extent of 1 part in 10^{14} in pitchblende, but abundances of this order are unlikely to cause any serious error. Plutonium-239 is produced during neutron irradiation of uranium-238, but the amount formed depends directly on the amounts of uranium present and in any case is insignificant during a short irradiation.

The (*n*, 2*n*) reaction for thorium-232 has a threshold energy of 6.3 MeV and a cross-section of 12.4 millibarns[34]. Our irradiations were carried out in a graphite facility of HIFAR, in which the residual fission flux is about $3 \cdot 10^5$ neutrons/cm²/sec[35]. Only 2.05% of fission neutrons have energies above 6.3 MeV[34], therefore the effective flux giving rise to the ^{232}Th (*n*, 2*n*) reaction is only $6 \cdot 10^3$ neutrons/cm²/sec. A flux of this magnitude will not produce a significant amount of protactinium-231 from the small amounts of thorium present in the sample during irradiation for a fortnight.

The threshold energy for the reaction ^{238}U (*n*, 2*n*) ^{237}U is about 6 MeV and the cross-section reaches a maximum of 1.5 barns at a neutron energy of 10 MeV[36]. The extremely low flux of high-energy neutrons combined with the small amount of target nuclide present and the long half-life of neptunium-237 ($2.2 \cdot 10^6$ years) produce insignificant activities of this nuclide and interference from this reaction can be ignored.

The production of neptunium-237 by a second order reaction

$$^{235}\mathrm{U}\ (n,\gamma)\ ^{236}\mathrm{U}\ (n,\gamma)\ ^{237}\mathrm{U} \xrightarrow[6.75\ \text{days}]{\beta^-} {}^{237}\mathrm{Np}$$

may be postulated, but it can be calculated that 1 µg of natural uranium irradiated for two weeks in a similar flux to that used in these determinations, produces an activity of neptunium-237 of less than one disintegration per year.

Protactinium-231 is present in the decay chain of uranium-235. The specific activity of ^{235}U is $4.74 \cdot 10^3$ disintegrations per min per mg, therefore the activity of ^{231}Pa in equilibrium with 1 µg of natural uranium is $3.4 \cdot 10^{-2}$ disintegrations per min. As the amounts of sample used contain less than 1 µg of uranium, and 100 counts per min (efficiency = 0.5) of protactinium-231 are added as tracer, the error introduced by the presence of naturally occurring ^{231}Pa is considerably less than 0.1%.

Thorium-230 (ionium) is present in the decay chain of ^{238}U, and protactinium-231 is formed during neutron irradiation by an (*n*, γ) reaction on this nuclide. The cross-section of this reaction for thermal neutrons is 35 barns. The amount of protactinium-231 activity formed by this reaction in a thermal flux of $6 \cdot 10^{12}$ neutrons/cm²/sec on the thorium-230 in equilibrium with 1 µg of natural uranium during irradiation for 14 days is approximately $5 \cdot 10^{-4}$ disintegrations per min. This level is too low to cause any significant interference.

The effect of neutron self-shielding in the samples is not considered significant because of the small sample size and the low cross-section of the major matrix materials.

The small amounts of thorium and uranium in the comparator standards combined with their comparatively low cross-section for thermal neutrons reduce the probability of self-shielding in this energy region to a negligible level; however, there is the possibility of self-shielding for neutrons in the epithermal energy range owing to resonance capture. In the irradiation position used, the ratio of total epithermal neutron density to total thermal neutron density is $4.0 \cdot 10^{-4}$. From this it can be calculated[35] that resonance capture by ^{238}U produces only about 5% of the total neptunium-239, and by ^{232}Th only 0.6% of the protactinium-233 activity. It can be seen that self-shielding for resonance energy neutrons would have to be very serious to cause a significant error in the uranium determinations and would cause no serious error in the thorium determinations.

CONCLUSION

The method described for the determination of thorium and uranium in rocks has been applied at the microgram and submicrogram levels. The chemical separations are performed carrier-free and produce radiochemically pure sources with adequate recovery. There appears to be no interference from nuclear reactions on other elements or on thorium or uranium. Results obtained for the rocks G1 and W1 are generally in good agreement with those obtained by other workers.

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SUMMARY

A neutron activation method is described for the determination of thorium and uranium in rocks at the microgram and submicrogram levels. Radiochemical separations are carried out using the alpha-active nuclides protactinium-231 and neptunium-237 as tracers. The method is applied to the standard granite G1 and the standard diabase W1.

RÉSUMÉ

Une méthode par activation au moyen de neutrons est décrite pour le dosage de traces de thorium et d'uranium, dans des roches. On utilise le protactinium-231 et le neptunium-237 comme traceurs pour les séparations radiochimiques.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Thorium und Uran in Gesteinen durch Aktivierung mit Neutronen. Die radiochemischen Trennungen wurden mit Protaktinium-231 und Neptunium-237 als Tracer durchgeführt.

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LEWIS ACID-BASE TITRATIONS EMPLOYING MEGACYCLE-FREQUENCY OSCILLATORS

PART III. PREPARATION, ISOLATION AND CHARACTERIZATION OF SOME ADDUCTS PREDICTED FROM TITRATION CURVES

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During an investigation of the use of megacycle-frequency oscillators to follow Lewis acid-base titration reactions[1,2], it was noted that precipitates frequently formed during the course of the titration, especially when aluminum chloride was used as the Lewis acid. While the adducts involving stannic chloride as the Lewis acid were usually soluble at the concentrations and in the solvents used, insoluble products could be obtained by changing the solvent, increasing the concentrations of the reactants, or a combination of the two.

The isolation in pure form of several of these reaction products was then attempted; one reason was the desire to verify the composition of adducts indicated by the characteristic shapes of the megacycle-frequency titration curves. Isolation of several of the adducts of interest has been reported in the literature, but characterizing data such as elemental composition and melting point are lacking for most of these.

Consequently, a number of adducts involving aluminum chloride and stannic chloride, and various nitrogen and oxygen bases were prepared, generally by mixing solutions containing the probably stoichiometric amounts of acid and base dissolved in acetonitrile, benzene or *n*-heptane.

DISCUSSION AND CONCLUSIONS

Thirteen stannic chloride–oxygen base adducts were prepared and analyzed for tin

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TABLE I

NATURE AND COMPOSITION OF SOLID STANNIC CHLORIDE–OXYGEN BASE ADDUCTS

Base used	*Character of precipitate*	*M.P.*^{b} (°)	*Analysis*^{c} *Cl(%)*	*Analysis*^{c} *Sn(%)*	*Cl : Sn ratio*	*Possible product* (%)^d	*purity* (%)^e
Diethyl ether	White powder	78–80	34.3	28.1	4.08	99	97
$SnCl_4 \cdot 2Et_2O^a$			34.7	29.0	4		
n-Dibutyl ether	White needles	37–39	24.2	21.1	3.84	89	92
$SnCl_4 \cdot 2Bu_2O^a$			27.2	22.8	4		
Tetrahydrofuran	White powder	S : 165–175	35.0	29.1	4.01	100	99
$SnCl_4 \cdot 2THF^a$			35.0	29.3	4		
p-Dioxane	White powder	S : 175–195	38.0	31.3	3.85	94*	92
$SnCl_4 \cdot \overline{D}$*			40.6	33.9	4		
$SnCl_4 \cdot 2\overline{D}$			32.3	27.1	4		
Methyl alcohol	Pasty white solid	98–103	42.8	36.4	3.96	98*	100
	White crystals^f	175–200	36.8	40.1	3.07	100**	97
$SnCl_4 \cdot 2MeOH$*			43.7	36.6	4		
$SnCl_3 \cdot OMe \cdot MeOH$**			36.9	41.2	3		
Ethyl alcohol	Pasty white solid	53–56	38.0	33.1	3.85	95*	98
	White needles^g	191–193	33.8	37.5	3.02	101**	100
$SnCl_4 \cdot 2EtOH$*			40.2	33.1	4		
$SnCl_3 \cdot OEt \cdot EtOH$**			33.8	37.5	3		
n-Propyl alcohol	White crystals	95–98	36.9	30.9	4.00	99*	99
	White crystals^f	182–184	30.9	34.0	3.05	100**	99
$SnCl_4 \cdot 2PrOH$*			37.3	31.2	4		
$SnCl_3 \cdot OPr \cdot PrOH$**			30.9	34.5	3		
iso-Propyl alcohol	White powder	103–106	37.1	31.5	3.95	100*	101
	White needles^f	104–106	36.8	30.8	4.00	99*	99
$SnCl_4 \cdot 2PrOH$*			37.3	31.2	4		
$SnCl_3 \cdot OPr \cdot PrOH$			30.9	34.5	3		
n-Butyl alcohol	White needles	?	33.8	29.0	3.91	97*	100
$SnCl_4 \cdot 2BuOH$*			34.7	29.0	4		
$SnCl_3 \cdot OBu \cdot BuOH$			28.6	31.9	3		
$SnCl_3 \cdot OBu$			35.7	39.8	3		
tert.-Butyl alcohol	White powder	70^i	33.5	37.2	3.01	94*	93
$SnCl_4 \cdot 2BuOH$			34.7	29.0	4		
$SnCl_3 \cdot OBu \cdot BuOH$			28.6	31.9	3		
			35.7	39.8			

Water	White crystals[h]	56–58	40.9	34.9	3.93	101*	103
						96**	98
$SnCl_4 \cdot 6H_2O$			38.5	32.2	4		
$SnCl_4 \cdot 5H_2O$			40.5	33.9	4		
$SnCl_4 \cdot 4H_2O$**			42.6	35.7	4		
Acetone	White powder	94–96	37.0	31.3	3.93	98	99
$SnCl_4 \cdot 2\bar{A}$			37.7	31.5	4		
Cyclohexanone	Tan granular solid	74–76	39.4	24.6	3.98	95	95
$SnCl_4 \cdot 2\overline{CH}$			31.0	26.0	4		

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[a] Possible compositions of solid, which precipitated from heptane solution, are given in every case.

[b] Sublimation temperature designated by a prefix "S".

[c] Each percentage is the average of duplicate determinations; the average deviation was frequently less than 0.1%.

[d] Based on the ratio of chloride in the product formed to the chloride in a possible species indicated by * or ** when more than one possible species is given.

[e] Based on the ratio of tin in the product formed to the tin in a possible species indicated by * or ** when more than one possible species is given.

[f] Product initially prepared was then recrystallized from heptane.

[g] Product initially prepared was then recrystallized from benzene.

[h] Prepared by bubbling moist air through a benzene solution of stannic chloride.

[i] Decomposed, *i.e.*, turned brown; did not melt even at higher temperatures.

and chloride ion; melting or sublimation points were determined for ten of them. Table I summarizes the data obtained and includes calculated percentages of tin and chlorine corresponding to possible formulas for the adducts, the Cl : Sn ratio found, and purities calculated on the basis of the ratios of Sn and Cl in the product obtained to the Sn and Cl in a possible product.

Stannic chloride–ether adducts

Molecular addition compounds involving stannic chloride and oxygen bases were reported in the literature as early as 1841, when a $SnCl_4$–Et_2O adduct was reported but not characterized[3]. Much later, stable addition compounds of stannic chloride and various esters, as well as diethyl ether, were reported[4]. More recently, SISLER and coworkers[5–9] have systematically studied the molecular addition compounds of the Group IV tetrahalides with ethers. Addition compounds of stannic chloride reported are a AB_2 adduct with diphenyl ether[8], AB and AB_2 adducts with methyl *m*-cresyl ether[9] and AB_2 adducts with both tetrahydrofuran (THF) and tetrahydropyran[6]. Melting points were given for several of these compounds.

Adducts of stannic chloride with diethyl ether, *n*-dibutyl ether, and THF prepared in the present study were all AB_2 adducts based on the Sn and Cl content. While the megacycle-frequency response curve for the addition of THF to $SnCl_4$ in benzene[2] had a maximum at the 1 : 1 molar ratio, it was not possible to isolate a solid AB species. Even when mixtures containing a considerable molar excess of $SnCl_4$ over THF were used, the adduct formed was always the AB_2 product. This, of course, does not mean that the AB adduct does not exist in solution, but merely indicates the greater stability and/or lower solubility of the AB_2 adduct over the AB adduct.

The only adduct of stannic chloride and *p*-dioxane that could be isolated was the AB compound. Attempts to isolate the AB_2 and A_2B adducts were unsuccessful. These results are in agreement with the megacycle-frequency response curve for the addition of pure *p*-dioxane to stannic chloride in benzene; a definite break in the curve occurs only at the 1 : 1 molar ratio[2]. ZENCHELSKY *et al.*[10] also reported 1 : 1 stoichiometry for thermometric titration involving stannic chloride and *p*-dioxane. Formation only of a AB species is in conformity with the behavior of *p*-dioxane as a diacid Lewis base. The resulting $SnCl_4$–dioxane compound then has hexacoordinate tin with the dioxane most likely serving as a bridging ligand between two tin atoms, which would result in a linear polymeric molecule (*cf.* ref.[2]).

The melting points obtained for the $SnCl_4$–Et_2O and $SnCl_4$–THF adducts agree well with those reported in the literature; the $SnCl_4$–*n*-Bu_2O adduct is a new compound. Analytical and melting point data have not been previously reported for the $SnCl_4$–*p*-dioxane adduct.

Stannic chloride–alcohol adducts

An adduct reported in 1884[11] involving stannic chloride and ethyl alcohol was assigned the formula $SnCl_3(OEt)(EtOH)$. The simple dialcoholate was subsequently prepared[12]. More recent investigation[13] indicates that $SnCl_3(OR)ROH$, $SnCl_4 \cdot 2ROH$, or a mixture of the two is generally obtained. The latter, when heated, gave a sublimate of the simple dialcoholate. When pure $SnCl_3(OMe)MeOH$ was heated under reduced pressure, the volatile $SnCl_4 \cdot 2MeOH$ was obtained, probably by a disproportionation,

$$2SnCl_3(OMe)MeOH \rightarrow SnCl_4(MeOH)_2 + SnCl_2(OMe)_2 \qquad (1)$$

$SnCl_3(OEt)EtOH$ was shown to be dimeric in boiling benzene, with tin exhibiting the coordination number of six as in the monomeric tetrachloride dialcoholates. The initial products for *tert.*-butyl and *tert.*-amyl alcohols were again mixtures, but under pressure monoalcoholates sublimed; the latter likely formed in preference to the characteristic dialcoholates because of the steric effect of the tertiary alkyl group in preventing the approach of the second alcohol molecule.

The composition of the adducts formed by stannic chloride with methyl, ethyl, *n*-propyl and *n*-butyl alcohols in the present study seem to be temperature-dependent and are generally in good agreement with those reported by BRADLEY, CALDWELL AND WARDLAW[13]. Initial precipitates obtained at room temperature were the simple AB_2 adduct, *i.e.*, $SnCl_4 \cdot 2ROH$. Upon recrystallization from boiling solvent, these products change to $SnCl_3(OR)ROH$ through the elimination of a molecule of hydrogen chloride. The *n*-butyl alcohol adduct seemed to decompose when recrystallization was attempted; a product was not obtained.

The simple iso-propyl alcohol adduct, $SnCl_4 \cdot 2C_3H_7OH$, apparently underwent no change upon recrystallization. In the case of *tert.*-butyl alcohol, the adduct initially formed analyzed for $SnCl_3 \cdot OC_4H_9$ and did not change upon recrystallization.

It seems clear that alcohols tend to form the simple dialcoholate with stannic chloride. This was predicted by the characteristic curve maxima at 2 : 1 molar ratio (ROH : $SnCl_4$) in the megacycle-frequency response curves for the addition of alcohols to stannic chloride in benzene (*cf.* ref.[2]).

Whether or not a molecule of hydrogen chloride can be eliminated from the dialcoholate seems to depend on the nature of the alcohol involved and the temperature. In the case of *tert.*-butyl alcohol, the failure to form the AB_2 adduct is likely due to the influence of steric factors, which prevent the approach of more than the one alcohol molecule to the stannic chloride molecule.

DEVLIN AND PEPPER[14] report a AB_3 adduct of stannic chloride and ethyl alcohol, but this conclusion does not seem justified. The formula was based solely on a chlorine analysis of the adduct. Although the 35.5% Cl found is very close to the 35.7% calculated for the AB_3 adduct, it is not too far from that calculated for $SnCl_3(OC_2H_5)$-C_2H_5OH (33.6%). Since a tin determination was not made on the product, a Cl : Sn ratio of 4 : 1 was not substantiated. The melting point reported by DEVLIN AND PEPPER for their product is the same as that obtained for the $SnCl_3(OC_2H_5)C_2H_5OH$ compound in the present study. It, therefore, seems quite possible that DEVLIN AND PEPPER were working with the latter compound instead of $SnCl_4 \cdot 3C_2H_5OH$.

Other stannic chloride adducts

The adduct formed between stannic chloride and water appears to be $SnCl_4 \cdot 4H_2O$, $SnCl_4 \cdot 5H_2O$ or a mixture of the two, based on both analysis and melting point. Acetone and cyclohexanone clearly form AB_2 adducts with stannic chloride.

Aluminum chloride adducts

Anhydrous aluminum chloride readily combines with ammonia. While the mono- and triammines are the most stable[15], other adducts have been reported[16]. Although ELEY[17] states that evidence indicates that only the 1 : 1 adducts of aluminum chloride with nitrogen bases, other than ammonia, have been isolated, VAN DYKE and co-workers[18,19] report conductance measurements and vapor pressure studies, which indicate the formation of AB_2 adducts with trimethylamine, pyridine and benzonitrile in nitrobenzene and benzonitrile. However, the solid adducts were not actually isolated and analyzed.

Table II summarizes the analyses of the three aluminum chloride–nitrogen base adducts prepared in the present study, the Cl : Al ratios found along with the Cl : Al ratios for possible formulas, and the calculated purity based on the ratios of Al and Cl in the product obtained to those in a possible product.

Acetonitrile forms a AB_2 adduct with aluminum chloride. It was impossible, by the technique used, to isolate a 1 : 1 adduct. The unexpected AB_3 adduct seems to have formed in the reaction of piperidine with aluminum chloride. These two adducts support the view that aluminum chloride can form adducts with nitrogen bases in other than a 1 : 1 ratio.

The reaction of aluminum chloride with pyridine gives an interesting product; it is clear that two chlorine atoms have been removed from the aluminum chloride molecule as the 1 : 1 pyridine–aluminum chloride adduct has formed, since the Cl : Al ratio in the adduct is 1 : 1. The AB_2 aluminum chloride–pyridine adduct could not be prepared by the technique used, although the megacycle-frequency response curve for the addition of pyridine to a solution of aluminum chloride in acetonitrile[1] indicates the formation of both the AB and AB_2 adducts.

TABLE II

NATURE AND COMPOSITION OF SOLID ALUMINUM CHLORIDE–NITROGEN BASE ADDUCTS

Base used	*Analysis*		*Cl : Al ratio*	*Possible product purity*	
	Cl(%)	*Al(%)*		*(%)*[c]	*(%)*[c]
Acetonitrile	47.6	12.7	2.85	96*	101
$AlCl_3 \cdot \overline{AC}$[a]	61.0	15.5	3		
$AlCl_3 \cdot 2\overline{AC}$*	49.4	12.5	3		
Piperidine	25.8	6.4	3.06	94*	92
$AlCl_3 \cdot$ pip	48.6	12.4	3		
$AlCl_3 \cdot$ 2pip	35.1	8.9	3		
$AlCl_3 \cdot$ 3pip*	27.4	7.0	3		
Pyridine	25.1	20.1	0.96	99	105
$AlCl \cdot$ py	25.2	19.2			

[a] Possible compositions of solid, which precipitated from heptane solution, are given in every case.

[b] Based on the ratio of chloride in the product formed to the chloride in a possible species indicated by * when more than one possible species is given.

[c] Based on the ratio of aluminum in the product formed to the aluminum in a possible species indicated by * when more than one possible species is given.

EXPERIMENTAL

Chemicals

n-Heptane (Eastman Kodak yellow label) was purified as follows[20]. 1 l was vigorously stirred with 200 ml of concentrated sulfuric acid for at least 4 h, washed twice with water, dried over anhydrous calcium sulfate, and distilled through an 18-inch Fenske column; the absence of unsaturated contaminants was verified by the ultraviolet spectra. Other chemicals used were identical to those used in the titration studies[1,2].

Preparation of adducts

Ten to 20 mmoles of pure oxygen base was added to 10–20 mmoles of stannic chloride in 20 ml of *n*-heptane or benzene contained in a 50-ml glass-stoppered flask; in every case the solid adduct obtained was independent of the proportions used. Immediate precipitation occurred except with stannic chloride and *n*-dibutyl ether; the latter mixture required cooling with Dry Ice–acetone for precipitation to occur. Precipitates were filtered, washed with pure solvent, and air-dried before being transferred to weighing bottles. All operations except Dry-Ice cooling were carried out in a dry box. During the cooling operation the reaction mixture was kept in a glass-stoppered conical flask, and then immediately returned to the dry box for filtration and further processing.

Use of a special sintered glass filtering crucible (Fig. 1) permitted preparation, washing, drying and weighing of the aluminum chloride–nitrogen base adducts without contact with the atmosphere. Twenty to 30 ml of approximately 0.4 M aluminum chloride in acetonitrile was delivered from an automatic buret to a 125-ml separatory funnel; a two or three molar excess of 0.1 M base in acetonitrile was immediately added. After brief shaking, the funnel was connected to the previously weighed filtering crucible; the precipitate was filtered by suction, washed with anhydrous solvent from the dropping funnel, and dried by drawing dry air through the apparatus for 10–15 min (a 4-ft. length of 18-mm glass tubing filled with anhydrous calcium sulfate served as the drying column). After closing of the stopcocks, the filtering crucible was detached and reweighed to determine the weight of the adduct.

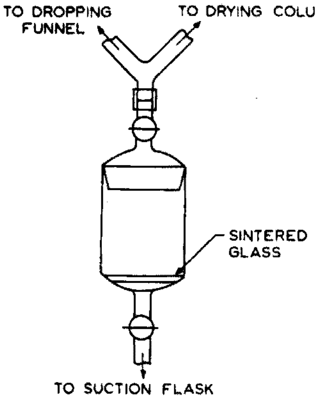

Fig. 1. Sintered glass filtering crucible used in the preparation of aluminum chloride–nitrogen base adducts.

The adduct from aluminum chloride and acetonitrile was formed by pumping off excess solvent from a 25-ml portion of 0.175 M aluminum chloride in acetonitrile, using a side-arm tube attached to a vacuum pump. A glass-like solid remained as the container approached constant weight.

Analysis of the adducts

Samples of the stannic chloride–oxygen base adducts were weighed out from weighing bottles, which were tightly stoppered and stored in a desiccator. Tin was determined gravimetrically, following hydrolysis to the hydrous oxide in boiling aqueous 2% ammonium nitrate solution; the precipitate was filtered through Whatman No. 41H paper, washed free of chloride with 2% ammonium nitrate solution, ignited, and weighed as SnO_2. Chloride was determined in the filtrate by potentiometric titration with 0.1 *M* silver nitrate.

In the case of the aluminum chloride–nitrogen base adducts, the crucible containing the weighed product was placed in a 250-ml beaker containing water. After soaking for several minutes, the crucible was removed with thorough rinsing with distilled water to remove all of the product. A slight excess of dilute ammonia and filter pulp were added; the solution was boiled for 1 min to coagulate the hydrous alumina precipitate, which was filtered through Whatman No. 41H paper, washed with hot 2% ammonium nitrate solution until washings were chloride-free, ignited, and weighed as Al_2O_3. The accuracy of this method for the determination of aluminum was verified by a control determination on reagent grade aluminum chloride hydrate. One ml of 6 *M* nitric acid was added to the filtrate from the aluminum filtration and the chloride titrated potentiometrically with 0.1 *M* silver nitrate.

Melting points of the adducts were taken by the conventional capillary technique. A Thiele tube, containing dibutyl phthalate and heated with a microburner, served as the bath. The 250° thermometer used was calibrated against one certified by the National Bureau of Standards. Because of the extreme reactivity of the aluminum chloride adducts with atmospheric moisture, their melting points could not be determined by the technique employed.

The authors wish to thank the U. S. Atomic Energy Commission, which helped support the work described.

SUMMARY

Adducts of stannic chloride with thirteen oxygen bases, isolated as solids from benzene or heptane solution, were characterized by analysis and melting point behavior; several of these are new compounds. Diethyl ether, *n*-dibutyl ether and tetrahydrofuran form AB_2 adducts; *p*-dioxane, in conformity with its being a diacid base, forms only a 1 : 1 species. Methyl, ethyl, *n*-propyl and *n*-butyl alcohols form simple AB_2 adducts at room temperature which on recrystallization from boiling solvent give $SnCl_3(OR)ROH$; iso-propyl alcohol gives only the AB_2 adduct; *tert.*-butyl alcohol only forms $SnCl_3 \cdot OC_4H_9$ (steric hindrance probably prevents formation of the AB_2 adduct). Water gives a AB_4 or AB_5 adduct.

Adducts of aluminum chloride with three nitrogen bases were similarly prepared from acetonitrile solution. Pyridine forms a 1 : 1 species. Acetonitrile itself forms a AB_2 species. Piperidine forms a AB_3 species. The latter two adducts support the view that $AlCl_3$ can form other than 1 : 1 adducts with nitrogen bases.

RÉSUMÉ

Les auteurs ont effectué la préparation, la séparation et la caractérisation des produits d'addition du chlorure stannique, obtenus avec 13 bases oxygénées. Plusieurs d'entre eux sont des composés nouveaux. De même, les produits d'addition du chlorure d'aluminium avec 3 bases azotées ont été préparés.

ZUSAMMENFASSUNG

Beschreibung der Herstellung, Trennung und Eigenschaften der Additionsprodukte von Zinntetrachlorid mit Sauerstoffbasen sowie von Aluminiumchlorid mit Stickstoffbasen.

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PARTITION CHROMATOGRAPHY ON ION-EXCHANGE RESINS

SEPARATION OF SUGARS

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Strongly polar non-electrolytes such as sugars and polyalcohols can be taken up effectively from mixed solvents by means of ion-exchange resins[1,2]. Only a few chromatographic separations based upon this sorption mechanism have been reported[3,4]. A systematic study of the factors which govern this sorption has been carried out (*cf.*[5]). Based upon this work a study of the chromatographic separation of sugars has been started. The results given in this paper demonstrate that this type of separation offers great possibilities in practical analytical work.

CHROMATOGRAPHIC PROCEDURE

The experiments were carried out according to the standard procedure recommended for chromatographic separations of similar solutes by means of ion-exchange chromatography. Precautions were taken to avoid gas bubbles in the resin bed[5]. The resin (Dowex 1 X-8) was classified hydraulically to obtain the fraction 45–75 μ and was used in its sulfate form. The dimensions of the resin bed were 10 × 840 mm. The height of the resin bed as well as the particle dimensions were determined after the resin had been conditioned in 74% ethanol.

The sugars were dissolved in water and the aqueous solution diluted with 99% ethanol to obtain a concentration of 75% alcohol (by weight); 5 ml of this solution containing 20–50 mg of sugar were introduced on to the top of the column and pressed into the resin bed by nitrogen pressure. A few ml of the eluant were used to wash the walls of the column. The eluant was fed on to the column with a pump at constant flow rate[5]. When not otherwise mentioned the flow rate was 0.8 ml/cm^2/min. The temperature was kept constant at 28°.

ANALYSIS OF THE ELUATE

During the first part of this investigation the eluate fractions were analyzed by the phenol method[6]. One ml of a 5% phenol solution was added to 1 ml of an eluate fraction followed by 5 ml of concentrated sulfuric acid. The light absorption was measured in an Evelyn Photometer at 490 mμ.

The fractions were later analyzed automatically using a Technicon AutoAnalyzer consisting of sampler, proportioning pump, heating bath, colorimeter, and recorder. A procedure was used permitting an acid hydrolysis of the sugar solution in order to increase the amount of reducing sugars in the sample solution. The hydrolysis to monosaccharides is not complete, but despite this fact reproducible results were obtained. In a second step the solution is oxidized in alkaline medium with ferricyanide and the decrease in ferricyanide concentration determined colorimetrically (*cf.*[7]). The flow diagram and the internal diameter of the different pump tubes are given in Fig. 1. All tubings were made of Tygon.

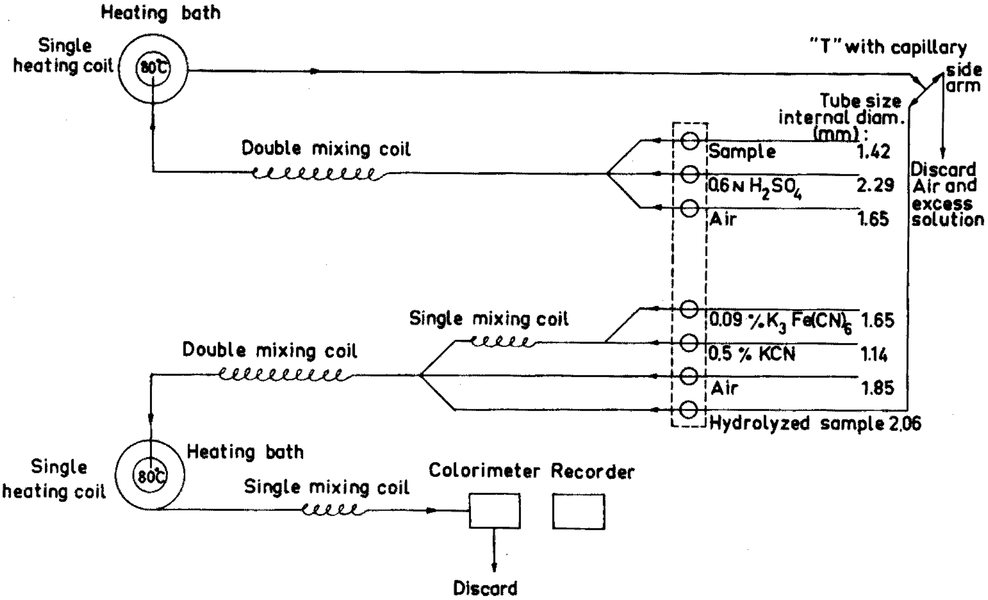

Fig. 1. Determination of sugar in the eluate by means of the Technicon AutoAnalyzer.

The sample was mixed with 0.6 *N* sulfuric acid solution and divided into alternating segments of liquid and air inside a Tygon tube. The reaction time in the heating bath was about 5 min. The acid solution leaving the heating bath was deaerated and divided into two streams in a T-fitting. Part of the solution (the rest was discarded) was mixed with 0.09% potassium ferricyanide in 2 *N* sodium hydroxide solution, 0.5% potassium cyanide solution and air. The alkaline solution was divided into segments of liquid and heated to 80° for about 5 min and the light absorption was then measured in the colorimeter at 440 mμ. The cell length was 10 mm.

RESULTS AND DISCUSSION

A study of the kinetics of the sorption of polar non-electrolytes on ion-exchange resins from ethanol–water solutions has shown that the diffusion within the resin phase is comparatively slow[1,2]. For this reason extremely small resin particles were chosen in the present work. In experiments with glucose it was demonstrated that the rate of sorption decreases rapidly for an increased ethanol concentration, whereas the equilibrium uptake increases[1]. In almost water-free medium the rate of sorption is extremely low. For this reason too high ethanol concentrations should be avoided.

The results given in Fig. 2 confirm the fact that the sorption of glucose and cellobiose increases for an increased ethanol concentration. In 70% ethanol the separation factor is too low to permit a quantitative separation, whereas a clear-cut separation is obtained in 74% ethanol.

Similarly, a quantitative separation of glucose from lactose is obtained at this

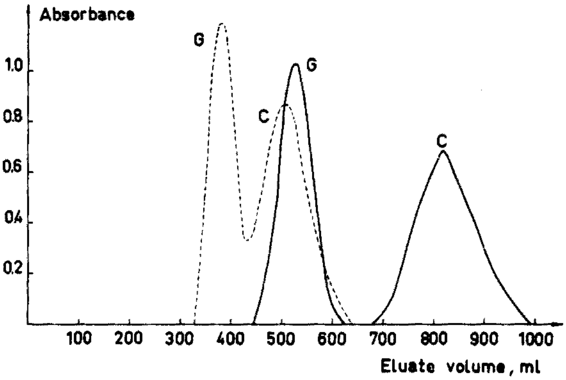

Fig. 2. Influence of the alcohol concentration on the separation of 10 mg glucose (G) from 10 mg cellobiose (C). --- 70% ethanol; —— 74% ethanol.

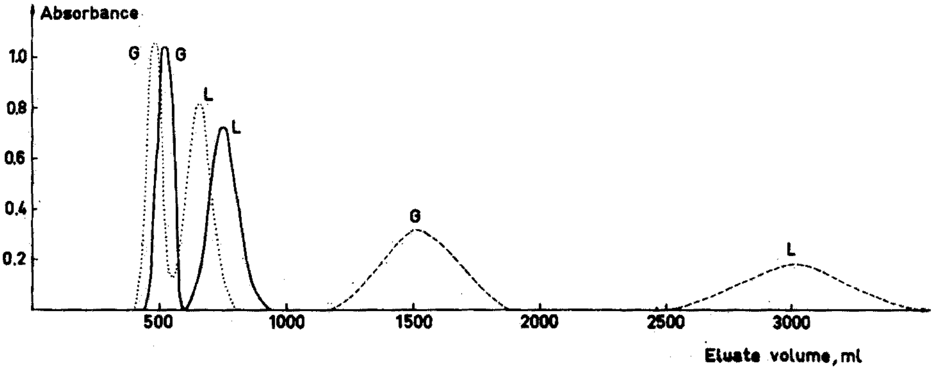

Fig. 3. Influence of the alcohol concentration on the separation of 10 mg glucose (G) from 10 mg lactose (L)···· 72% ethanol; —— 74% ethanol; --- 82% ethanol.

concentration (Fig. 3), whereas in 72% ethanol the elution bands overlap. A further increase in alcohol concentration results in an increased separation factor, but as shown in the experiments with 82% ethanol the elution bands broaden. This is explained by the increased distribution coefficients (*cf.*[5]) and the decreased rate of diffusion inside the resin particles.

As can be expected from the kinetic investigation referred to above it must be expected that the flow rate will be a critical variable. The results presented in Fig. 4 show that a decreased flow rate results in a sharpening of the elution bands and in an improved separation of glucose and sucrose. At the higher flow rate an improved separation can be obtained when smaller amounts are to be separated (Fig. 5). The influence of the loading of the column is demonstrated also by the results given in Fig. 6, which show that 10 mg of glucose can be satisfactorily separated from 10 mg of cellobiose at the higher flow rate, whereas a large overlapping is obtained if the quantities are doubled.

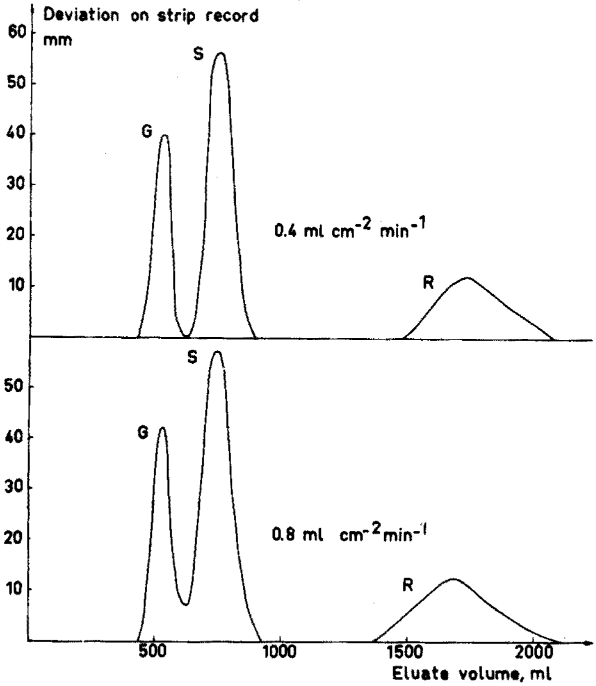

Fig. 4. Influence of the flow rate on the separation of 10 mg glucose (G) from 20 mg sucrose (S) and 20 mg raffinose (R). Eluant: 74% ethanol.

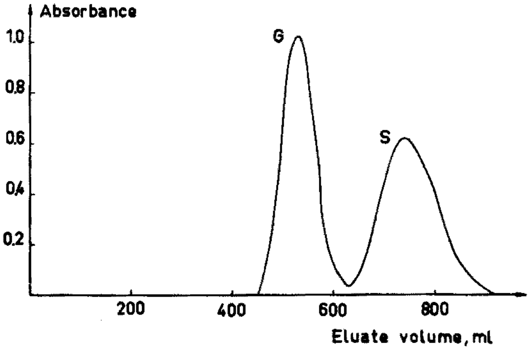

Fig. 5. Separation of 10 mg glucose (G) from 10 mg sucrose (S). Eluant: 74% ethanol.

In all experiments the monosaccharide appears ahead of the disaccharide. From Fig. 4 it is seen that the trisaccharide raffinose appears as a separate band after sucrose. Experiments with the tetrasaccharide stachyose and the pentasaccharide verbascose showed that these appear after the trisaccharide. These are held very strongly by the resin at the ethanol concentrations used in the experiments hitherto described. In order to avoid an excessive broadening of the elution bands the ethanol concentration has to be decreased. With a mixture containing these sugars as well as mono- and disaccharides it is recommended to start the elution at a higher eluant concentration and to decrease the ethanol concentration either stepwise or by the gradient elution technique.

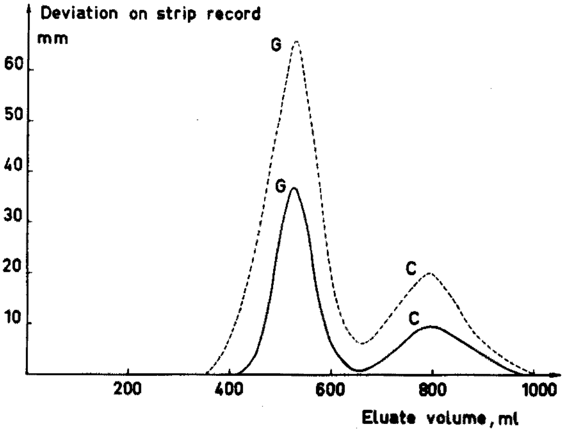

Fig. 6. Influence of the amounts of sugar on the separation of glucose (G) from cellobiose (C). Eluant: 74% ethanol. —— 10 mg of each sugar; --- 20 mg of each sugar.

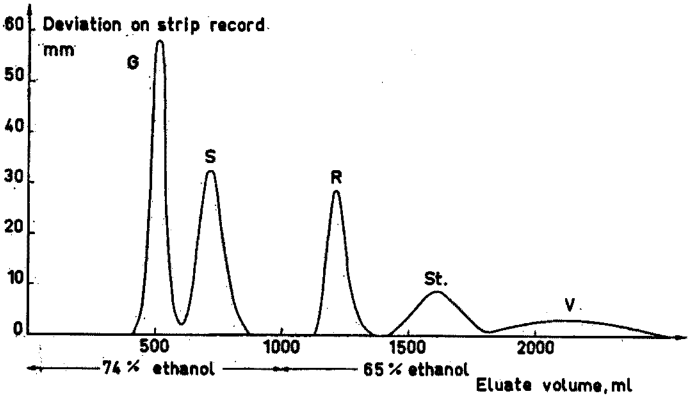

Fig. 7. Stepwise elution of glucose (G), sucrose (S), raffinose (R), stachyose (St.) and verbascose (V) (10 mg of each).

The results given in Fig. 7 show that a satisfactory separation is obtained with a mixture of glucose, sucrose, raffinose, stachyose, and verbascose by using stepwise elution. These sugars appear in the order of their molecular weights, the monosaccharide appearing first in the eluate.

Individual differences between various mono-, di-, and trisaccharides have been observed. Separate experiments showed that xylose, arabinose, and mannose are held less strongly than glucose and can be separated easily as a group. Similarly, the trisaccharide melezitose can be separated from raffinose even at the higher flow rate

(Fig. 8). Melezitose appears between sucrose and raffinose and its separation from sucrose is less satisfactory under these conditions. A complete separation can be achieved by decreasing the flow rate and increasing the column length.

The peak elution volumes observed in experiments with a single sugar agree well with those obtained when several sugars are separated. Values obtained in the experiments described in detail in this paper as well as in some other experiments carried out with the same column are shown in Table I. These data can be used to estimate column dimensions when it is desired to use the method in other separations than those reported in this paper.

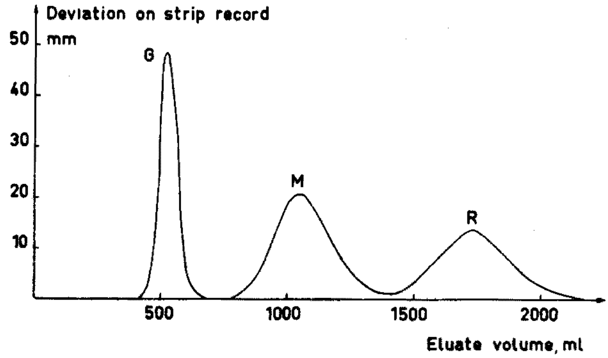

Fig. 8. Separation of 10 mg glucose (G), 20 mg melezitose (M) and 20 mg raffinose (R). Eluant: 74% ethanol.

TABLE I

PEAK ELUTION VOLUMES (ml) AT VARIOUS ETHANOL CONCENTRATIONS (wt. %)

	65%	70%	72%	74%	82%
Xylose				360	
Glucose	280	380	470	530	1500
Cellobiose		510		800	
Lactose			660	760	3000
Maltose				760	
Sucrose			620	740	
Melezitose					1060
Raffinose	450				1730
Stachyose	780				
Verbascose	1320				

The chromatographic separation described in the present work requires a fairly long period of time, but can be run without attendance. The analysis of the eluate by means of the AutoAnalyzer is very convenient. In the present work 40 fractions were analyzed per hour. The effective time for a complete analysis is, therefore, comparatively short.

According to the experience gained so far, the method presented above is a valuable complement to the anion-exchange separations in borate medium which were first suggested by KHYM, ZILL AND COHN (*cf.*[8]). Separations in aqueous solution based upon differences in the exclusion of sugars by ion-exchange resins have been reported by several authors (*cf.*[9,10]). This method is extremely simple and has the advantage that large amounts of sugars can be handled, but in most systems the results are less favorable, owing to the limited spectrum of distribution coefficients; in this method disaccharides appear ahead of monosaccharides, whereas in our method the order is reversed.

The financial support of the Swedish State Technical Research Council is gratefully acknowledged.

SUMMARY

Factors affecting the chromatographic separation of sugars in ethanol–water solutions by means of anion-exchange resins in the sulfate form have been studied. When proper conditions are chosen a satisfactory separation of mono-, di-, tri-, tetra-, and pentasaccharides from one another can be achieved. In some cases it is possible to separate sugars of similar molecular weight.

RÉSUMÉ

Une étude a été effectuée sur la séparation chromatographique de sucres, au moyen de résine (échangeur d'anions). Il est possible de séparer mono-, di-, tri-, tétra- et pentasaccharides. Dans certains cas, des sucres de même poids moléculaire peuvent être séparés.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung der Zuckerarten mit Anionenaustauscherharzen. Unter geeigneten Bedingungen können mono-, di-, tri-, tetra-, und pentasaccharide sowie auch Zucker von ähnlichem Molekulargewicht voneinander getrennt werden.

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ETHYLENEGLYCOL-BIS(AMINOETHYL)TETRAACETIC ACID IN THE AMPEROMETRIC TITRATION OF CADMIUM IN THE PRESENCE OF ZINC

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The titrimetric determination of cadmium in the presence of zinc or *vice versa* is difficult because of the close resemblance of the two metal ions in their analytical behavior. Predominantly, instrumental methods and especially amperometric methods have been used to attack the problem; most of these have involved precipitation titrations. The available methods have recently been reviewed by FERNANDO AND FREISER[1]. The introduction of chelons has offered new possibilities for such a determination. SWEETSER AND BRICKER[2] were the first to propose a method using EDTA as the titrant. Selectivity was achieved by working in strongly alkaline medium where zinc is present as the zincate; a photometric end-point was employed (236 mμ) and cadmium was kept in solution by adding potassium cyanide, the amount of which was critical. Diethylene-triaminepentaacetic acid (DTPA) was used in a photometric titration with copper acting as the photometric indicator[3]. Appropriate adjustment of the ammonia concentration brought about the desired order of the relevant apparent stability constants. Since the absolute constants of the cadmium- and zinc-DTPA complexes are close, the amount of ammonia is critical. Ethyleneglycol-bis(aminoethyl)tetraacetic acid (EGTA) is more advantageous since the absolute constants of the cadmium and zinc complexes differ considerably, making EGTA a remarkable exception in this respect compared with other chelons. This approach was used by FLASCHKA AND GANCHOFF[4], and as expected, the ammonia concentration could be varied in a much wider range without the slightest effect on the correctness of the results. A photometric end-point (742 mμ) was employed.

Under the conditions of the titration auxiliary complex formers are required to prevent the precipitation of the hydroxides of metal ions, such as iron, aluminium or titanium. Masking agents can be employed, but in general are undesirable because most of them also form complexes to a certain degree with cadmium and zinc and act in such a manner as to decrease the difference of their apparent stability constants. It seemed, therefore, to be of interest to study the applicability of an amperometric procedure instead of a photometric procedure, because the former is not affected by precipitations except through errors caused by coprecipitation of the metal to be titrated. In addition to this, the diffusion current of cadmium itself can be used to follow the titration, since cadmium is reduced at a more positive potential than zinc. It would also be possible to use the "chelon wave" method, recently investigated by REILLEY AND CAMPBELL[5], for locating the end-point, though this did not form part of the present investigation. Since the "chelon wave" is actually the anodic dissolution wave of mercury, it is subject to changes caused by the presence of other complex formers, especially chloride ion which in practice is very frequently a component of the sample solution.

Titration with copper as amperometric indicator

In order to benefit from the theoretical considerations and practical experience gained in the photometric titration where copper was used as the indicator ion[4], this method was considered first for adaptation to an amperometric end-point. The theoretical principle is as follows. Comparison of the effective stability constants of the EGTA chelonates in 0.1 *M* ammonia at pH 10 (Table I) shows the order to be Cd > Cu > Zn. The cadmium constant is larger than that of copper by about 4 logarithmic units, and cadmium is thus titrated before copper with EGTA. The difference in the effective stability constants is of sufficient magnitude to allow an amperometric end-point detection. A potential of −0.30 V *vs.* the S.C.E. was chosen for the amperometric titration. This corresponds to the reduction of copper(II) to copper(I). At this relatively low potential only a few ions are electroactive. Notably also, the second reduction wave of oxygen is avoided, so that titration in the presence of dissolved oxygen is feasible. After the cadmium has been complexed, copper starts to react and thus indicates the end-point. The slope of the copper curve is dependent on the concentration of ammonia and decreases with increasing ammonia concentration, since the effective stability constant of the copper complex decreases. Thus, a

TABLE I

LOGARITHMS OF THE STABILITY CONSTANTS OF THE EGTA COMPLEXES OF SOME METALS

Metal	*log K_{abs}*	*log K_{eff} at pH 10 in ammoniacal solution*		*Reference*
		0.1 M	*1.0 M*	
Cd^{2+}	16.7	13.6	9.9	12
Zn^{2+}	12.8	8.1	4.1	11
Cu^{2+}	17.8 (17.5)[a]	9.5	5.6	10
Ca^{2+}	11.0	—	—	12
Mg^{2+}	5.4	—	—	12
Ba^{2+}	8.4	—	—	12
Pb^{2+}	14.6	—	—	10

[a] Value obtained by the present authors from the shift in half-wave potential.

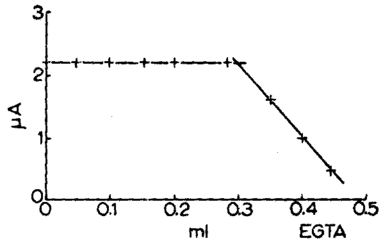

Fig. 1. Titration curve for the determination of cadmium in ammoniacal solution at pH 10 using copper as amperometric indicator.

small slope of the titration curve after the end-point and a steep curvature in its vicinity are observed in solutions of high ammonia concentration.

The slope is also reduced by the presence of cations whose effective stability constants are comparable to that of the copper complex. However, the position of the cadmium end-point is not affected by the slope of the indicator curve. A titration curve of this type is shown in Fig. 1: the horizontal segment of the curve corresponds to the titration of cadmium and the sloped segment to the titration of copper; the intersection of the two lines indicates the cadmium end-point.

Some representative results obtained by this method are shown in Table II.

TABLE II

TITRATION OF CADMIUM AT pH 10 USING COPPER AS AMPEROMETRIC INDICATOR

Cd^{2+} taken (mg)	*ml 0.1000 M EGTA*			*Metal (X) added (mg)*	*Appr. mole ratio X:Cd*	*Remarks*
	Calc.	*Found*	*Diff.*			
1.19	0.106	0.106	±0.000	—	—	—
3.57	0.318	0.315	−0.003	—	—	—
4.77	0.424	0.422	−0.002	—	—	—
5.96	0.530	0.530	±0.000	—	—	—
9.54	0.849	0.854	+0.005	—	—	—
5.96	0.530	0.528	−0.002	—	—	O$_2$ not removed
5.96	0.530	0.529	−0.001	—	—	O$_2$ not removed
5.96	0.530	0.532	+0.002	Zn(3.1)	1:1	—
5.96	0.530	0.530	±0.000	Zn(6.2)	2:1	—
5.96	0.530	0.528	−0.002	Zn(12.4)	4:1	—
5.96	0.530	0.534	+0.004	Zn(30.9)	10:1	—
5.96	0.530	0.526	−0.004	Zn(124)	40:1	—
2.28	0.203	0.208	+0.005	Zn(1545)	500:1	—
5.96	0.530	0.531	+0.001	Fe(1.2)	2:5	Lactate masking
5.96	0.530	0.531	+0.001	Fe(1.8)	3:5	Lactate masking
5.96	0.530	0.524	−0.006	Fe(0.6)	1:5	Lactate masking
5.96	0.530	0.525	−0.005	Fe(0.6)	1:5	Lactate masking
5.96	0.530	0.531	+0.001	Fe(3.0)	1:1	Tartrate masking
5.96	0.530	0.530	±0.000	Fe(1.5)	1:2	Tartrate masking
5.96	0.530	0.530	±0.000	Ca(2.1)	1:1	—
1.19	0.106	0.105	−0.001	Ca(0.8)	2:1	—
4.77	0.424	0.426	+0.002	Ca(17.0)	10:1	—

Indication by cadmium in ammoniacal solution

Omitting copper as the indicator and using cadmium itself for the indication should have definite advantages as far as stability constants are concerned (see Table I). Accordingly, a higher ratio of zinc to cadmium should be tolerable with less curvature around the end-point; this was proved experimentally (Table III). With respect to the potential, however, more species were potential interferences since the titration has to be performed at −0.90 V *vs.* the S.C.E.

Indication by cadmium in acetate medium

The EDTA titration of cadmium with an amperometric end-point was first studied by PŘIBIL AND MATYSKA[6]. They found no particular difficulty except that high

TABLE III

TITRATION OF CADMIUM IN AMMONIACAL SOLUTION AT pH 10

Cd^{2+} taken (mg)	*ml 0.1000 M EGTA*			*Metal (X) added (mg)*	*Appr. mole ratio X:Cd*
	Calc.	*Found*	*Diff.*		
2.16	0.192	0.190	−0.002	—	—
3.25	0.289	0.291	+0.002	—	—
3.92	0.349	0.349	±0.000	—	—
9.15	0.814	0.816	+0.002	—	—
11.78	1.046	1.047	+0.001	—	—
4.58	0.407	0.409	+0.002	Zn (2.7)	1:1
2.87	0.255	0.256	+0.001	Zn(16.7)	10:1
5.73	0.510	0.512	+0.002	Zn(333)	100:1
5.73	0.510	0.510	±0.000	Zn(333)	100:1
2.16	0.192	0.190	−0.002	Ca(0.8)	1:1
2.16	0.192	0.190	—0.002	Ca(38.5)	50:1
2.16	0.192	0.195	+0.003	Ca(77.0)	100:1
1.79	0.159	0.159	±0.000	Ba(109)	50:1
5.73	0.510	0.512	+0.002	Mg(12.4)	10:1
5.73	0.510	0.508	−0.002	Mg(124)	100:1

chloride concentrations impaired the results. A later investigation of the method by TANAKA *et al.*[7] revealed that several kinetic processes were involved at the electrode; slightly high results were obtained unless a rather high gelatin concentration was maintained.

With EGTA as the titrant, a similar situation was encountered, but it was found that at a sufficiently positive potential, the same kinetic wave was of no consequence even with the usual small concentration of gelatin or sometimes no gelatin at all. However, as a safeguard 0.005% gelatin was generally used in the experiments. Since the maximum suppressor, especially in high concentrations, caused undue foaming of the solution during the necessary deaeration, General Electric Antifoam 60 was added in an amount of approximately 0.005%. It was found that this Antifoam can itself act as an effective maximum suppressor and gelatin was therefore omitted in many cases. Closer investigation of these possibilities is in progress.

TABLE IV

TITRATION OF CADMIUM IN ACETATE BUFFER pH 5

Cd^{2+} taken (mg)	*ml 0.1000 M EGTA*			*Metal (X) added (mg)*	*Appr. mole ratio X:Cd*	*remarks*
	Calc.	*Found*	*Diff.*			
1.08	0.096	0.100	+0.004	—	—	—
3.25	0.289	0.291	+0.002	—	—	—
5.73	0.510	0.510	±0.000	—	—	—
9.15	0.814	0.816	+0.002	—	—	—
11.76	1.047	1.047	+0.001	—	—	—
16.29	1.449	1.459	+0.010	—	—	—
5.73	0.510	0.505	−0.005	Zn(33.3)	10:1	—
5.40	0.480	0.478	−0.002	Zn(31.4)	10:1	—
2.74	0.244	0.245	+0.001	Zn(160)	100:1	—
5.40	0.480	0.479	−0.001	Fe(2.7)	1:1	Ascorbic acid masking
5.40	0.480	0.479	−0.001	Fe(26.8)	10:1	Ascorbic acid masking
5.40	0.480	0.470	−0.010	Fe(26.8)	10:1	Ascorbic acid masking
5.40	0.480	0.488	+0.008	Fe(268)	100:1	Ascorbic acid masking

The titration in acetate medium was carried out at a potential of −0.70 V *vs.* the S.C.E. At this potential cadmium is reduced but zinc is inactive at the electrode. Representative data obtained by this method are collected in Table IV.

EXPERIMENTAL

Apparatus

A Sargent Model XV recording polarograph was used. Titrations were performed in a 200-ml beaker equipped with a medium porosity glass frit bottom through which nitrogen could be passed for deaeration. A Sargent automatic burette was employed to deliver the titrant.

Reagents

Solutions of metal ions and complexing reagent were prepared from Reagent Grade material and standardized according to well-established procedures[9,10]. Buffer pH 10 was prepared by dissolving 70 g of ammonium chloride and 570 ml of concentrated ammonia and diluting to 1 l with deionized water. The acetate buffer was prepared by mixing equal amounts of 2 *M* sodium acetate and 2 *M* acetic acid. A 0.5% stock solution of gelatin was prepared daily from bacteriological gelatin. A 0.5% stock solution of G. E. Antifoam 60 was prepared by diluting 0.5 ml of the commercial emulsion to 100 ml with deionized water.

Procedure

Accurately measured amounts of metal solutions were pipetted into the titration cell. The necessary amount of acetate or ammonia buffer, 10 ml of 1 *M* potassium nitrate and either 1 ml of gelatin or 1 ml of Antifoam 60 or both were added and the mixture was diluted to 100 ml with deionized water. After deaeration for not less than 15 min, the titration was performed; nitrogen was allowed to bubble for 3 min after each addition of titrant. (For deoxygenation with ascorbic acid, see below.) Plotting of data and obtaining the end-point was performed in the usual manner. In the case of the amperometric indicator method, 5 ml of a 0.010 *M* copper nitrate solution was added before the initial deaeration.

DISCUSSION

As can be seen from Tables II–IV, the accuracy and precision of the three methods are approximately the same; an average deviation of about 0.002 ml of a 0.1 *M* titrant may be expected in a practical application.

The choice of the modification to be applied is closely related to the problem of the interfering metal ions. Three groups of interferences may be differentiated. Firstly, metal ions whose EGTA complexes have an effective stability constant higher than or similar to that of the cadmium complex will be co-titrated so that only the sum of cadmium plus the interfering metal or metals can be obtained. The second group includes metal ions which are polarographically active under the conditions of the titration; the determination of cadmium may still be performed in the presence of such an interference but it is necessary to work against a current background and, depending on the amount of interfering metal, a more or less reduced accuracy and precision may result. The last group of interferences includes metal ions which form precipitates under the conditions of the titration; such metals do not generally hamper an amperometric titration except by coprecipitation of the metal to be determined or by adsorption phenomena at the mercury drop. Here the amount of interfering metal plays the deciding role.

In practical applications of the method, there are many possible combinations of interferences and a special investigation must be made in each particular case in order to ascertain the permissible limits. Some assistance for such investigations is available in the form of calculations from known stability constants, β-factors, and values of the half-wave potentials of the metal ions concerned; hence thorough investigations were not made in the present work and only a few typical interferences were studied in more detail.

With regard to the exclusion of interferences by co-titration, the modification involving acetate-buffered medium is preferable, because at the lower pH the selectivity of EGTA is greater. Magnesium and the alkaline earths can be tolerated to a much higher degree than in ammoniacal solution. With respect to the second group, the use of copper as amperometric indicator is of advantage because the applied potential is low and thus fewer substances are polarographically active.

The influence of calcium has been studied in some detail because it is a frequent component of substances to be analysed or it may be introduced as an impurity during the course of the analysis. As long as only cadmium and zinc are present, the ammonia concentration is not very critical, but in the presence of calcium this concentration becomes extremely important. With moderate concentrations of ammonia the apparent stability constant of the Cd–EGTA complex is lowered so that it becomes very close or equal to that of the calcium complex and the titration curve shows only one break which indicates the sum of cadmium and calcium. If a high ammonia concentration (above 1.5 *M*) is maintained, the apparent stability constant of the cadmium complex is lowered to such a degree that the calcium is titrated before the cadmium and a curve of the type shown in Fig. 2 is obtained. Thus it is possible to titrate the two elements successively (Table V).

Magnesium, barium and strontium exhibit similar behavior; but the effects are not so pronounced as is to be expected from the considerably lower stability constants.

Another element which frequently accompanies cadmium and zinc is lead. So far no method of masking or application of the β-factor has been successful in preventing its cotitration. However, the lead can be titrated in another aliquot of the sample after cadmium and zinc have been masked with cyanide; the sum of cadmium and

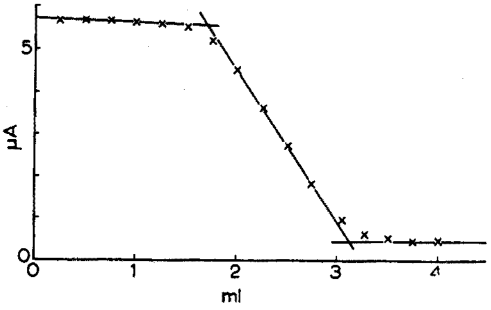

Fig. 2. Curve for the successive titration of calcium and cadmium in 1.5 *M* ammoniacal solution.

TABLE V

CONSECUTIVE TITRATION OF CALCIUM AND CADMIUM IN 1.5 *M* AMMONIA

Cd^{2+} *taken* (*mg*)	*ml 0.1000 M EGTA*			Ca^{2+} *taken* (*mg*)	*ml 0.1000 M EGTA*		
	Calc.	*Found*	*Diff.*		*Calc.*	*Found*	*Diff.*
0.80	0.200	0.197	−0.003	2.23	0.198	0.202	+0.004
0.80	0.200	0.199	−0.001	2.23	0.198	0.192	−0.006
2.04	0.510	0.512	+0.002	1.51	0.312	0.310	−0.002
0.44	0.110	0.106	−0.004	1.69	0.150	0.148	−0.002

lead is then obtained amperometrically and cadmium is calculated by difference.

Similar procedures can be applied in other similar cases by appropriate use of the methods developed for general complexometric titrations, thus aiding in the resolution of multicomponent systems.

Some effort was devoted to a study of the interference of iron. In ammoniacal solution moderate amounts of iron (and aluminium) can be tolerated. The precipitate as such has no influence on the result of the cadmium titration. With higher amounts, however, coprecipitation of cadmium with the iron becomes noticeable and low results are found; this is less noticeable in the presence of high concentrations of zinc. An effective method of masking iron is to reduce it with ascorbic acid to the divalent state which does not interfere. The reduction has to be performed in acidic solution at a pH of about 1.5; after the iron has been reduced by addition of a spatula-full of ascorbic acid the solution is neutralized and the desired buffer is added.

Ascorbic acid has the additional advantage of providing an effective "chemical deaeration", thus permitting the omission of the tedious bubbling with nitrogen. The reaction between ascorbic acid and oxygen in ammoniacal solution is extremely rapid. The method, however, cannot be applied when copper is used as the indicator because copper is slowly reduced to the monovalent state. In acidic medium the reaction between oxygen and ascorbic acid is very slow. Addition of one drop of 0.001 *M* copper salt solution, however, catalyzes the reaction so that the removal of oxygen is practically instantaneous. The amount of copper is so small that no correction of the cadmium titration is necessary and, moreover, the copper is reduced and thus rendered inactive.

The amperometric titration is thought to be complementary to the photometric titration described earlier[4]. The photometric titration, while sensitive to the presence of precipitates and of light-absorbing substances, is not hampered by polarographically active substances. Both methods in combination with other chelometric approaches, and in complicated cases with the addition of a separation step which isolates both cadmium and zinc from the bulk of interfering ions, should allow advantageous application to many problems of practical analysis.

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SUMMARY

Cadmium can be titrated amperometrically with EGTA in the presence of zinc; three modifications of the titration are described. The diffusion current of cadmium may be used to follow the titration at −0.90 or −0.70 V *vs.* the S.C.E. in ammoniacal or acetate-buffered medium respectively. The titration may also be performed in ammoniacal solution at −0.30 V *vs.* the S.C.E., using copper as the amperometric indicator. The influence of iron, aluminium, magnesium, alkaline earths and lead was studied. Ascorbic acid could be used to mask iron and as an effective remover of oxygen. Under appropriate conditions cadmium could be titrated in the presence of 500-fold amounts of zinc. The titration error is approximately 0.002–0.003 ml of a 0.1 *M* titrant solution.

RÉSUMÉ

Le cadmiun peut être dosé, en présence de zinc, par titrage ampérométrique au moyen de l'acide éthylèneglycol-bis(aminoéthyl)tétracétique (EGTA). Le courant de diffusion du cadmium peut servir à suivre le titrage, à −0.9 ou −0.7 V (*vs.* E.C.S.), en milieu tampon, respectivement ammoniacal ou acétique. Le titrage peut également s'effectuer en solution ammoniacale, à −0.3 V (*vs.* E.C.S.), en utilisant le cuivre comme indicateur ampérométrique. L'influence de Fe, Al, Mg, alcalino-terreux et Pb a été examinée. L'acide ascorbique permet de masquer le fer et d'éliminer l'oxygène dissous dans la solution. Dans certaines conditions, le cadmium peut être dosé en présence de zinc, en quantités 500 fois plus grandes.

ZUSAMMENFASSUNG

Kadmium kann amperometrisch mit GlAeDTE in Gegenwart von Zink titriert werden. Kadmium kann eingesetzt werden um den Verlauf der Titration zu verfolgen, wobei −0.90 oder −0.70 V (gegen ges. Calomel) in ammoniakalischer bzw. azetatgepufferter Lösung titriert wird. Bei −0.30 V kann Kupfer als amperometrischer Indikator verwendet werden. Der Einfluss von Eisen, Aluminium, Magnesium, Erdalkalien und Blei wurde studiert. Ascorbinsäure wurde als Maskierungsmittel für Eisen und zur Entfernung von gelöstem Luftsauerstoff angewendet. Unter Einhalten der entsprechenden Bedingungen kann Kadmium in Gegenwart eines 500fachen Überschusses an Zink bestimmt werden. Die Methode ist auf etwa 0.002–0.003 ml einer 0.1 molaren Titrationslösung genau.

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POLAROGRAPHY OF THE FRUCTOSE-BORATE SYSTEM

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It is well known that most aldehydes are easily reducible at the dropping mercury electrode (DME), whereas only a few particular ketones (such as those having a point of unsaturation in the vicinity of the carbonyl groups) can be reduced at the DME. However, with respect to sugars, ketoses are the more easily reducible species. HEYROVSKÝ AND SMOLER[1] showed that aldoses, such as glucose, galactose, mannose, rhamnose, 1-arabinose, and lyxose cannot be reduced at the DME. On the other hand, they found that in neutral or alkaline media fructose and sorbose gave well-defined polarographic waves. The reduction waves for the two ketones started in the vicinity of −1.80 V *vs.* the saturated calomel electrode and were proportional to the concentration of the respective sugars. SWANN *et al.*[2] utilized the depression of the fructose wave by borate for the determination of small amounts of boron by an amperometric titration procedure; the depression of the fructose wave is caused by the formation of a complex between fructose and borate ions. TORSSELL[3] assumed that the complex was formed between the carbonyl group of the fructose and the borate ion. From the depression of the polarographic wave of the fructose by the borate ions, he was able to calculate the equilibrium constant of the system.

The objective of the work reported in this paper was to study a little more thoroughly the polarographic behavior of the fructose-borate system.

Apparatus

"Leeds and Northrup" *Electro-Chemograph*, type E.

Indicating electrode. Dropping mercury electrode consisting of a standard glass capillary tubing purchased from the Fisher Scientific Company and connected to a mercury reservoir (500-ml dropping funnel) with about four feet of Tygon tubing.

Reference electrode. Silver-silver chloride electrode with a 1 *N* LiCl salt bridge.

pH-meter. "Leeds and Northrup" pH-meter, Model 7664.

Electrodes, pH. Conventional blue glass-calomel electrode system, purchased from Leeds and Northrup Company.

Reagents

Lithium chloride, lithium hydroxide and boric acid were "Baker Analyzed" reagents. Fructose (Pfanstiehl Laboratories, Inc., Waukegan, Illinois) was listed as being

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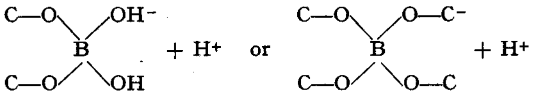
better than 99% pure and had the following specifications: molecular weight 180.13, specific rotation 92°, residue after ignition 0.05%, moisture < 0.1%.

Polyhydroxy alcohols and borate

The interaction between polyhydroxy alcohols and borate ions in solution has long been known. As far back as 1842, BIOT[4] reported that a solution of boric acid became acid to litmus upon the addition of sugars. Additional demonstrations, such as increase in mutual solubility, change in optical rotation, increase in conductivity have all served to indicate the formation of a complex between the borate ions and hydroxy compounds. A number of workers have proposed structures of these complexes based upon systematic studies of their stoichiometry by physical measurements. The structures proposed by HERMANS[5] are accepted by many as being most plausible, although with some reservations. He has shown that 1,2- and 1,3-diols will generally form complexes with boric acid which may often be isolated. He assigns two structures to these complexes. One is an ester formed by splitting out two molecules of water between one hydrated borate ion and one molecule of a glycol. The other is formed by splitting out four molecules of water between one hydrated borate ion and two molecules of glycol. The two structures are shown below.



TUNG AND CHANG[6] studied the boric acid–mannitol complex by measuring the pH of various solutions using the quinhydrone electrode. They postulated the reaction to be $B^- + nM = BM_n^-$, where B^- represents the borate ion, n an integer, M the mannitol, and BM_n^- the complex ion. By a graphical solution of an equation derived from the mass-action expression, n was found to be 2 and the equilibrium constant K for the reaction was $2.75 \cdot 10^6$.

These results were rejected by DEUTSCH AND OSOLING[7] with respect to both the constant and formulation. The latter authors employed conductivity and pH measurements on a series of mannitol–boric acid solutions. They concluded that mannitol reacts with borate ions to form two complexes, according to the following equations:

$$HB = H^+ + B^-$$

$$B^- + M = BM^-, \; K_1$$

$$B^- + 2M = BM_2^-, \; K_2$$

where HB represents boric acid, B^- the borate ion, M the mannitol, BM^- and BM_2^- the complexes, and the K's are the mass-action constants, the reactions being assumed to proceed from left to right. The mass-action constants calculated from their data were $K_1 = 3 \cdot 10^2$ and $K_2 = 5.1 \cdot 10^4$.

In the case of polarography the existence of the interaction between fructose and borate ions is manifested by a decrease in the polarographic wave of an alkaline fructose solution after the addition of borate ions. The first question that was considered concerned whether or not the depressed wave in the presence of borate ions was still the polarographic wave of fructose or was it that of a complex species.

Fructose wave in the presence and absence of borate

It was decided to compare the polarographic characteristics of the fructose wave in the presence and absence of the borate ions. If these characteristics are the same, then it can be assumed that fructose is the reducible species in both cases and that the complex is not directly involved in the reduction process.

The polarographic wave of fructose in a 0.1 M lithium chloride, 0.01 M lithium hydroxide supporting electrolyte is shown in Fig. 1. The concentration of the fructose in this solution was 2.15 mmoles/l, the mercury height 54 cm, mercury flow rate 1.98 mg/sec and temperature 30 ± 0.1°. The resulting wave was corrected for both residual current and I.R. drop (cell resistance 415 ohms). It is noticed that the reduction starts in the vicinity of -1.70 V which is in qualitative agreement with the work of HEYROVSKÝ AND SMOLER[1]. These authors also found a considerable variation in the magnitude of the fructose wave with temperature, about 15% increase per degree rise in temperature, whereas the normal increase for a diffusion-controlled process is from 1.3 to 2.3% per degree. They attribute this abnormal temperature coefficient to the fact that the reduction process is at least in part kinetically controlled and must be considered irreversible.

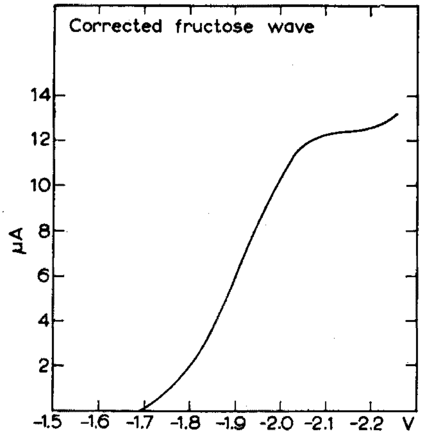


Fig. 1. Polarographic wave of fructose in 0.1 M LiCl–0.1 M LiOH.

In general, the relationship between current and potential for an irreversible electrode process may be expressed[8] as follows:

$$i = kC^{\circ} \exp \frac{(\alpha nEF)}{RT},$$

where α is the transfer coefficient, n is the number of electrons transferred in the rate-determining step, C° is the concentration of the electroactive substance at the surface of the electrode, and RT and F retain their usual electrochemical significance. From the above, one can obtain a polarographic equation that is analogous to the Nernst equation for diffusion-controlled and reversible electrode reactions. This modified equation is:

$$E_{de} = E_{1/2} + \frac{RT}{\alpha F} \ln \frac{i}{(i_d - i)}$$

where E_{de} is the potential of the dropping mercury electrode, i is the polarographic current corresponding to E_{de}, i_d the limiting current, and $E_{1/2}$ the half-wave potential. For a reversible process, the αn in the polarographic equation is replaced by n, an integer, which represents the number of electrons transferred in the over-all electrode reaction. In the case of an irreversible process in which n is known, α will be a numerical measure of the deviation from reversibility. Data obtained from the fructose polarogram shown in Fig. 1 were used to make the plot E_{de} *vs.* $\log i/(i_d - i)$ shown in Fig. 2. From this straight-line plot the value of $E_{1/2}$ was found to be -1.91 V and that of α to be 0.212 after assigning to n a value 2.

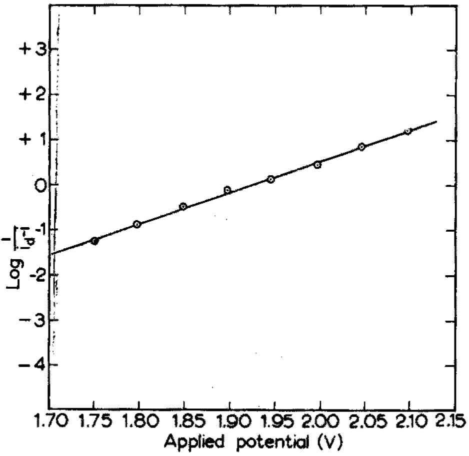


Fig. 2. Plot of E_{de} *vs.* $\log i/(i_d - i)$.

Another solution containing both fructose and borate ions in the same supporting electrolyte was prepared. The concentrations of fructose and borate were $3.0 \cdot 10^{-6}$ M and $1 \cdot 10^{-2}$ M respectively. A polarogram of this solution was made. A comparison of the measured limiting current compared with that of the wave in the absence of borate ions indicated a 67% depression in wave height. The straight-line plot of E_{de} *vs.* $\log i/(i_d - i)$ of the depressed wave gave an $E_{1/2}$ of -1.90 V and a transfer coefficient α of 0.215. The fact that the transfer coefficients and the half-wave potentials do not change upon the addition of borate indicates that the reducible species has not changed by the addition of the borate ions. The only apparent difference is the amount of the reducible species present.

Further evidence that the complex formed is not directly involved in the electroreduction is shown by the effect of the mercury height on the diffusion current. The mercury pressure will, of course, be proportional to the height of the column of mercury above the electrode. It is well-known that for true diffusion currents as defined by the Ilkovic equation the diffusion current varies directly with the product $m^{2/3}t^{1/6}$ where m is equal to the weight of mercury issuing from the capillary per sec in mg and t is the drop time in sec. Because m varies directly with the mercury pressure P (generally expressed as mercury column height in cm) and t varies inve sely with mercury pressure, the resulting current is proportional to the square root of the mercury pressure as shown below:

$$i_d = KP^{1/2}$$

WIESNER[9] in a study of kinetically controlled processes, reported that the limiting current i_k is governed by the following equation:

$$i_k = Km^{2/3}t^{2/3}$$

Inserting the equivalent pressure relationships, the following equation is obtained:

$$i_k = K$$

Thus, if the electrode process is 100% kinetically controlled, the limiting current will not change in magnitude as a result of changing the height of the mercury column.

A third type of electrode process produces what is known as an adsorption current. In this type, the limiting current has been shown[8] to be directly proportional to $m^{2/3}t^{-1/3}$. After converting to units of pressure, the value of the limiting current may be expressed as follows:

$$i_a = KP$$

The three equations relating limiting current to mercury pressure or height may be expressed with the following general equation:

$$i = KP^x$$

or

$$\log i = \log K + X \log P$$

in which case a diffusion-controlled process will have a value of 0.5 for X; for kinetically and adsorption controlled processes the values of X are zero and one respectively.

TABLE I

RELATIONSHIP BETWEEN MERCURY PRESSURE AND LIMITING CURRENT OF FRUCTOSE WAVE

Mercury height (cm)	*i (μA)*
51	15.2
46	14.5
41	13.8
36	13.2
31	12.2

The above concepts were applied to the fructose wave. Several polarograms were made of the same fructose solution, each at different settings of the mercury level. This solution was $3.1 \cdot 10^{-3}$ M with respect to fructose in the 0.1 M LiCl–0.01 M LiOH electrolyte. The temperature was controlled at 30°. The comparison between limiting current and mercury height is shown in Table I. The plot of log of mercury height against log of limiting current is shown in Fig. 3. The slope of this curve has a value of 0.40. Since, as indicated earlier, a slope of 0.50 signifies a diffusion-controlled process and a value of 0.00 signifies a purely kinetically controlled process, the experimental value of 0.40 points to a process that is both diffusion and kinetically controlled.

Again, for the purpose of comparison, an evaluation of the relationship between the mercury pressure and the limiting current was made for fructose in the presence of a considerable quantity of borate. The concentrations of the fructose and borate ions were $3.0 \cdot 10^{-3} M$ and $1 \cdot 10^{-2} M$ respectively; the supporting electrolyte was 0.1 M LiCl and 0.01 M LiOH; the temperature was controlled at 30°. The values for the limiting currents corresponding to the various mercury levels are tabulated in Table II. A plot of log of mercury height against log of limiting current gave a straight line with a slope of 0.40 which, of course, is identical with the value obtained for fructose in the absence of borate ions.

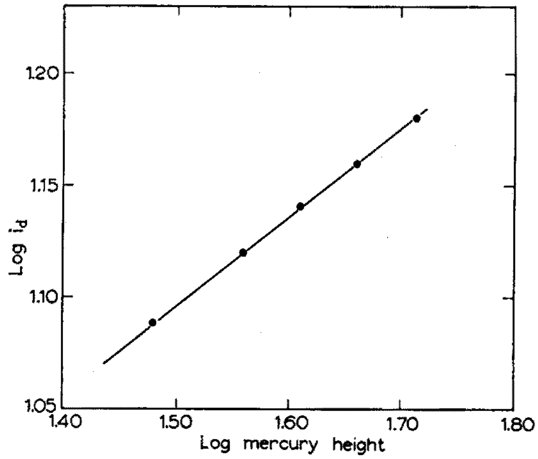


Fig. 3. Plot of log (mercury height) *vs.* log (limiting current).

TABLE II

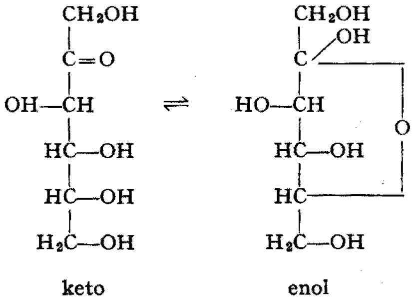
RELATIONSHIP BETWEEN MERCURY PRESSURE AND LIMITING CURRENT OF FRUCTOSE WAVE IN THE PRESENCE OF BORATE IONS

Mercury height (cm)	*i (μA)*
50	5.00
45	4.72
40	4.50
35	4.31
30	4.03

It is noted that the magnitude of the current values in Table II is much less than that of the current values for the corresponding mercury height settings in Table I. This, of course, is due to the borate present which has effectively removed a considerable amount of the reducible fructose by complex formation. However, the relationship of rate of change of current with mercury height is the same in both systems which is the factor that classifies the electrode process.

Method of complex formation

Because the depressed polarographic wave has the same characteristics as the original fructose wave, it is postulated that in both cases the same species is being reduced. Thus, the borate ions function to reduce the concentration of reducible fructose. The reason for the reduction in concentration by the presence of borate ions may be explained by the fact that fructose exists in two tautomeric forms. The two forms are the keto and enol forms, represented as follows:



The keto form having the free carbonyl group is polarographically reducible, whereas the enol form is inert. The reduction in the concentration of the keto form upon the addition of borate ions is probably caused by the formation of a complex between the enol form (a polyhydroxy alcohol) and the borate ions. This formation, of course, will shift the above equilibrium to the right, thus effectively decreasing the concentration of the reducible fructose (keto form).

Although the fructose wave is partially kinetically controlled, the limiting current is proportional to the fructose concentration as shown by HEYROVSKÝ AND SMOLER[1] and later verified by SWANN *et al.*[2]. This means that one cannot determine the ratio of enol and keto forms of the fructose from the simple polarographic wave of fructose, but, owing to the existence of the direct proportionality, one can utilize the decrease in the limiting current of the wave (caused by the introduction of borate ions) to calculate the proportion of fructose that has entered into complex formation. This is the basis for the calculation of the equilibrium constant described in the following section.

Calculation of equilibrium constant from polarographic data

Since the limiting current of the fructose wave is directly proportional to the concentration of the keto form, any decrease in this limiting current will be a direct measure of the amount of the keto form that has been transformed into a non-reducible species. Assuming, of course, that the borate ions tie up the enol form of the fructose, then this decrease in limiting current will also be an indirect measure of the amount of the enol form that has been complexed. In other words, two equilibrium states are postulated for before and after the addition of borate ions.

(*1*) Before the addition of borate ions: $\text{Fructose}_{(\text{enol form})} \rightleftharpoons \text{Fructose}_{(\text{keto form})}$.

(*2*) After the addition of borate ions: $\text{Fructose–borate complex} \rightleftharpoons \text{Fructose}_{(\text{enol form})} \rightleftharpoons \text{Fructose}_{(\text{keto form})}$. If one assumes a 1 : 1 addition, *i.e.*, one borate ion to one mole of fructose and ignores the enol form, then the over-all equation may be expressed as follows:

$$F + B \rightleftharpoons FB$$

in which F represents the reducible fructose. FB is the fructose–borate complex and its concentration will be proportional to the decrease in the limiting current of the fructose originally present, *i.e.*, before the addition of the borate. B represents the borate ions that have not complexed with the fructose. Its magnitude is equivalent to the difference between the amount of borate added and the value of FB as determined by the decrease in limiting current. Thus, the following equilibrium constant can be calculated:

$$\frac{(\mathrm{F\,B})}{(\mathrm{F})\,(\mathrm{B})} = K$$

For experimental verification, a series of solutions were prepared; each solution was $6.6 \cdot 10^{-4}$ *M* with respect to fructose, 0.1 *M* with respect to LiCl and 0.01 *M* with respect to LiOH. To each solution, a different amount of borate was added. Polarograms were made and the equilibrium constants calculated. The data used in the calculation and the results are shown in Table III. As can be seen, the values of *K*, assuming a 1 : 1 addition, were relatively constant. Two other sets of *K* values were calculated, assuming the following modes of addition:

TABLE III

CALCULATION OF K FOR REACTION $\mathrm{F} + \mathrm{B} \rightleftharpoons \mathrm{F\,B}$

Initial concn. fructose	*Initial concn. borate*	*Wave height (μA)*	*Concn. of complex*	*Concn. of free fructose*	*Concn. of free borate*	$K \cdot 10^2$
$6.6 \cdot 10^{-4}$	—	1.75	—	—	—	—
$6.6 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	1.46	$1.1 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	12.5
$6.6 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	1.25	$1.9 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	13.0
$6.6 \cdot 10^{-4}$	$7.5 \cdot 10^{-4}$	1.01	$2.8 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$	13.0
$6.6 \cdot 10^{-4}$	$12.5 \cdot 10^{-4}$	0.80	$3.6 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	$8.9 \cdot 10^{-4}$	13.5
$6.6 \cdot 10^{-4}$	$22.5 \cdot 10^{-4}$	0.55	$4.5 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$18.0 \cdot 10^{-4}$	12.0
					Average	12.8

Est. $K = 13 \cdot 10^2$

$$\mathrm{F} + 2\mathrm{B} \rightleftharpoons \mathrm{B\,F\,B} \quad \text{or} \quad K_a = \frac{(\mathrm{B\,F\,B})}{(\mathrm{B})^2\,(\mathrm{F})}$$

$$2\mathrm{F} + \mathrm{B} \rightleftharpoons \mathrm{F\,B\,F} \quad \text{or} \quad K_b = \frac{(\mathrm{F\,B\,F})}{(\mathrm{B})\,(\mathrm{F})^2}$$

The values of $K_a + K_b$ are tabulated in Table IV. The fact that the $K_a + K_b$ values are far from constant indicates that the first relationship, *i.e.*, $\mathrm{F} + \mathrm{B} = \mathrm{F\,B}$, best describes at least the predominant reaction.

RESULTS AND CONCLUSION

In view of the fact that the characteristics for the fructose wave and the depressed fructose wave are the same, *i.e.*, with respect to half-wave potential, transfer coefficient, and response to mercury pressure, it is concluded that the materials involved in the electro-reduction are identical. The only cause for the depression of the wave is the reduction in quantity of the reducible form of fructose present. Thus, it is postulated that the borate ions form a complex with the enol form of fructose, causing a shift to the right in the enol–keto equilibrium, producing a net decrease in the keto (reducible species) concentration. In other words borate ions form a complex with the fructose in the same manner as with mannitol or any other polyhydroxy alcohol.

TABLE IV

TABULATION OF VALUES CALCULATED FOR K_a AND K_b

K_a	K_b
$7.8 \cdot 10^6$	$2.29 \cdot 10^6$
$4.2 \cdot 10^6$	$2.77 \cdot 10^6$
$3.3 \cdot 10^6$	$4.16 \cdot 10^6$
$1.5 \cdot 10^6$	$4.52 \cdot 10^6$
$0.6 \cdot 10^6$	$5.70 \cdot 10^6$

In this respect we differ from TORSSELL[3] who assumes that the boric acid is bound to the second carbon atom (the carbonyl group) of the fructose. The only other evidence that the borate will combine with carbonyl groups was shown by VON PASTERNAK[10] who constructed a complex between boric acid and benzil. However, since benzil has two adjacent carbonyl groups, it must be considered as a special case.

Equilibrium constants, calculated from the magnitude of the depression, indicated that a 1 : 1 addition of the borate ions to the enol form of the fructose was the predominant method of addition. The value of the equilibrium constant calculated from our experiments at 30° ($K = 13 \cdot 10^2$) agrees favorably with the constant ($K = 7 \cdot 10^2$) reported by TORSSELL[3] from data acquired at 20°.

SUMMARY

The polarographic characteristics of the fructose wave in the presence and absence of borate ions were studied. The borate ions form a complex with fructose in a manner very similar to that formed with the simple polyhydroxy alcohols, such as mannitol. The polarographic data indicate that the predominant complex is a 1 : 1 addition. The equilibrium constant for this complex was calculated at 30°.

RÉSUMÉ

Les auteurs ont examiné les caractéristiques polarographiques du fructose, en présence et en l'absence de borate. Il y a formation d'un complexe entre le fructose et le borate, analogue à ceux obtenus avec des alcools polyhydroxylés (par exemple le mannitol).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das polarographische Verhalten von Fructose in Gegenwart und Abwesenheit von Borat. Dieses bildet mit Fructose ähnliche Komplexe wie mit den einfachen Polyhydroxyalkoholen. Es wurde festgestellt, dass der gebildete Komplex vorwiegend ein 1 : 1 Verhältnis aufweist.

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THE DIRECT FLAME PHOTOMETRIC DETERMINATION OF STRONTIUM: CALCIUM RATIOS IN THE ASH OF HUMAN BONES AND TEETH

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In recent years the physiological effects produced by the radioactive fission products from atomic weapons have necessitated an intensified study of the metabolism of strontium in animals and plants. Some years ago this laboratory developed spectrographic methods[1] in response to a demand for the determination of this element in a variety of biological materials. At that time it was found that by using an integrating flame photometer with an automatic background correcting device[2] adequate sensitivity was obtained for the determination of strontium in the calcium oxalate fractions separated from milk and vegetation. The suppressing effect of the phosphate component in the ash of bones and teeth precluded the use of this technique for the direct determination of strontium in solutions of these materials and the sample was buffered with a mixture of graphite and copper sulphate and the spectrum excited by means of a d.c. arc. Whilst the latter method has given results of good accuracy and reasonable reproducibility, the determination of strontium: calcium ratios in human bones and teeth has necessitated a separate determination of the calcium content by chemical methods and in consequence the process has been somewhat time-consuming. In view of recent developments in flame photometry it was decided to see whether these could be extended and used to re-investigate the problem with a view to determining the strontium: calcium ratios directly.

The ashes of human teeth and bones have strontium: calcium ratios of approximately 1 :4000 and there are two factors which contribute to the lack of sensitivity for the determination of strontium in the presence of calcium phosphate by direct flame photometry, namely, the inhibition of spectral emission of the alkaline earths in the presence of the phosphate and the presence of a high background in the vicinity of the strontium line at 4607.3 Å owing to a calcium oxide band system.

The strong suppressing effect of various anions, and of phosphate in particular, on the emission of the alkaline earths has been known for a long time[3] and has been the subject of many investigations[4-8]. This type of interference has been explained in terms of the comparatively low rate of volatilisation of the solid particles resulting when the solvent has evaporated from the spray droplets produced by the atomiser system[4,6,8]. It has been shown that the effect can be reduced by the addition of various substances to the solution to be atomised, *e.g.* iron[9], magnesium[10], EDTA[11] and sucrose[8]. Recently, however, it has been suggested that an improvement in sensitivity could be obtained for many elements dissolved in aqueous and organic solutions in flame photometry, by surrounding a Beckman-type atomiser burner system with a sheath of oxygen to prevent the nitrogen in the air from cooling the flame[12,13]. Since it would be an advantage to overcome the phosphate interference by means of a modified burner system rather than by the addition of extraneous materials to the sample to be analysed, experiments were directed towards investigating the effect of an oxygen mantle upon the phosphate interference in the determination of alkaline earths.

PRELIMINARY STUDIES

Fig. 1 shows the water-cooled burner used in the flame photometer constructed in this laboratory. Direct atomisation was accomplished by means of the reduction in pressure created at the top of the solution capillary by the oxygen blast. The atomised solution was injected into a pre-mixed oxygen–propane flame which was stabilised by means of an outer cone of filtered air. An oxygen mantle around the flame was thus easily obtained by replacing the air feed to the outer jacket with one of oxygen.

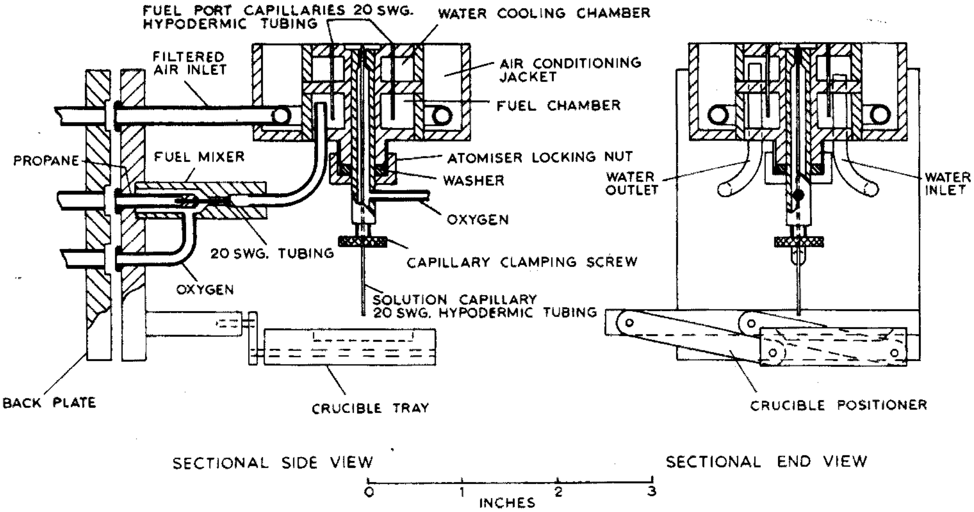

Fig. 1. Burner atomiser unit.

Initial experiments were conducted to determine the effect of oxygen and air mantles respectively on the spectral emission of the strontium line at 4607.3 Å using a 10 p.p.m. aqueous solution of strontium as chloride in the presence of varying amounts of phosphoric acid. In the flame photometer used for these experiments[2] one photomultiplier was arranged to receive the radiation from strontium at the appropriate wavelength, whilst another photomultiplier monitored the adjacent background. The outputs from the two photomultipliers were fed into Miller-type integrator-amplifiers and the difference in intensity levels after a fixed integration period was shown on a meter. The results obtained are indicated in Fig. 2 showing that when the oxygen jacket was used the apparent suppression caused by the phosphoric acid was considerably less than when air was used as a mantle.

The exclusion of nitrogen from the exterior of the flame had apparently increased the temperature of the flame sufficiently to overcome the effects of the low rate of volatilisation of the solid particles of strontium phosphate formed when the solvent had evaporated from the spray droplets in the flame. It was then necessary to determine whether there were any spectrographic inter-element effects between the strontium and the calcium phosphates which would be present in the samples, and the experiment was repeated using varying amounts of calcium phosphate dissolved in the minimum amount of hydrochloric acid in place of phosphoric acid; the results are shown in Fig. 3. It will be noticed that in the presence of calcium and an oxygen mantle considerable enhancement of the strontium line occurs. From this it would appear that, in these circumstances, not only is a high proportion of the molecules of alkaline earth phosphate volatilised and dissociated, but some of the calcium atoms are probably ionised, giving rise to an enhancement of the strontium arc line at 4607.3 Å. This hypothesis tends to be confirmed by the fact that a very similar effect is

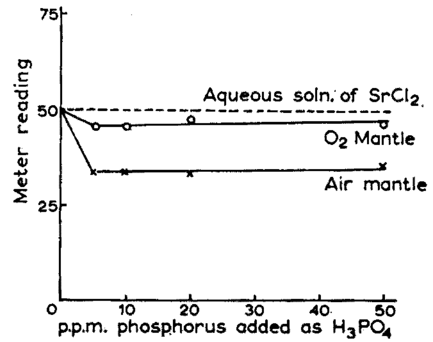

Fig. 2. Effect of phosphoric acid on the emission of strontium 4607.3 Å (10 p.p.m. solution).

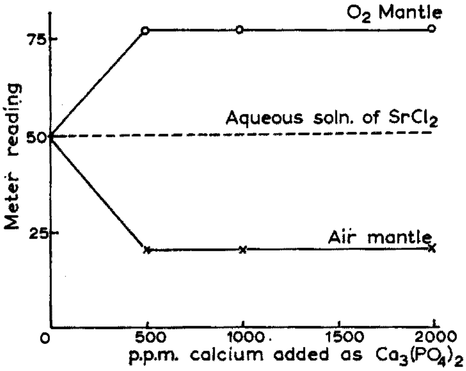

Fig. 3. Effect of calcium phosphate on the emission of strontium 4607.3 Å (1 p.p.m. solution).

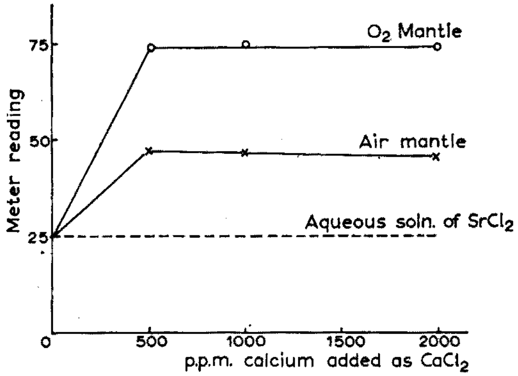

Fig. 4. Effect of calcium chloride on emission of strontium 4607.3 Å (1 p.p.m. solution).

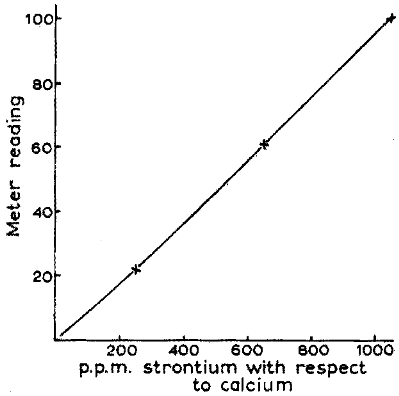

Fig. 5. Calibration curve of 20–1000 p.p.m. strontium with respect to calcium.

obtained by the addition of calcium chloride in place of calcium phosphate in the experiment described above (Fig. 4).

Since the integrating flame photometer[2] had provision for an internal standard channel, selected by means of interference filters, it was possible to avoid the effects of long period source fluctuations and to determine strontium: calcium ratios directly by using the calcium present in bones and teeth as internal standard and measuring the intensity of the strontium line at 4607.3 Å in relation to that of the calcium band head at 5473 Å.

Previous experience had shown that the lowest concentration of strontium in bone ash was 30 p.p.m. (*ca.* 75 p.p.m. of strontium with respect to calcium) and it was necessary to determine whether adequate sensitivity could be attained using the proposed modification to the flame photometric technique. A solution containing 0.1% of calcium as tribasic phosphate, free from strontium[14,15], was made up in 5% hydrochloric acid and the limit of detection, defined as twice the standard deviation of the background radiation of this blank material, was determined at 4607.3 Å. The results are indicated in Table I and show that adequate sensitivity was obtained.

TABLE I

EFFECT OF AIR AND OXYGEN MANTLES ON SENSITIVITY

Conditions mantle gas	*Limit of detection*	
	p.p.m. Sr w.r.t. Ca	*p.p.m. Sr in ash*
Air 20 l/min	140	54
Oxygen 20 l/min	20	8

STANDARDISATION AND MATRIX EFFECTS

The ashes of bones and teeth consist essentially of calcium phosphate and since it had been established that there was little variation in the concentration of the major constituents, standardisation of the method was comparatively straight-forward.

A calibration curve (Fig. 5) was constructed over the range 20–1000 p.p.m. of strontium with respect to calcium using synthetic standards made from analytical grade orthophosphoric acid and strontium-free calcium carbonate, such that each standard contained 0.1% of calcium as tribasic phosphate, 5% of hydrochloric acid and the appropriate amount of strontium chloride.

The effect of variations in the composition of the matrix upon the accuracy of the strontium results obtained was investigated. Small variations in the calcium and phosphorus content, of the order normally encountered in human bones and teeth were found to have a negligible effect whilst the presence of up to 20% of sodium was tolerated.

EXPERIMENTAL

An 0.1% calcium solution is prepared by dissolving 25.8 mg of bone or tooth ash in 0.5 ml of concentrated hydrochloric acid and making up to 10 ml with redistilled water. The strontium : calcium ratio is determined directly by flame photometry using automatic background correction and calcium as internal standard. An oxygen–propane flame surrounded by an oxygen mantle is used. The instrument is calibrated with synthetic standards prepared from strontium-free calcium carbonate and orthophosphoric acid solution.

Reagents

Hydrochloric acid, concentrated, d. 1.16.

Calcium carbonate, strontium-free, dried to constant weight at 100°.

Strontium carbonate, dried to constant weight at 100°.

Orthophosphoric acid, d. 1.75, 90% H_3PO_4.

Whenever possible reagents should be of AnalaR quality and the use of redistilled or demineralised water is implied throughout.

Standards

Master standards: *Strontium, 1000 p.p.m.* Weigh 0.169 g of strontium carbonate into a beaker, cover with 10–20 ml of water and add concentrated hydrochloric acid dropwise until dissolved. Make up to 100 ml with water to give a master solution containing 1000 p.p.m. of strontium. Dilute this master solution as necessary to give working standard solutions.

Calcium, 1%. Weigh 4.994 g of calcium carbonate (strontium-free) into a beaker, cover with 10–20 ml of water and dissolve in just sufficient concentrated hydrochloric acid. Make up to 200 ml with water.

Orthophosphoric acid, 1.63%. Weigh 3.62 g of orthophosphoric acid (90% H_3PO_4) into a beaker and make up to 200 ml with water.

Working standards: *Blank solution.* Measure 10 ml of the 1% calcium solution into a 100-ml flask, and add 5 ml of concentrated hydrochloric acid and 10 ml of the 1.63% phosphoric acid solution. Make up to 100 ml with water.

1000 p.p.m. strontium with respect to calcium solution. Proceed as for the preparation of the blank solution above, but before making up to 100 ml add 10 ml of 10 p.p.m. strontium solution. Additional standards for use in constructing a calibration curve are prepared in a similar way.

Preparation of sample

Dissolve 25.8 mg of the sample in 0.5 ml of concentrated hydrochloric acid and 1 ml of water, heat if necessary and allow to cool. Make up to 10 ml with water.

Flame photometry

Adjust the flame photometer for optimum operating conditions at 4607.3 Å (for a full description of the flame photometer and detailed operating instructions see ref. [2]). Obtain duplicate readings for each sample solution in turn and repeat to obtain a total of eight readings. Calculate the mean and read the strontium to calcium ratio from the calibration curve (Fig. 5).

ACCURACY AND REPRODUCIBILITY

The accuracy of the method was assessed by analysing samples the strontium content of which had already been determined by the techniques of neutron activation, emission spectroscopy and X-ray fluorescence. As can be seen from Tables II and III no significant bias was evident. An additional check on accuracy was obtained by a comparison of the results obtained on 150 samples analysed by both the flame photometric and the emission spectrographic techniques. No significant difference was found between these pairs of results.

TABLE II

COMPARISON OF RESULTS OBTAINED FOR BONES

Sample	*p.p.m. Strontium in bone ash*			
	Flame photometry	*Neutron activation*	*Emission spectroscopy*	*X-ray fluorescence*
I	165	145	175	—
II	150	146	170	—
III	160	148	165	—
M.1229	100	106	100	106
M.918	215	229	235	235
M.5747	100	—	95	105
M.5750	95	—	95	90
M.5752	125	—	130	115
M.5753	185	—	185	170

TABLE III

COMPARISON OF RESULTS OBTAINED FOR TEETH

Sample	*p.p.m. Strontium in tooth ash*		
	Flame photometry	*Emission spectroscopy*	*X-ray fluorescence*
Incisor ash	145	130	150
Molar ash	110	105	110

The reproducibility of the method was determined by the replicate analysis of a sample of bone ash containing 260 p.p.m. of strontium with respect to calcium. The standard deviation, calculated from the results of some sixty determinations obtained upon this sample over a period of four months, was 10 p.p.m. of strontium with respect to calcium. Further, replicate determinations upon the synthetic standards used to establish the calibration curve indicated that the standard deviation remains constant over the range 20–1000 p.p.m. of strontium with respect to calcium.

SUMMARY

Samples of bone or tooth ash are dissolved in hydrochloric acid and the strontium : calcium ratio is determined directly by flame photometry using an oxygen–propane flame, surrounded by a mantle of oxygen in order to eliminate the suppressing effect of phosphate. The effective concentration range is 20–1000 p.p.m. of strontium with respect to calcium and the standard deviation, which remains constant over this range, is 10 p.p.m. of strontium with respect to calcium.

RÉSUMÉ

Une méthode est décrite pour la détermination du rapport strontium : calcium dans la cendre d'os ou de dent. L'échantillon est dissous dans l'acide chlorhydrique; la détermination peut se faire directement par photométrie de flamme, en utilisant une flamme d'oxygène–propane, entourée d'oxygène, afin d'éliminer l'influence du phosphate.

ZUSAMMENFASSUNG

Beschreibung einer flammenphotometrischen Methode zur Bestimmung des Mengenverhältnisses Strontium : Calcium in Knochen- oder Zahn-Asche. Durch Anwendung einer Sauerstoff-Propanflamme, die mit einem Sauerstoffmantel umgeben ist, kann die Störung durch Phosphat ausgeschaltet werden.

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ATOMIC ABSORPTION STUDIES USING A HOLLOW-CATHODE TUBE AS AN ABSORPTION SOURCE*

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It has been shown by WALSH[1] and other investigators in the field of atomic absorption that a flame can be used as an absorption source for elements that are readily dissociated from their compounds. Except for some work done by RUSSELL AND WALSH[2], GATEHOUSE AND WALSH[3], with hollow-cathode absorption tubes, and L'vov with graphite crucibles[4], little has been published about the use of an absorption source other than the flame for atomic absorption work.

Because our laboratory is confronted with a variety of samples, some of which are not readily dissociated from their compounds in the flame, and many of which are radioactive, it was decided to investigate sources other than the flame to obtain limits of detection for elements of interest. It was thought that a hollow-cathode tube would serve our need, since the sputtering action of the discharge in the hollow cathode might dissociate even the refractory elements, as indicated by our previous experience of exciting refractory uranium alloys in a Schüler-Gollnow water-cooled hollow-cathode tube, and, also the radioactivity might be confined to the closed tube[5]. Since a number of Schüler-Gollnow water-cooled tubes were readily available at this laboratory, it was decided to use one as an emission source, and the other as an absorption source, after it was modified, to study absorption characteristics and limits of detection for a few elements.

EXPERIMENTAL

Apparatus

A schematic diagram illustrating the operation of the atomic absorption technique used for this investigation is shown in Fig. 1. The Schüler-Gollnow water-cooled tube[6]

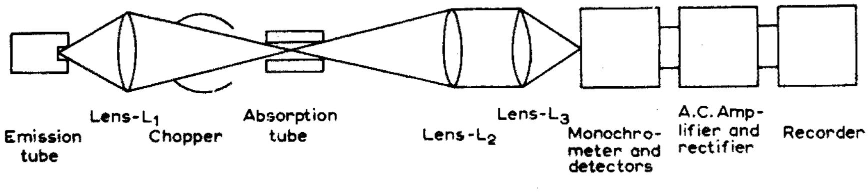

Fig. 1. Schematic diagram illustrating apparatus used for atomic absorption studies.

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

is also described by TOLANSKY[7]. It emitted steady light that was modulated by a 60-cycle mechanical chopper and was focussed on the hole of the cathode electrode of the absorption tube, by means of a lens, L_1, with a focal length of 200 mm. With two lenses, L_2, L_3, in series, of focal length 250 and 200 mm, respectively, the transmitted light coming from the absorption tube was focussed on the 20-μ slit, completely illuminating the collimator of a Jarrell-Ash monochromator, Model 82-000, equipped with 1P21 and 1P28 photo-multiplier tubes. The a.c. signal from the detector was amplified and rectified, and then transmitted to a Brown recorder. The emission and absorption tubes had independent conventional circulating systems[5] using neon as a carrier gas. Two conventional d.c. power supplies were used. To study the emission characteristics of the absorption tube, the mechanical chopper was placed between the absorption tube and the monochromator.

Emission tube

The Schüler-Gollnow emission tube used to obtain constant radiation had an anode and cathode made of 2S aluminum. O-Ring seals, instead of wax seals, were used at the ends of the glass tube that separated the cathode and anode. The connection of the hollow-cathode tube to the circulating system was made through O-ring seals and Sylphon bellows.

To obtain stable radiation from the hollow-cathode emission tube, a sample was sputtered in a cathode crater of the emission tube using the technique employed for the analysis of uranium alloys[5]. Approximately 30 min was required to sputter milligram quantities of elements (magnesium, calcium, beryllium and silicon) in the respective cathode craters of the emission tube to obtain stable radiation. For compounds, the sputtering time was somewhat longer. Approximately 1–2 h was required to obtain stability with sodium fluoride. However, once a sample was sputtered on the walls of the cathode crater, a reproducible light source was obtained that lasted 2–3 days when a low current of about 30 mA was used.

The first element investigated for atomic absorption studies using two hollow-cathode tubes was sodium. The source of sodium was sodium fluoride, since the purified compound is available in this laboratory, and it is used as a carrier for the determination of impurities in graphite[8]. The sodium line chosen for investigation was the strong 5890 D line; maximum absorption was expected from this line, and other investigators[9,10] found it to be very sensitive for analysis of sodium by atomic absorption techniques using a flame as an absorption source.

Since the lower limit of detection for an element of interest by atomic absorption techniques is dependent on the shape of the line emitted from the emission tube[11], studies were made of the emission tube to determine the optimum operating conditions required to obtain a strong sodium-D line having the maximum intensity with the minimum amount of self-absorption for the analysis of sodium.

In the absence of self-absorption in a hollow-cathode tube, the strong sodium-D line is twice as intense as the weak sodium-D line; as a result, a straight line can be drawn over a range of intensities, going through the origin (Fig. 2). Thus, to determine the optimum operating conditions for the emission tube to obtain the maximum intensity of the strong sodium-D line with the minimum amount of self-absorption, it was decided to perform studies comparing the intensities of the two sodium-D lines over a range of currents up to 120 mA using a new cathode containing 0.5 mg of sodium in the bottom of the electrode, and operating the tube using neon, as a carrier gas, at 2, 3, and 5 mm of Hg, respectively; the results were compared with the theoretical curve shown in Fig. 2. No attempt was made to obtain results using neon at a pressure lower than 2 mm of Hg, since at a lower pressure the discharge in the tube was unstable. To minimize any possible interferences from spectral lines and background for this work, the entrance and exit slit widths used on the monochromator were 20 and 45 μ, respectively.

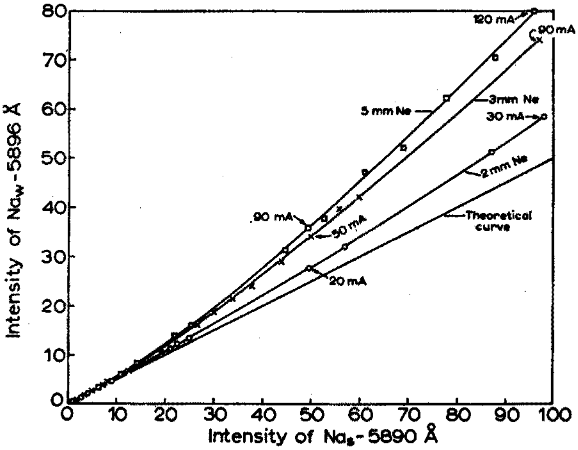

Fig. 2. The effect of neon pressure on the emission intensities of the sodium-D lines for the emission tube.

The results illustrated in Fig. 2 indicate that for a comparable intensity of the strong sodium-D line, using neon at 2, 3, and 5 mm of Hg, respectively, the minimum amount of self-absorption for the strong sodium-D line was obtained using neon at 2 mm of Hg, the lowest pressure; the maximum self-absorption was obtained using neon at 5 mm of Hg, the highest pressure. As a result, to obtain the desired sensitivity for the analysis of sodium, the emission tube was operated using neon at a pressure of 2 mm of Hg and a minimum current of approximately 30 mA.

Absorption tube

The modified water-cooled Schüler-Gollnow absorption tube used as the absorption source was similar in all respects to the emission tube with the exception of the cathode assembly shown in Fig. 3. The cathode itself, made of 2S aluminum, in some respects resembled the one used in the emission tube since both had the same length and outside diameter. The cathode in the absorption tube had a hole 1/4 in. in diam. and 1 in. long, for the purpose of retaining an evaporated liquid sample. A 1/4 in. portion of the cathode was threaded and screwed into a brass tube used to pass incident radiation from the emission tube, and, also to space the cathode 1/4 in. from the anode. The brass tube had a wall thickness of 3/32 in., and six radial holes, like those used in the emission cathode electrode, drilled around a circular groove to allow the carrier gas to circulate through the tube and the vacuum system. Two quartz windows, 1/8 in. thick and 3/4 in. diam., held in place by Apiezon W wax, were used at the front and rear of the absorption tube to allow light from the emission tube to pass through the absorption tube, as described previously.

To determine the optimum operating conditions for the absorption tube to obtain the desired sensitivity for sodium, a test similar to that used for the emission tube was performed. The 60-cycle mechanical chopper was placed between the absorption tube and the monochromator, and a new cathode, containing 0.5 mg of sodium fluoride was used when the tube was operated with neon at 2, 3, and 5 mm of Hg, respectively. The results of this investigation are shown in Fig. 4; they indicate that at a comparable intensity of the strong sodium-D line, using neon at 2, 3, and 5 mm of Hg in the absorption tube, the minimum amount of self-absorption was obtained using neon at 2 mm of Hg, while the maximum self-absorption was obtained using neon at 5 mm of Hg. Therefore, to obtain the desired sensitivity for sodium, the absorption tube was operated at 100 mA using neon at 2 mm of Hg as the carrier gas, because at this pressure the strong sodium-D line was relatively free of self-absorp-

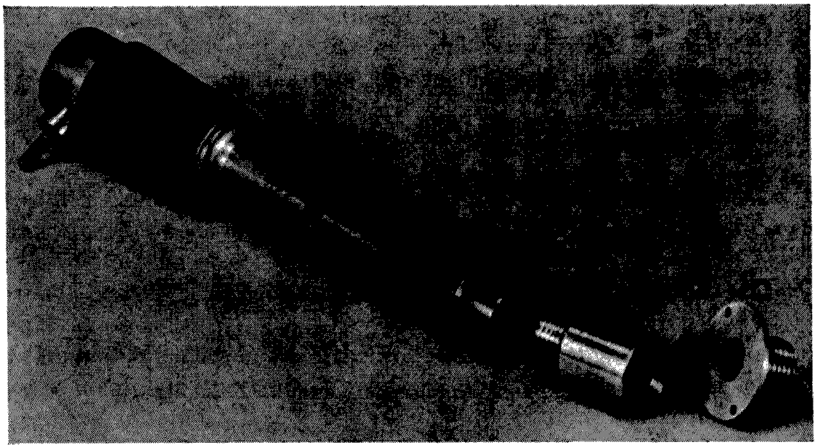

Fig. 3. Electrode assembly used in absorption tube.

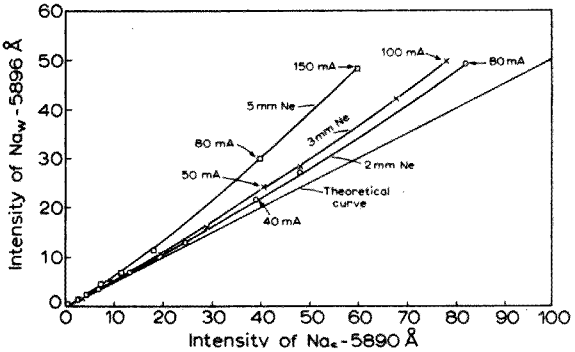

Fig. 4. The effect of neon pressure on the emission intensities of the sodium-D lines for the absorption tube.

tion, and therefore was more like the emission line. As a result, the maximum amount of incident radiation from the emission tube was absorbed by the absorption tube.

Procedure

Fig. 5 illustrates a recorder tracing obtained for a sodium sample. The initial intensity of the strong sodium-D line was obtained by shining light from the emission tube through the inactive absorption tube and on to the monochromator preset at the peak intensity of the strong sodium-D line. Subsequently, the absorption tube, containing a uniformly deposited sample in the hole of the cathode, was activated by turning on the current to 100 mA quickly, and the current was held steady at 100 mA until the maximum absorption was observed on the recorder in about 5 sec. The current in the absorption tube was then reduced to zero quickly, and the initial intensity from the emission tube was recorded again. By this technique of absorbing the emitted light from the emission tube, many absorption readings were obtained quickly, and any drifting of the light intensity of the emission tube was readily detected by observing two consecutive initial peak intensities of the emission tube. To demonstrate that this rapid technique was reliable, absorption readings were obtained for the same sample by keeping the current in the absorption tube on, at 100 mA, for 1 min. The results of this test are also included in Fig. 5; they indicate that the average absorption values obtained by keeping the absorption tube on for 1 min, and the average absorption value of a number of tracings obtained by keeping the absorption tube on for about 5 sec, are practically the same.

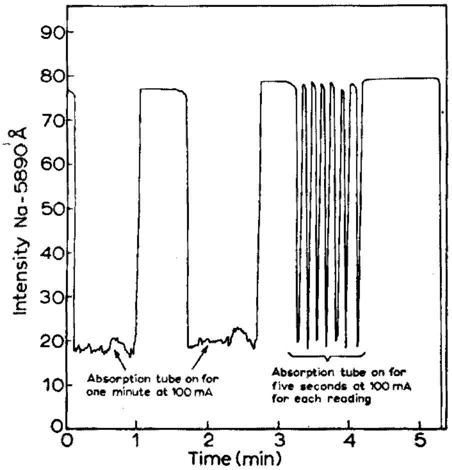

Fig. 5. Absorption tracing of a sodium sample using two hollow-cathode tubes.

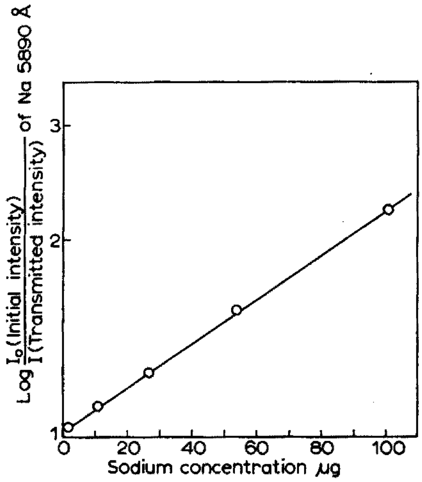

Fig. 6. Analytical curve for sodium.

RESULTS

To obtain an analytical curve for sodium, 0.1 ml of standard aqueous sodium fluoride solutions, ranging from about 1 to 100 μg of sodium, was evaporated under a heat lamp in the respective cathodes of the absorption tube electrodes. A uniformly deposited sample of sodium fluoride was obtained in the hole of the cathode electrodes by rolling the cylindrical electrodes, containing a liquid sample, back and forth on a smooth reflecting surface under a heat lamp while the solution was evaporating, to distribute and dry the solutions over the entire surface of the cathode hole. Subsequently absorption values were obtained for the standards, a blank 2S aluminum cathode, and a blank 2S aluminum cathode with 0.1 ml of distilled, deionized water evaporated in it. The blank electrodes, with and without the evaporated water, gave about the same absorption reading, which was appreciably lower than the absorption reading obtained for the cathode with 1 μg of sodium. The blank, however, was subtracted from all standards, and an analytical curve was obtained (Fig. 6). Each point on the curve is an average of at least five absorption values. Since a straight line was obtained by plotting the logarithm of the initial intensity over the transmitted intensity against concentration of the absorbing material, Beer's law was obeyed at the concentrations shown. A number of points obtained by evaporating standards containing more than 100 μg of sodium in the cathode crater of the absorption tube, fell below the curve. A repeat analysis of these standards showed the same trend; as a result, these points were excluded from Fig. 6, and it was decided to limit the sample in the absorption tube to approximately 100 μg of sodium to obtain reproducible results.

Effect of increasing the current in the absorption tube

The lower limit of detection for sodium can be further extended (Fig. 7) by increasing the current in the absorption tube, *i.e.* increasing the number of atoms in the ground state in the light path. Each point shown in Fig. 7 was an average of a number of absorption values obtained by the previously described techniques, using a new cathode electrode in the absorption tube containing 10 μg of sodium, in the form of sodium fluoride, with currents of 25, 50, 100, 200, 300, and 400 mA, respectively, in the absorption tube. The results indicate that the maximum absorption was obtained

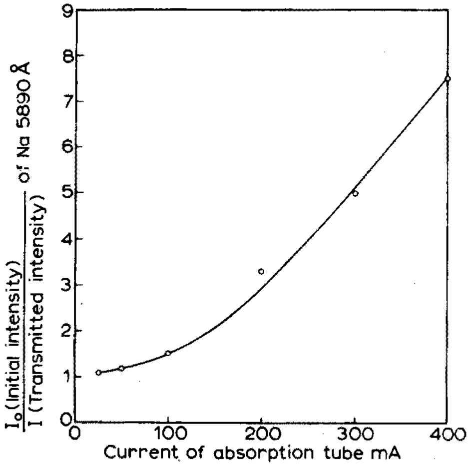

Fig. 7. The effect of increasing the current in the absorption tube.

using the highest current. However, since the sample in the absorption tube was sputtered away faster at a higher current, fewer reproducible absorption tracings like those shown in Fig. 5 were observed.

Reproducibility

To test the reliability of analyzing for sodium using a hollow-cathode tube as an absorption source, five absorption tube electrodes were loaded with 27 µg of sodium, and the average of the logarithms of initial intensity over transmitted intensity of five consecutive absorption readings was obtained for each electrode using the procedure described. The results (Table I) were obtained from the previously prepared analytical curve. For five independent analyses, the average percent deviation from the mean was ± 8.0%.

TABLE I

REPRODUCIBILITY TEST FOR SODIUM

Sample no.	*Na in absorption tube (µg)*	*Na detected (µg)*	*Difference (µg)*	*% Rel. dev.*
1	27.0	27.0	0.0	0.0
2	27.0	26.0	−1.0	−3.7
3	27.0	31.0	+4.0	+14.7
4	27.0	30.0	+3.0	+11.0
5	27.0	30.0	+3.0	+11.0
				% Average dev. ± 8.0%

To check further on the reliability of the method for obtaining absorption values for sodium using two hollow-cathode tubes, data corresponding to those in Table I were obtained in another way. If I_1 is the intensity recorded from the emission tube alone, I_2 is the intensity recorded from the absorption tube alone with the chopper placed in front of each tube, operated using the previously determined conditions, and I_{1+2} is the intensity recorded when both are operating and the chopper is placed in front of the two tubes, then $(I_1 + I_2 - I_{1+2})$ is the amount of incident light absorbed by the absorption tube. The absorption value obtained in this way was in good agreement with that obtained previously when the chopper was placed between the two tubes, for the same sample in the absorption tube; this indicates that a negligible fraction of the re-emitted light[12] from the absorption tube entered the monochromator when the emission and absorption tubes were operated simultaneously.

Effects of extraneous elements, lithium and magnesium, on sodium in the absorption tube

Lithium and magnesium which are commonly associated with sodium, were investigated to determine what influence they had on the absorption values of sodium. The sodium was kept constant at 10 µg in the absorption tube, and the lithium, in the form of lithium fluoride, was varied from 0.1 to 100 µg, in the absorption tube. The results (Fig. 8, curve 1) indicated that lithium suppressed the absorption values for sodium, even at the smallest concentration of lithium, 0.1 µg.

Other investigators analyzing sodium by emission techniques, using the d.c. arc, a.c. spark and flame, have found that lithium enhanced the strong sodium-D line.

Therefore it was thought desirable to investigate the effect of lithium on the emission intensity of the strong sodium-D line obtained from the absorption tube. This investigation was carried out by simply placing the chopper between the absorption tube and monochromator; thus the emitted intensity from the absorption tube was detected and observed. The results (Fig. 8, curve 2) indicate that lithium suppressed the emission intensity of the strong sodium-D line also, and curves 1 and 2 have about the same shape.

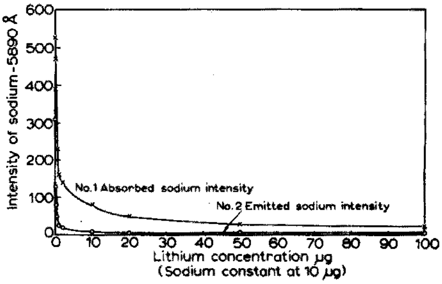

Fig. 8. Influence of lithium on sodium.

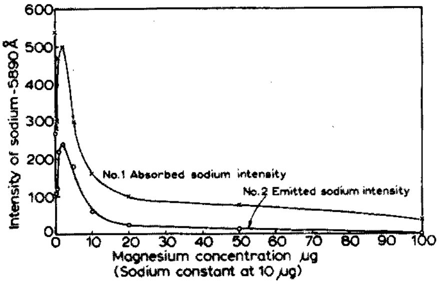

Fig. 9. Influence of magnesium on sodium.

Fig. 9, curve 1 shows the effect of magnesium in the absorption tube on the absorption values of sodium. The results indicated that magnesium, as magnesium chloride, suppressed the sodium absorption values. Curve 2 (Fig. 9) illustrates the effect of magnesium on the emission intensity of sodium from the absorption tube, using the absorption tube as an emission source as discussed previously. The results indicated that the emission of the strong sodium-D line was also suppressed when magnesium was added to the absorption tube; curves 1 and 2 in Fig. 9 have about the same shape.

The effect of the various concentrations of lithium fluoride and magnesium chloride on the absorption and emission values of sodium is not entirely understood, since the mechanism of the discharge in a hollow-cathode tube is quite complex and involved. For example, in discussing the spectra of metals in a hollow-cathode tube, TOLANSKY[7] has indicated that spark spectra are favored using a light carrier gas, helium, and the arc spectra are favored using a heavier carrier gas, argon. More recently, MITCHELL[13], working with an iron hollow cathode, found that the ionization was least ("most arc-like") when argon was used as a carrier gas, but that ionization was greatest ("most spark-like") when xenon, a relatively heavier carrier gas, was used.

Since the two sets of curves (Figs. 8 and 9) have different shapes, it is apparent that the compounds, lithium fluoride and magnesium chloride, responsible for the interference effects, can be put into two separate categories: lithium fluoride progressively lowers the absorption and emission values of sodium as the concentration of the compound is increased in the absorption tube, whereas magnesium chloride lowers the absorption and emission values of sodium irregularly as the concentration of the compound is increased. The minimum and maximum interferences occur at 2 and 100 µg of magnesium in the absorption tube.

Investigation of other elements

A limited amount of work has been done to determine the lower limit of detection for a number of elements, calcium, magnesium, beryllium, and silicon, that form refractory compounds, and have a relatively simple spectrum. Standard aqueous solutions, ranging from 1 to 100 μg of these elements were made, using compounds that were water-soluble for convenience, and evaporated in craters of cathode electrodes. Absorbance values were obtained using electrodes containing standards and blanks, and differences in absorbances were observed between respective standards and blanks. Table II shows the approximate lower limit of detection for these elements. The lines used for the initial investigation were the obvious strong lines normally expected to be used for flame work. However, because the hollow-cathode excitation is quite different from flame excitation, it is possible that more sensitive lines are available; thus before the maximum sensitivity and accuracy are realized for these elements, a thorough investigation of a number of lines should be performed for each element.

TABLE II

LOWER LIMIT OF DETECTION FOR A NUMBER OF ELEMENTS INVESTIGATED USING A HOLLOW-CATHODE TUBE AS AN ABSORPTION SOURCE

Element	*Lower limit*	*Wavelength of line used (Å)*	*Compound used in absorption tube*	*Current and slit width*
Magnesium	Appr. 1 μg	2852.1	Magnesium chloride	100 mA, 50 μ
Calcium	Appr. 1 μg	4226.7	Calcium chloride	100 mA, 50 μ
Beryllium	Appr. 1 μg	2348.6	Beryllium chloride	300 mA, 150 μ
Silicon	Appr. 1 μg	2881.6	Sodium metasilicate	300 mA, 150 μ

CONCLUSION

It has been shown that even at water-cooled temperatures, a hollow-cathode tube is a very sensitive absorption source for the detection of refractory and non-refractory type elements. However, since small amounts of extraneous elements affect the absorption values, it appears that carefully controlled standardization is necessary to obtain accurate results. A buffering technique might minimize inter-element effects and thus improve the accuracy, since the results shown in Figs. 8 and 9 indicate that the absorption values for sodium change at a smaller rate when large amounts of lithium and magnesium are present in the sample of the absorption tube.

At this point in our work, it appears that a water-cooled hollow-cathode tube may have some advantages over a hot hollow-cathode tube used as an absorption source when small amounts of samples are analyzed, since the sample in the water-cooled tube is not consumed too rapidly; as a result many more reproducible absorption observations may be obtained for a given sample.

The authors thank Drs. H. CLAASEN and P. F. A. KLINKENBERG, resident research associates of our laboratory staff, for helpful discussions, and E. E. KLOCEK of our machine shop for assistance with the absorption tube electrode assembly.

SUMMARY

When hollow-cathode tubes are used as the emission source and as the absorption source, atomic absorption studies reveal microgram quantities of several elements; sodium, magnesium, calcium, beryllium, and silicon were detected in the discharge of the absorption tube. Conventional, independent circulating systems and d.c. power supplies were used with each tube, along with other readily available equipment. An analytical curve plotted for sodium over the range 0–100 μg, obeys Beer's law. Lithium and magnesium suppress the sodium absorption values, thus careful standardization is necessary. The average percent deviation from the mean for a number of sodium samples analyzed was ± 8.0%.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'absorption atomique, en utilisant des tubes cathodiques creux comme source d'émission et source d'absorption. On peut ainsi déceler des microquantités de nombreux éléments. Na, Mg, Ca, Be et Si ont été détectés dans la décharge du tube d'absorption. Une courbe analytique tracée pour le sodium (de 0 à 100 μg) obéit à la loi de Beer. Li et Mg diminuent les valeurs d'absorption du sodium; un étalonnage précis est nécessaire.

ZUSAMMENFASSUNG

Wenn hohle Kathodenröhren für Emission und Absorption verwendet werden, können damit Mikrogramm-Mengen verschiedener Elemente bestimmt werden. So wurden Natrium, Magnesium, Calcium, Beryllium und Silicium bei der Entladung des Absorptionsrohres nachgewiesen. Eine analytische Kurve für Natrium im Mengenbereich von 0–100 μg folgt dem Beer'schen Gesetz. Da Lithium und Magnesium die Absorptionswerte für Natrium stark erniedrigen, ist eine sorgfältige Standardisierung notwendig.

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EIN VERFAHREN ZUR HALBQUANTITATIVEN PHOTOGRAPHISCHEN β-STRAHLENMESSUNG MIT HILFE DER RINGOFENMETHODE

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Wie bereits früher gezeigt wurde[1], können radioaktive Substanzen in sehr geringer Aktivität mit Hilfe der Ringofenmethode[2] autoradiographisch nachgewiesen werden. Aus dieser Möglichkeit heraus wurde eine, „Chronoautoradiographie" genannte, Methode entwickelt[3-5], mit deren Hilfe es gelang, geringe β-Aktivitäten halbquantitativ mit den in der Ringofentüpfelkolorimetrie[6-9] üblichen Fehlergrenzen zu bestimmen. MALISSA UND LOLEY[10] wendeten das Verfahren auf die Untersuchung schwach radioaktiver Lösungen und Abwässer an. Bereits in der ersten Veröffentlichung zur Chronoautoradiographie[3] wurde darauf hingewiesen, dass es prinzipiell möglich sei, die Ringofentüpfelkolorimetrie, *d.h.* den Vergleich von drei Proberingen mit einer Standardskala, sinngemäss auf die halbquantitative Autoradiographie mit Hilfe des Ringofens zu übertragen. In diesem Falle würden dann nicht Proberinge und Standardringe, sondern die aus diesen durch Exposition und Entwickeln erhaltenen Schwärzungen miteinander verglichen. Da jedoch die Herstellung der Autoradiogramme von den in Betracht gezogenen schwachen Aktivitäten mehrere Stunden bis Tage dauert, und da man üblicherweise in einer Voruntersuchung zunächst feststellen muss, wie stark die Probeaktivität im Vergleich zur Standardaktivität ungefähr ist[3], schien der notwendige Zeitaufwand gegenüber den praktischen Erfordernissen unverhältnismässig hoch zu sein. Im folgenden soll jedoch gezeigt werden, dass es ohne Zeitverlust möglich ist, schwache β-Aktivitäten auch ohne ein spezielles Expositionsgerät durch direkte Autoradiographie halbquantitativ zu bestimmen.

PRINZIP DER METHODE

Aus einer unbekannten Lösung des β-aktiven Isotops A werden fünf Proberinge mit 1, 4, 8, 16 und 20 Tropfen (Kapillarpipette) gewaschen. Zu einem Zeitpunkt t_0 legt man die Filterpapiere mit den Proberingen einzeln auf geeignet zugeschnittene Röntgenfilmstücke R_u und klemmt jedes Film-Filter-Paar auf einer ebenen Bodenplatte (Bakelit) fest. Die obere Seite jedes Filters wird mit einem gleich grossen Röntgenfilm R_0 abgedeckt und das Ganze in geeigneter Weise beschwert. Auf Grund dieser Anordnung werden nun jeweils *zwei* Röntgenfilme von *einem* Probering „belichtet". Nach 1 Stunde Expositionszeit entfernt man den oberen Film R_0 vom Probering 20 (*d.i.* der aus 20 Tropfen hergestellte Probering) – ohne dass sich dabei der untere Film R_u und das Filter, die weiterhin miteinander in Kontakt bleiben, verschieben – und entwickelt ihn. Die erhaltene Schwärzung ordnet man überschlagsweise in eine Standardskala ein, die mit Proberingen aus 1, 2, 4, 6, 8, 10, 13, 16 und 20 Tropfen einer bekannten Standardlösung des Isotops A in 20 Stunden Expositionszeit hergestellt wurde. Mit Hilfe dieser Grobschätzung lässt sich bereits die der Probe angemessene Gesamtexpositionszeit (vom Zeitpunkt t_0 an gerechnet) festlegen, an deren Ende dann alle Filme R_u entwickelt werden. Diese Zeit muss so bemessen sein, dass wenigstens 3 Probeschwärzungen in den Bereich der Standardskala fallen (*vgl.* Ringofentüpfelkolorimetrie[7,9]). Sollte nach 1 Stunde Expositionszeit der Film R_0 vom Probering 20 nur eine sehr schwache oder gar keine Schwärzung aufweisen, so verfährt man nach weiteren 11 Stunden, also nach insgesamt 12 Stunden Expositionszeit, mit dem Film R_0 vom Probering 16 in gleicher Weise. Bei Proben von noch geringerer Aktivität müssen schliesslich nach 48 bzw. 125 Stunden Expositionszeit die Filme R_0 von den Proberingen 8 bzw. 4 auf ihre Schwärzung hin geprüft werden.

Zweck der beschriebenen Versuchsführung ist es, die Aktivität der unbekannten Probe im Vergleich zur Standardaktivität und damit die erforderliche Expositionszeit *während* der laufenden Exposition abzuschätzen. Die Festlegung der Tropfenzahlen und der Zwischenzeiten, nach denen die oberen Filme R_0 entwickelt werden, erfolgte unter der Voraussetzung, dass das Reziprozitätsgesetz gültig ist. Dieses sei für den vorliegenden Fall folgendermassen formuliert:

$$\text{Schwärzung S} = \text{f}\,(z \cdot a \cdot t)$$

und bei gleicher Schwärzung von Standard- und Probe-Autoradiogramm

$$z_s \cdot a_s \cdot t_s = z_p \cdot a_p \cdot t_p$$

t_s = Expositionszeit für die Standardringe
t_p = Expositionszeit für die Proberinge
a_s = Aktivität eines Tropfens der Standardlösung ($\approx$ 50 pC/μl)
a_p = Aktivität eines Tropfens der Probelösung
z_s = Tropfenzahl der Standardringe
z_p = Tropfenzahl der Proberinge.

Die Standardlösung ist so beschaffen, dass nach 20 Stunden Expositionszeit die den Werten $a_s \cdot 20$, $2a_s \cdot 20$, $4a_s \cdot 20$, $6a_s \cdot 20$, $8a_s \cdot 20$, $10a_s \cdot 20$, $13a_s \cdot 20$, $16a_s \cdot 20$, $20a_s \cdot 20$ entsprechenden Schwärzungen eine brauchbare Standardskala ergeben. (Die 9 Filter mit den Standardringen werden auf *einen* Filmstreifen gelegt, mit einem zweiten Filmstreifen abgedeckt und mit einer Beschwerung versehen, die etwa den gleichen Auflagedruck ausübt wie die Beschwerung bei den Proberingen.) Mit den Proberingen erhält man nach t_p Stunden Expositionszeit Schwärzungen, die folgenden Werten entsprechen:

$$a_p \cdot t_p \quad 4a_p \cdot t_p \quad 8a_p \cdot t_p \quad 16a_p \cdot t_p \quad 20a_p \cdot t_p$$

Mit Hilfe der *einen* Standardaktivität ist es nun innerhalb vernünftiger Expositionszeiten ohne weiteres möglich, unbekannte Aktivitäten im Bereich von $a_p = 1/50\ a_s$ bis $a_p = 50a_s$ (also 1 :2500!) halbquantitativ zu bestimmen. Im ersten Fall ($a_p = 1/50\ a_s$) rücken nach $t_p = 125$ Stunden Expositionszeit die von den Proberingen 8, 16 und 20 herrührenden Schwärzungen gerade schon in die Standardskala, während im zweiten Fall ($a_p = 50a_s$) nach $t_p = 1$ Stunde Expositionszeit die von den Proberingen 1, 4 und 8 stammenden Schwärzungen eben noch innerhalb der

Standardskala liegen. Für jeden beliebigen, zwischen diesen beiden Extremen liegenden Wert von a_p kann man unter Anwendung des Reziprozitätsgesetzes leicht berechnen, dass nach 1 oder 12 oder 125 Stunden Expositionszeit wenigstens 3 der 5 Probeschwärzungen in den Bereich der Standardskala fallen müssen. Damit sind die für die Ringofentüpfelkolorimetrie geltenden Bedingungen erfüllt und man erhält den gesuchten Wert a_p/a_s nach

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

Σz_s (Σz_p) = Summe der Tropfenzahlen der Standardringe (Proberinge), deren Autoradiogramme zur Berechnung herangezogen werden.

Die Zwischenzeit von 48 Stunden, an deren Stelle auch andere passende Zeitspannen treten können, wurde nur vorgeschlagen, um unnötig lange Expositionszeiten zu vermeiden. Bei der Festlegung der Expositionszeit für die Proberinge sollte man darauf achten, dass nicht nur 3 Probeschwärzungen innerhalb der Standardskala liegen, sondern dass diese Probeschwärzungen auch einen möglichst weiten Bereich der Skala überstreichen. Bei unbekannten Aktivitäten in der Nähe der Extremwerte $a_p = 1/50\ a_s$ bzw. $a_p = 50 a_s$ kann man dieser Forderung dadurch gerecht werden, dass man die Expositionszeit für die Standardskala (20 Stunden) verkürzt bzw. verlängert.

Um den Einfluss des photographischen Entwicklers auf die Bestimmungen auszuschalten, wurde die Herstellung der Standardskalen so geleitet, dass mit den Probefilmen stets ein Standardfilm mitentwickelt werden konnte. Dabei wurden immer wieder die gleichen Standardringe verwendet. Alle Versuche wurden mit ADOX-DONEO-Röntgenfilmen (Hersteller: ADOX-Fotowerke Dr. C. Schleusner GmbH., Frankfurt/Main) und mit dem auf das Doppelte verdünnten Entwickler Ilford ID-19 (Entwicklungszeit bei 20° 5 min) durchgeführt.

ERGEBNISSE UND DISKUSSION

In Tabelle I sind einige Ergebnisse aufgeführt, die mit der beschriebenen Methode erhalten wurden.

TABELLE I

ANALYSENERGEBNISSE

Probe		*Standard*		a_p/a_s		*Fehler (%)*
Isotop	t_p *(h)*	*Isotop*	t_s *(h)*	*Sollwert*	*Gefunden*	
^{45}Ca	2.5	^{45}Ca	20	6.250	6.13	−2.0
^{45}Ca	18.75	^{45}Ca	20	1.000	1.00	±0
^{45}Ca	1.5	^{45}Ca	20	32.600	32.30	−0.9
^{137}Cs	8.5	^{137}Cs	20	2.000	1.94	−3.0
^{137}Cs	86	^{137}Cs	15	0.100	0.096	−4.0
^{137}Cs	7.25	^{137}Cs	20	3.500	3.27	−6.6
^{110}Ag	60	^{110}Ag	20	0.250	0.238	−4.8
^{110}Ag	185	^{110}Ag	15	0.021	0.021	±0
^{110}Ag	88	^{110}Ag	15.5	0.063	0.062	−1.6
^{204}Tl	87.75	^{204}Tl	18	0.050	0.051	+2.0
^{204}Tl	7.75	^{204}Tl	20	2.000	2.175	+8.8
^{90}Sr/Y	21.5	^{90}Sr/Y	20	1.000	1.032	+3.2

Die Mehrzahl aller durchgeführten Versuche lieferte Ergebnisse, deren Abweichungen vom Sollwert innerhalb der für die Ringofentüpfelkolorimetrie als befriedigend angesehenen ± 10%-Fehlergrenzen lagen. Es traten jedoch, besonders während der warmen Sommermonate, auch Abweichungen auf, welche deutlich über diese Grenzen hinausgingen, und deren Ursache nicht in der Methode gefunden werden konnte. Auffallend war, dass besonders bei schwach aktiven Proben, für die eine lange Expositionszeit erforderlich war, die Resultate gelegentlich mit starken Minusfehlern behaftet waren. Derartige Effekte traten bei Proben, deren Aktivitäten der Standardaktivität gleich oder nahezu gleich waren, und für die dementsprechend auch Expositionszeiten von ungefähr 20 Stunden gewählt wurden, nicht auf. Alles deutete darauf hin, dass es sich bei dem erwähnten Effekt um einen Latenzbildschwund, ein sog. „Fading" handeln musste.

Das Fading und seine Abhängigkeit von Temperatur, Luftfeuchtigkeit und der Beschaffenheit des Filmmaterials sind zwar schon seit längerem bekannt (*vgl.* bei YAGODA[11] und BECKER[12]), jedoch liegen speziell über die Verhältnisse bei latenten β-Strahlen-„Bildern" kaum Informationen vor[11]. Auf den ersten Blick hat es den Anschein, als ob durch den Fadingeffekt die Gültigkeit des Reziprozitätsgesetzes in Frage gestellt würde. Das Fading ist jedoch kein Reziprozitätsfehler im eigentlichen Sinn, sondern wird erst sekundär durch chemische Einflüsse auf das latente Bild hervorgerufen[12].

Als besonders krasses Beispiel für den Fadingeffekt ist in Tabelle II die halbquantitative Bestimmung einer schwach aktiven Sr/Y-90-Probe unter verschiedenen Bedingungen aufgeführt.

TABELLE II

EINFLUSS DES FADINGEFFEKTES

Nr.	*Probe*		*Standard*		a_p/a_s		*Fehler (%)*	*Bedingn.*
	Isotop	t_p *(h)*	*Isotop*	t_s *(h)*	*Sollwert*	*Gefunden*		
1	^{90}Sr/Y	114	^{90}Sr/Y	20	0.100	0.064	—36.0	RT[a]
2	^{90}Sr/Y	117	^{90}Sr/Y	117.3	1.000	1.000	± 0	RT
3	^{90}Sr/Y	100.7	^{90}Sr/Y	20	0.100	0.107	+ 7.0	T[b]

[a] Probe und Standard bei Raumtemperatur (20–22°) und ≈ 70% relat. Luftfeuchtigkeit exponiert.

[b] Probe und Standard in einer Tiefkühltruhe bei —21° exponiert.

Aus Tabelle II kann entnommen werden, dass der Fadingeffekt keine Rolle spielt, wenn Probe und Standard gleiche Aktivität besitzen, und demzufolge die Expositionszeiten für Probe- und Standardringe kaum voneinander verschieden sind (Nr. 2). Das Fading wird für die halbquantitative Autoradiographie mit Hilfe des Ringofens bedeutungslos, wenn man die Expositionen bei tiefen Temperaturen ausführt (Nr. 3). Dieser Befund konnte durch weitere Experimente, über deren Ergebnisse in einer späteren Mitteilung berichtet werden soll, bestätigt werden.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur halbquantitativen, autoradiographischen Bestimmung von radioaktiven Isotopen mit Hilfe der Ringofenmethode beschrieben. Dabei wird die Arbeitsweise der Ringofentüpfelkolorimetrie in modifizierter Form übernommen. Ein spezielles Expositionsgerät ist nicht erforderlich. Einige Ergebnisse, das Auftreten von Fadingeffekten sowie die Möglichkeit zur Verhinderung dieser Effekte werden mitgeteilt.

SUMMARY

A method for the semiquantitative autoradiographic determination of radio-isotopes by β-ray measurement is proposed. The techniques of ring-oven spot colorimetry are applied in a modified form and no special exposure device is needed. The occurrence of a fading effect and its avoidance are discussed.

RÉSUMÉ

Une méthode est proposée pour le dosage autoradiographique semiquantitatif de radio-isotopes, par mesure du rayonnement β. On utilise un procédé colorimétrique (technique du ,,ring-oven"). Les auteurs traitent aussi de l'effet de fading et de la façon de l'éviter.

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TOTAL LUMINESCENCE OF ORGANIC MOLECULES OF PETROCHEMICAL INTEREST

PART I. NAPHTHALENE, PHENANTHRENE AND 1,2,4,5-TETRAMETHYLBENZENE

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The use of phosphorimetry for analytical purposes was first suggested and applied by KEIRS, BRITT AND WENTWORTH[1], whose work demonstrated the feasibility of using spectroscopic resolution of phosphorescence and the time discrimination of a phosphoroscope to identify and quantify the components of various binary mixtures. No published work has thus far utilized selective excitation techniques (*i.e.* variation of the exciting wavelength) in conjunction with phosphorimetry to identify and quantify components of a mixture similarly; nor has any attempt been made to compare the sensitivities of room-temperature fluorescence (35°C), low-temperature fluorescence (−195.8°C), low-temperature phosphorescence (−195.8°C) and room-temperature absorption (35°C) with regard to their qualitative and quantitative capabilities. Such is the aim of the present work.

It is as well to point out that the present authors regard low-temperature fluorimetry and phosphorimetry as being mutually complementary rather than independent techniques. Maximum usefulness results from quantification of the fluorescence, phosphorescence, and the excitation spectra of the pure components, and any mixture of these luminescent species may then be readily analyzed and quantified. Only in the rare event that *all spectra* of two substances are completely superposable would their mutual analysis in a mixture be rendered impossible by this method, and in this case time-resolution of the phosphorescence should generally suffice to make it possible again.

In this investigation the fluorescence (at 77°K in a glass matrix and at 35°C in a liquid solution) and the phosphorescence of naphthalene, phenanthrene and 1,2,4,5-tetramethylbenzene were studied. The quantitative data so obtained were then applied to the analysis of a blend in which the ratio by weight of these three components was 1:1:1.

EXPERIMENTAL

Apparatus

An Aminco–Keirs Spectrophosphorimeter and an Aminco–Bowman Spectrophoto-

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fluorimeter in combination with an X–Y recorder and an RCA 1P–28 photomultiplier tube were used to obtain spectra and decay curves. The sample geometry for both 77°K and 35°C experimentation is shown in Fig. 1. The cylindrical quartz tubes employed at the former temperature were of 2 mm internal diameter; at 35°C 1 cm^2 quartz cells were used. Ultraviolet absorption spectra were obtained at room temperature using a Cary–14 Spectrophotometer with both 1 and 0.1 cm quartz cells.

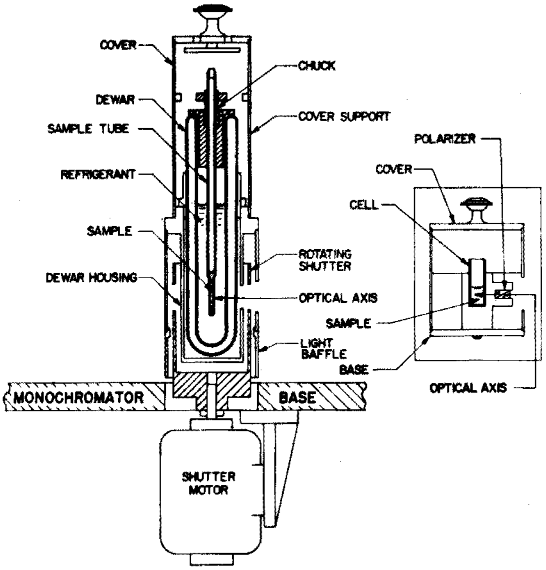

Fig. 1. Left: Sample geometry for phosphorescence at 77°K. This same geometry, with the rotating shutter remover, was used for fluorescence at 77°K. The diagram is self-explanatory. Right: Sample geometry for fluorescence at 35° C. The use of polarizers enables one to eliminate scatter; they were not used, nor was such use necessary, in the present work.

Materials

The low-temperature glass matrix consisted of EPA obtained from The American Instrument Company*. The background luminescence of this glass was observable only at the most sensitive settings of the luminescence metering systems. The room-temperature solvent was a Harleco fluorimetric grade *n*-heptane**; there was no observable luminescence and only slight scatter from this solvent at room temperature with the slits employed throughout this work.

Procedure

Excitation and emission spectra in both fluorescence and phosphorescence were obtained at 77°K for each of the three compounds and suitable excitation and emission wavelengths were chosen. A series of solutions of varying concentrations in EPA mixed solvent was then prepared for each of the compounds. The intensity of emission at the optimum wavelengths was measured for the individual solutions. To obtain easily reproducible and accurate results, it was found necessary to remove the cover

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* The American Instrument Company, 8030 Georgia Avenue, Silver Spring, Maryland.
** Hartmann–Leddon Company, Philadelphia, Pennsylvania.

from the sample compartment of the instrument, and, having provided suitable shielding from stray room light, to rotate manually the chuck which holds the sample tube until a maximum intensity reading was obtained.

A series of solutions of varying concentration in *n*-heptane was prepared for each compound and emission intensities were measured at room temperature (35°C) for the solutions. No difficulties were encountered in the placement of the 1 cm^2 cell.

RESULTS

The phosphorescence decays of the three compounds in EPA at 77°K are shown in Fig. 2. The lifetimes are tabulated in Table I. Since all three lifetimes are relatively long and not too different, no significant discrimination may be effected by variation of phosphoroscope speed.

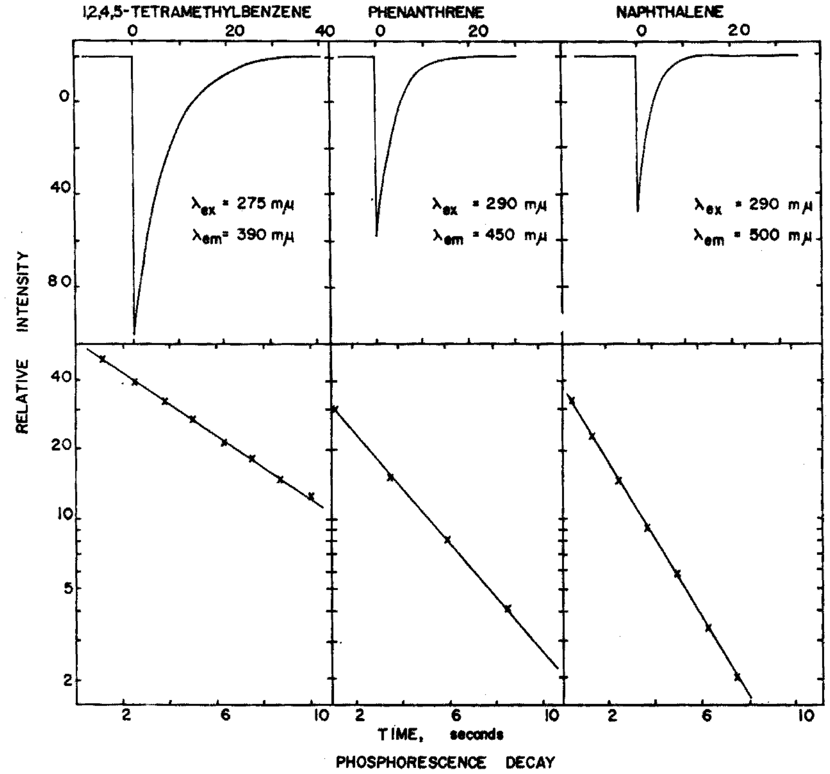

Fig. 2. The phosphorescent decay of naphthalene (right), phenanthrene (middle) and 1,2,4,5-tetramethylbenzene (left).

The various emission and excitation spectra of the pure compounds are shown in Figs. 3, 4 and 5. The wavelengths of the maxima of intensities are tabulated in Table I. A reproducible linear relationship between emitted radiant intensity and concentration was found for each of the three compounds. The maximum and minimum concentrations which may be accurately determined under the conditions of the experiment are shown in Table II, and the work curves are given in Figs. 6–8. It is

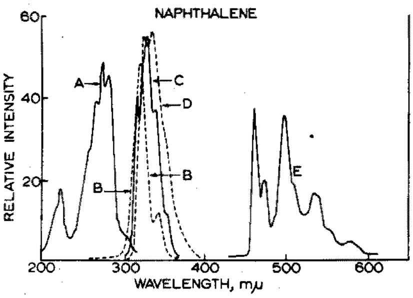

Fig. 3. The fluorescence excitation spectrum (A), the fluorescence spectrum (C) and the phosphorescence spectrum (E) of naphthalene at 77°K in EPA; the fluorescence excitation spectrum (B) and fluorescence spectrum (D) of naphthalene in *n*-heptane at 35°C. It is not intended that this diagram reflect true relative intensities and the spectra are presented merely to show the spectral discrimination which is possible. Quantitative data are available from Fig. 6 and Table II.

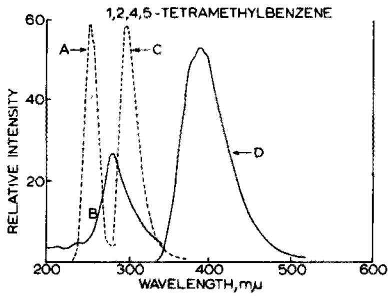

Fig. 5. Phosphorescence excitation spectrum (B) and phosphorescence spectrum (D) of 1,2,4,5-tetramethylbenzene in EPA at 77°K; fluorescence excitation spectrum (A) and fluorescence spectrum (C) of 1,2,4,5-tetramethylbenzene in *n*-heptane at 35°C. It is not intended that this diagram reflect true relative intensities and the spectra are presented merely to show the spectral discrimination which is possible. Quantitative data are available from Fig. 8 and Table II.

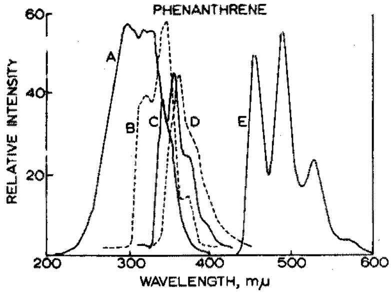

Fig. 4. Fluorescence excitation spectrum (A), fluorescence spectrum (C) and phosphorescence spectrum (E) of phenanthrene at 77°K in EPA; fluorescence excitation spectrum (B) and fluorescence spectrum (D) of phenanthrene in *n*-heptane at 35°C. It is not intended that this diagram reflect true relative intensities and the spectra are presented merely to show the spectral discrimination which is possible. Quantitative data are available from Fig. 7 and Table II.

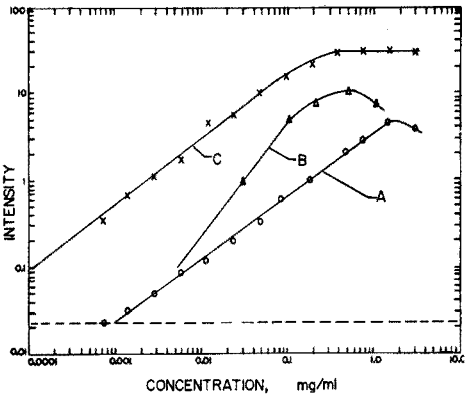

Fig. 6. Work curves for naphthalene. A, Phosphorescence at 77°K; B, fluorescence at 35°C, C, fluorescence at 77°K. The excitation and emission wavelengths were set at 310 and 475 mμ respectively for curve A, 310 and 335 mμ respectively for curve B; and 300 and 342 mμ respectively for curve C. The slits used are specified on Table II.

possible to conclude from the data of Table II that phosphorimetry is of comparable sensitivity to any of the other techniques, and that it may be used to higher concentrations than fluorimetry, presumably because of less self-absorption. It is further evident from Figs. 3, 4 and 5 that the phosphorescence spectrum contains more *apparent* resolution than the fluorescence spectrum, and that it should, if anything, be a better characterization spectrum than fluorescence.

Analysis of the previously specified blend was attempted. It is clear from Figs. 3, 4 and 5 that 340 mμ excitation should produce only phenanthrene emission since neither

TABLE I

PHOSPHORESCENCE LIFETIMES AND VIBRONIC PEAKS

Compound	$\tau\frac{1}{2}$ *(sec)*	*LTF*[a] *(mμ)*	*LTP*[b] *(mμ)*	*LTE*[c] *(mμ)*
Naphthalene	1.75	314 327[d] 335 342	463[d] 474 497 580	221 267 275[d] 282
Phenanthrene	2.6	348 354 363[d] 382 405	462[d] 470 498[d] 538	305[d] 325 332 340
Tetramethylbenzene	4.5	310[d]	375 387[d] 392	225 275[d]

[a] Low-temperature fluorescence (77°K).

[b] Low-temperature phosphorescence (77°K).

[c] Low-temperature excitation (77°K).

[d] These wavelengths are the most intense, and therefore most sensitive analytically.

TABLE II

A COMPARISON OF METHODS OF DETERMINATION[a]

Compound	*1,2,4,5-Tetramethylbenzene*	*Naphthalene*	*Phenanthrene*
Low-temperature phosphorescence Slits[b]: 5–2–4–3	λ_{ex} = 275 mμ λ_{em} = 392 mμ Max. = 1.34 mg/ml Min. = 0.0018 mg/ml	λ_{ex} = 310 mμ λ_{em} = 475 mμ Max. = 1.4 mg/ml Min. = 0.0007 mg/ml	λ_{ex} = 340 mμ λ_{em} = 465 mμ Max. = 0.5 mg/ml Min. = 0.001 mg/ml
Low-temperature fluorescence Slits[b]:3–2–2–1–0.5	λ_{ex} = 225 mμ λ_{em} = 285 mμ Max. = 1.00 mg/ml Min. = 0.0007 mg/ml	λ_{ex} = 275 mμ λ_{em} = 320 mμ Max. = 0.100 mg/ml Min. = 0.00058 mg/ml	λ_{ex} = 300 mμ λ_{em} = 340 mμ Max. = 0.03 mg/ml Min. = 0.0002 mg/ml
Room-temperature fluorescence Slits[c]: 5–2–2–2–2–3–2	λ_{ex} = 260 mμ λ_{em} = 298 mμ Max. = 0.50 mg/ml Min. = 0.001 mg/ml	λ_{ex} = 310 mμ λ_{em} = 335 mμ Max. = 0.100 mg/ml Min. = 0.005 mg/ml	λ_{ex} = 325 mμ λ_{em} = 368 mμ Max. = 0.500 mg/ml Min. = 0.0015 mg/ml
Ultraviolet absorption 275 mμ Using 1 cm and 0.1 cm cells only	Max. = 0.6 mg/ml Min. = 0.01 mg/ml	Max. = 0.400 mg/ml Min. = 0.0007 mg/ml	Max. = 0.100 mg/ml Min. = 0.0015 mg/ml

[a] The phosphorescence results for the three compounds are intercomparable, as are both sets of fluorescence results. However, one set is not strictly comparable with another set since different slit widths were used. However, in a practical sense the use of larger slit widths should not have significantly increased the sensitivity of either method, since there are background scatter and spurious emission effects to be contended with. It is implied then that the three sets of data (*i.e.* phosphorescence, fluorescence and room-temperature fluorescence) are indeed truly comparable.

[b] The order of slits is A, B, C, D and E; the numbers quoted are slit widths in mm; the position of these slits is described in the operating instructions for the Aminco–Keirs Spectrophosphorimeter.

[c] The order of slits is 1, 2, 3, 4, 5, 6, 7; the numbers quoted are slit widths in mm; the position of these slits is described in the operating instructions for the Aminco–Bowman Spectrophotofluorimeter.

of the other two components absorb in this region. That such is the case is very clearly illustrated in Fig. 9, and the resulting phosphoroscopic analysis for phenanthrene is shown in Table III. Excitation at 275 mμ enables one to excite the tetramethylbenzene luminescence, and to distinguish the phosphorescence spectrally. Excitation at 275 mμ maximizes the naphthalene fluorescence which is spectrally

TABLE III

DETERMINATION OF PHENANTHRENE IN A THREE COMPONENT MIXTURE OF 1 PART PHENANTHRENE: 1 PART NAPHTHALENE: 1 PART 1,2,4,5-TETRAMETHYLBENZENE[a]

Known concentration (mg/ml)	*Concentration as determined from working curve (mg/ml)*
0.010	0.010
0.0010	0.0011
0.0005	0.0007
0.0001[b]	0.0002

[a] $\lambda_{ex} = 340$ mμ; $\lambda_{em} = 460$ mμ.

[b] Smaller than minimum amount that may be determined under the given conditions.

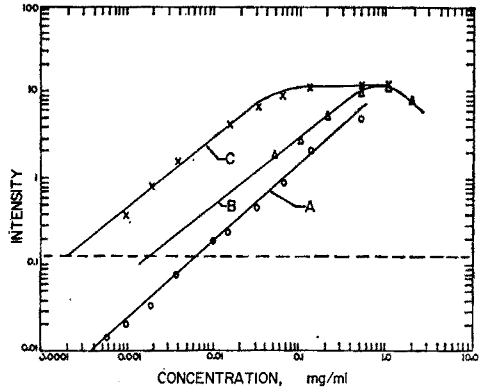

Fig. 7. Work curves for phenanthrene. A, Phosphorescence at 77°K; B, fluorescence at 35°C; C, fluorescence at 77°K. The excitation and emission wavelengths were set at 340 and 465 mμ respectively for curve A, 325 and 368 mμ respectively for curve B, and 300 and 340 mμ respectively for curve C. The slits used are specified in Table II.

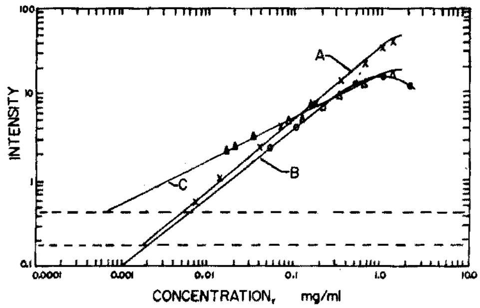

Fig. 8. Work curves for 1,2,4,5-tetramethylbenzene. A, Phosphorescence at 77°K; B, fluorescence at 35°C; C, fluorescence at 77°K. The excitation and emission wavelengths were set at 275 and 392 mμ respectively for curve A, 260 and 298 mμ respectively for curve B, and 225 and 285 mμ respectively for curve C. The slits used are specified in Table II.

quite distinct (see excitation at 290 mμ in Fig. 9). There should then be no difficulty in determining any component of the ternary solution; an effort to do this resulted in the data of Table IV. At concentrations above 0.01 mg/ml, competitive absorption processes made estimation of both naphthalene and tetramethylbenzene impossible, while at concentrations much below 0.01 mg/ml the sensitivity decrease rendered the accuracy poor.

TABLE IV

DETERMINATION OF PHENANTHRENE, NAPHTHALENE AND 1,2,4,5-TETRAMETHYLBENZENE IN THE BLEND

Component *Technique*	*Naphthalene* *Fluorescence*	*Phenanthrene* *Phosphorescence*	*Tetramethylbenzene* *Phosphorescence*
λ_{ex} (mμ)	375	340	275
λ_{em} (mμ)	320	460	392
Introduced (mg/ml)	0.01	0.01	0.01
Measured (mg/ml)	0.006	0.01	0.007

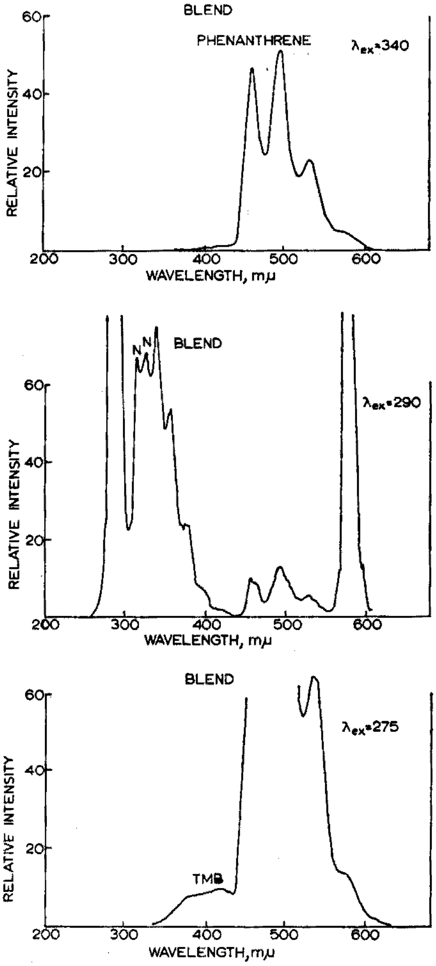

Fig. 9. Phosphorescence of blend excited at 340 mμ (top), phosphorescence of blend excited at 275 mμ (bottom) and total emission of blend excited at 290 mμ (middle). It is to be noted that the top spectrum is the phosphorescence of phenanthrene only, that the bottom spectrum contains the phosphorescence of 1,2,4,5-tetramethylbenzene well-resolved spectrally and that the fluorescence of naphthalene (denoted N) is quite distinct, spectrally, on the middle spectrum.

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SUMMARY

Total emission, phosphoroscopically resolved emission, excitation and mean lifetime in the excited triplet state were measured for three organic molecules of petrochemical interest in EPA rigid glass at 77° K. Fluorescence was also measured at room temperature in *n*-heptane. Methods for the determination of these three molecules in individual solutions are presented and compared with known methods by absorption spectroscopy. An attempt was made to quantify a blend of the three components by luminescence techniques.

RÉSUMÉ

Les auteurs ont effectué une étude sur la luminescence totale de molécules organiques présentant un intérêt en pétrochimie: naphtalène, phénanthrène et tétraméthyl-1,2,4,5-benzène. La fluorescence a également été mesurée dans le *n*-heptane. Des méthodes pour le dosage de ces 3 substances sont proposées et comparées à des méthodes connues par spectroscopie d'absorption.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendbarkeit der Lumineszenzerscheinungen von Naphthalin, Phenanthren und 1,2,4,5-Tetramethylbenzol zu deren quantitativen Bestimmung im Gemisch. Fluoreszenz, Phosphoreszenz und die Anregungsspektren der reinen Substanzen wurden gemessen und mit den Werten verglichen, die durch Absorptionsspektroskopie erhalten wurden.

REFERENCE

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A STUDY OF THE FERROCYANIDE–FERRICYANIDE SYSTEM WITH APPLICATION TO THE DETERMINATION OF ZINC BY NULL-POINT POTENTIOMETRY

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Zinc in concentrations greater than 10^{-3} *M* has been determined by titration with ferrocyanide[1–3]. The end-point is often detected by the sudden change in potential of a platinum electrode immersed in the ferrocyanide solution to which a small amount of ferricyanide has been added. Concentrations greater than 0.1 *M* can be determined within an accuracy of 1% by a direct titration with ferrocyanide. Concentrations below 0.01 *M* must be back-titrated with standard zinc solution after an addition of excess ferrocyanide. The accuracy of the latter case is about 5%, and the limit of detection is slightly less than 10^{-3} *M* zinc.

This paper describes an investigation of the factors affecting the potential of a platinum electrode immersed in a ferrocyanide–ferricyanide solution. The effect of pH, potassium ion concentration and the stability of ferrocyanide and ferricyanide solutions are considered in detail. This study was done in order to choose the proper experimental conditions for applying the very rapid, accurate and sensitive null-point potentiometric technique to the determination of zinc. The precision null-point potentiometric method was first used by MALMSTADT AND WINEFORDNER[4–6] for the determination of chloride and has been subsequently used for other determinations[7–9]. The determination of zinc is based on an indirect application of the null-point principle. Zinc in the unknown solution is precipitated by addition of an excess of ferrocyanide. This solution also contains a known concentration of ferricyanide and buffer. The concentration of ferrocyanide in a reference solution, which also contains the same concentration of ferricyanide and buffer, is then changed by dilution, with a solution containing the same concentration of ferricyanide and buffer but no ferrocyanide, until it contains the same concentration of ferrocyanide as the unknown. From the initial concentration of ferrocyanide in the reference solution, the initial volume of reference solution, the volume of diluent added and the ratio of zinc to ferrocyanide in the precipitate, the concentration of zinc in the unknown solution can be calculated. Zinc can be determined with an accuracy of about 10% in solutions containing as little as 10^{-5} *M* and with an accuracy of 5% in solutions containing 10^{-4} *M* or higher. The reproducibility of measurement is 1% or better for all solutions 10^{-4} *M* and larger. This technique also has the advantage of requiring small volumes of sample so that only 5 to 50 µg of zinc is required for an analysis. However, the null-point method as well as the titration method are susceptible to cationic interferences, especially divalent and trivalent cations which precipitate or complex with ferrocyanide. The effect of various cations on the null-point technique and a possible means of compensating or correcting for several of the interferences is discussed.

Dependence of potential of ferricyanide–ferrocyanide system on pH and potassium ion concentration

A thorough investigation of the effect of pH and potassium ion concentration was necessary in order to determine the optimum range of experimental conditions for the analysis of zinc by the use of null-point potentiometry. An initial study showed that the potential of the ferricyanide–ferrocyanide system was approximately constant over a range of pH from 12 or higher down to about 4. Below 4 the potential of the system increased quite rapidly as the pH decreased. KOLTHOFF[10] studied the effect of concentrated acid on the ferricyanide–ferrocyanide system and developed an empirical equation which approximately described the acid effect. MULLER[11] also studied the effect of acidity as well as potassium ion concentration on the ferricyanide–ferrocyanide system and gave empirical relations for the dependence of potential on pH at constant potassium concentration and the dependence of potential on potassium ion concentration at constant pH. Because the above equations were empirical and applied only to specific systems, a detailed study of the potential, E, of a platinum electrode immersed in ferricyanide–ferrocyanide solutions (measured with respect to the normal hydrogen electrode) *vs.* pH at various values of potassium ion concentration and at approximately constant ionic strength was carried out.

Potassium ferrocyanide is the salt of a weak acid. NEKRASOV AND ZOTOV[12] found that the dissociation of the first two hydrogens of $H_4Fe(CN)_6$ was essentially complete whereas the last two hydrogens were only slightly dissociated. The dissociation equilibria and constants for the final two hydrogens are given below.

$$H_2Fe(CN)_6{}^{2-} \rightleftharpoons HFe(CN)_6{}^{3-} + H^+ \quad K_3 = 10^{-3} = \frac{[H^+][HFe(CN)_6{}^{3-}]}{[H_2Fe(CN)_6{}^{2-}]} \tag{1}$$

$$HFe(CN)_6{}^{3-} \rightleftharpoons Fe(CN)_6{}^{4-} + H^+ \quad K_4 = 5\cdot 10^{-5} = \frac{[H^+][Fe(CN)_6{}^{4-}]}{[HFe(CN)_6{}^{3-}]} \tag{2}$$

DAVIES[13] measured the dissociation constant for the following equilibrium,

$$KFe(CN)_6{}^{3-} \rightleftharpoons Fe(CN)_6{}^{4-} + K^+ \quad K_5 = \frac{[K^+][Fe(CN)_6{}^{4-}]}{[KFe(CN)_6{}^{3-}]} \tag{3}$$

and determined the value of K_5 to be $6 \cdot 10^{-3}$. Using the above three equilibria, the material balance expression for ferrocyanide, namely

$$C_{red} = [Fe(CN)_6{}^{4-}] + [HFe(CN)_6{}^{3-}] + [H_2Fe(CN)_6{}^{2-}] + [KFe(CN)_6{}^{3-}]$$

where C_{red} is the analytical concentration of ferrocyanide (the reduced form) and the Nernst equation for the ferricyanide–ferrocyanide system, namely

$$E = E^\circ + 0.059 \log \frac{[Fe(CN)_6{}^{3-}]}{[Fe(CN)_6{}^{4-}]} \tag{5}$$

where E° is the standard potential (European Convention) which was determined by

KOLTHOFF[14] and found to be +0.356 V, the following equation relating potential to pH was derived.

$$E = E^\circ + 0.059 \log \frac{C_{ox}\{[H^+]^2 + K_3[H^+] + (K_3K_4/K_5)C_K + K_3K_4\}}{C_{red}K_3K_4} \tag{6}$$

C_{ox} is the analytical concentration of ferricyanide (oxidized form) and C_K is the analytical concentration of potassium ion. In the derivation of eqn. 6, it is assumed that the equilibrium concentrations of ferricyanide and potassium are equal to their analytical concentrations, respectively. These two assumptions are certainly valid. BRIGANDO[15] has shown that $H_3Fe(CN)_6$ is essentially completely dissociated. The species $KFe(CN)_6^{2-}$ will certainly be dissociated to a much greater extent than $KFe(CN)_6^{3-}$ because of the smaller charge on the ferricyanide than on the ferrocyanide. The potassium ion concentration initially added will also be changed only slightly due to loss as $KFe(CN)_6^{3-}$, since in all cases studied the potassium ion concentration was much larger than the initial ferrocyanide concentration, *i.e.*, the initial ferrocyanide concentration was 10^{-3} *M* but the potassium concentration was 1 *M*, 0.1 *M* and 0.03 *M* in the cases studied.

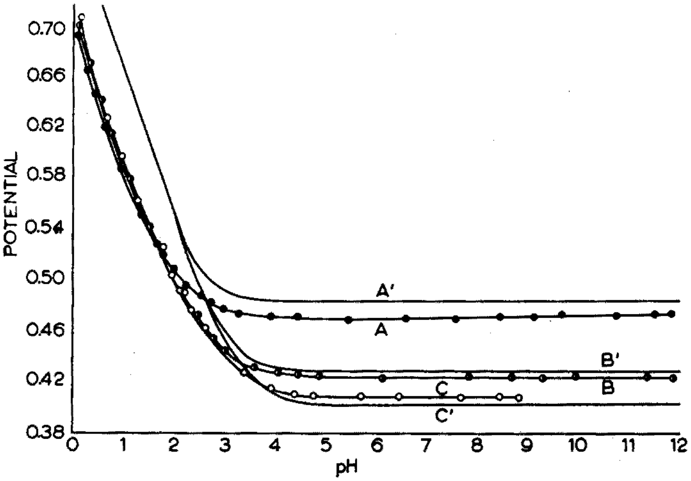

Fig. 1. Potential of ferricyanide–ferrocyanide system as a function of pH for several different potassium ion concentrations. Curve A, $[K^+] = 1.00$ *M*. Curve B, $[K^+] = 0.100$ *M*. Curve C, $[K^+] = 0.0300$ *M*. Primed letters are for theoretical curves. Unprimed letters are for experimental curves.

In Fig. 1 the experimental curves of potential *vs.* pH are given for three different concentrations of potassium ion, namely 1 *M*, 0.1 *M*, and 0.03 *M*. For each experimental curve, the ferricyanide and ferrocyanide concentrations were both 10^{-3} *M* at the start but decreased slightly during the study as acid was added to change the pH from 12 to 0; however, the ratio of ferricyanide to ferrocyanide remained constant throughout. The change in C_{red} and C_{ox} as a result of dilution is accounted for in Fig. 1. Also, in Fig. 1 theoretically derived curves using eqn. 6 are given. As can be seen, the fit is quite good, especially with respect to the general shape. Therefore, it is possible to predict the region of invariant potential as a function of pH and potassium concentrations. An even better correlation would possibly result if activity coefficient data were available for the ionic strengths involved. Also, it is quite possible that the acid constants or potassium constant for ferrocyanide may be somewhat in error.

From the experimental as well as theoretical curves, it can be seen that the potential is no longer a function of pH above a pH of about 4. If a null-point potentiometric analysis were to be run at a pH of less than 4, errors would result if the unknown and reference solutions were not precisely at the same pH. Also, if the pH were to go above 6, there is danger of precipitating the zinc as zinc hydroxide for solutions in which the zinc concentration of the unknown is greater than 0.005 *M*. The optimum range of pH for a null-point potentiometric analysis is therefore 4 to 6, and so a pH of 5 was chosen for all null-point analyses because the solution could be easily buffered at this pH using acetic acid and sodium acetate.

Principles of null-point potentiometric method for zinc

The general principles of the null-point potentiometric method have already been discussed with regard to the analysis of chloride[4]. The analysis of zinc by the same technique differs slightly from the chloride method. In the determination of chloride, a pair of silver–silver chloride indicator electrodes is used, one being placed in a reference chloride solution and one in an unknown chloride solution. Both solutions have a high ionic strength which is maintained constant throughout the analysis. The chloride concentration of the unknown solution is then changed until the concentration of chloride in the unknown is the same as the reference solution which is indicated when the potential difference between the two silver–silver chloride electrodes becomes zero. The determination of zinc differs from this in that both members of the potential-determining couple, the ferricyanide–ferrocyanide system, are soluble, and so a pair of platinum electrodes is used. The zinc is only indirectly involved in that it removes part of the ferrocyanide from the unknown solution, and this results in a change of the potential of the platinum electrode in the unknown solution. The ferrocyanide concentration in the reference solution is then changed until it is equal to that in the unknown solution.

The change in potential involved in the null-point method described is about 30 mV or less. Because the potential difference is only 30 mV, it is essential — as in any null-point potentiometric method — that the ionic strength and temperature of the unknown and reference solutions be the same. Actually this is quite a simple matter to achieve. To keep the same ionic strength in all solutions, all solutions contain a large and equal concentration of a strong electrolyte. In this case a mixture of potassium chloride and sodium acetate is added. In order to maintain the pH at 5 all solutions also have a certain concentration of acetic acid. Keeping the temperature the same is no problem with the setup used here because the sample half-cell is a small tube (isolation compartment) which is immersed in the reference solution and which therefore has the same temperature as the reference at the time of measurement. Electrical contact is made between the unknown solution in the isolation compartment and the reference solution in a beaker by means of either a cracked glass bead or an asbestos fiber at the tip of the isolation compartment. This hole is too small to permit significant mixing of the two solutions.

In determining zinc by the null-point method, the potential-determining couple is the ferricyanide–ferrocyanide system.

$$\mathrm{Fe(CN)_6^{3-}} + e^- \rightleftharpoons \mathrm{Fe(CN)_6^{4-}} \qquad E^{\circ\,14} = 0.356$$

The zinc in the unknown solution removes some of the ferrocyanide as precipitate and thereby changes the potential of the platinum electrode in the unknown half-cell. The ferricyanide concentration as well as the buffer concentration is maintained constant in both half-cells and in all added solutions. The reference half-cell consists of a solution containing the same concentration of ferricyanide and buffer as the unknown solution and the same concentration of ferrocyanide as the unknown if no zinc were present in the unknown. The potential difference between the two platinum electrodes, one being placed in the unknown and one in the reference solution for a concentration cell without liquid junction potential (the liquid junction potential is negligible since the ionic strength is maintained large and constant in all solutions) is given by

$$E = \left(E^\circ + 0.059 \log \frac{a_{\mathrm{ox}}}{a_{\mathrm{red}}}\right)_{\mathrm{Refn}} - \left(E^\circ + 0.059 \log \frac{a_{\mathrm{ox}}}{a_{\mathrm{red}}}\right)_{\mathrm{Unkn}}$$

$$= 0.059 \log \frac{a_{\mathrm{ox})_{\mathrm{Refn}}}}{a_{\mathrm{ox})_{\mathrm{Unkn}}}} + 0.059 \log \frac{a_{\mathrm{red})_{\mathrm{Unkn}}}}{a_{\mathrm{red})_{\mathrm{Refn}}}}$$

$$= 0.059 \left[\log \frac{C_{\mathrm{ox})_{\mathrm{Refn}}}}{C_{\mathrm{ox})_{\mathrm{Unkn}}}} + \log \frac{f_{\mathrm{ox})_{\mathrm{Refn}}}}{f_{\mathrm{ox})_{\mathrm{Unkn}}}} + \log \frac{C_{\mathrm{red})_{\mathrm{Unkn}}}}{C_{\mathrm{red})_{\mathrm{Refn}}}} + \log \frac{f_{\mathrm{red})_{\mathrm{Unkn}}}}{f_{\mathrm{red})_{\mathrm{Refn}}}}\right] \qquad (7)$$

where *a*, *C* and *f* correspond, respectively, to activity, concentration and activity coefficient of the species in concern. The symbols ox and red refer, respectively, to ferricyanide and ferrocyanide, and Refn and Unkn refer, respectively, to reference and unknown solutions. The Nernst factor 0.059 is given for 25°. Because the ionic strength in the two half-cells is the same, the activity coefficient of each ion is the same in the two half-cells. The concentration of ferricyanide is also the same in both half-cells, and so eqn. 7 reduces to

$$E = 0.059 \log \frac{C_{\mathrm{red})_{\mathrm{Unkn}}}}{C_{\mathrm{red})_{\mathrm{Refn}}}} \qquad (8)$$

Therefore, the null-point is reached when the potential difference, *E*, is equal to zero. At this point the concentration of ferrocyanide is the same in the reference as in the prepared unknown solution.

The null-point is reached experimentally by adding a dilution solution to a prepared reference solution from a buret. The dilution solution contains no ferrocyanide but does contain the same concentration of ferricyanide and ionic buffer as the prepared reference solution. Also, it is not critical whether or not the prepared reference solution contains the potassium zinc ferrocyanide precipitate, since in all cases studied the concentration of ferrocyanide is in excess which represses the solubility of the precipitate in the unknown solution. Even in cases where the zinc concentration is as low as $3 \cdot 10^{-5}$ *M*, the solubility of the precipitate contributes a negligible concentration of ferrocyanide to the total unprecipitated ferrocyanide concentration in the solution as will be indicated later in the paper.

The reaction of zinc with ferrocyanide[1,16] is given below

$$(4y - 2x)\mathrm{K}^+ + x\mathrm{Zn}^{2+} + y\mathrm{Fe(CN)}_6^{4-} \rightleftharpoons \mathrm{K}_{4y-2x}\mathrm{Zn}_x[\mathrm{Fe(CN)}_6]_y \tag{9}$$

where $x = 3$ and $y = 2$ if the precipitation is carried out in the presence of excess potassium and in acid solution, and $x = 2$ and $y = 1$ if the precipitation is carried out in a solution containing a deficiency of potassium at a low acidity. In this study the former case ($x = 3$, $y = 2$) is used. Because the zinc and ferrocyanide do not react in a 1 : 1 ratio and because ferrocyanide, not zinc, is the measured species, the equation for calculating the unknown zinc concentration is somewhat more involved than the chloride case[4]. The equation for the zinc concentration, C_{zinc}, in the unknown is given below

$$C_{\mathrm{zinc}} = kC_{\mathrm{red}})_{\mathrm{Refn}} \left(\frac{V_a}{V_0 + V_a}\right) \tag{10}$$

where V_0 is the initial volume of *reference* solution before dilution, V_a is the volume of dilution solution added from the buret, k is the ratio of zinc ions to ferrocyanide ions in the precipitate and $C_{\mathrm{red}})_{\mathrm{Refn}}$ is the concentration of ferrocyanide in the Reference solution before diluting with water to form the *reference* solution. The derivation of the above equation is similar to that given for chloride[4] and will not be given here. In order to avoid terminology confusion, the measured reference solution in the beaker is designated *reference* whereas the reference solution which is used to prepare the *reference* is designated Reference. The prepared sample solution containing the potassium. zinc ferrocyanide and which is placed in the isolation compartment is designated *sample*. The reader is referred to the sections on *Solutions* and *Experimental procedure of analysis* for the use of these terms.

EXPERIMENTAL

Apparatus

Null detector. The potential between the platinum electrodes was measured by a null detector, consisting of a high input impedance, d.c. chopper amplifier (Model M-10 of Houston Instrument Corporation, Houston, Texas) with a zero center, 100 μA meter in series with a 1000-ohm resistor across the output terminals. Although a zero-adjust circuit which would supply a maximum of 10 mV of bucking voltage was present, it was not needed in this work. The null detector and zero-adjust circuit are discussed in more detail by MALMSTADT AND WINEFORDNER[5].

Electrodes. The platinum indicator electrodes consisted of a strip of platinum plate sealed in the tip of a glass tube. The exposed plate on each measured about 0.4 by 1 cm. Connections to the platinum plate were made by platinum wire. The electrodes were kept in distilled water when not in use.

Isolation compartment. Two types of isolation compartments are suitable for maintaining electrical contact between the sample and reference solutions while preventing mixing. These are the asbestos fiber type and the cracked glass type which have been previously discussed by MALMSTADT AND WINEFORDNER[4,5].

Stirrers. The *reference* solution, in a 100-ml beaker, was stirred by a magnetic stirrer with a teflon-coated stirring bar. The magnetic stirrer had no effect on the null-point reading using the null detector described above. However, when the electrodes were connected to a recorder the magnetic stirrer caused a continuous wavering of the recorder pen. Because the null detector was used throughout, the magnetic stirrer gave adequate stirring and no interference. However, a more efficient stirring system as well as one which can be used without producing recorder noise has been used by MALMSTADT AND WINEFORDNER[5,6].

The sample solution in the isolation compartment also had to be stirred. This was accomplished by connecting the platinum electrode to a vibrator such as found in some electric razors and allowing the electrode to vibrate parallel to the flat plate surface. This was done to prevent bending of the platinum plate during vibration.

Volumetric glassware. A 25-ml automatic refilling buret (Fischer–Porter) was used for adding the Dilution solution to the *reference* solution. A 10-ml automatic refilling pipet (Fischer–Porter) was used for measuring the ferrocyanide. The sidearms of the buret and pipet were connected to reservoirs containing Dilution and Reference solutions, respectively.

Solutions

Stock buffer solution. This solution is used as both a pH buffer and ionic strength buffer. To prepare the stock solution, 895 g of reagent-grade potassium chloride, 1633 g of reagent-grade sodium acetate trihydrate and 360 g of reagent-grade glacial acetic acid were dissolved in enough distilled water to make a final volume of about 6 l. The concentrations of the materials in the buffer as prepared above were 2 M potassium chloride, 2 M sodium acetate and 1 M acetic acid. The same batch of stock buffer solution must be used to prepare each pair of solutions listed below because the ionic strength of the buffer will certainly vary slightly from one batch to the next. However, one batch of buffer solution is good for a large number (about 500) of determinations, and so this is not a significant disadvantage.

Stock ferrocyanide solution. 0.1000 M, 0.02000 M and 0.002000 M. An acculute (Anachemia Chemicals Ltd., Montreal) of 0.1000 M potassium ferrocyanide was used to prepare the 0.1000 M ferrocyanide stock solution. Several liters of 0.02000 M and 0.002000 M ferrocyanide were also prepared by diluting the 0.1000 M ferrocyanide with deionized water.

Stock ferricyanide solution. 0.02000 M and 0.002000 M. One l of 0.02000 M potassium ferricyanide was prepared by weighing out 6.586 g of $K_3Fe(CN)_6$ (reagent grade) and diluting to volume with deionized water. Several liters of 0.002000 M ferricyanide were prepared by diluting the 0.02000 M with deionized water.

Standard zinc solution. One l of 2000 p.p.m. ($3.060 \cdot 10^{-2}$ M) zinc solution was prepared by dissolving 2.4894 g of reagent-grade zinc oxide in the least amount of reagent-grade hydrochloric acid and diluting this solution to volume with deionized water. Several liters of 200.0 p.p.m. ($3.060 \cdot 10^{-3}$ M) and 20.00 p.p.m. ($3.060 \cdot 10^{-4}$ M) were also prepared by diluting the 2000 p.p.m. zinc stock solution with deionized water.

Reference solutions. $2.000 \cdot 10^{-3}$ M and $2.000 \cdot 10^{-4}$ M. For each l of $2.000 \cdot 10^{-3}$ M Reference solution, 500.0 ml of stock buffer solution, 100.0 ml of $2.000 \cdot 10^{-2}$ M ferrocyanide stock solution and 100.0 ml of $2.000 \cdot 10^{-2}$ M ferricyanide stock solution were added to a liter volumetric flask and diluted to volume with deionized water. Similarly, for each l of $2.000 \cdot 10^{-4}$ M Reference solution, 500.0 ml of stock buffer solution, 100.0 ml of $2.000 \cdot 10^{-3}$ *M* ferrocyanide stock solution and 100.0 ml of $2.000 \cdot 10^{-3}$ *M* ferricyanide stock solution were added to a liter volumetric flask and diluted to volume with deionized water.

Dilution solutions. $1.000 \cdot 10^{-3}$ *M* and $1.000 \cdot 10^{-4}$ *M*. For each l of $1.000 \cdot 10^{-3}$ *M* Dilution solution, 250.0 ml of stock buffer solution and 50.0 ml of $2.000 \cdot 10^{-2}$ *M* ferricyanide stock solution were added to a liter volumetric flask and diluted to volume with deionized water. At least 2 l of this solution should be prepared. For each l of $1.000 \cdot 10^{-4}$ *M* Dilution solution, 250.0 ml of stock buffer solution and 50.0 ml of $2.000 \cdot 10^{-3}$ *M* ferricyanide stock solution were added to a liter volumetric flask and diluted to volume with deionized water. Again, at least 2 l should be prepared.

Experimental procedure of analysis

Except for the stirrers, the apparatus was set up in the same manner as is shown for the determination of chloride in water samples[5]. The stirrers were described above.

In all the experiments performed, the *sample* solution with the precipitate was placed in the isolation compartment rather than the beaker. Since the isolation tube is much smaller than the beaker, this permits the use of a much smaller sample volume. The *sample* solution was prepared for analysis by pipetting 10.00 ml of Reference solution into a 100-ml beaker and then with stirring, pipetting 10.00 ml of unknown sample solution into the same beaker. The isolation compartment was rinsed out with 2–3 ml of the precipitated *sample* solution and then about 1 ml of *sample* solution was placed into the compartment. The compartment was mounted in the reference beaker (a 100-ml beaker) so that the tip of the isolation compartment was about 1 cm below the *reference* solution level. The *reference* solution was prepared by pipetting 10.00 ml of Reference solution and 10.00 ml of deionized water into the reference beaker. A large quantity of *reference* solution could be prepared if desired. Initially, the meter needle of the microammeter was off-scale. Dilution solution was then added to the *reference* solution in the beaker until the null-point was reached, which occurred when the meter needle returns to zero. Because there was only a small or no asymmetry potential difference (*i.e.*, if the precipitated *sample* solution was placed in the reference beaker as well as the isolation compartment, the potential difference was always close to zero — in fact the slight asymmetry potential difference corresponded to a volume of Dilution solution which was less than the experimental error) the null-point was always taken as zero. Between determinations, the electrodes, isolation compartment and reference beaker should be rinsed with deionized water, and the electrodes should be dried off by touching Kleenex gently to the surfaces. A clean, dry, 100-ml reference beaker should be used for the next determination, and the sample isolation compartment should again be rinsed out with 2–3 ml of prepared *sample* solution.

If a sample were to contain too large a concentration of zinc, then virtually all the ferrocyanide would be removed from the precipitated *sample* solution and a null-point might never be reached by dilution. Therefore, if in the course of a determination, large amounts of Dilution solution are added without reaching a null-point, the precipitated sample should be discarded, and a new precipitated sample should be prepared from the original sample after diluting it several fold with deionized water. The $2.000 \cdot 10^{-3}$ *M* Reference solution is appropriate for zinc in the concentration range of 10–100 p.p.m., and the $2.000 \cdot 10^{-4}$ M Reference solution is useful for zinc in the concentration range of 1–10 p.p.m.

RESULTS AND DISCUSSION

Precipitation conditions and stability of ferrocyanide solutions

At least two zinc ferrocyanide salts have been reported in the literature[16-18]. These are $Zn_2Fe(CN)_6$ and $K_2Zn_3Fe[(CN)_6]_2$. Various factors such as other ions in solution, acidity and method of precipitation have been reported to favor the formation of one or the other of these salts, but there is probably no set of conditions that favors the formation of one to the complete exclusion of the other. In addition to the fact that the precipitate is composed of two salts, there is a possibility of further variation in composition due to the adsorption of $K_4Fe(CN)_6$ on the precipitate[16]. However, even if the precipitate were not formed stoichiometrically, this does not interfere with this method of analysis as long as $kC_{red})_{Refn}$ is known and remains constant from one precipitate to the next during a series of analyses.

From a survey of the literature[16-18], it seemed that in order to form precipitates with k being the same each time, the precipitate should be formed under reproducible conditions. Therefore, each time an unknown solution was analyzed for zinc, the same procedure was followed. This involved addition of Reference solution to a 100-ml beaker, and then with rapid stirring an equal volume of the unknown sample was added by pipet at the point where stirring seemed to be greatest. The solution from most 10-ml pipets drains slow enough to allow stirring by a magnetic stirring assembly to be effective. Because the unknown solution is always added to the ferrocyanide, there is always an excess of ferrocyanide and never an excess of zinc which minimizes any possibility of forming the undesirable $Zn_3[Fe(CN)_6]_2$ precipitate.

The order of addition of reagents was experimentally checked. Strangely enough, the same results were obtained whether the zinc was added to the ferrocyanide or ferrocyanide to the zinc. Because ferrocyanide solutions decompose slowly and because the exact value of k has not been definitely proven, the value of $kC_{red})_{Refn}$ was determined (using eqn. 10) for six identical samples in which 10.00 ml of a zinc solution of concentration $1.53 \cdot 10^{-3}$ M was added rapidly with good stirring to 10.00 ml of the $2.000 \cdot 10^{-3}$ M Reference solution. Similarly, the same Reference solution was added rapidly with good stirring to the zinc solution and the values of $kC_{red})_{Refn}$ (using eqn. 10) for six identical samples were determined. The data for this study are given in Table I. It should be kept in mind when eqn. 10 is used that $C_{red})_{Refn}$ corresponds to the initial concentration of ferrocyanide in the Reference solution, in this case $2.000 \cdot 10^{-3}$ M, and C_{zinc} corresponds to the zinc concentration in moles per liter in the initial unknown solution before preparation for analysis, in this case $1.53 \cdot 10^{-3}$ M. As can be seen from Table I, the value of $kC_{red})_{Refn}$ is the same within experimental error whatever the order of addition of reagents. This means that the same precipitate formed whether zinc was added first or second. This is probably due to the large excess of potassium and the relatively small amount of acetic acid forcing the $K_2Zn_3[Fe(CN)_6]_2$ precipitate to form.

Because ferrocyanide solutions decompose slowly, the value of $kC_{red})_{Refn}$ decreases slowly as was determined experimentally and is shown in Fig. 2. It was not possible to extrapolate back to zero time to find the value of k for the initial concentration of ferrocyanide which is known at zero time. The extrapolation was not possible because

TABLE I

REPRODUCIBILITY OF THE NULL-POINT POTENTIOMETRIC METHOD FOR A STANDARD ZINC SAMPLE AS A FUNCTION OF METHOD OF ADDITION OF REAGENTS

Method of addition	$kC_{\mathrm{red})\mathrm{Refn}} \cdot 10^3$	*Deviation* · 10^3
Zinc to ferrocyanide	2.473	0.030
Zinc to ferrocyanide	2.495	0.008
Zinc to ferrocyanide	2.505	0.002
Zinc to ferrocyanide	2.508	0.005
Zinc to ferrocyanide	2.519	0.016
Zinc to ferrocyanide	2.517	0.014
	Average = 2.503	0.012
	Coefficient of variation = 0.7%	
Ferrocyanide to zinc	2.481	0.007
Ferrocyanide to zinc	2.485	0.003
Ferrocyanide to zinc	2.499	0.011
Ferrocyanide to zinc	2.472	0.016
Ferrocyanide to zinc	2.501	0.013
Ferrocyanide to zinc	2.488	0.000
	Average = 2.488	0.008
	Coefficient of variation = 0.4%	

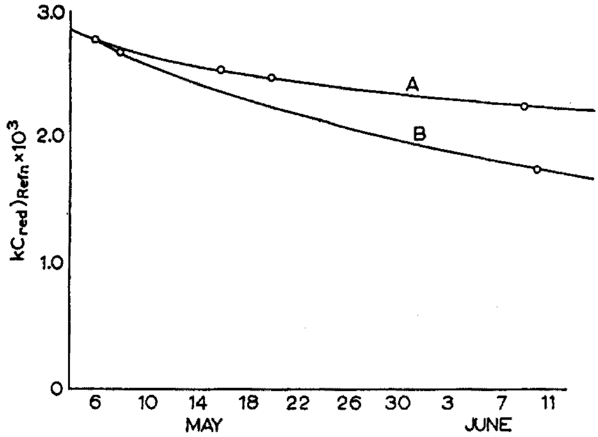

Fig. 2. Time study of ferrocyanide solutions. Curve A, All solutions prepared from the $2.000 \cdot 10^{-3}\,M$ Reference. Curve B, All solutions prepared from the $2.000 \cdot 10^{-4}\,M$ Reference.

the stock solutions of ferrocyanide, which were used to prepare the solutions used to obtain Fig. 2, were prepared from a more concentrated stock solution which had been standing for some time. The rate of decomposition of ferrocyanide is certainly a function of the ferrocyanide concentration as will be shown later. However, if it is assumed that the decomposition rate is nearly the same in all concentrations of ferrocyanide and if the time between preparation of the fresh stock solution and the measured samples is small (less than 2 weeks), then upon extrapolation of a straight line drawn through the curve A points in Fig. 2 back to the solution preparation date (April 25), k is found to be about 1.5. Because k is approximately 1.5, the dominant form of the precipitate is most probably $K_2Zn_3[Fe(CN)_6]_2$ (*i.e.*, $k = x/y = 3/2 = 1.5$) and not $Zn_2Fe(CN)_6$ (*i.e.*, $k = x/y = 2/1 = 2.0$).

The most reasonable explanation of the change in $kC_{red})_{Refn}$ with time is due to a change in the ferrocyanide concentration of the stock solution which was used in preparing the measured solutions, *i.e.*, the *reference* and *sample* solutions, and not due to a change in k with time .It is quite reasonable that the concentration of ferrocyanide would decrease with time either due to decomposition or to oxidation to ferricyanide[10]. In any analysis of zinc it is not necessary to know the exact values of k and $C_{red})_{Refn}$ but only the product $kC_{red})_{Refn}$ in order to use eqn. 10 for calculating C_{zinc}. Even though it is reasonable to assume that $k = 1.50$ and that the entire variation in $kC_{red})_{Refn}$ with time is due to $C_{red})_{Refn}$, nevertheless it has not been adequately shown for this work that k is 1.50. Thus in all calculations (using eqn. 10), the term $kC_{red})_{Refn}$ is determined daily by running a standard zinc solution because it has been shown that $kC_{red})_{Refn}$ is certainly constant over a period of several hours (see Table I). Then whatever the form of the precipitate and whatever the concentration of ferrocyanide, accurate results can be found simply by measuring $kC_{red})_{Refn}$ before a series of determinations. If a large number of samples are run over a period of days or weeks, it is recommended that a plot of $kC_{red})_{Refn}$ *vs.* time be made as in Fig. 2 by analyzing a standard zinc sample every other day. Actually it is possible to find accurate values of $kC_{red})_{Refn}$ from a time plot as in Fig. 2 by extrapolating the $kC_{red})_{Refn}$ curve for periods up to five or six days. In this case it would then be necessary to run a standard only about every five days.

Fig. 2 contains two curves corresponding to two different Reference solutions. In curve A, the $2.000 \cdot 10^{-3}$ M Reference solution is used whereas in curve B the $2.000 \cdot 10^{-4}$ M Reference solution is used. It can be seen that the rate of decomposition of the ferrocyanide in the more dilute Reference solution is certainly more rapid than in the concentrated solution. Therefore, any time a new Reference solution is prepared and used in a series of analyses, it is essential that a new $kC_{red})_{Refn}$ *vs.* time curve be run or at least that $kC_{red})_{Refn}$ be determined daily.

Reproducibility, accuracy, speed and sensitivity of the null-point method for zinc

The reproducibility of analysis is given in Table I. Whether zinc is added to ferrocyanide or ferrocyanide to zinc, the reproducibility is shown to be excellent (coefficient of variation of 0.7% in one case and 0.4% in the other) for the determination of a zinc solution containing $1.53 \cdot 10^{-3}$ M. In cases in which duplicates are made on the same zinc sample solution the results fall within 1% of each other when the zinc concentration is about 10 p.p.m. or higher and within several per cent of each other when the zinc is in the range of 1–10 p.p.m.

The accuracy of the null-point method and further checks on reproducibility are given in Table II (the coefficient of variation on data 9–14 is 0.8%). When using a Reference solution of $2.000 \cdot 10^{-3}$ M, zinc concentrations of about 100 p.p.m. can be determined with a precision and accuracy of about 1%. When the concentration of zinc is as low as 20 p.p.m., the error is about 5%. When using a Reference solution of $2.000 \cdot 10^{-4}$ M the error is about 10% even on solutions containing only 3 or 4 p.p.m. of zinc. The reproducibility on three zinc samples containing only $1.53 \cdot 10^{-4}$ M (10 p.p.m.) was better than 2%. All results in Tables I and II are determined by the use of eqn. 10.

TABLE II

DETERMINATION OF ZINC BY NULL-POINT POTENTIOMETRY

Sample no.	$[Fe(CN)_6^{4-}]$ *in reference soln.* (*M*)	*Zinc concn. taken* (*p.p.m.*)	(*M* · *10*^{3})	*Zinc concn. found* (*p.p.m.*)	(*M* · *10*^{3})	*Error* (%)
1[a]	0.001000	66.7	1.020	66.0	1.009	−1.1
2	0.001000	50.0	0.765	50.3	0.770	+0.6
3	0.001000	50.0	0.765	47.7	0.760	−0.6
4	0.001000	33.3	0.510	34.8	0.533	+4.4
5	0.001000	25.0	0.383	26.6	0.407	+6.5
6	0.001000	20.0	0.306	20.7	0.317	+3.7
7	0.001000	20.0	0.306	21.7	0.332	+8.6
8	0.001000	10.0	0.153	13.9	0.212	+38.6
9[a]	0.001000	50.0	0.765	51.0	0.780	+1.9
10	0.001000	50.0	0.765	50.0	0.765	0.0
11	0.001000	50.0	0.765	50.2	0.769	+0.5
12[b]	0.001000	50.0	0.765	49.9	0.764	−0.1
13	0.001000	50.0	0.765	49.9	0.764	−0.1
14[b]	0.001000	50.0	0.765	50.2	0.769	+0.5
15[a]	0.0001000	10.0	0.153	10.1	0.154	+0.6
16	0.0001000	10.0	0.153	10.1	0.154	+0.6
17	0.0001000	10.0	0.153	9.9	0.151	−1.2
18[b]	0.0001000	6.67	0.102	6.1	0.0928	−9.0
19[b]	0.0001000	5.00	0.0765	5.0	0.0765	0.0
20	0.0001000	4.00	0.0612	4.5	0.0682	+10.2
21	0.0001000	3.33	0.0510	3.7	0.0572	+12.2
22[b]	0.0001000	2.00	0.0306	3.1	0.0470	+53.6

[a] The groups of data (1–8, 9–14, 15–17, 18–22) were obtained on different days and so the value of $kC_{red})_{Refn}$ for each group differed slightly. In samples 1–8 the value of $kC_{red})_{Refn}$ was calculated from an average of samples 2 and 3. In samples 9–14 the value of $kC_{red})_{Refn}$ was calculated from sample 10. The coefficient of variation for samples 9–14 is 0.8%. In samples 15–17 the value of $kC_{red})_{Refn}$ was calculated from the average of the three samples. In samples 18–22 the value of $kC_{red})_{Refn}$ was calculated from sample 19.

[b] These samples were determined with a small amount of zinc ferrocyanide precipitate in the *reference* solution. All other samples were determined using a *reference* solution containing no precipitate.

From the above results it is evident that in all cases the reproducibility of analysis was somewhat better than the accuracy of analysis. In each series of results the value of *k* was found from the second most concentrated solution (for the $2.000 \cdot 10^{-3}$ *M* Reference, the $0.765 \cdot 10^{-3}$ *M* zinc solution was used to find *k*). Also in each series it is noted that the concentrations of zinc found become increasingly greater than the actual experimental concentration of zinc used to prepare the solutions. A possible reason for this large positive error is that the solubility of the zinc precipitate in the isolation compartment increases, when the $2.000 \cdot 10^{-4}$ *M* ferrocyanide Reference solution is used, as the zinc concentration decreases. However, it has been shown both experimentally and theoretically that the solubility effect is negligible. In Table II results 12, 14, 18, 19, and 22 were determined by adding some of the unknown precipitate to the *reference* solution as well as to the isolation compartment. As can be seen, no improvement in the accuracy of results occurred. This study of the effect of solubility was necessary because no unambiguous data for the solubility or solubility product of $K_2Zn_3[Fe(CN)_6]_2$ could be found in the literature. However, according to GRIEB AND CONE[19] the solubility is quite low and so the ferrocyanide produced by the solubility of $K_2Zn_3[Fe(CN)_6]_2$ should be quite negligible. Because the decrease of ferrocyanide concentration is accounted for and the solubility effect is negligible in nearly all cases studied, the positive error in Table II is probably due to a slightly greater ferricyanide concentration in the Reference than in the Dilution solutions. It is quite likely that the ferricyanide concentration is higher in the Reference than Dilution solutions as a result of oxidation of ferrocyanide or as a result of a decomposition process which removes ferricyanide faster in the absence of ferrocyanide than in its presence.

The determination of zinc by the null-point technique can generally be done in about 10 min. This time includes preparation of the zinc precipitate, cleaning out the isolation compartment and beaker, filling the isolation compartment with the zinc solution, pipetting the appropriate solutions into the reference beaker, diluting the *reference* solution and calculating the results.

The precipitate was placed in the isolation compartment rather than in the beaker for several reasons. One of the advantages is that only a small volume of sample is needed. For example, if a 5-ml zinc sample contained only 1 p.p.m. of zinc, then only about 5 μg of zinc are needed for the analysis. In addition, the rate of attainment of equilibrium is also faster by this method since no precipitate is put into the beaker. In the beaker only a mixture of ferricyanide–ferrocyanide is present in addition to the buffer, and it is well known that the ferricyanide–ferrocyanide system is quite reversible[20]. A precipitate in the beaker would certainly result in a slower approach to equilibrium, and therefore the addition of the Dilution solution would undoubtedly have to be much slower. The addition of the Dilution solution for all determinations in this paper was done at the maximum rate allowable by the buret, *i.e.*, about 20 ml per min, until the meter needle of the null detector came on scale. Then the Dilution solution was added slowly until the null-point was reached. Because the zinc precipitate for the isolation compartment is prepared first and because the ferrocyanide is usually in appreciable excess in the sample solution, the sample solution is essentially at equilibrium when the Dilution solution is added to the *reference* solution. This was evident experimentally because the null-detector meter reading remained at the null-point for more than 10 min after the null-point was reached even for solutions containing only 10^{-4} *M* ferricyanide–ferrocyanide. An additional advantage of placing the sample in the isolation compartment is that it is possible to cover a large concentration range with good accuracy. For example, as seen in Table II, a ten-fold concentration range of zinc can be covered quite readily.

Interferences

Most previous papers on the determination of zinc by direct or indirect titration with ferrocyanide completely neglect the effect of cationic interferences on the accuracy of the zinc analysis. For example, ferrocyanide has been also used for the quantitative determination of copper[21], indium, lead and gallium[2]. A number of other cations including Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cd^{2+}, UO_2^{2+} and Hg^{2+} also form ferrocyanide precipitates[22]. However, of the listed metal ions, only several usually occur in appreciable concentrations in samples containing zinc, *e.g.*, blood and plant material. These include Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+} and Co^{2+}, all of which form ferrocyanide precipitates. Of these five cations Fe^{3+} (or Al^{3+}) can be removed by filtering out as the oxide at a pH of 5 or by suitable complexation. Of the remaining four, Cu^{2+}, Co^{2+} and Ni^{2+} can generally be removed, if necessary, by controlled potential electrolysis. The Mn^{2+}, in most cases, can remain since its ferrocyanide is much more soluble[22] than the zinc ferrocyanide precipitate.

Ions such as Mg^{2+} and Ca^{2+}, if in large amounts, may also interfere because they form incompletely dissociated molecules with ferrocyanide[13], as does potassium. One way to avoid this problem is to prepare the *reference* solution with approximately the same concentrations of calcium and magnesium as found in the *sample* solution. The addition of small amounts of solid calcium and magnesium salts to a ferricyanide–ferrocyanide solution caused only a slight change in the potential. Large amounts of solid salts of magnesium and calcium caused a significant change in the potential. However, this was certainly due to a change in the ionic strength of the solution as well as a possible change due to formation of a non-dissociating complex.

SUMMARY

The effect of pH and potassium ion concentration on the potential of the ferricyanide–ferrocyanide system and the stability of solutions of ferricyanide and ferrocyanide were studied. An equation relating the potential of the system to pH and potassium ion concentration was derived and agreed well with experimental data. The proper experimental conditions for applying the very rapid, accurate and sensitive precision null-point potentiometric technique to the determination of zinc were then chosen. Zinc in the concentration range of 1–100 p.p.m. was determined with good accuracy within 10 min; as little as 5 μg of zinc can be determined. The stability of solutions, the type of precipitate, the rate of attainment of equilibrium, the accuracy and reproducibility, and the effect of cationic interferences were studied.

RÉSUMÉ

Les auteurs ont étudié l'effet du pH et de la concentration en potassium sur le potentiel du système ferricyanure/ferrocyanure. L'équation établie correspond bien aux valeurs trouvées expérimentalement. Une méthode de dosage potentiométrique du zinc est proposée, avec indication de la stabilité des solutions, du type de précipité, de la vitesse d'équilibre, de la précision, de la reproductibilité et de l'influence des cations gênants.

ZUSAMMENFASSUNG

Der Einfluss von pH und Kaliumkonzentration auf das Potential des Ferricyanid–Ferrocyanid Systems und die Stabilität der Lösungen wurde untersucht. Eine mathematische Beziehung zwischen Potential des Systems gegenüber pH und Kaliumkonzentration wurde abgeleitet und stimmt gut überein mit den Versuchsergebnissen. Auf dieser Grundlage wurde dann eine schnelle und genaue potentiometrische Methode zur Bestimmung von Zink im Bereich von 1–100 p.p.m. ausgearbeitet. Die Stabilität der Lösungen, Art des Niederschlags, Gleichgewichtseinstellung, Genauigkeit und Reproduzierbarkeit sowie der Einfluss von Fremdionen wurde untersucht.

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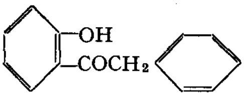
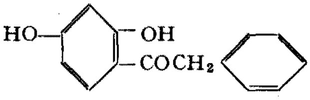
Short Communications

The detection of titanium with hydroxyphenylbenzyl ketones

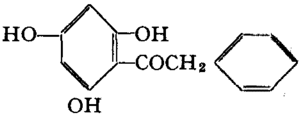
All the spot tests available for the detection of titanium either do not have sufficiently low identification limits, or several other metal ions found commonly with titanium interfere. In the present investigation, 2-hydroxy- (I), 2,4-dihydroxy- (II) and 2,4,6-trihydroxy- (III) phenylbenzyl ketones were studied for the detection of titanium.



I



II



III

All these compounds give yellow complexes with titanium, but the sensitivity increases with increasing number of phenolic-OH groups. With (III) as little as 0.05 μg of titanium can be detected in one drop of solution. The colour developed may be due to reaction with the phenolic-OH group or chelation with the enolic form of the ketone. Phenylbenzyl ketone itself does not give any colour with titanium whereas phenol, resorcinol and phloroglucinol give light brown complexes with appreciably larger amounts of titanium; these observations indicate that chelation is responsible for the colour test. The other reagents available[1] have two adjacent phenolic-OH groups; in the present case there is only one phenolic-OH group available for chelation. The other hydroxyl group is alcoholic in nature and is made available by enolization. Hydrogen bond formation between the phenolic-OH and keto groups would tend to stabilize the keto form of the reagent but the present test indicates that either the enolic form does exist in the case of phenylbenzyl ketones or the addition of titanium leads to the conversion of the keto form to enolic form.

Detection of titanium when present alone

Procedure: Place a drop of titanium solution on the centre of Whatman filter paper

(No. 1, 9 cm diameter), dry with hot air and add a drop of the reagent solution. Dry the spot and compare the colour produced with that of the blank.

Reagent: 0.1% solution of 2,4,6-trihydroxyphenylbenzyl ketone in ethyl alcohol.

By this method 0.05–2 µg of titanium can be detected and estimated semiquantitatively by comparing the spots obtained with those of a standard solution.

The identification limit is 0.05 µg and the dilution limit is 1 : 1,000,000. Both these limits are better than those reported for any other reagent.

Iron(III) gives a light violet colour with the reagent but iron(II) gives no colour. Complex formation with citric or tartaric acid prevents the reaction of iron(III). Reduction of iron(III) with hydrazine or phenylhydrazine reduces the sensitivity of the test. Cerium gives a brownish yellow spot. Coloured ions such as chromate can be washed away from the spot, thus preventing interference. Aluminium, mercury, magnesium, calcium, copper, lead, silver, cobalt, molybdate and thorium, as well as formaldehyde, form no colours with the reagent.

Detection of titanium in steel

Titanium is used as an alloying metal in stainless steel. This reagent was therefore used for detecting titanium in the stainless steel. A synthetic mixture and blank of the following composition were prepared:

Metals	*Synthetic mixture, µg/drop*	*Blank, µg/drop*
Iron (as ferric chloride)	180	180
Chromium (as dichromate)	45	45
Nickel (as chloride)	25	25
Manganese (as manganous sulphate)	5	5
Titanium (as chloride)	1	—

Procedure: 1–2 µg of titanium is required to carry out this test satisfactorily. Place 2 drops of 5% citric acid solution on the centre of a Whatman No. 1 filter paper and add a drop of test solution over it. Dry the spot and add 2 drops of the reagent solution. After 3 min, wash the spot with a jet of water so as to wash out the iron citrate complex as well as the chromate. Carry out a blank similarly. A yellow spot was obtained in the sample.

The above procedure was adopted to detect the titanium steel SS321 out of a batch containing SS 302, 304, 316 and 347. One drop of 1 : 1 nitric acid was placed over the metal piece. After 2–3 min, it was transferred to a filter paper by means of a capillary and the above procedure was followed.

All these reagents were prepared by methods given in the literature[2-4].

Conclusion

2,4,6-Trihydroxyphenylbenzyl ketone is a sensitive reagent for titanium. The identification limit is 0.05 µg of titanium, and the dilution limit is 1 : 1,000,000. The reagent can also be employed to detect 1–2 µg of titanium in the presence of other constituents of stainless steels.

Our thanks are due to SHRI H. N. SETHNA for his interest shown in this work.

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S. D. PAUL
M. S. KRISHNAN

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(Received September 15th, 1962)

Anal. Chim. Acta, 28 (1963) 494–496

Observations on the fluorescence of some tetracyanoethylene complexes

Since the first description of the synthesis and chemistry of tetracyanoethylene[1] (I) considerable interest in its possible use as a general analytical reagent has been demonstrated. Tetracyanoethylene forms highly colored π-complexes with a variety of aromatic compounds, and also reacts with certain other types of structures to yield colored products[2]. Because of its ability to form colored complexes, it has been suggested as a reagent in a variety of applications including detection of nitrogen compounds in petroleum[3], development of paper chromatograms[4], colorimetric determination of anthracene[5] and the titrimetric estimation of dienes via the Diels–Alder reaction[6]. In these studies the detection signal has been based on the absorption of light or a visible color change. Tetracyanoethylene would possess added versatility if light emission could be used as an adjunct to visible color. We wish to report on the fluorescence of I, in that our observations may be of some practical value and may stimulate a more detailed theoretical investigation.

The residue deposited by the evaporation of a benzene solution of I fluoresces yellow when exposed to ultraviolet light. Infrared spectra were obtained in potassium bromide for both the fluorescent and nonfluorescent residues. There was no spectral evidence that tetracyanoethylene was associated with benzene. Actually the only difference in the two spectra was the splitting of the 8.64 μ and 12.5 μ bands in the case of the fluorescent material. This splitting phenomenon sometimes occurs with materials that possess different crystal forms and the existence of a metastable crystalline form of I was considered tentatively as an explanation for the fluorescence.

In an attempt to support this hypothesis, the following experiment was performed. Separate beakers of benzene and I powder were placed under a bell jar and allowed to stand for two days. It was thought that under these conditions I, although exposed to benzene vapor, would not change readily in crystal structure. Although the powder seemed unchanged after exposure to benzene vapors, it did fluoresce light yellow under ultraviolet light using a 366 mμ filter. Hence, it was concluded that only a trace of benzene is necessary to cause the fluorescence and that a crystal structure modification probably is not involved.

Several experiments were then carried out in an attempt to estimate the quantity of benzene necessary for the fluorescence. A saturated solution of I in benzene was allowed to evaporate to dryness. The residue after standing at room temperature for 3 h still fluoresced. The material was then placed in a small test tube, capped with a septum and allowed to stand for several hours. When the atmosphere above I was examined by gas–liquid chromatography, using a 0.5 ml sample, the presence of a considerable quantity of benzene in the vapor above the sample was established. In fact, benzene was also detected, although in lesser amounts, in the vapors above a sample which still fluoresced even after standing overnight (15–16 h). In a third experiment, a benzene solution of I was placed in a rotating evaporator and the benzene was evaporated under water aspirator vacuum. After removal of the solvent, aspiration was continued for an additional 5 h. This material no longer fluoresced, although gas–liquid chromatography still detected benzene in the vapors above the sample. On the basis of these observations, it was concluded that benzene must be an integral part of fluorescent I, and that the small quantity of benzene involved explains its absence from the infrared spectrum of the fluorescent sample.

It was also noticed that the solids obtained by cooling benzene solutions of I to dry-ice temperature fluoresced yellow-green under ultraviolet light. The temperature does not appear critical; only solidification is needed. Further studies of this phenomenon included determining the concentration of I necessary for fluorescence, and to establish whether or not solutions of I other than in benzene cooled below their melting points, could be made to fluoresce. Solutions of I in benzene were prepared in concentration ranges of 0.1 M to $1.0 \cdot 10^{-6}$ M in decreasing steps by a factor of 10. These were cooled and the resulting solids were irradiated with an ultraviolet light (366 mμ filter). Only the more concentrated solutions (0.1 M and 0.01 M) emitted light in the solid state. None of the solutions exhibited visible fluorescence as liquids. Solutions of I in toluene and xylene were, in turn, cooled below their melting points and then exposed to ultraviolet light, but fluorescence was not observed. However, while evaporating toluene and xylene solutions of I on filter paper, brief but bright yellow and orange flashes, respectively, were observed under ultraviolet light. Fluorescence was not visible under the same conditions using cumene or ethylbenzene. In addition the infrared absorption spectra of samples of I from toluene and xylene solutions did not exhibit splitting of the 8.65 μ and 12.5 μ bands. A fluorescent sample of I became nonfluorescent when deposited from a toluene solution.

A nuclear magnetic resonance spectrum was next obtained of benzene and benzene saturated with I in an effort to detect the shift in the proton resonance of the benzene. However, both spectra were identical, thus indicating that the complex formation does not involve a *major* withdrawal or addition of electrons to the electron cloud of the benzene ring.

Some of the experiments with I were repeated easily using ultra-pure benzene[7]. Therefore, the fluorescence properties do not appear to be due to impurities in benzene.

Our general observations on fluorescence indicate the potential of rendering tetracyanoethylene yet more useful as an analytical reagent. It may be that the fluorescence is of a charge-transfer nature such as that reported by McGlynn *et al.*[8] for certain charge-transfer complexes. However, we did not obtain emission spectra even for the solutions which did emit light. A quantitative spectral study in a variety of solvents may help to elucidate further the observed phenomenon.

We wish to acknowledge receipt of a generous sample of tetracyanoethylene from Dr. W. J. MIDDLETON, E. I. Du Pont de Nemours & Co.

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Edgewood Arsenal, Maryland (U.S.A.)

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[1] T. L. CAIRNS *et al.*, *J. Am. Chem. Soc.*, 80 (1958) 2775.
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(Received November 2nd, 1962)

Book Reviews

Electrochemical Reactions, the Electrochemical Methods of Analysis, G. CHARLOT, J. BADOZ-LAMBLING AND B. TRÉMILLON, Elsevier, Amsterdam, 1962, pp. ix + 376, Dfl. 40.—

This is a translation of "Les Reactions Electrochimiques" published by Masson in 1959, and as such is welcome in making this useful and stimulating test available to a wider public. It is a literal translation in that no alteration or revision has been made, and, although revealing an occasional touch of Gallic flavour, is done into generally excellent English. The translator is not named and one is tempted to ascribe the work to a ghost because it is difficult to believe that the original authors could have resisted making some revision, addition or correction during preparation of the work for press. The literature coverage stops abruptly in 1958, which was admirable in the original edition, but leaves obvious gaps in the more rapidly advancing fronts of the subject. There are a few minor changes of layout and citation numbering, and the author index has, regrettably, been dropped, but otherwise there is little to add to the review of the original edition (*Analyst* 85 (1960) 690). An original and refreshing attempt to appraise the field of electroanalytical chemistry in terms of current–potential relationships or polarisation-curves of electrodes, this book claims the attention of all whose work embraces this subject.

E. BISHOP (Exeter)

Treatise on Analytical Chemistry, édité par I. M. KOLTHOFF et P. S. ELVING avec la collaboration de E. B. SANDELL, Part II, *Analytical Chemistry of the Elements*, Vol. 2, Interscience–Wiley, New York, 1962, 471 pp., 135 s.

Les divers volumes de ce remarquable ouvrage sortent de presse à un rythme régulier et rapide.

Dans ce deuxième volume de la deuxième partie, six auteurs: Messieurs C. V. Banks, J. M. Dale, L. M. Melnick, J. R. Musgrave, Hiroshi Onishi et H. R. Shell traitent de huit éléments: le gallium, l'indium, le thallium, le silicium, le germanium, le fer, le cobalt et le nickel.

On retrouve, dans cet ouvrage, les mêmes rubriques que dans les volumes précédents. Une fois de plus nous admirons la qualité des exposés mais nous regrettons quelque peu le manque d'homogénéité qui aurait pu être facilement évité. C'est ainsi, à titre d'exemple, que les tableaux des propriétés ne sont pas comparables d'un élément à l'autre et les diverses parties inégalement développées. La bibliographie va jusqu'en 1960: un choix a été fait qui nous parait judicieux.

Cet ouvrage renferme une foule considérable de renseignements tant en ce qui concerne les propriétés physiques et chimiques des éléments que les méthodes de séparation et d'identification. Toutes les méthodes de dosages actuellement en usage sont citées et décrites.

Nous avons particulièrement apprécié les paragraphes intitulés: "procédés de laboratoire recommandés" où chacun y trouvera sans peine la méthode qui lui est utile avec tous les détails nécessaires.

En fait chaque chapitre est traité de telle sorte que le lecteur pourra très rapidement se faire une idée générale des conditions de séparation et de dosage de l'élément considéré.

D. MONNIER (Genève)

Anal. Chim. Acta, 28 (1963) 499

Radiochimica Acta, Band 1, Heft 1 (48 pages), (September 1962). Akademische Verlagsgesellschaft, Frankfurt A.M., and Academic Press, New York – London. Price per volume (4 issues) DM 72, $ 18.

Most chemists will be dismayed by the appearance of yet another journal. *Radiochimica Acta* is concerned with rather a special branch of chemistry but it is one of increasing importance having points of contact with many others. This new publication is introduced by Otto Hahn; the first issue contains a dozen papers on subjects ranging from the radiation chemistry of high polymers to the production and separation of isotopes. If the quality of its contributions is maintained, this journal will have to be added to the reading lists of chemists interested in any aspect of radiochemistry.

Some of the papers in this first issue are dated late 1961 but others are as recent as June 1962. It is to be hoped that the editors will be able to promise speedy publication but that they will insist on careful preparation and checking of manuscrips. We do not wish to have another journal containing brief accounts of work "to be described in detail elsewhere".

The notice to authors indicates that papers in German, French and English may be accepted; summaries of all papers are printed in the three languages. There is evidently a generous allowance of free reprints.

J. C. BEVINGTON (Birmingham)

Anal. Chim. Acta, 28 (1963) 499–500

Progress in Infra-red Spectroscopy, Volume 1, Edited by H. A. SZYMANSKI, Plenum Press, New York, 1962, pp. iv + 446, $ 16.00.

This volume is sub-titled "Proceedings of the Sessions of the 5th Annual Infra-red Spectroscopy Institute, Canisius College, Buffalo, N.Y." and this origin doubtless accounts for some of its remarkable features. Some twenty contributions of an average length of ten pages precede two longer articles on Group Theory (50 pp. by J. Ziomek) and Analytical Applications of Ultra-violet, Visible and Infra-red Spectrophotometry (78 pp. by R. G. White). How these come under the title of this volume is an open question. The former is a condensed summary of the use of group theory in relation to molecular symmetry and vibrations, with relevant examples. Very useful as a set of notes to anyone teaching the subject, it is too brief for introductory presentation. The second paper (White) is essentially a condensed *vade-mecum* on visible and uv spectrophotometric analysis with some examples of near infra-red spectra thrown in. Despite the 717 references with which the chapter is replete, it in no way deals with "Progress in Infra-red Spectroscopy".

Of the items which come under the title, some thirty pages on applications in the inorganic field might be mentioned, and forty pages (four brief contributions) on far infra-red methods are certainly relevant. The remainder of the contents are suggested by the titles "Infra-red correlations of plastics and resins"; "Raman spectroscopy at Canisius College".

There may well be a case for publishing material of this kind — it could be useful, although also otherwise available, in some industrial laboratories. With its misleading title and fair proportion of trivial items, the price of the present volume makes it an imposition on unsuspecting librarians.

MANSEL DAVIES (Aberystwyth)

Anal. Chim. Acta, 28 (1963) 500

Publications received

Deoxyribonucleic acid: Structure, Synthesis and Function, Proceedings of the 11th Annual Reunion of the Societé de Chimie Physique, June 1961, Pergamon Press, Oxford, 1962, pp. ix + 235, 60 s.

Méthodes d'Analyse – Cetama 1962: Méthodes 1 à 100, Commissariat à l'Energie Atomique: Commission d'Etablissement des Méthodes d'Analyse, Presses Universitaires de France, Paris, 1962, pp. 428 (no price given).

Etude Histochimique du Foyer Otospongieux, L. G. CHEVANCE avec la collaboration de P. CLERC et J. BOUCHE, Librairie Arnette, Paris, 1962, pp. 132, Br. 50 NF.

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Anal. Chim. Acta, 28 (1963) 500

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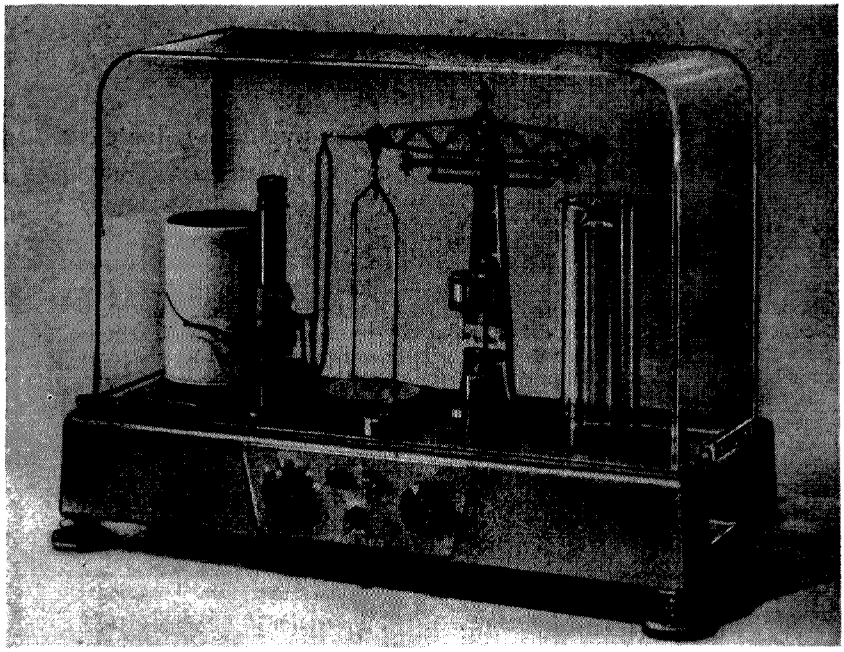

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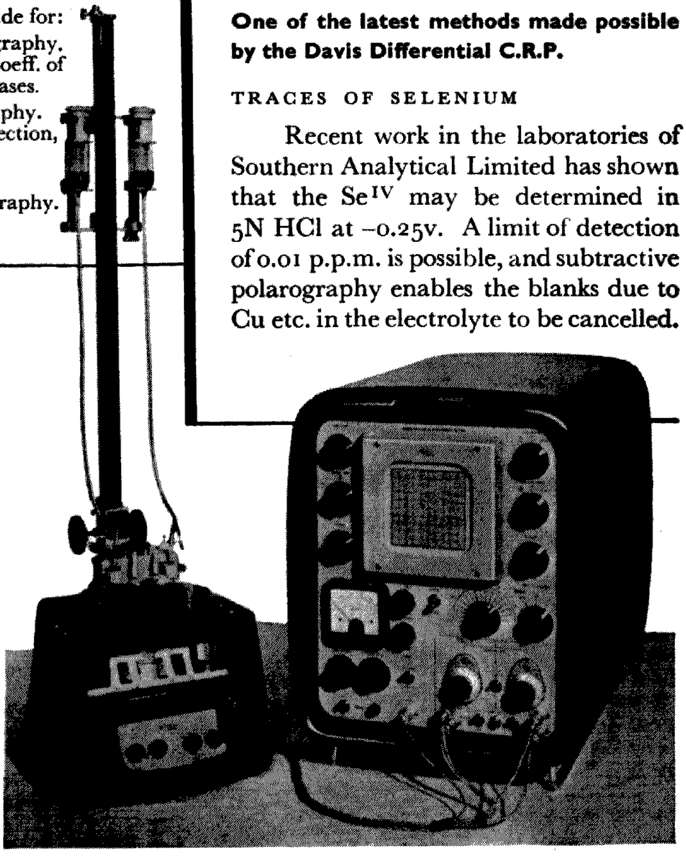

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