ANALYTICA CHIMICA ACTA

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

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 33, No. 6, 577–696, December 1965
Completing Vol. 33 (1965)

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 33, No. 6, December 1965

THE INFLUENCE OF POLYNUCLEAR ZIRCONIUM SPECIES ON DIRECT TITRATION OF ZIRCONIUM WITH EDTA

Accurate results in EDTA titration of zirconium at all concentration levels can only be obtained if zirconium ions are converted to a depolymerised form. Treatment with strong sulphuric acid is more generally applicable for this conversion than treatment with other mineral acids which fail to depolymerise highly polymerised zirconium sulphate systems. To avoid the zirconium species becoming repolymerised under the conditions required for a direct titration, EDTA is added at high acidity (1–2 *N* sulphuric acid, depending on zirconium concentration). At an appropriate stage of the titration, easily determined by a colour change obtained with xylenol orange indicator, a single addition of a fixed quantity of ammonia solution establishes the correct pH for a sharp end-point. Results are quantitative and amounts of zirconium from 10 μg to 500 mg can be determined with appropriate standard EDTA solutions.

E. S. Pilkington and W. Wilson,
Anal. Chim. Acta, 33 (1965) 577–585

THE USE OF A LITHIUM-DRIFTED GERMANIUM DIODE TO DETERMINE CARBON IN STEELS BY MEASUREMENT OF PROMPT γ-RADIATION

A lithium-drifted germanium p–i–n diode was used as detector to measure the prompt radiation emitted by the reaction ^{12}C (d,p) ^{13}C during the irradiation of steels with low-energy deuterons. Typical spectra obtained using a diode and a thallium-activated sodium iodide crystal are compared, and results given for a number of standard steel samples.

T. B. Pierce, P. F. Peck, W. M. Henry and B. W. Hooton,
Anal. Chim. Acta, 33 (1965) 586–592

THE SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH 8-HYDROXYQUINOLINE

A superior spectrophotometric method is proposed for determining small amounts of zirconium as the 8-hydroxyquinolinate in chloroform, measured at 386 mμ. The molar absorptivity is 14,700. In contrast to other available methods, anions such as chloride, sulfate, perchlorate, tartrate, oxalate, and fluoride do not interfere.

R. T. van Santen, J. H. Schlewitz and C. H. Toy,
Anal. Chim. Acta, 33 (1965) 593–596

DETERMINATION OF TITANIUM AND ZIRCONIUM IN MOLYBDENUM BASE ALLOYS BY ION EXCHANGE

The anion-exchange behavior of titanium, zirconium and molybdenum in sulfuric–oxalic acid system was studied. The systematic use of distribution coefficients defined conditions for a simple method for the analysis of zirconium and titanium in molybdenum base alloys. Less than 0.1% zirconium and 0.1% titanium can be determined. Molybdenum, among the three, was found to form the most stable anionic species with oxalic acid.

M. SHAKASHIRO AND H. FREUND,
Anal. Chim. Acta, 33 (1965) 597–601

APPLICATIONS OF THE POLAROVOLTRIC METHOD

A STUDY OF TITRATION CURVES IN THE DETERMINATION OF ORGANIC DIBASIC ACIDS WITH BASES AND THE INFLUENCE OF ADDED SALTS

(in French)

The polarovoltric titration curves obtained in a study of the reaction of organic dibasic acids, both saturated (*e.g.* malonic, succinic and adipic acids) and unsaturated (*e.g.* maleic, fumaric and *o*-phthalic acids) with basic reagents in N,N-dimethylformamide were different for each acid. It was possible to classify these curves in 4 distinct groups.

The individual acidic functions for all of the acids studied, except fumaric and adipic acids, could be detected by a suitable choice of titration conditions. The first acid function in fumaric and adipic acids could not be titrated.

When tetrabutylammonium hydroxide was incapable of indicating the second end-point, this end-point could be detected either by changing the reagent (*e.g.* using MeONa) or by adding a salt (*e.g.* $NaClO_4$) to the solution.

J. E. DUBOIS AND P. C. LACAZE,
Anal. Chim. Acta, 33 (1965) 602–611

THE SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF PRIMARY AND TERTIARY AMINES IN AQUEOUS SOLUTION WITH COPPER–(ETHYLENE DINITRILO)TETRAACETIC ACID

The preferential coordination of primary amines to the copper–EDTA complex and the resulting fall in absorbance at 720 mμ is used as a basis for the accurate determination of both primary and tertiary amines in mixed aqueous solutions. The total amine content is first determined by spectrophotometric titration of the mixed amine solution with the dibasic copper–EDTA complex (or *vice versa*). Then the mixed solution of amines is diluted to a definite total amine concentration, and its absorbance at 720 mμ is again measured after the addition of a definite amount of the tetrasodium salt of EDTA complexed with copper, $(CuY)^{2-}$. This absorbance is located on a suitable varying concentration ratio curve, and the concentrations of both primary and tertiary amines in the solution being analyzed can be read directly from the curve.

I. M. CITRON AND D. DOLAN,
Anal. Chim. Acta, 33 (1965) 612–618

THE DETERMINATION OF GLYCOLLIC ACID IN SOLUTIONS PREVIOUSLY IN CONTACT WITH ION-EXCHANGE RESINS

Two methods were examined for the determination of glycollic acid which had been in contact with polystyrene-type cation-exchange resins. For resins with high degrees of cross-linking (8% DVB or greater), a titration based on oxidation with dichromate was satisfactory but for resins with lower cross-linking, variable 'blank' values caused difficulties. A spectrophotometric method with chromotropic acid was shown to be applicable to solutions from any resin irrespective of the cross-linking, and also to the determination of glycollic acid in the presence of lactic acid if the glycollic: lactic ratio (w/w) was not less than 4:3.

S. J. Lyle and A. R. Sani,
Anal. Chim. Acta, 33 (1965) 619–624

TRIARYLMETHANE DYESTUFFS AS REDOX INDICATORS

The redox properties of a number of triarylmethane dyestuffs have been studied in conventional redox titrations and their usefulness as redox indicators has been assessed. None is superior to the established indicators for titrations involving cerium(IV) and chromium(VI) as oxidising titrants. One dyestuff, Regina Purple (C.I. 4215), is strongly recommended for use in the Andrews' iodate titration and another, Basic Blue 11 (C.I. 44040), for the iodine–thiosulphate titration. Certain commercially available phthalocyanine dyestuffs have also been studied as redox indicators and their behaviour is compared with that of the triarylmethane type.

J. N. Brazier and W. I. Stephen,
Anal. Chim. Acta, 33 (1965) 625–638

A RAPID METHOD FOR THE DETERMINATION OF SUBSTANCES RESOLVED ON THIN-LAYER PLATES

A method is described for the removal of spots from thin-layer plates, which, when used in conjunction with spectral reflectance, makes possible the rapid analysis of substances resolved on chromatoplates. Data are provided which indicate that the surfaces laid down by a commercial applicator are, with certain limitations, satisfactory for use with this technique.

V. T. Lieu, R. W. Frei, M. M. Frodyma and I. T. Fukui,
Anal. Chim. Acta, 33 (1965) 639–647

SOLUTION OF ROCKS AND REFRACTORY MINERALS BY ACIDS AT HIGH TEMPERATURES AND PRESSURES

DETERMINATION OF SILICA AFTER DECOMPOSITION WITH HYDROFLUORIC ACID

A modified Morey bomb was designed which contains a removable nichrome-cased 3.5-ml platinum crucible. This bomb is particularly useful for decompositions of refractory samples for micro- and semimicro-analysis. Temperatures of 400–450° and pressures estimated as great as 6000 p.s.i. were maintained in the bomb for periods as long as 24 h. Complete decompositions of rocks, garnet, beryl, chrysoberyl, phenacite, sapphirine, and kyanite were obtained with hydrofluoric acid or a mixture of hydrofluoric and sulfuric acids; the decomposition of chrome refractory was made with hydrochloric acid. Aluminum-rich samples formed difficultly soluble aluminum fluoride precipitates. Because no volatilization losses occur, silica can be determined on sample solutions by a molybdenum-blue procedure using aluminum(III) to complex interfering fluoride.

I. May and J. J. Rowe,
Anal. Chim. Acta, 33 (1965) 648–654

PROOF OF ULTRAPURITY IN ZONE-REFINED NAPHTHALENE

Zone-melting as an ultrapurification technique for organic substances has recently received much attention but *proof* of ultrapurity in final measurements has often been lacking. The numerous difficulties encountered in *proof* of ultrapurity narrowed the present study to only one compound, naphthalene. The use of only one analytical procedure has serious disadvantages. It was shown that gas–liquid chromatographic analysis and thermal analysis measurements can be deceptive. However, a combination of "absolute methods" of ultrapurity analysis (thermal analysis, gas–liquid chromatography, phase solubility methods) that measure *total* impurities can yield a reliable picture of the sample.

Whether the zone-melted naphthalene sample used is 100.00000 mole-% pure, or 99.9999 mole-% pure as given by the thermal analysis data, is uncertain. The thermal analysis and DTA method were capable of detecting 0.00008 mole-% of impurities. However proof of ultrapurity is dependent upon a combination of measurements *via* several ultrapurification processes and several methods of assay.

R. FRIEDENBERG AND P. J. JANNKE,
Anal. Chim. Acta, 33 (1965) 655–669

SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM(III) WITH AZIDE

Sodium azide was shown to be a sensitive reagent for the spectrophotometric determination of rhodium(III). The coloured complex showed absorption maxima at 405 mμ and at 480 mμ. At both wavelengths, the system obeyed Beer's law from 2 to 40 p.p.m. of rhodium. The percent relative error for the optimum range (6 to 40 p.p.m.) was 2.73. Both 1:1 and 1:2 complexes appear to be formed in solution, but in pyridine only one complex is formed. A scheme for the separation of rhodium from all other ions, involving ion-exchange and solvent-extraction processes, is proposed.

A. K. MAJUMDAR AND B. K. MITRA,
Anal. Chim. Acta, 33 (1965) 670–676

SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 2-AMINO-8-NAPHTHOL-6-SULPHONIC ACID

(Short Communication)

GR. POPA AND C. LAZĂR,
Anal Chim. Acta, 33 (1965) 676–678

SPECTROPHOTOMETRIC DETERMINATION OF CHLOROPICRIN IN WATER

(Short Communication)

J. A. CASTRO AND H. GODOY,
Anal. Chim. Acta, 33 (1965) 679–683

DETERMINATION OF MICRO QUANTITIES OF NIOBIUM IN URANIUM

(Short Communication)

S. K. SHRIMAL AND M. S. VARDE,
Anal. Chim. Acta, 33 (1965) 683–685

THE INFLUENCE OF POLYNUCLEAR ZIRCONIUM SPECIES ON DIRECT TITRATION OF ZIRCONIUM WITH EDTA

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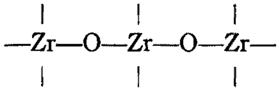
(Received April 5th, 1965)

Since the first work on zirconium–EDTA titrations reported in 1954, indirect titration[1-7] has been favoured because of the difficulties (attributed to hydrolysis) which arose when direct titrations were first attempted[2,6,7]. It is evident that direct titrations would be more convenient but a preliminary examination of procedures reported in the literature[8-17] revealed that in no case could the dual objectives of a sharp end-point and acceptable accuracy be achieved simultaneously. Results were always lower than theoretical to an extent which varied with the solution concentration of zirconium and with the previous history of treatment with respect to temperature and pH.

Our investigations showed that the inconsistencies which had been a feature of direct EDTA zirconium titrations are directly attributable to the formation of polynuclear zirconium species ("polymerisation") and that proper attention to depolymerisation procedures is an essential pre-requisite to the titration of zirconium in solution. Polymerisation, as a development of hydrolysis of zirconium ions in aqueous solutions is well known and many papers have reported the conditions under which this phenomenon occurs[18-24]. The polymerisation, derived from oxygen bridging, gives species of the general type



$$-\underset{|}{\overset{|}{\mathrm{Zr}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Zr}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Zr}}}-$$

possessing a high degree of stability. Depolymerisation is in general a slower or more difficult reaction to carry out than polymerisation although the rate is influenced by whether zirconium concentration or pH or temperature was the predominant factor in causing the original polymerisation[22].

It is well established that polymerisation occurs readily and to an increasing extent as (*a*) zirconium concentration is increased and (*b*) temperature and pH are raised. The main concern to the analyst is that the resultant polymeric species reacts with EDTA in a variety of ratios other than a 1:1. Since the conditions required for direct EDTA titrimetry (moderately acid solutions, heated in the pH 0–1.5 region) are virtually ideal for rapid formation of polymeric species, it becomes extremely easy to lose 1:1 stoichiometry with EDTA in any attempt at unmodified direct titration. Errors from loss of stoichiometry may also derive from the zirconium solution being inadvertently polymerised during preparation. Tests showed that at a concentration range of the order of 1 mg/ml, all zirconium solutions prepared by dissolving chloride, nitrate or sulphate salts in dilute acids will contain a certain proportion of polymeric material.

If polymerisation is slight, the ability of EDTA to effect some measure of depolymerisation at a slow rate has produced reasonable results and has allowed this special problem of zirconium titrimetry either to be overlooked or, if recognised, to impose serious restrictions on the permissible amounts of zirconium.

The role of sulphate ion

Several early papers reported the formation of a white precipitate when EDTA was added to zirconium solutions containing sulphate ions[2,5]; this caused a serious interference with both direct and indirect titrimetry. Such precipitates, which we find can only be obtained when polynuclear zirconium ions react with EDTA in sulphate systems, contain sulphate, zirconium and EDTA in readily variable ratios up to as high as 40:1 Zr: EDTA[25]. One procedure introduced by earlier workers to prevent this type of precipitation in the presence of sulphate was to add tartrate prior to EDTA, adjust to pH 2 and back-titrate the excess of EDTA with bismuth(III) solution[3,26]. In the present work, it was shown that tartrate does in fact lead to clear solutions on addition of EDTA but does not depolymerise zirconium polynuclear species sufficiently for a 1:1 Zr: EDTA stoichiometry to be obtained in all cases, particularly at the higher concentrations of zirconium which are more highly polymerised (0.1 *M* titrant).

Several workers have noted that regardless of precipitate formation, the presence of sulphate ion still causes serious interference in any form of EDTA titrimetry of zirconium[2,4,7,15]. MILNER AND PHENNAH[4] avoided the interference by fuming with sulphuric acid before adding excess EDTA and back-titrating. Heating to fumes with sulphuric acid was also adopted by MILNER AND EDWARDS[5] to prevent formation of zirconium–EDTA precipitates in an improved back-titration procedure.

Although certain workers have implied that direct titrimetry of zirconium with EDTA in sulphate systems is virtually impossible[2,7,15], the present work has shown that the technique of MILNER AND PHENNAH which amounts to a depolymerisation reaction can be used in a modified form as a preliminary to the development of a workable direct titration procedure.

EXPERIMENTAL

Depolymerisation in sulphate systems

Zirconium sulphate (TAMCO "low-hafnium" grade, 0.05% HfO_2 in oxides) was recrystallised as described by CLABAUGH AND GILCHRIST[27] and dissolved in cold 0.1 *N* sulphuric acid, without heating, to prepare several standard solutions ranging from 0.001 *M* to 0.1 *M* Zr concentration. Exact standard values were established by mandelic acid precipitation[28].

To observe depolymerisation effects more clearly, the standard 0.1 *M* solution was firstly "highly" polymerised. The procedure was to raise the pH to 1.8 (approximately the highest value permissible to retain a clear solution) and heat at 90° for 30 min. The polymerised zirconium species formed by this technique remained in clear solution indefinitely at pH 1.8 in contrast to monomer or less highly polymerised species which, if adjusted to pH 1.8 at 0.1 *M* concentration, deposited a zirconium sulphate complex after several days.

Instead of depolymerising by evaporating to fumes with sulphuric acid, solutions were heated for a fixed time with increasing concentrations of sulphuric acid. Determinations of the polymeric state of the zirconium species before and after the sulphuric acid treatment were made by adding excess EDTA to the cooled solutions from the digestions, ignoring any precipitate which formed; adjusting to pH 5.6 with acetate buffer; boiling for several minutes; cooling, and titrating excess of EDTA with zinc standard solution using xylenol orange indicator.

Zirconium recoveries are shown in Table I. Test (*a*) shows the recovery obtained without a depolymerisation step and test (*b*) shows that further heating in the absence of sulphuric acid decreased the recovery as additional polymerisation occurred. Precipitates which formed on the addition of EDTA redissolved when the solutions were buffered at pH 5.6 for the zinc back-titration, but their initial formation always indicated that poor recoveries would be obtained. It is evident that a digestion with sulphuric acid, at a concentration in the solution of not less than 5 *N*, was required to give quantitative recoveries. The digestion time of 15 min represents a minor improvement on the MILNER AND PHENNAH fuming technique which is equally quantitative.

TABLE I

DEPOLYMERISATION OF POLYMERIC ZIRCONIUM SPECIES

(Zr taken: 92.1 mg (10-ml aliquot of 0.1 *M* zirconium sulphate polymerised at pH 1.8 at 90°); solution volume in digestion with sulphuric acid: 20 ml; zirconium concentration: $5 \cdot 10^{-2}$ *M*)

H_2SO_4 20 N added (ml)	*Acidity or pH*	*Boiling time (min)*	*Zr found (mg)*	*Zr recovery (%)*
Nil (a)	1.8	Nil	29.9	32.5
Nil (b)	1.8	15	25.3	27.5
1	1 *N*	15	79.5	86.3
3	3 *N*	15	88.3	95.8
4	4 *N*	15	91.0	98.8
5	5 *N*	15	92.1	100.0
10	10 *N*	15	92.1	100.0

As an example of zirconium solutions which may frequently be encountered in the laboratory, stock solutions were prepared without a deliberate polymerisation technique, by dissolving zirconium sulphate in 0.1 *N* sulphuric acid without heating. Solutions of this relatively low acidity tend towards the polymeric state in a slow process of ageing. This is illustrated by the results in Table II, obtained by the zinc back-titration procedure as for Table I. The low recovery confirms the presence of

TABLE II

EFFECT OF AGEING 0.1 *M* ZIRCONIUM SULPHATE SOLUTION AT ROOM TEMPERATURE
(Acidity: H_2SO_4 0.1 *N*; Zr taken: 92.1 mg)

Age of solution (days)	*Zr found (mg)*	*Zr recovery (%)*
1	44.0	47.8
6	22.8	24.8
13	19.1	20.8

polymeric species in an ordinary preparation using 0.1 *N* sulphuric acid as the dissolving medium. Even a 0.5 *N* sulphuric acid medium did not prevent polymerisation of 0.1 *M* zirconium solutions and serious errors would therefore arise with the otherwise reliable back-titration procedure; a test of recovery from a cold 0.5 *N* sulphuric acid medium gave only 94% for 92.1 mg Zr. Heating at this concentration of acid only caused further polymerisation and a still lower recovery. To ensure a quantitative recovery in any EDTA back-titration procedure for zirconium, digestion at not less than 5 *N* sulphuric acid concentration would appear to be an essential preliminary step.

Attempts to depolymerise sulphate systems with other strong acids, *e.g.* hot concentrated 11 *N* hydrochloric acid or evaporation to fumes with perchloric acid were completely unsuccessful as the zirconium–EDTA–sulphate precipitate still formed after such digestions on the addition of EDTA. Thus, to establish a direct titration procedure, only sulphuric acid depolymerisation has the widest possible application to all zirconium systems regardless of concentration of zirconium and any unknown previous ageing characteristics.

Direct titration of zirconium with EDTA in sulphate systems

The sharpest indicator changes with any feasible metal indicator occurring simultaneously with a quantitative EDTA reaction take place at the pH which provides ideal conditions for polymerisation even in solutions which have been freshly depolymerised. This was readily shown qualitatively by evaporating an aliquot of zirconium sulphate solution (0.1 *M*) representing 90 mg Zr to fumes with 3 ml of sulphuric acid and diluting to 2 *N* acidity. EDTA added to one portion of solution yielded a clear solution; EDTA added to another which had been adjusted to pH 1.0 produced the white precipitate, indicating that repolymerisation occurred at this pH even without heating.

The major barrier to a successful direct EDTA titration therefore lies in the fact that the pH for an optimum end-point cannot be established at the start of the titration. The alternative of titrating at a higher acidity is likewise unacceptable as the acidities required to preserve the depolymerised state (1–3 *N* H_2SO_4) are too high for any indicator to function satisfactorily, or for the EDTA reaction to be quantitative.

It has, however, been possible to work out a satisfactory and completely reliable procedure which is based on the following observations:

(*a*) Solutions of low zirconium concentration are polymerised less readily than solutions of higher concentration.

(*b*) Xylenol orange indicator can give useful, though not sharp, colour reactions with zirconium ions at the high levels of acidity required to preserve the depolymerised state.

(*c*) EDTA is also of value in preserving a depolymerised state.

EXPERIMENTAL

Direct titration procedure A

For EDTA titrant 0.1 *M*. Amount of ZrO_2: 60–600 mg.

Reagents. Disodium EDTA 0.1 M. Dissolve 37.2 g recrystallised Na_2EDTA in distilled water to 1 litre volume.

Xylenol orange indicator. 0.1% aqueous. Certain commercial products may be of unsatisfactory quality.

Method. Measure an aliquot of zirconium solution, ideally 10 ml (or larger volumes evaporated to this volume) into 150-ml Erlenmeyer or wide-mouth conical beaker. Add 10 ml of 10 *N* sulphuric acid and boil gently for 15 min. Add slowly 40 ml of water, or dilute to 60 ml, add 8 drops (0.4 ml) of xylenol orange indicator and heat to boiling. Commence titrating with EDTA at 1.7–2 *N* acidity to a colour change from purple to a pale orange. Cool somewhat, add 10 ml of 7 *N* ammonia solution and reboil to restore or establish a strong purple. Titrate to a sharp change to lemon yellow.

Confirm the end-point by adding 1–2 ml of the ammonia solution and reheating. No further change from the lemon yellow indicates a true end-point. (Excessive use of ammonia solution produces an alkaline indicator purple.)

Notes: (*a*) Loss of volume in the depolymerisation digestion is immaterial, as evaporation to fumes is equally effective.

(*b*) 100 meq. of sulphuric acid is a desirable maximum, and prior evaporation of an aliquot if necessary to establish the 5 *N* acid concentration is preferable to using additional acid.

(*c*) Titration with EDTA should be commenced at an acidity not less than 2 *N* for amounts of zirconium above 60 mg in order to avoid repolymerisation.

(*d*) The amount of ammonia solution specified when related to 100 meq. of sulphuric acid places the end-point pH satisfactorily about pH 1.2 yielding a sharp end-point.

Procedure B

For EDTA titrant 0.01 *M*. Amount of ZrO_2: 1–60 mg.

Identical with Procedure A; the starting colour is brown-orange rather than purple which is obtained later in the titration on ammonia addition.

Procedure C

For EDTA titrant 0.001 *M*. Amount of ZrO_2: 0.1–6 mg.

Decrease the amount of sulphuric acid to 10 meq. and depolymerise by evaporation just to fumes. Cool, add 25 ml of hot water, boil and titrate as in Procedure A using only 1 ml of 7 *N* ammonia solution to establish the purple colour necessary to complete the titration. Reboil to confirm the end-point.

RESULTS

Colour at beginning of titration

When the amount of zirconium involved is insufficient to produce a purple or reddish colour at the start it may be necessary to add a portion of the allocated quantity of ammonia solution. This does not cause repolymerisation if used only sufficiently to establish a purple colour, as the amount of zirconium indicated by the absence of a purple colour is then not at a sufficiently high concentration to suffer a polymerisation error.

Effect of addition point of ammonia solution on titrating accuracy

Although it has not been found necessary to add ammonia early in the titration the effect of adding various proportions of the allocated quantity at the beginning was studied for each of the 3 zirconium concentration levels. The amounts of zirconium taken were equivalent to a theoretical volume of titrant of 10.04 ml for each case involving 0.1 *M*, 0.01 *M* and 0.001 *M* EDTA. Depolymerisation was effected with 100 meq. of sulphuric acid for 0.1 *M* and 0.01 *M* tests and with 10 meq. for the 0.001 *M* (0.9 mg Zr) test. Results are shown in Fig. 1. For highest accuracy, it can be seen that addition of more than 25% of the required ammonia at the beginning of the titration should be avoided. There is in fact no difficulty in recognising the colour changes and avoiding any addition of ammonia until approximately 90% of the required volume of EDTA has been added.

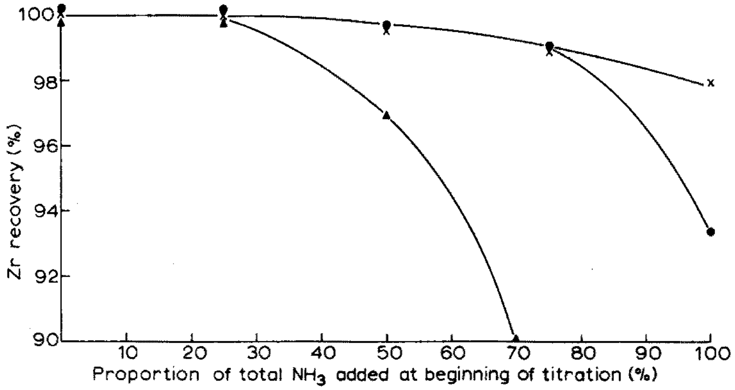


Fig. 1. Effect of addition of ammonia solution at beginning of titration. ● 91.6 mg Zr: commencing acidity 2 *N*; × 9.16 mg Zr: commencing acidity 2 *N*; ▲ 0.92 mg Zr: commencing acidity 0.4 *N*.

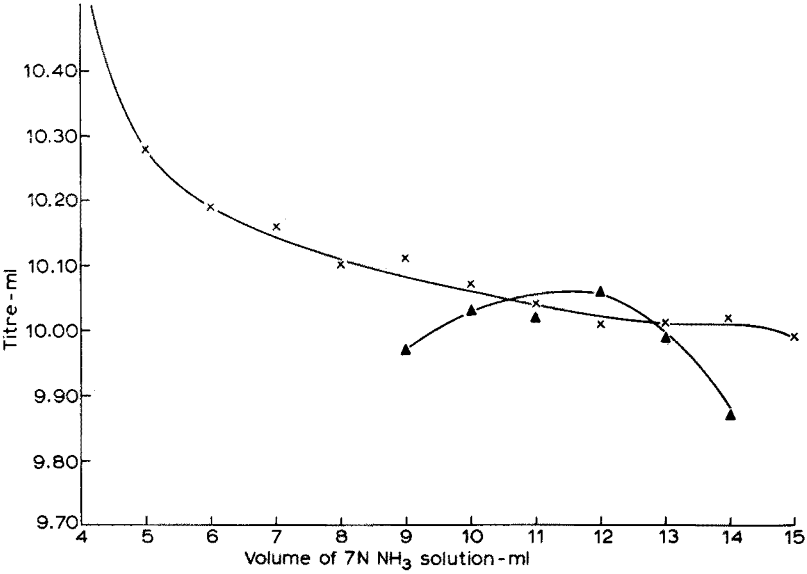


Fig. 2. Effect of quantity of ammonia solution on zirconium recovery. × 10.06 ml 0.1 *M* (theoretical volume); ▲ 10.06 ml 0.01 *M* (theoretical volume).

Quantity of ammonia

The effect of varying the quantity from the 10 ml of 7 *N* ammonia solution found ideal for 100 meq. of sulphuric acid was examined in tests using 10 ml of 0.1 *M* and 0.01 *M* zirconium solution. After depolymerisation and dilution to 50 ml, 95% of the expected volume of EDTA was added to each of a series of solutions in which the volume of ammonia solution was varied from 5 to 15 ml for 0.1 *M* EDTA titrant and from 6 to 14 ml for 0.01 *M* EDTA titrant. Solutions were reheated and titrated to the best available end-points. Results are shown in Fig. 2.

These data indicate that a tolerance of 9–12 ml of ammonia solution is allowable at both concentration ranges for errors not greater than ±0.5%. When the correct amount is used, significantly improved accuracy covering the range 6–600 mg ZrO_2 is obtainable.

TABLE III

ZIRCONIUM RECOVERIES USING DIRECT EDTA TITRATION: PROCEDURES A, B AND C

EDTA concentration (M)					
0.1		*0.01*		*0.001*	
Zr taken (mg)	*Zr found (mg)*	*Zr taken (mg)*	*Zr found (mg)*	*Zr taken (mg)*	*Zr found (mg)*
46.2	46.2	9.21	9.22	0.046	0.044
92.5	92.5	18.45	18.52	0.185	0.181
191.5	192.0	36.90	36.96	0.462	0.459
365.0	366.0			0.925	0.922
636.0	638.0			1.85	1.85
				4.60	4.58

Typical recoveries from aliquots of zirconium sulphate solutions using the recommended procedures for the 3 levels of EDTA concentration are shown in Table III.

DISCUSSION

The studies have shown that sulphate systems involving strong sulphuric acid depolymerisation of polynuclear zirconium species are essential for the determination of amounts of zirconium by direct EDTA titration over a wide range, conveniently representing 1 ml 0.001 *M* to 50 ml 0.1 *M* titrant or 120 μg to 600 mg ZrO_2. (With 0.001 *M* titrant in a microburette 10 μg Zr can be reliably titrated.) Reports that sulphate ion causes interference with indirect titrimetry and renders direct titrimetry impossible can now be modified. It is to be noted, however, that sulphuric acid systems improperly handled after depolymerisation can repolymerise to an extent causing greater errors than may arise from weakly polymerised systems of other acids. This factor has resulted in a number of workers restricting themselves to non-sulphate systems in which a measure of success is only obtained at very low zirconium concentrations (the less than 35 mg amounts in 200-ml volume sometimes quoted). Such solutions are not highly polymerised, provided that they have not been heated at low acidities (0.1–0.5 *N*), and in many cases they can be almost completely depolymerised during a slow EDTA titration or by heating with excess EDTA. If however solutions of any zirconium concentration are polymerised strongly by heating at low acidities (0.1–0.5 N) the limitations of the published direct titration procedures would become even more obvious. With such solutions, depolymerisation by digestion with strong acids such as hydrochloric, nitric or even fuming with perchloric acid is quite ineffective particularly at 0.01 to 0.1 M zirconium concentrations. With the exception of hydrofluoric acid[29], which is inapplicable in zirconium–EDTA systems, only sulphuric acid is in our experience completely effective for depolymerisation in all systems. It has the additional value of extending direct and indirect titrimetry to sulphate-bearing materials which are extensively employed commercially and frequently encountered analytically as a result of pyrosulphate fusions.

The virtually unique property of sulphuric acid to effect chain cleavage of polynuclear zirconium species at sufficiently high concentrations (>5 N) arises from the ability of sulphate ion to form complexes with zirconium, a property not shared to the same extent by other acids permissible in the EDTA system. After depolymerisation it is important, particularly with zirconium concentrations higher than 0.01 M, that the acidity should be approaching 2 N in sulphuric acid for the addition of EDTA. As only depolymerised species are present under such conditions no precipitates are formed and, if excess EDTA is added, the pH may be raised to any value between 2 and 6 for a back-titration procedure. This approach has been used in the several back-titration procedures that have been found satisfactory[1,4,5].

The failure of the previous attempts at direct titrimetry derives from the fact that it was apparently not considered possible to add EDTA at acidities higher than 1 N, a requirement which had to await the introduction of an indicator such as xylenol orange to have a possibility of success. The ability of this indicator to determine a suitable stage in the titration for the adjustment of pH to the optimum end-point value allows a single addition of ammonia to be made without a pH measurement being required and confers essential simplicity on the new procedure.

SUMMARY

Accurate results in EDTA titration of zirconium at all concentration levels can only be obtained if zirconium ions are converted to a depolymerised form. Treatment with strong sulphuric acid is more generally applicable for this conversion than treatment with other mineral acids which fail to depolymerise highly polymerised zirconium sulphate systems. To avoid the zirconium species becoming repolymerised under the conditions required for a direct titration, EDTA is added at high acidity (1–2 N sulphuric acid, depending on zirconium concentration). At an appropriate stage of the titration, easily determined by a colour change obtained with xylenol orange indicator, a single addition of a fixed quantity of ammonia solution establishes the correct pH for a sharp end-point. Results are quantitative and amounts of zirconium from 10 μg to 500 mg can be determined with appropriate standard EDTA solutions.

RÉSUMÉ

Pour obtenir des résultats précis lors du dosage du zirconium par l'EDTA, il est nécessaire de procéder à une dépolymérisation du zirconium. Pour cela, on effectue généralement un traitement à l'acide sulfurique concentré. L'EDTA est ensuite ajouté en milieu très acide (H_2SO_4 1–2 *N*). A un moment déterminé du titrage, fixé par un changement de coloration du xylénol-orange, on ajoute une certaine quantité d'ammoniaque, permettant d'obtenir le pH nécessaire pour un virage net. Les résultats sont quantitatifs et des teneurs de 10 μg à 500 mg de zirconium peuvent être dosées.

ZUSAMMENFASSUNG

Genaue Ergebnisse bei der EDTA-Titration von Zirkonium bei allen Konzentrationsbereichen erhält man nur, wenn die Zirkoniumionen in eine depolymerisierte Form umgewandelt werden. Die Behandlung mit starker Schwefelsäure ist dazu besser geeignet als mit anderen Mineralsäuren, die bei der Depolymerisation hochpolymerisierter Zirkoniumsulfatsysteme versagen. Um die Repolymerisation bei der Titration zu vermeiden, wird EDTA bei hoher Säurekonzentration (1–2 *N* Schwefelsäure, je nach Zirkonium konzentration) zugegeben. Bei einer geeigneten Stufe der Titration, die leicht durch einen Farbwechsel, den man mit einem Xylenolorange-Indikator erhält, bestimmt werden kann, ergibt eine einmalige Zugabe einer bestimmten Menge Ammoniaklösung den genauen pH-Wert für einen scharfen Endpunkt. Die Ergebnisse sind quantitativ und Zirkoniummengen von 10 μg bis 500 mg können mit geeigneten EDTA-Lösungen bestimmt werden.

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THE USE OF A LITHIUM-DRIFTED GERMANIUM DIODE TO DETERMINE CARBON IN STEELS BY MEASUREMENT OF PROMPT γ-RADIATION

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(Received March 26th, 1965)

Nuclear methods of instrumental analysis relying on γ-ray spectroscopy of an intact sample after irradiation, often require the analysis of complex spectra, but their application is frequently limited by the resolution attainable by thallium-activated sodium iodide or similar scintillators.

Recently solid state radiation detectors have been produced which can provide high resolution of γ-rays, and in particular the lithium-drifted germanium diode is potentially a most useful detector for γ-ray spectroscopy[1-6]. However, the efficiency of the small solid state detectors at present generally available is very much lower than can be achieved with a thallium-activated sodium iodide scintillator, and whilst this is offset to some extent by the reduced energy spread of the γ-peak, low sensitivity has restricted their use. Nevertheless, when samples of high γ-activity are available, the diodes can be usefully applied to γ-ray spectroscopy, for the sharp peaks, which often lie on a relatively smooth background, frequently permit easy calculation of the counts under the peak.

A possible application of these detectors is to the determination of carbon in steels by measurement of the prompt γ-radiation emitted during deuteron bombardment[7], for the yield of 3.09-MeV prompt γ-rays is often high, and although the excellent resolution of the diode is not required to isolate the carbon activity from other γ-rays emitted by steels when the carbon content is high, the sharp peaks obtained simplify calculation of total carbon counts. In this paper, the use of a lithium-drifted germanium diode for this type of carbon determination is reported.

EXPERIMENTAL

Targets

Steel samples from 3 different sources were used as targets. In addition to spectrographic standards SS 31-35 (Bureau of Analysed Samples Ltd.), and steel discs cut from a range of analysed samples supplied by A.E.R.E. Outstation, Chatham, used previously for other prompt radiation experiments[7], a number of steel samples from the range of British Chemical Standards (Bureau of Analysed Samples Ltd.) were available. These were in the form of turnings and were compressed into discs of 0.75 in. diameter and 0.1 in. thickness, by applying a load of 15 tons with the aid of a hydraulic press. The compacted steel samples and the small discs of massive steel were held in the well of a target backplate by a knurled ring as reported earlier[7].The backplate was mounted in a standard target holder on an "O"-ring seal, the complete assembly being held together by a locking ring.

The spectrographic samples, being of 1.75 in. diameter, were substituted for the backplate, and placed directly on the "O"-ring seal of a modified target holder.

Experimental arrangement

A diagram of the flight tube, target and detector is shown in Fig. 1. The deuteron beam from the 90° analysing magnet of the Van de Graaff accelerator was collimated by 1/8-in. diameter tantalum stops before striking the target. The target holder was mounted on an insulating flange connected to the flight tube by flexible bellows, so that the target could be mechanically oscillated to increase the area irradiated. A lead from the target holder carried the charge falling on to the target to a current integrator in the counting room.

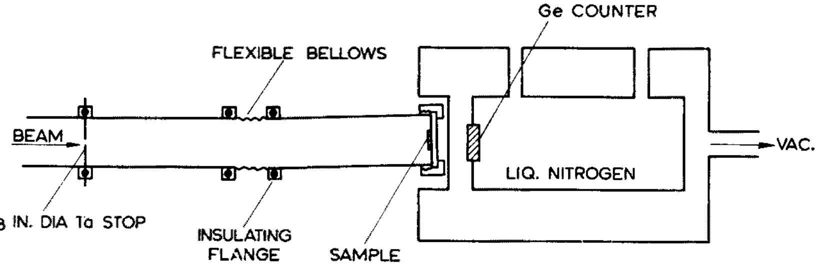

Fig. 1. Diagram of target and detector assembly.

The lithium-drifted germanium diode, housed in a cryostat, was positioned as close to the target as possible, without requiring counting geometry to be disturbed by target changes. The germanium counter used in these experiments was prepared by drifting lithium into gallium-doped germanium and had a sensitive area of 2 cm^2 and a thickness of about 3.5 mm. Operating at liquid nitrogen temperature, the resolution of the system (detector plus electronics) was about 8 keV on 1.33-MeV γ-rays. Full details of the preparation and performance of this type of counter are described elsewhere[8].

The electronics associated with the detector are shown in block form in Fig. 2. The diode was operated at a negative bias voltage of 150 V, and the charge produced by an incident γ-ray amplified using a low-noise, charge-sensitive amplifier type 1786C. Two methods were used to obtain estimates of the 3.09-MeV γ-ray intensity. One method was to analyse the pulse-height spectrum obtained with a 1024-channel analyser; the other was to count the number of events in a particular energy interval. The energy interval was defined using two discriminators, each governing a separate scaler, one set just below, and the other just above the 2.07-MeV double escape peak. Discriminator levels were adjusted to the correct value, using test pulses injected at the input of the pre-amplifier, and the pulses calibrated by means of the multichannel analyser. An immediate measure of the count of the double escape peak could then be obtained by subtracting the smaller from the larger scaler reading.

RESULTS AND DISCUSSION

Typical differences in the γ-spectra obtained from the deuteron irradiation of carbon steels using a 3 × 3″ thallium-activated sodium iodide crystal and a 2 cm² × 3.5 mm lithium-drifted germanium diode as detectors, can be seen by comparing Figs. 3 and 4. In both cases plot A refers to the prompt spectrum and plot B to the spectrum obtained from a count started immediately the irradiation was completed. In both cases the major activity remaining after irradiation gives a γ-peak at an energy of 0.51 MeV, corresponding to the annihilation of positrons, emitted during the decay of neutron-deficient nuclides which are formed during deuteron bombardment (*e.g.* ^{12}C (d,n) ^{13}N). There is, however, considerable difference in the energies of the main carbon peaks in the two prompt spectra. The absorption, in matter, of a γ-ray, with an energy greater than 1.02 MeV can occur by pair production in which the photon is replaced by an electron–positron pair, and in addition to registering a full-energy γ-

(2)

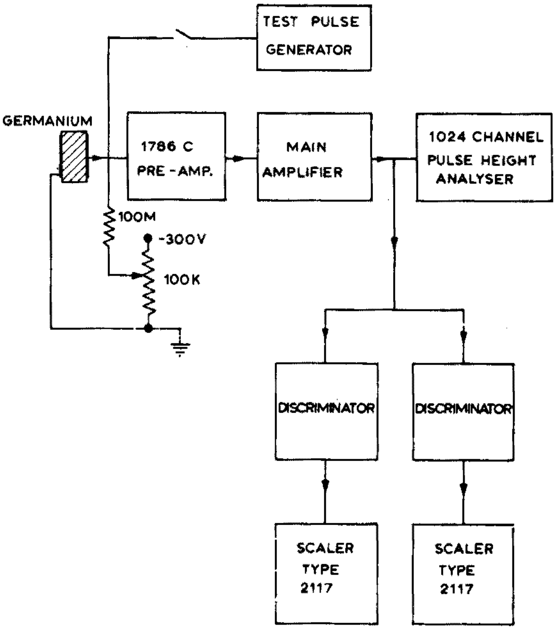

Fig. 2. Block diagram of electronic equipment.

(3)

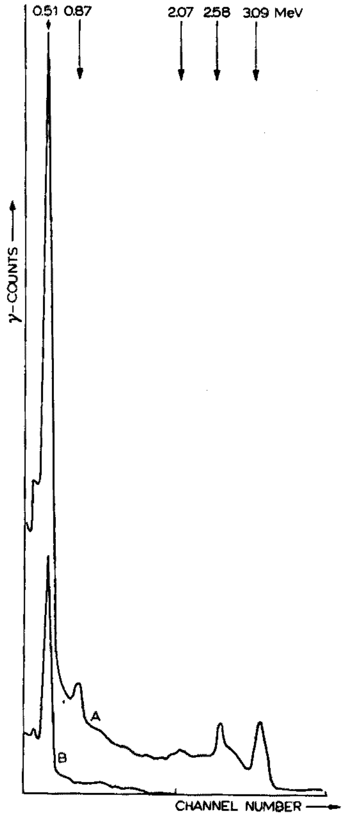

Fig. 3. Typical spectrum of steel irradiated with 1.5-MeV deuterons as detected by a 3 × 3″ NaI (Tl) scintillator. Plot A, prompt spectrum; plot B, spectrum obtained by counting immediately after the completion of irradiation.

peak at E_γ MeV, where E_γ is the total energy of the incident photon, the detector may give peaks at $E_\gamma - 0.51$ MeV and $E_\gamma - 1.02$ MeV due to escape of one or both of the γ-quanta resulting from annihilation of the positron. When a 3 × 3″ thallium-activated sodium iodide crystal is used to detect the prompt spectrum emitted by a steel irradiated with deuterons (Fig. 3, plot A) a peak is obtained at 3.1 MeV corresponding to the full energy of the first excited-to-ground state transition in ^{13}C from the reaction ^{12}C (d,p) ^{13}C, together with single- and double-escape peaks on the Compton continuum at 2.6 and 2.1 MeV respectively. With the thin diode, however, where escape is more probable, the 2.1-MeV double-escape peak provides the major contribution due to carbon to the prompt spectrum, and in the results reported here, the counts in the 2.1-MeV double-escape peak were used as the basis of the determinations. Irradiations usually took about 2 min.

Figure 4 also shows the relatively smooth background on which the double-escape peak stands, thus simplifying calculation of counts in the peak. The further peak at 0.87 MeV, which can be seen in Figs. 3 and 4, is due to the first excited-to-ground state transition in ^{17}O induced by the reaction ^{16}O (d,p) ^{17}O.

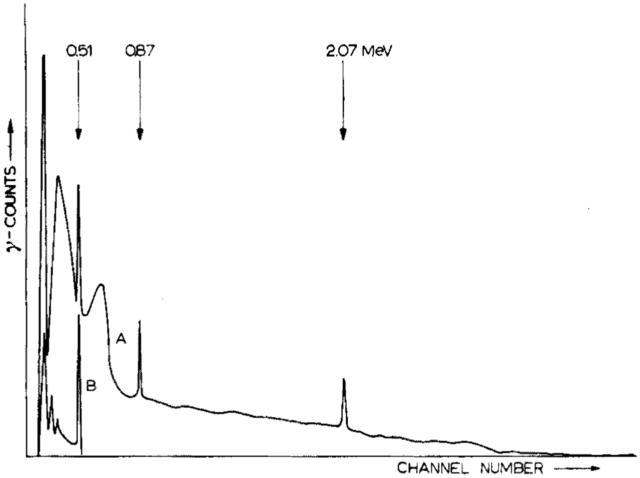

Fig. 4. Typical spectrum of steel irradiated with 1.5-MeV deuterons as detected by a lithium-drifted germanium diode. Plot A, prompt spectrum; plot B, spectrum obtained by counting immediately after the completion of irradiation.

Throughout the experiments reported in this paper, the diode was found to give results (calculated from the 2.1-MeV double-escape peak) which were consistent with the known carbon content of the sample, although slight gain shifts were observed which were attributed to amplifier instability.

Once the diode had been installed and cooled, it was kept at liquid nitrogen temperature for the period during which accelerator time was available, to avoid any deterioration that might occur at room temperature.

Effect of beam current variations

Beam current may vary during irradiation as a result of machine instability, or it may be deliberately altered between successive runs to compensate for changes in the element content of the samples. The count rate of the γ-ray which is to be measured, as recorded by the counting equipment, should therefore be proportional to beam current over the range of currents used. A 0.34%-carbon steel disc was irradiated with deuterons at beam currents varying from 1.0 to 20.0 μA and the count rate of the 2.1-MeV double-escape γ-rays plotted against the deuteron beam current. Results showed that direct proportionality between deuteron current and γ-ray yield was maintained over the range of currents investigated and subsequent experiments with a number of steels of different carbon contents confirmed that counts in the carbon peak for samples irradiated to the same particle dose, were independent of the dose rate.

Irradiation of steel samples of varying carbon content

A thick target excitation curve was obtained for the 3.09-MeV ^{13}C γ-ray, with incident deuteron energies varying from 0.8 to 2.0 MeV. The form of the curve was similar to that already published[9], showing a rapid rise up to about 0.9 MeV, and a further sharp rise above 1.5 MeV, with a rather smaller increase in between. As sufficient sensitivity was achieved with the deuteron energy E_d MeV in the range $1.0 < E_d < 1.5$ MeV no higher energies were used.

The usual method of measuring the prompt γ-rays emitted from the ^{12}C (d,p) ^{13}C reaction during deuteron bombardment of the sample was to total the counts under the 2.1-MeV double-escape peak, from the spectrum recorded by a 1024-channel pulse-height analyser; in Fig. 5 the counts obtained by irradiating samples to a deuteron dose of 600 μc are plotted against the known carbon content of the samples. A good linear dependency was found for spectrographic standards and steel samples supplied by A.E.R.E., Chatham, which were discs of solid steel with a fresh face cut directly before irradiation. Within the limits of experimental error results did not vary as successive faces were cut on the same samples. However, discs of compacted B.C.S. steels for which the surfaces could not be so carefully prepared, were found to

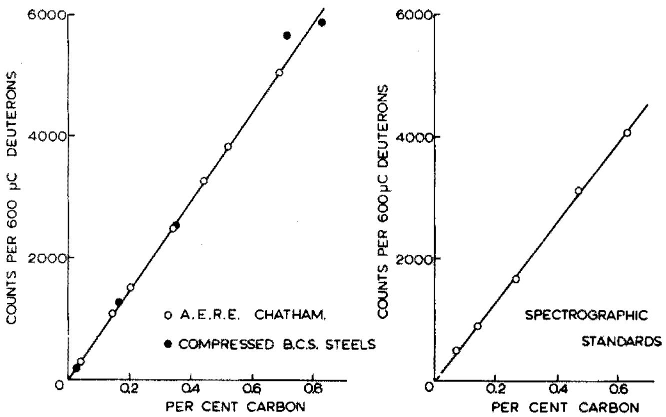

Fig. 5. Plot of count under the 2.1-MeV double-escape peak against known carbon content of the samples. Irradiation with 1.5-MeV deuterons.

give less consistent results. In a separate series of irradiations at reduced geometry but to a deuteron dose of 2000 μc, the standard deviation for 14 successive runs on a 0.69%-carbon steel was ±2.6% and for 12 runs on a 0.34%-carbon steel was ±3.3%. Irradiation of 6 different samples of 0.34%-carbon steel gave a standard deviation of ±4.9%. The type of measurement described above would correspond to an analytical technique dependent upon the use of external standards for calibration.

In order to avoid using a multi-channel pulse-height analyser, a second series of results was obtained by subtracting the count of a scaler with a discriminator set just above the double-escape peak from one with a discriminator set just below. Again a straight line was obtained when the count difference of the scalers was plotted against the known carbon content of the samples, but in this case the line did not pass through the origin, and showed an appreciable background count.

CONCLUSION

The high resolution of the lithium-drifted germanium diode can show an advantage over scintillation detectors applied to counting prompt γ-rays, when the intensity of γ-radiation is sufficiently high to offset the effects of low sensitivity. The feasibility of using this type of counter in an analytical method has been demonstrated in a straightforward case, and its potential uses in resolving more complex prompt γ-spectra, which are frequently encountered, and in simultaneous analysis for more than one element, are apparent.

SUMMARY

A lithium-drifted germanium p–i–n diode was used as detector to measure the prompt radiation emitted by the reaction ^{12}C (d,p) ^{13}C during the irradiation of steels with low-energy deuterons. Typical spectra obtained using a diode and a thallium-activated sodium iodide crystal are compared, and results given for a number of standard steel samples.

RÉSUMÉ

Une diode lithium–germanium p–i–n est utilisée comme détecteur pour mesurer la radiation immédiate émise par la réaction ^{12}C(d,p)^{13}C au cours de l'irradiation d'aciers avec des deutérons de faible énergie. Les spectres typiques obtenus à l'aide d'une diode et d'un cristal thallium–iodure de sodium activé sont comparés. On donne les résultats pour un certain nombre d'étalons en acier.

ZUSAMMENFASSUNG

Eine Lithium–Germanium-p–i–n-Diode wurde als Detektor zum Messen der Strahlung benutzt, die bei der Reaktion ^{12}C(d,p)^{13}C während der Bestrahlung von Stählen mit niederenergetischen Deuteronen emittiert wird. Typische Spektren, die mit einer Diode und einem talliumaktivierten Natriumjodidkristall erhalten wurden, werden verglichen. Für eine Anzahl Standardstahlproben werden die Ergebnisse angegeben.

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THE SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH 8-HYDROXYQUINOLINE

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(Received January 6th, 1965)

Determination of trace zirconium in refractory alloys has always been a difficult analytical problem. Although SANDELL[1] includes a number of colorimetric reagents for the determination of trace zirconium, many lack either sensitivity or selectivity. Others[2-8] suffer from serious interference of one or more of the anions: sulfate, fluoride, oxalate, tartrate, or citrate.

Xylenol orange, which has the desired sensitivity and selectivity, was used by CHENG[4]. Difficulty was experienced in this laboratory in obtaining reproducible results, presumably because of insufficiently pure reagent. Consequently, a search was initiated for a superior reagent.

HYNECK AND WRANGELL[9] noted the serious positive interference of zirconium in the aluminum–oxine determination. Their data suggested that zirconium may be precipitated with oxine. Although SANDELL[1] includes a summary of various metal oxinate precipitates, no information regarding applications are available. An investigation of the zirconium–oxine system brought the following results.

EXPERIMENTAL

Apparatus and reagents

Beckman Model DU or equivalent, with 1-cm quartz absorption cells.

Zirconium standard (40 µg/ml). Dissolve exactly 0.1413 g of nuclear grade zirconium oxychloride octahydrate in 50 ml of 1:1 perchloric acid. Dilute to 1 l with 1:1 perchloric acid.

Ammonium chloride–ammonium tartrate solution. Dissolve 120 g of ammonium chloride and 120 g of ammonium tartrate in water and dilute to 1 l.

Dilute hydrofluoric acid. Dilute 48% hydrofluoric acid 1:10 and store in polyethylene.

Recommended procedure

Transfer a sample solution containing 20–200 µg zirconium (which may be the effluent from an ion exchange or other separation, and comprised of a solution of a mineral acid, oxalic acid, hydrofluoric acid, or a mixture of the above) to a 150-ml beaker. Add 10 ml of dilute hydrofluoric acid, if not present, and 10 ml of ammonium chloride–ammonium tartrate solution. Make approximately neutral with ammonia water and dilute to *ca.* 50 ml with water. Adjust the pH to 8.9±0.1 with ammonia.

Add 1 ml of a 5% solution of 8-hydroxyquinoline in acetone and allow to stand for 30 min. Transfer to a 125-ml separatory funnel and extract with three 10-ml portions of chloroform, shaking for 30 sec each time. Combine the chloroform extracts in a 50-ml volumetric flask, and dilute to the mark. Add *ca.* 1 g of anhydrous sodium sulfate to the flask to remove any trace of water. Carry a reagent blank through the same procedure. Measure the absorbance of the extract at 386 mμ using chloroform as the reference. Subtract the reagent blank absorbance from the sample and determine the amount of zirconium from a calibration curve prepared previously from standard zirconium solutions.

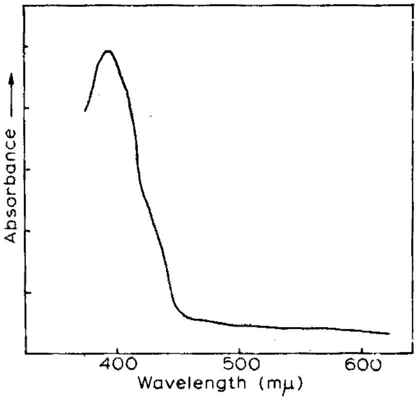
RESULTS AND DISCUSSION

Absorption curve

The absorption spectrum for zirconium–oxine complex is shown in Fig. 1, with a maximum appearing at 386 mμ. A calibration curve followed Beer's law up to a concentration of 6 μg/ml, with a molar absorptivity of 14,700.

Effect of pH

A series of samples containing 100 μg of zirconium was prepared, adjusting samples to pH 6 and below with an ammonium acetate–acetic acid buffer, and to pH 8 and above with an ammonia–ammonium chloride buffer. Figure 2 shows a maximum absorbance at a pH of 8.9.



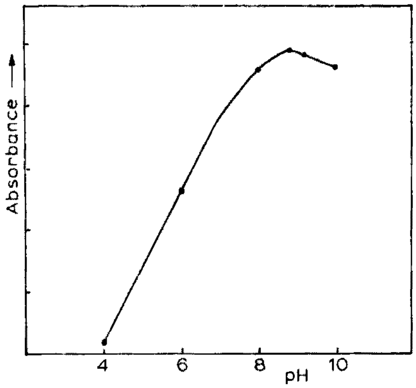


Fig. 1. Absorption spectra of zirconium–oxine complex in chloroform.

Fig. 2. pH Dependence of the formation of the zirconium–oxine complex.

Development of complex with time

The minimum time for complete development of the zirconium–oxine complex, before extraction with chloroform, was 30 min. The system was found to be stable for at least an additional 30 min. The addition of oxine to an aqueous solution to develop the zirconium–oxine complex before extracting with chloroform is felt to be an advantage over the method of extracting the sample with oxine dissolved in chloroform, because equilibrium is reached more rapidly.

Prevention of hydrolysis

A suitable complexing agent is required, during adjustment of pH, to prevent the hydrolysis of zirconium. Oxalic and tartaric acids were reported by STARY[10] in his study of metal oxinates. SHAKASHIRO AND FREUND[11] used an oxalic acid system with success. Initial studies in this laboratory employed tartaric acid in varying amounts, resulting in the above procedure. A minimum of 4 ml of 20% tartaric acid was required to prevent hydrolysis.

Later studies revealed that fluoride ion worked equally well, if not better, in this capacity. A test was made by adding various amounts of fluoride to different sets of reagent blanks and zirconium standards. The recommended procedure was followed, except for one set in which the tartrate was deleted. The results, as represented by Table I, show that fluoride had no adverse effects on the determination.

TABLE I

EFFECT OF FLUORIDE ON ABSORBANCE

Sample	*Amount of F^- added*	*Absorbance*	
		Gross	*Net*
Reagent blank	0	0.061	
210 μg Zr	0	0.722	0.661
210 μg Zr	1000 μg as NaF	0.733	0.672
Reagent blank	20 ml of 1% HF	0.027	
210 μg Zr	20 ml of 1% HF	0.704	0.677
210 μg Zr	20 ml of 1% HF	0.702	0.675
Reagent blank[a]	2 ml of conc. HF	0.028	
210 μg Zr[a]	2 ml of conc. HF	0.696	0.668
210 μg Zr[a]	2 ml of conc. HF	0.698	0.670
Reagent blank	0	0.050	
250 μg Hf	0	0.447	0.397
Reagent blank	2 ml HF	0.017	
250 μg Hf	2 ml HF	0.414	0.397

[a] No tartaric acid added.

Interferences

Sulfate, fluoride, oxalate, tartrate and citrate anions could all be tolerated in gross amounts in this method. Phosphate did not interfere when present in amounts of 1.5 mg or less.

No extensive study of interferences by metals was made because of the extensive studies of SANDELL[1] and STARY[10]. Some tests were made during which a suspected interference from titanium and niobium was confirmed. Also, it was found that aluminum interference was eliminated by the addition of fluoride. This probably accounts for the decrease in reagent blank upon addition of fluoride as shown in Table I, aluminum being a common impurity in many reagents and a constituent of most glassware. Table I includes a set of samples of hafnium, indicating that hafnium may be determined equally well by the same method.

SUMMARY

A superior spectrophotometric method is proposed for determining small amounts of zirconium as the 8-hydroxyquinolinate in chloroform, measured at 386 mμ. The molar absorptivity is 14,700. In contrast to other available methods, anions such as chloride, sulfate, perchlorate, tartrate, oxalate, and fluoride do not interfere.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique du zirconium sous forme d'hydroxy-8-quinoléate, dans le chloroforme, à 386 mμ. Le coefficient d'extinction molaire est de 14,700. Contrairement à d'autres méthodes, les anions: chlorure, sulfate, perchlorate, tartrate, oxalate et fluorure ne gênent pas.

ZUSAMMENFASSUNG

Es wird eine spektralphotometrische Methode zur Bestimmung kleiner Zirkoniumgehalte als 8-Hydroxychinolin in Chloroform vorgeschlagen. Gemessen wird bei 386 mμ. Der molare Extinktionskoeffizient beträgt 14700. Im Gegensatz zu anderen verfügbaren Methoden stören die Anionen Chlorid, Sulfat, Perchlorat, Tartrat, Oxalat und Fluorid nicht.

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DETERMINATION OF TITANIUM AND ZIRCONIUM IN MOLYBDENUM BASE ALLOYS BY ION EXCHANGE

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(Received January 6th, 1965)

The demand of the aero-space industry for thermally resistant materials of construction has led to the development of many new alloys. Molybdenum, alloyed with small amounts of titanium and zirconium, exhibits desirable properties at high temperature. Despite their growing importance, very little has been published on the analysis of such refractory alloys. Ion exchange, using mixtures of hydrofluoric–hydrochloric acids and the strongly basic resin Dowex-1, has been used[1–3]. Oxalic acid is known to form stable complexes with titanium, molybdenum, and zirconium, but because the complexes are very stable large volumes of eluants are required for stripping. This problem has been attacked either by using low concentrations of the oxalic acid or by the use of an oxalic–inorganic acid mixture. WACKER AND BALDWIN[4] found that niobium is taken up on Dowex-1 from 0.4 *M* oxalic acid and eluted with 1 *M* hydrochloric–0.01 *M* oxalic acid solution. SPEEKE AND HOSTE[5] have also shown that niobium and tantalum can be separated either with 0.01 *M* oxalic–2 *M* hydrochloric solution or 0.5 *M* oxalic–1 *M* hydrochloric solution on a Dowex 1–X8 column. BANDI *et al.*[6] used different oxalic–citric–hydrochloric acid mixtures and hydrogen peroxide to separate zirconium, titanium, niobium, tantalum, tungsten and molybdenum, with the zirconium and titanium coming out in the same fraction. Thus a second anion-exchange step was required. Very little work has been done, however, in the sulfuric–oxalic acid medium.

After a systematic study of the distribution coefficients of titanium, zirconium and molybdenum, a simple procedure was developed to determine as little as 0.05% Ti, 0.05% Zr in a molybdenum base alloy. This procedure was applied to the analysis of the TZM alloy and gave results reproducible within 1%. The procedure was extended to the determination of high levels of zirconium and titanium in molybdenum alloys.

EXPERIMENTAL

Apparatus

Ion-exchange column. A conventional glass column, 23 cm high, 1.9 cm inside diameter, was pulled to a tip and plugged with glass wool at the outlet. The eluant was introduced through a 500-ml separatory funnel whose stem was attached to a 5-cm capillary tube by a small piece of rubber tubing. The flow rate was controlled by the height of the funnel and the bore of the capillary tube. An automatic fraction collector was connected electrically with a 20-ml syphon pipet.

Spectrophotometers. Both Beckman Models B and DB were used. The measurements were carried out at wavelengths of 410 mμ (titanium–tiron[7]), 386 mμ (zirconium–oxine[8]) and 330 mμ (molybdenum–hydrogen peroxide[9]), using 1-cm cells.

Reagents

Metal stock solutions. Zirconium and titanium solutions containing 1 mg/ml were prepared from the pure metals by solution in 1:1 nitric acid and a few drops of hydrofluoric acid, followed by fuming with sulfuric acid to dryness. The residue was dissolved in 5% sulfuric acid. The 1 mg/ml molybdenum solution was prepared by dissolving the pure metal in 1:1 sulfuric acid and a minimum amount of nitric acid. After fuming, the residue was dissolved in 5% sulfuric acid.

Ion-exchange resin. The strongly basic Dowex 1-X8 chloride form (200–400 mesh) was used throughout this work. The pretreatment of the resin and its transfer into the sulfate form was done as described by MACHLAN AND HAGUE[10], with a final resin bed height of 16 cm. When the column was not in use, it was washed with 200 ml of deionized water[11]. To prepare the column for a run, 250 ml of 6% sulfuric–0.025 *M* oxalic acid solution was passed. For the distribution coefficient measurements the sulfate form of the resin was air-dried to a constant weight.

Solutions. The eluant, 6% sulfuric–0.025 *M* oxalic acid solution, was prepared by mixing 60 ml of concentrated sulfuric acid with about 800 ml of water in a 1-l volumetric flask. After cooling, 25 ml of 1 *M* oxalic acid was added and the volume was adjusted to 1 l with water. The 10% sulfuric–0.025 *M* oxalic acid solution was prepared in a similar manner. Solutions necessary for spectrophotometric determinations were prepared from Reagent-Grade materials.

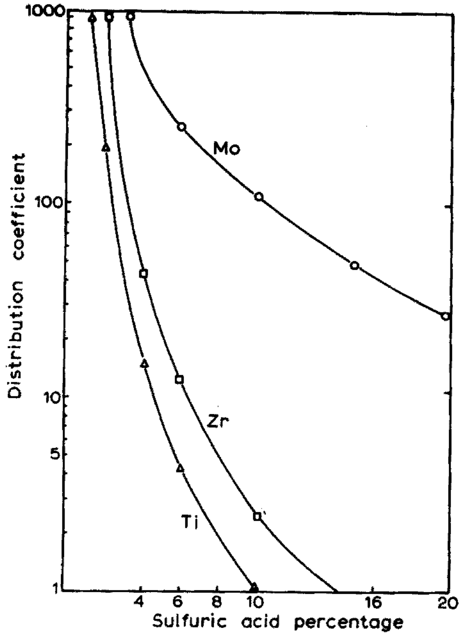
Determination of distribution coefficients

Approximately 1 g of the air-dried resin was placed in a 125-ml glass-stoppered Erlenmeyer flask, followed by pipetting 5 ml of the metal stock solution and the proper amount of dilute acids and water to a final volume of 50 ml. The stoppered flask was shaken for 10 h and an aliquot from the supernatant liquid was analyzed for its metal ion content by the appropriate colorimetric method. The results of these studies are shown in Figs. 1 and 2.

Separation procedures

For a molybdenum base alloy containing less than 1% titanium and 1% zirconium. Weigh accurately 100 mg of the alloy and dissolve it in a platinum dish with 10 ml of 1:1 sulfuric acid, 1 ml of nitric acid and 2 drops of hydrofluoric acid. Fume to dryness and dissolve the residue in 50 ml of the 6% sulfuric–0.025 *M* oxalic acid solution. Transfer to the 16-cm resin bed column and collect the eluate. Complete the titanium elution by passing 110 ml of the 6%–0.025 *M* solution at a flow rate of 1.5–2 ml/min. The combined 160 ml contains the titanium fraction, which is determined spectrophotometrically with tiron. A concentration step, such as evaporation, might be necessary if the titanium content of the sample is less than 0.5 mg. It was noticed that equally good results were obtained whether or not the oxalate content of the titanium aliquot was destroyed by nitric acid. Hence a higher oxalate level than originally pointed out by YOE AND ARMSTRONG[7] can be tolerated.

Next, elute the zirconium with 160 ml of 10% sulfuric–0.025 *M* oxalic acid solution, also at a flow rate of 1.5–2 ml/min. As with titanium, a concentration step is



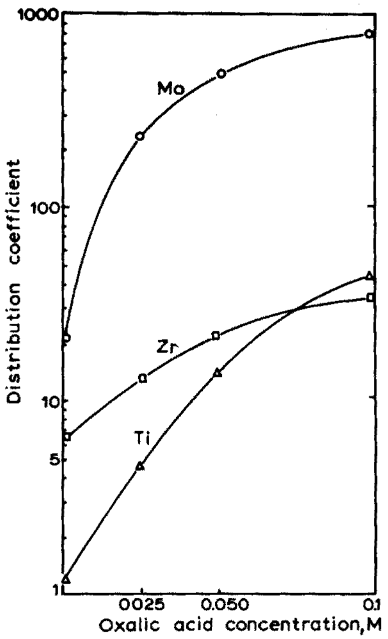


Fig. 1. Distribution coefficients of titanium, zirconium and molybdenum *vs.* sulfuric acid percentage in 0.025 *M* oxalic acid solution.

Fig. 2. Distribution coefficients of zirconium, titanium and molybdenum *vs.* oxalic acid concentration in the 6% sulfuric acid solution.

necessary if less than 0.5 mg of zirconium is present in the original sample. Determine zirconium spectrophotometrically with oxine. Finally elute molybdenum with 500 ml of 20% sulfuric acid.

For a molybdenum alloy containing larger amounts of titanium and zirconium. Some modifications of the above procedure are necessary because of the broadening of the elution curves. A 10–20 mg sample size is quite adequate; this is put in 25 ml of the 6%–0.025 *M* sulfuric oxalic acid solution. Elution of titanium is complete with 165 ml of the 6%–0.025 *M* acid mixture; 200 ml of the 10%–0.025 *M* solution elutes zirconium and finally 300 ml of the 20% sulfuric acid solution removes molybdenum from the column.

Table I shows analytical results obtained on several synthetic alloys and a

TABLE I

ANALYSIS OF MOLYBDENUM ALLOYS

Sample weight (mg)	*Titanium*			*Zirconium*		
	Present (mg)	*Found (mg)*	*Recovery (%)*	*Present (mg)*	*Found (mg)*	*Recovery (%)*
100	0.05	0.05	100	0.08	0.079	98.8
50	0.20	0.195	97.5	0.40	0.404	101
20	1.00	0.99	99	1.00	0.98	98
20	3.50	3.45	98.6	2.1	2.12	101
10	4.00	3.94	98.5	0.2	0.196	98
15	0.50	0.52	104	5.0	4.97	99.4

TZM alloy obtained from Wah Chang Corporation, Albany, Oregon. Every "found" value represents the average of 3 experiments.

RESULTS AND DISCUSSION

Although distribution coefficients could be used to calculate the volume of eluant required to elute a metal ion from a given column[12], it is more reliable to determine this volume by collecting actual fractions from the column and analyzing them separately. The D values in this respect would rather predict the optimum conditions for the separation. In our case, as an example, the 6%–0.025 *M* solution looked promising because it indicated that titanium was not absorbed strongly on the column ($D \approx 4$) while zirconium was absorbed moderately ($D \approx 14$) and molybdenum was held tightly ($D \approx 250$).

It is clear from Fig. 1 that no significant level of titanium anionic species is present in the 6%–0.025 *M* solution. This is in agreement with BABKO AND DUBOVENKO[13] who found that at $pH < 1$ titanium forms the simple complex $TiOC_2O_4$ with oxalic acid. Although their studies were conducted in the non-complexing medium of perchloric acid, sulfuric acid at the 6% level does not form any anionic species with titanium ($D \approx 1$ from Fig. 2). BEUKENKAMP AND HERRINGTON[14] found that titanium is present in the form of $Ti(OH)_3^+$, $Ti(OH)_2^{2+}$, $Ti(OH)_2HSO_4^+$, and $Ti(OH)_3HSO_4$ in sulfuric acid solution. Zirconium also seems to form very stable complexes in 0.025 *M* oxalic acid. The stability of these complexes decreases as the concentration of sulfuric acid increases, but apparently no significant zirconium anionic species are present in the 10%–0.025 *M* solution. KORKISCH AND FARAG have demonstrated[15] that less than 10% of the zirconium is absorbed from 4 *N* sulfuric acid solution. Dilute sulfuric acid, however, is known to form anionic species with zirconium and a separation scheme of zirconium and hafnium is based on this principle[10]. Of the three elements, molybdenum seems to form the most stable anionic complexes with oxalic acid, species which persist even at high sulfuric acid concentrations ($D \approx 110$ in 10% sulfuric–0.025 *M* oxalic acid solution).

The authors are grateful to Mr. RICHARD VAN SANTEN and coworkers in the analytical laboratory of Wah Chang Corporation, Albany, Oregon, for their gift of the pure elements and their many helpful suggestions.

SUMMARY

The anion-exchange behavior of titanium, zirconium and molybdenum in sulfuric–oxalic acid system was studied. The systematic use of distribution coefficients defined conditions for a simple method for the analysis of zirconium and titanium in molybdenum base alloys. Less than 0.1% zirconium and 0.1% titanium can be determined. Molybdenum, among the three, was found to form the most stable anionic species with oxalic acid.

RÉSUMÉ

Les auteurs ont examiné le comportement du titane, du zirconium et du molybdène sur échangeur d'anions, en système acide sulfurique–acide oxalique. Il a été possible d'établir les conditions d'analyse du zirconium et du titane dans des alliages à base de molybdène. On peut ainsi doser moins de 0.1% de zirconium et de titane. Le molybdène donne le composé le plus stable avec l'acide oxalique.

ZUSAMMENFASSUNG

Das Austauscherverhalten von Titan, Zirkonium und Molybdän in einem System aus Schwefel- und Oxalsäure wurde untersucht. Aus Untersuchungen über die Verteilungskoeffizienten ergaben sich die Bedingungen für eine einfache Methode zur Analyse von Zirkonium und Titan in Molybdängrundlegierungen. Es können weniger als 0.1% Zirkonium und 0.1% Titan bestimmt werden. Von den 3 Elementen bildete Molybdän die stabilsten Anionen mit Oxalsäure.

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APPLICATION DE LA METHODE POLAROVOLTRIQUE

MORPHOLOGIE DES COURBES DE DOSAGE DE DIACIDES ORGANIQUES EN FONCTION DE LA BASE TITRANTE ET DES EFFETS DE SEL

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(Reçu le 7 avril, 1965)

Nous avons étudié dans l'article précédent la courbe de dosage polarovoltrique de l'acide maléique dans le N,N-diméthylformamide (DMF) en présence de perchlorate de sodium et par l'addition de réactifs basiques[1]. Le choix de ce diacide a été retenu pour la forme caractéristique de sa courbe de dosage, dont l'étude a permis d'expliquer les différentes variations de tension aux électrodes au voisinage de chaque acidité.

Une notation symbolique destinée à rappeler l'origine de ces variations de potentiel a également été proposée et sera étendue dans le présent travail à d'autres diacides organiques.

L'étude effectuée dans le cas de l'acide maléique permet dès maintenant d'envisager différents types de courbes de dosages qui peuvent être rencontrés pour d'autres diacides organiques. Nous avons en effet la possibilité théorique de doser soit la première acidité, soit les deux comme pour l'acide maléique, soit encore la somme des deux, ce qui laisse prévoir plusieurs types fondamentaux de courbes de dosages.

Afin de vérifier cette proposition nous avons choisi quelques diacides organiques particuliers dans les séries aliphatique saturée (malonique, succinique, adipique), éthylénique (maléique et fumarique) et aromatique (*o*-phtalique), et étudié à l'aide de ces exemples les modifications de courbes de dosages consécutives à des effets de sel et de réactif titrant.

Nous montrerons ainsi que le choix du réactif titrant, ou l'addition d'un sel indifférent à la solution à doser peut conduire à diverses possibilités de dosage des deux acidités, c'est-à-dire à différents types fondamentaux de courbes.

Ces variations ne peuvent pas être obtenues en changeant les caractéristiques électriques du circuit d'électrolyse, qui n'entraînent que des variations secondaires de la morphologie. Aussi pour tous les dosages décrits par la suite, nous avons conservé les valeurs électriques indiquées pour le polarovoltmètre standard ($U = 3$ V et $R = 0.5$ mégohm)[2].

EFFETS DE SEL ET DE RÉACTIFS TITRANTS APPLIQUÉS AUX DOSAGES DE DIACIDES ORGANIQUES EN SOLUTION DANS LE N,N-DIMÉTHYLFORMAMIDE

L'addition d'un sel indifférent à la concentration 0.5 et 1 M, n'a généralement aucune incidence sur les courbes de dosages de solutions d'acides ou de bases dans l'eau. Des modifications appréciables ne sont obtenues généralement que dans le cas où on ajoute un sel possédant un ion commun avec l'acide ou la base, et à des concentrations très élevées, comprises entre 5 M et 8 M.

Ainsi, comme l'ont montré Rosenthal et Dwyer[3], la courbe de neutralisation de l'aniline par HCl et par la méthode pH-métrique peut être fortement améliorée par addition de LiCl 8 M à la solution d'amine.

Dans des solvants non aqueux, très peu de sels peuvent être considérés, même à faible concentration, comme des électrolytes indifférents.

En effet, dans le cas des courbes polarovoltriques de dosages, en plus de l'effet d'augmentation de conductibilité, qui se traduit par la suppression du saut de potentiel correspondant à l'addition des premières fractions de réactif dans un solvant peu conducteur, s'ajoutent des effets spécifiques qui modifient complètement les formes de courbes à l'endroit du point équivalent.

Ainsi, nous avons vu précédemment[1], qu'il était possible de déterminer les deux acidités de l'acide maléique en présence de perchlorate de sodium, en utilisant comme réactif, soit le méthylate de sodium (MeONa), soit l'hydroxyde de tétrabutylammonium (TBA-OH).

En l'absence de ce sel, et par l'emploi de TBA-OH, on constate alors qu'il n'est plus possible de doser les deux acidités. La modification de la courbe est si profonde, que seule la première acidité est mise en évidence.

Pour d'autres types de diacides comme l'acide succinique, l'utilisation du solvant sans sel, permet au contraire de doser séparément par l'emploi du TBA-OH les deux acidités. Si on ajoute du perchlorate de sodium à la solution de ce diacide, la détection de la première acidité est alors supprimée, et seul est possible le dosage global de la somme des deux acidités.

De même, si au lieu d'utiliser le titrant TBA-OH, on dose le même diacide à l'aide du titrant MeONa, *en présence ou non de* $NaClO_4$, on ne peut alors détecter que l'ensemble des deux acidités.

Ces quelques exemples montrent combien peut apparaître complexe, sinon confus, le problème du dosage des diacides au moyen d'électrodes de platine polarisées.

Afin de donner un aperçu d'ensemble des résultats expérimentaux, nous avons groupé dans le Tableau I les dosages relatifs à ces diacides.

TABLEAU I

EFFETS DE RÉACTIFS ET DE SELS APPLIQUÉS AUX DOSAGES DE DIACIDES ORGANIQUES EN SOLUTION DANS LE DMF

Les acidités sont numérotées 1 et 2. Le signe + ou — indique que la détermination de l'acidité correspondante est possible ou non. Ces résultats correspondent au cas où l'électrode tournante est l'anode

Acidités	*DMF*				*DMF +* $NaClO_4$ *0.5 M*			
	TBA-OH		*MeONa*		*TBA-OH*		*MeONa*	
	1	*2*	*1*	*2*	*1*	*2*	*1*	*2*
Malonique	+	—	—	+	—	+	+	+
Succinique	+	+	—	+	—	+	—	+
Adipique	—	+	—	+	—	+	—	+
o-Phtalique	+	—	+	+	+	+	+	+
Maléique	+	—	+	+	+	+	+	+
Fumarique	—	+	—	+	—	+	—	+

Les résultats sont obtenus à l'aide de 2 électrodes dissymétriques, précédemment décrites[1]: l'anode est une électrode tournante, la cathode est une électrode fixe de grande surface.

Ce montage présente généralement l'avantage d'améliorer la détection de la seconde acidité (au détriment de la première) et par suite d'augmenter la précision des dosages.

L'application aux électrodes de polarités inverses est également intéressante dans le cas où l'on veut arrêter le dosage à la demi-neutralisation de l'acide. Cette dernière remarque a fait l'objet d'essais systématiques qui seront exposés par ailleurs.

Les résultats du Tableau appellent les remarques suivantes:

(*1*) avec le réactif MeONa, on dose toujours la somme des deux acidités, alors qu'avec TBA-OH on peut doser soit la première, soit la somme des deux acidités;

(*2*) l'addition de perchlorate de sodium à la solution de DMF a pour effet de rendre possible le dosage de la somme des deux acidités, pour tous les diacides étudiés;

(*3*) avec les réactifs TBA-OH et MeONa, la possibilité de dosage de la première acidité en présence de $NaClO_4$ ne subsiste que pour les acides maléique et *o*-phtalique;

(*4*) exception faite des acides adipique et fumarique, il est toujours possible par le choix des conditions expérimentales de doser les deux acidités.

INTERPRÉTATION DES DIFFÉRENTS TYPES DE COURBES

Comme nous avons pu le voir pour le tracé des courbes de polarisation de l'acide maléique[1], le problème du dosage de la première acidité ne dépend uniquement que de la présence en solution des ions H^+ ou des protons solvatés SH^+, qui sont réduits sur platine suivant la réaction $SH^+ + e \rightleftarrows S + \frac{1}{2} H_2$.

La disparition de ces ions par neutralisation produit à la cathode un saut de potentiel, que nous avons noté symboliquement $E_C{}^{H^+ \to S}$ pour rappeler que ce signal correspond à une transition du potentiel de la cathode, de la vague de réduction de SH^+ ou H^+ à celle du solvant S.

Suivant le type de diacide, plusieurs possibilités sont à envisager quant aux forces relatives des deux acidités.

La discussion reste cependant formelle, et l'emploi des constantes thermodynamiques de dissociation de chaque acidité, n'est guère applicable.

En effet, d'une part les dosages ont lieu dans un solvant dont la composition varie progressivement en fonction de Z (ainsi une solution initiale 10^{-2} M de diacide dans le DMF est transformée avec nos conditions expérimentales pour $Z=1$ en un mélange ternaire: DMF 83%, benzène 15% et méthanol 2%) et d'autre part, comme nous le verrons par la suite, la dissociation de ces acides dépend à la fois du choix de la base titrante et de la présence en solution d'un électrolyte.

Malgré cela, on peut cependant envisager qualitativement les cas suivants:

(*a*) les deux acidités sont équivalentes, toutes deux fortement dissociées;

(*b*) la première acidité est forte, la deuxième acidité n'est pas dissociée, mais est neutralisée par le réactif;

(*c*) la première acidité est également forte, la deuxième non dissociée ne réagit pas sur la base titrante;

(*d*) les deux acidités sont de même force et faiblement dissociées, mais sont neutralisées par la solution titrante.

Pour chacune de ces possibilités, il apparaît qu'on puisse retenir un type de courbe de dosage.

Dans le cas (*a*) les deux acidités étant dissociées, le signal $E_C{}^{H^+\rightarrow S}$ ne se produit qu'après la neutralisation des deux acidités, et est suivi immédiatement par le signal $E_A{}^{S\rightarrow OH^-}$ du réactif en excès qui réagit à l'anode. On a alors les courbes du type (*a*) de la Fig. 1. Elles ont la forme d'un V renversé, d'autant plus aigu que les deux acidités sont plus fortes. C'est le cas de l'acide fumarique en présence de $NaClO_4$ (Fig. 2), et également d'acides organiques simples comme l'acide benzoïque, monochloroacétique ou dichloroacétique.

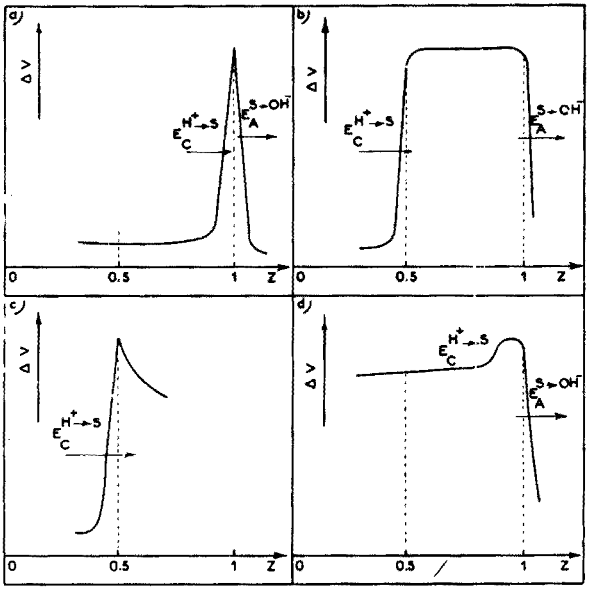


Fig. 1. Types de courbes de dosages polarovoltriques de diacides.

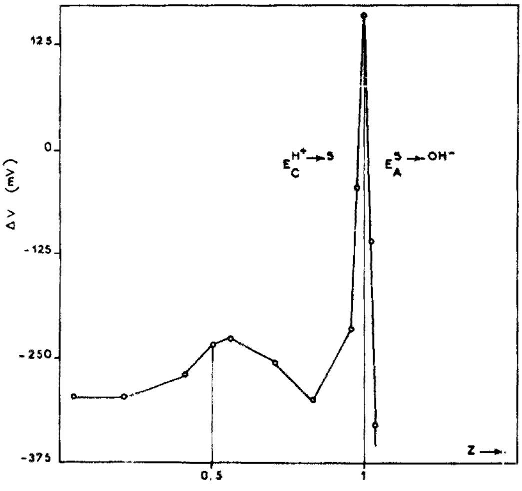
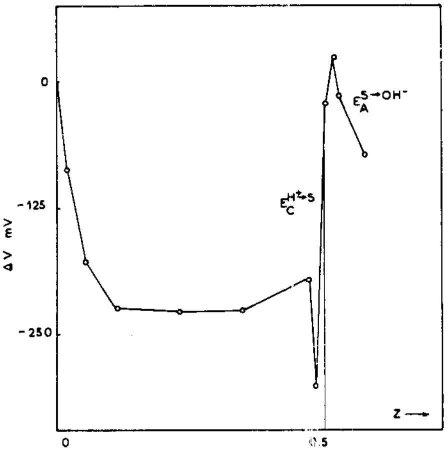


Fig. 2. Courbe de dosage de l'acide fumarique. Solvant, 40 ml DMF + $NaClO_4$ 0.5 *N*; réactif, méthylate de sodium 0.1 *N*.

Dans le cas (*b*) le signal $E_{C}{}^{H^+\to S}$ se produit après la neutralisation de la première acidité; le deuxième hydrogène, peu dissocié, ne peut réagir électrochimiquement, du fait de sa trop faible concentration. Il peut cependant être neutralisé par la base, et par suite le signal $E_{A}{}^{S\to OH^-}$ apparaît pour Z supérieur à 1, ce qui donne les courbes du type (*b*) observées avec les acides maléique et *o*-phtalique en présence de $NaClO_4$ et par l'emploi des réactifs TBA-OH ou MeONa.

En absence de $NaClO_4$ et avec le réactif TBA-OH, on observe les courbes du type (*c*) dans le cas des acides maléique, malonique et *o*-phtalique. Le signal utilisable est celui de la première acidité $E_{C}{}^{H^+\to S}$; il y a neutralisation d'un peu d'ions H^+ de la deuxième acidité, mais très lente ce qui explique l'apparition du signal $E_{A}{}^{S\to OH^-}$ pour Z supérieur à $\frac{1}{2}$ (Fig. 3).



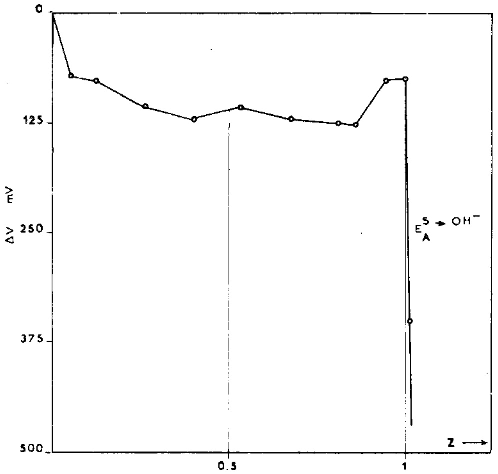


Fig. 3. Courbe de dosage de l'acide maléique. Solvant: 40 ml DMF; réactif, TBA-OH 0.1 *N*.

Fig. 4. Courbe de dosage de l'acide adipique. Solvant: 40 ml DMF + $NaClO_4$ 0.5 *N*; réactif, TBA-OH 0.1 *N*.

Dans le dernier cas (*d*), où les deux acidités sont équivalentes mais faiblement dissociées, le signal $E_{C}{}^{H^+\to S}$ est inexistant ou très faible. Il n'apparaît plus que le signal de la base $E_{A}{}^{S\to OH^-}$ pour Z supérieur à 1.

Ces courbes sont observées avec les acides adipique, fumarique et succinique (Fig. 4) dans les conditions chimiques indiquées sur le Tableau I.

INTERPRÉTATION DES EFFETS DE SEL ET DE BASE TITRANTE

D'après le Tableau I, nous voyons que l'emploi du méthylate de sodium ou l'addition du perchlorate de sodium à la solution de diacide, conduit à la possibilité de dosage de la deuxième acidité. Ceci est particulièrement net pour les acides malonique, *o*-phtalique et maléique, pour lesquels l'emploi du DMF et du réactif TBA-OH ne permet de doser que la première acidité.

Soit HCO_2-X-CO_2H un tel diacide. La réaction de neutralisation par les deux réactifs TBA-OH et MeONa, conduit à la formation des sels:

(*1*) $HCO_2-X-CO_2^-TBA^+$ et (*1'*) $TBA^+CO_2^-\ X-CO_2^-TBA^+$

(*2*) $HCO_2-X-CO_2^-Na^+$ et (*2'*) $Na^+CO_2^-\ X-CO_2^-Na^+$

Chacun de ces composés est en équilibre avec les ions provenant de sa dissociation.

En particulier, à la demi-neutralisation, nous avons les équilibres:

(1) $HCO_2{-}X{-}CO_2^-TBA^+ \rightleftarrows (3)\ HCO_2{-}X{-}CO_2^- + TBA^+$

ou (2) $HCO_2{-}X{-}CO_2^-Na^+ \rightleftarrows (3)\ HCO_2{-}X{-}CO_2^- + Na^+$

Pour que la neutralisation de la deuxième acidité soit possible, il faut que l'hydrogène des acides (*1*), (*2*) ou (*3*) puisse être dissocié.

Dans le cas de l'acide (*3*), la liaison hydrogène contribue en partie à rendre négligeable la dissociation du proton[4,5]; la neutralisation par un réactif basique n'est alors pas possible.

Les mêmes considérations restent valables pour l'acide (*1*). La grande taille du cation TBA^+ a pour effet d'éloigner la charge positive du groupe carboxylate, et par suite ce composé a un comportement analogue à celui de l'acide (*3*).

La dissociation de l'hydrogène reste donc faible pour les acides (*1*) et (*3*), ce qui peut expliquer que le réactif TBA-OH employé seul, ne puisse pas réagir sur la deuxième acidité des acides malonique, maléique et *o*-phtalique.

Au contraire, avec l'acide (*2*), on peut considérer, du fait de la faible distance séparant les ions $-CO_2^-$ et Na^+, que les charges électriques se neutralisent. Ceci a pour conséquence d'affaiblir la liaison hydrogène envisagée précédemment, et par suite de favoriser la dissociation du proton, dont la neutralisation par un réactif basique est alors possible.

En conséquence, si on ajoute à une solution d'un tel diacide, un sel minéral possédant un cation de petite taille, et fortement dissocié comme le perchlorate de sodium[6], il apparaît que le dosage de la deuxième acidité par deux réactifs aussi différents que MeONa et TBA-OH devient alors possible.

Dans les deux cas, nous avons en effet l'acide $HCO_2{-}X{-}CO_2Na$ dans la solution à doser, et dont la dissociation est comparable à celle d'un acide ordinaire.

Lorsque le perchlorate de sodium est ajouté à la solution de diacide, on observe après la demi-neutralisation de l'acide, la formation d'un léger précipité. Ce précipité qui n'apparaît pas lorsque le réactif TBA-OH est employé seul, prouve que la formation d'un sel de sodium est effective dans les deux cas.

Il présente d'autre part l'avantage de faciliter l'ionisation du deuxième hydrogène, par l'intermédiaire d'une réaction de déplacement.

En effet, nous avons les deux équilibres:

$$HCO_2{-}X{-}CO_2Na \rightleftarrows H^+ + NaCO_2{-}X{-}CO_2^-$$

$$NaCO_2{-}X{-}CO_2^- + Na^+ \rightleftarrows NaCO_2{-}X{-}CO_2Na$$

Or la concentration de $NaCO_2{-}X{-}CO_2Na$ est constante et définie par sa limite de solubilité, dès que le précipité est apparu. Pour toute la suite de la neutralisation, on peut considérer qu'il y a un déplacement continuel de H^+ par Na^+, par l'intermédiaire de la réaction:

$$HCO_2{-}X{-}CO_2Na + Na^+ \rightleftarrows H^+ + NaCO_2{-}X{-}CO_2Na$$

En conclusion, il apparaît que les effets observés au cours de dosages de diacides par le méthylate de sodium et l'hydroxyde de tétrabutylammonium, sont dûs en grande partie à la présence en solution de cations particuliers, dont l'action est mise en évidence par l'emploi du perchlorate de sodium.

Ces résultats ne sont d'ailleurs pas particuliers à l'emploi des électrodes métalliques polarisées. Des effets similaires ont été signalés récemment. En particulier MARPLE ET FRITZ[7] ont montré un "accroissement d'acidité" dans les dosages d'acides faibles, par addition de TBA^+Cl^- dans l'alcool tertiobutylique, et HARLOW[8] a montré l'influence de plusieurs réactifs basiques d'ammonium quaternaires dans les dosages de diacides dans l'alcool isopropylique, à l'aide de la méthode potentiométrique classique.

PARTIE EXPÉRIMENTALE

Appareillage et purification des produits chimiques

L'appareillage et la purification des produits ont été décrits précédemment, lors de l'étude de l'acide maléique[1].

Les diacides utilisés sont toujours des produits Prolabo pur ou R.P. que nous avons recristallisés et séchés avant de les utiliser.

Résultats des dosages

Tous les résultats, sauf indication contraire, ont été obtenus avec le montage électrode tournante fonctionnant en anode et l'électrode fixe en cathode. Ce montage a été précédemment décrit, de même que les conditions nécessaires à la réalisation d'un dosage[1].

Le Tableau II représente les dosages obtenus dans le DMF seul et avec les deux réactifs, le Tableau III ceux obtenus en présence de perchlorate de sodium 0.5 *N*.

Tous les nombres indiqués représentent des masses en mg: m_p est la masse de

TABLEAU II

DOSAGES DE DIACIDES EN SOLUTION DANS LE DMF (ÉLECTRODE TOURNANTE: ANODE)

Diacides	*TBA(OH)*			*MeONa*		
	m_p	m_1'	m_2'	m_p	m_1'	m_2'
Malonique	48.42	48.11	—[a]	48.77	—	48.74[a]
	60.11	60.12	—[a]	42.15	—	42.04[a]
Succinique	57.31	57.57	57.56[a]	55.40	—	55.60
	52.88	52.82	52.78[a]			
Adipique	78.79	—	78.45	32.08	32.40	32.41[b]
	79.27	—	78.92			
o-Phtalique	83.40	82.40	—[a]	26.61	—	26.90[a]
Maléique	36.67	37.87	—[a]	58.28	57.48	58.07[a]
	50.89	51.01	—[a]	58.28	57.34	58.28[a]
Fumarique	46.44	—	46.45	42.84	—	42.35
	47.23	—	46.87	46.50	—	47.02

[a] La détermination de la première acidité peut être effectuée ou améliorée si on utilise l'électrode tournante comme cathode.

[b] Le signal $E_C^{H^+ \to S}$ est faible, même lorsque l'électrode tournante est la cathode.

TABLEAU III

DOSAGES DE DIACIDES EN SOLUTION DANS LE DMF ET EN PRÉSENCE DE $NaClO_4$ 0.5 *M* (ÉLECTRODE TOURNANTE: ANODE)

Diacides	*TBA(OH)*			*MeONa*		
	m_p	m_1'	m_2'	m_p	m_1'	m_2'
Malonique	37.32	—	36.92	50.41	49.86	50.25[a]
	45.19	—	43.91	39.37	—	39.50
Succinique	54.14	—	54.10	35.68	—	35.32
	54.15	—	54.12	32.20	—	32.34
Adipique	58.69	—	58.90	54.60	—	55.00
	56.74	—	56.95	42.38	—	41.97
o-Phtalique	68.41	—	68.60[b]	27.54	27.65	28.20
	71.88	—	72.36[b]			
Maléique	45.91	—	45.85	35.75	36.75	35.81
	50.55	50.02	50.25	34.81	35.52	35.07
	48.03	48.01	48.57[c]			
Fumarique	53.13	—	52.94	37.47	—	37.30
	52.93	—	53.26	29.87	—	30.27
				29.82	—	30.24

[a] Le dosage a été réalisé en utilisant l'électrode tournante comme cathode, et $NaClO_4$ a été remplacé par Et_4NClO_4 0.5 *M*.

[b] Le signal $E_C^{H^+ \to S}$ existe lorsque l'électrode tournante est anode, mais l'erreur de titrage est importante.

[c] Le dosage a été effectué en utilisant successivement l'électrode tournante comme cathode pour la détermination de la première acidité, puis comme anode pour la détection de la deuxième acidité.

diacide pesée, m_1' et m_2' les masses expérimentales calculées respectivement à partir de la détermination de la première et de la deuxième acidité.

Les résultats des deux Tableaux indiquent que la précision du dosage de la somme des deux acidités est généralement meilleure que 1%, sauf pour l'acide malonique en présence de perchlorate de sodium lorsqu'il est neutralisé par le TBA-OH. La fin de réaction étant très lente et incomplète, l'erreur de titrage peut atteindre 2%.

La première acidité par contre est déterminée avec moins de précision; cela est dû en général à une moins bonne résolution du signal électrique $E_C^{H^+ \to S}$, comme c'est le cas pour l'acide malonique dosé par le réactif MeONa en présence de $NaClO_4$.

Correction d'essai blanc

La détermination du point équivalent correspondant à chaque acidité pose le problème de la nécessité d'effectuer un essai blanc.

Pour $Z = \frac{1}{2}$ on choisit comme point équivalent la valeur de potentiel la plus élevée de la courbe de dosage, et pour $Z = 1$ le point d'inflexion de la branche descendante. Pour cette dernière acidité qui correspond à un excès de réactif, il est nécessaire d'effectuer une correction, ce qui revient à déterminer la quantité de solution titrante qu'il faut ajouter à 40 ml de DMF en l'absence de diacide, pour obtenir la même variation de potentiel du signal $E_A^{S \to OH^-}$. Cette valeur est ensuite retranchée à celle obtenue pour le dosage de la deuxième acidité.

Influence de l'eau dans les dosages

Dans le cas du TBA-OH, nous avons constaté que l'addition de quantités d'eau croissantes sur une prise d'essai de DMF, ne modifiait en rien l'essai blanc, c'est-à-dire la quantité nécessaire de TBA-OH qu'il faut ajouter à la solution pour obtenir le signal $E_A{}^{S\rightarrow OH}$

Ainsi, pour un solvant DMF distillé en présence de benzène, donnant un essai blanc équivalent à 0.10 ml de TBA-OH 0.1 *N*, l'addition de 10 µl d'eau à 40 ml de DMF ne donne lieu à aucune modification.

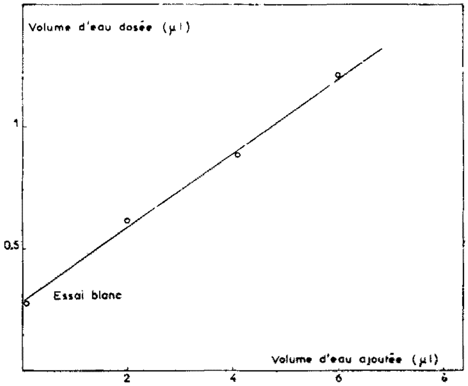


Fig. 5. Action de l'eau sur le méthylate de sodium. On a porté en abscisse la quantité d'eau ajoutée à 40 ml de DMF. Les valeurs portées en ordonnée représentent la quantité d'eau qui a réagi sur le méthylate de sodium.

Au contraire, dans le cas du méthylate de sodium, la teneur en eau du solvant joue un rôle important, ce qui justifie le procédé de l'essai blanc. Pratiquement, on constate que 15% de l'eau ajoutée réagit sur le titrant, comme le montre la courbe de la Fig. 5.

RÉSUMÉ

L'étude de quelques diacides organiques de la série aliphatique tels que l'acide malonique, succinique, adipique, et d'acides insaturés tels que les acides maléique, *o*-phtalique et fumarique a montré que les courbes de dosages obtenues dans le N,N-diméthylformamide, à l'aide de réactifs basiques et par la méthode polarovoltrique, différaient suivant le diacide choisi. La comparaison des résultats obtenus avec ces diacides a permis de classer ces courbes en 4 types distincts.

Exception faite de l'acide adipique et de l'acide fumarique, pour lesquels il n'est possible de doser que la somme des deux acidités, chaque fonction acide (première ou deuxième acidité) peut être mise en évidence par un choix convenable des conditions chimiques de dosage. En particulier, lorsque le réactif TBA-OH ne permet pas de doser la deuxième acidité, celle-ci peut être détectée, soit par un changement de réactif (MeONa), soit par addition de sel ($NaClO_4$) à la solution de diacide.

SUMMARY

The polarovoltric titration curves obtained in a study of the reaction of organic dibasic acids, both saturated (*e.g.* malonic, succinic and adipic acids) and unsaturated (*e.g.* maleic, fumaric and *o*-phthalic acids) with basic reagents in N,N-dimethylformamide were different for each acid. It was possible to classify these curves in 4 distinct groups.

The individual acidic functions for all of the acids studied, except fumaric and adipic acids, could be detected by a suitable choice of titration conditions. The first acid function in fumaric and adipic acids could not be titrated.

When tetrabutylammonium hydroxide was incapable of indicating the second end-point, this end-point could be detected either by changing the reagent (*e.g.* using MeONa) or by adding a salt (*e.g.* $NaClO_4$) to the solution.

ZUSAMMENFASSUNG

Die Untersuchung der Form der Titrationskurven zweibasischer Säuren in N,N-Dimethylformamid hat gezeigt, dass diese sich mit den Säuren ändert. Untersucht wurden sowohl aliphatische Säuren wie: Malonsäure, Bernsteinsäure und Adipinsäure als auch ungesättigte Säuren wie Maleinsäure, *o*-Phthalsäure und Fumarsäure. An Hand der Ergebnisse war es möglich, diese zweibasischen Säuren in 4 verschiedene Klassen zu unterteilen.

Beide Säuregruppen konnten durch Wahl der Titrationsbedingungen unabhängig voneinander bestimmt werden. Nur bei der Adipinsäure sowie der Fumarsaüre gelang es nicht, die erste Dissoziationsstufe zu bestimmen. Falls eine Titration mit TBA-OH nicht die zweite Dissoziationsstufe zu bestimmen erlaubt, kann dieses dennoch entweder durch Titration mit einem anderen Reagenz (MeONa) oder durch Zufügen eines indifferenten Salzes wie Natriumperchlorat erreicht werden.

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THE SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF PRIMARY AND TERTIARY AMINES IN AQUEOUS SOLUTION WITH COPPER-(ETHYLENE DINITRILO)TETRAACETIC ACID

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(Received February 11th, 1965)

The analytical method presented in this paper follows a related method by CITRON AND MILLS[1] for the determination of primary amines in aqueous solution. Both methods are based upon the findings of KIRSON AND CITRON[2] regarding the diminished absorption of the copper–EDTA complex at 720 mμ when small quantities of primary amines are added to the complex in aqueous solution and the absence of this effect when tertiary amines are added. These findings were later substantiated by CITRON[3] in an investigation in the infrared.

The present investigators felt that the difference in effect between primary and tertiary amines upon the absorbance of $(CuY)^{2-}$ could be the basis for an analytical determination of both types of amines in mixed aqueous solutions. It was found, however, that since tertiary amines do have a slight effect in lowering the absorbance of the $(CuY)^{2-}$ complex, it would be necessary to employ a two-step process in which total amine content was first determined by an acid–base neutralization involving CuH_2Y, and then the concentration of each type of amine determined by a varying ratio technique using standards in which the relative amounts of primary and tertiary amines vary but the total concentration remains the same. Both steps are spectrophotometric determinations and employ the same wavelength, 720 mμ.

EXPERIMENTAL

Apparatus and reagents

A Beckman model DB spectrophotometer with recorder and scale expansion accessory were used. The absorption cells were Beckman standard silica U cells, 1.0 cm in diameter. The reagents employed came from miscellaneous sources.

Cupric sulfate, anhydrous, Baker analyzed reagent (assay $CuSO_4$, 99.7%); (ethylenedinitrilo)tetraacetic acid, tetrasodium salt, and disodium salt, Matheson, Coleman and Bell; *n*-propylamine, triethylamine, benzylamine, isopropylamine, *tert.*-butylamine and tri-*n*-propylamine, all from Eastman Organic Chemicals.

Procedure

Determination of total amine content. With a pipet or buret, place 2.5 ml each of accurately prepared solutions of 0.1 *M* copper(II) sulfate and 0.1 *M* EDTA-disodium salt into a series of 6 or 8 25-ml volumetric flasks. Dilute the mixed primary plus tertiary amine solution to be analyzed to a concentration of about 0.2 M, and add exact portions varying from 1.0–3.0 ml to the volumetric flasks. Dilute all the flasks to the mark. Examine the series of solutions prepared above at 720 mμ. If a recorder is used, record only a small segment of the visible spectrum, say 760–680 mμ.

Plot absorbance *vs.* ml of amine solution for the series of solutions. The curve should include a maximum (intersection of two straight lines). The point of maximum absorbance corresponds to a ratio [total amine]/[CuH_2Y] = 2.00. Provided that the volumes and concentrations of solutions are employed exactly as outlined above, the molar concentration of total amine in the solution examined can be found from the expression:

$$[\text{total amine}] = \frac{0.5}{\text{ml of amine added at max. absorbance}}$$

The concentration of total amine in the original solution can be calculated by using the proper dilution factors.

Alternatively, the mixed amine solution may be titrated photometrically with CuH_2Y as titrant. Dilute the mixed amine solution to about 0.2 M. Add various measured portions of 0.1 M CuH_2Y, prepared as described previously, to a series of 2.0-ml portions of the amine solution placed in 25-ml volumetric flasks. Dilute each flask to the mark, and measure the absorbance values of the series at 720 mμ. Plot absorbance *vs.* ml of CuH_2Y added. In this case there will be no maximum absorbance, but a sharp break (change in slope) will occur in the curve at a ratio [total amine]/[CuH_2Y] = 2.00. Provided that the above directions are followed exactly, the concentration of total amine in the solution examined can be found from the expression:

$$[\text{total amine}] = (0.008)\ (\text{ml of } CuH_2Y \text{ added at break in curve}).$$

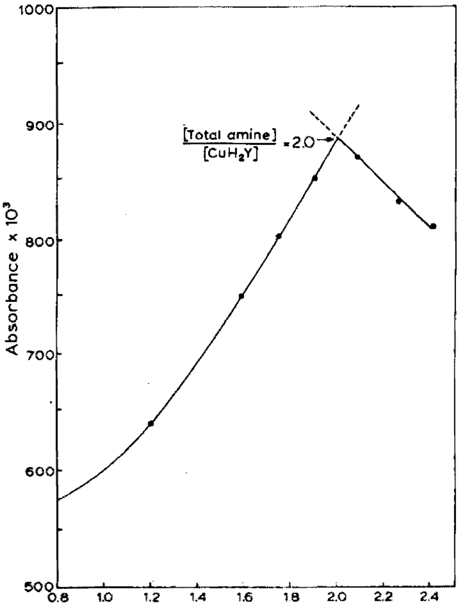
Use proper dilution factors to calculate total amine in the original solution.

Determination of primary and tertiary amine concentrations in the mixed solution. Into a series of 6 or 8 25-ml volumetric flasks add 2.5 ml of 0.1 M copper(II) sulfate solution and 2.5 ml of 0.1 M EDTA-tetrasodium salt (Na_4Y), accurately prepared. To the series of flasks add varied amounts of primary amine and tertiary amine of known concentration so that the total amine concentration in each flask upon dilution to the mark will be 0.010 M. For this purpose it is best to use the amines which are thought to be present in the mixed solution to be determined. However, this is not strictly necessary, as will be seen from the data later presented.

Add a calculated aliquot of the mixed amine solution (whose total amine content has been determined) to a 25-ml volumetric flask containing 2.5 ml of 0.1 M copper(II) sulfate and 2.5 ml of 0.1 M Na_4Y. The calculated aliquot should be so chosen that upon dilution to the mark, the total amine concentration here too will be 0.010 M. Measure the absorbance values of all the solutions at 720 mμ. Plot absorbance *vs.* molar concentration of primary amine or molar concentration of tertiary amine (or both), and locate the absorbance of the mixed solution to be determined on the curve. Read off the molar concentration of primary amine and/or tertiary amine in the solution examined from the curve. The concentration of the other amine, if only one is plotted, can be found by subtracting the concentration of the amine determined from 0.010. Account for all dilution factors used in calculating the concentrations of primary and tertiary amine in the original mixed solution.

RESULTS AND DISCUSSION

The method outlined above is limited to the analysis of mixed solutions of primary and tertiary monoamines. Diamines and polyamines would not only lower the absorption of the copper–EDTA complex, but would also shift the wavelength of maximum absorption from 720 mμ to shorter wavelengths[2]. Amino alcohols and amino acids would necessitate a modification in the method of determining total amine content. Further investigation will be necessary to extend the method to these types of amines.



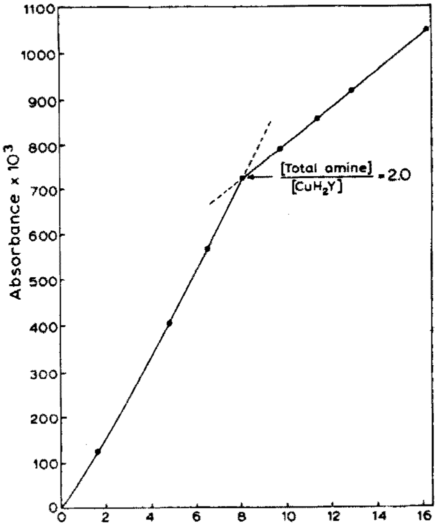


Fig. 1. Determination of total amine content: addition of mixed amine solution to solution in which $[CuH_2Y] = 0.0100\ M$.

Fig. 2. Determination of total amine content: addition of CuH_2Y to mixed solution in which [total amine] $= 0.0160\ M$.

Figure 1 shows a plot of absorbance *vs.* [total amine] when increasing increments of a mixed solution of primary and tertiary amines are added to a series of solutions in which CuH_2Y is held constant at 0.0100 M. The equivalence point corresponds to a maximum absorbance which occurs when [total amine]/$[CuH_2Y] = 2.00$. When the total amine concentration is unknown, the same type of curve can be plotted with ml of total amine as abscissa. Only a few points (3 or 4) on either side of the maximum absorbance are needed to determine the point of maximum absorbance accurately, provided that the points fall within the linear portion of the curve. Essentially the same curve is obtained for any mixture of those primary and tertiary amines tested at any given total concentrations.

Figure 2 shows the curve obtained when absorbance is plotted *vs.* $[CuH_2Y]$ for a series of solutions in which various amounts of CuH_2Y have been added to solutions in which [total amine] is held constant at a value of 0.016 *M*. At [total amine]/[CuH_2Y] = 2.00 there occurs a sharp change in the slope of the curve. A few points on either side of this change of slope, provided that the above ratio is not lower than 0.4 (below which the curve loses linearity), are sufficient to determine the point of change of slope. Again, the curve is essentially the same for all amine mixed solutions determined with the same concentration of CuH_2Y.

As indicated in the procedure, the individual amine concentrations are determined by varying the ratio of primary to tertiary in a series of standards to which the complex $(CuY)^{2-}$ has been added while keeping the total amine concentration constant in the standard solutions and the solutions to be analyzed (the total concentration in the latter having been determined). Typical varying ratio tests involving the mixtures of various primary and tertiary amines (Table I) revealed very similar absorbance values at each particular ratio. A typical varying ratio plot of absorbance *vs.* [primary amine] and [tertiary amine] is shown in Fig. 3. It is based

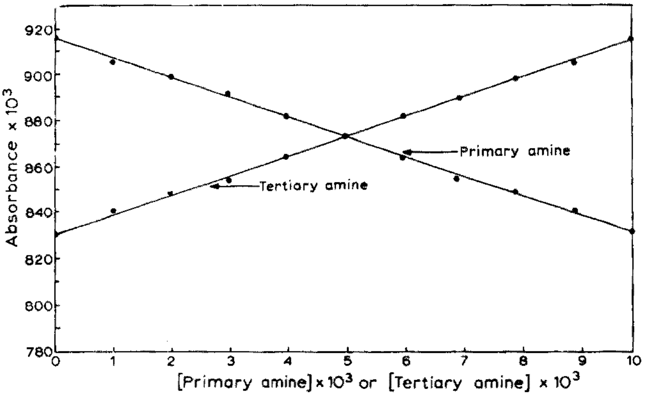


Fig. 3. Varying ratio plot to determine molar concentrations of primary amine and tertiary amine in mixed solutions. [total amine] = 0.0100 *M*; [$(CuY)^{2-}$] = 0.0100 *M*.

upon the average of absorbance values for all amine mixtures tested except those involving benzylamine for which a separate plot would give better results. Investigation indicated that, although the absorbance values for solutions containing benzylamine run somewhat higher than the absorbance values for other mixtures, the same varying ratio plot could generally be used at a given total amine concentration without regard to the particular primary and tertiary amines in the mixed solution. However, for utmost accuracy, the authors suggest that wherever possible the amines being investigated in the mixed solution be used to make up the standard solutions for the varying ratio tests.

The total amine concentration upon dilution in the varying ratio test need not necessarily be 0.010 *M* as shown in these data, but may be a constant value within the range 0.006 *M* and 0.014 *M*, a corresponding concentration of $(CuY)^{2-}$ also being maintained. Total amine concentrations below 0.006 *M* should not be used because there is too little spread in absorbance values for the varying ratio of primary to

TABLE I

SUMMARY OF RESULTS FOR 5 REPLICATE SAMPLES IN SEVERAL SERIES OF MIXED AQUEOUS AMINE SOLUTIONS

Solution no. [a]	*Taken (M)*			*Found (M)*									
				Total amine				*Individual amines*					
	[Total amine]	*[Pri mary amine]*	*[Tertiary amine]*	*Mean molarity*	*Range* $\cdot 10^3$	*Std. dev.* $\cdot 10^4$	*Relative std. dev.* (%)	*[Pri-mary amine]*	*[Tertiary amine]*	*Range* $\cdot 10^3$	*Std. dev.* $\cdot 10^3$	*Relative std. dev.* (%)	
												Primary amine	*Tertiary amine*
1	0.1000	0.0200	0.0800	0.1003	2.4	4.40	0.40	0.0205	0.0798	6.0	1.08	5.3	1.4
2	0.1000	0.0400	0.0600	0.1010	3.2	6.99	0.69	0.0413	0.0597	4.7	1.05	2.5	1.8
3	0.2000	0.0800	0.1200	0.2000	0.4	1.45	0.07	0.0784	0.1216	9.0	1.71	2.2	1.4
4	0.2000	0.1200	0.0800	0.1995	3.8	7.65	0.38	0.1200	0.0795	7.0	2.61	2.2	3.3
5	0.1000	0.0800	0.0200	0.1002	1.6	3.14	0.31	0.0807	0.0195	3.5	0.74	0.92	3.8
6	0.1000	0.0850	0.0150	0.1002	2.8	5.50	0.55	0.0845	0.0157	3.5	0.70	0.83	4.5
7	0.1000	0.0900	0.0100	0.1006	2.4	4.98	0.50	0.0914	0.0092	6.5	1.19	1.3	12.9
8	0.1000	0.0950	0.0050	0.0996	1.7	5.01	0.50	0.0948	0.0048	3.4	0.66	0.70	13.8

[a] Mixed amine solutions used:
Solution no. 1. *n*-Propylamine and triethylamine.
2. Benzylamine and triethylamine.
3. Isopropylamine and triethylamine.
4. *tert.*-Butylamine and triethylamine.
5. *n*-Propylamine and tri-*n*-propylamine.
6. Benzylamine and tri-*n*-propylamine.
7. Isopropylamine and tri-*n*-propylamine.
8. *tert.*-Butylamine and tri-*n*-propylamine.

tertiary amine, while at concentrations above 0.014 M, the linearity of the absorbance *vs.* molar concentration curve begins to break down.

Several series of tests on replicate samples were run to determine the precision of this analytical method. The precision in determining total amine content as well as the concentrations of the individual amines was evaluated for each series. The results appear in Table I.

In the method of analysis for primary amines only[1], the authors listed the effect of various anions upon the precision of the method. No significant change in these effects was observed for this method. The anions $C_2H_3O_2^-$, CO_3^{2-}, Cl^-, and NO_3^- present in amounts equimolar to the amount of total amine determined caused deviations in the maximum absorbance of less than 0.50% in each case. Cations in solution which complex strongly with EDTA would interfere seriously with the method and must be eliminated beforehand, especially if the concentration of the foreign cation exceeds one-tenth of the molar concentration of the copper–EDTA complex in the solutions examined.

Again, in this method, the authors have used equimolar amounts of copper(II) and EDTA (whether the disodium or tetrasodium salt) in making up the solutions of CuH_2Y for the determination of total amine and $(CuY)^{2-}$ for the determination of individual primary and tertiary amine concentrations. This was done to give results of highest reproducibility.

The authors are indebted to HAROLD WEINBERGER, Chairman of the Department of Chemistry, to KATHLEEN HILLERS, and to the faculty of the Department of Chemistry at Fairleigh Dickinson University for their support and encouragement during this research. A special acknowledgment is due to MARCY ROBINSON who performed a great many of the early experiments in the development of this method.

SUMMARY

The preferential coordination of primary amines to the copper–EDTA complex and the resulting fall in absorbance at 720 mμ is used as a basis for the accurate determination of both primary and tertiary amines in mixed aqueous solutions.The total amine content is first determined by spectrophotometric titration of the mixed amine solution with the dibasic copper–EDTA complex (or *vice versa*). Then the mixed solution of amines is diluted to a definite total amine concentration, and its absorbance at 720 mμ is again measured after the addition of a definite amount of the tetrasodium salt of EDTA complexed with copper, $(CuY)^{2-}$. This absorbance is located on a suitable varying concentration ratio curve, and the concentrations of both primary and tertiary amines in the solution being analyzed can be read directly from the curve.

RÉSUMÉ

Les auteurs ont examiné le dosage spectrophotométrique simultané d'amines primaires et tertiaires, au moyen du complexe cuivre–EDTA. On détermine la teneur totale en amines par titrage spectrophotométrique, au moyen de Cu-EDTA. Puis on mesure l'absorption à 720 mμ, après addition d'une quantité déterminée de Cu-EDTA.

Les concentrations en amines primaire et tertiaire sont lues directement sur la courbe.

ZUSAMMENFASSUNG

Die bevorzugte Koordination von primären Aminen am Kupfer–EDTA-Komplex und die resultierende Abnahme in der Absorption bei 720 mμ wurde als Grundlage für die genaue Bestimmung von primären und tertiären Aminen in wässrigen Lösungen benutzt. Zuerst wurde der gesamte Amingehalt durch spektralphotometrische Titration mit dibasischem Kupfer–EDTA-Komplex bestimmt. Dann wurden die Gemische der Amine bis zu einer bestimmten Gesamtaminkonzentration verdünnt und ihre Absorption bei 720 mμ nach Zugabe einer bestimmten Menge des Tetranatriumsalzes des EDTA als Komplex mit Kupfer erneut gemessen. Die Konzentrationen der primären und tertiären Amine können aus einer Eichkurve abgelesen werden.

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THE DETERMINATION OF GLYCOLLIC ACID IN SOLUTIONS PREVIOUSLY IN CONTACT WITH ION-EXCHANGE RESINS

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(Received March 22nd, 1965)

In connection with equilibrium studies involving glycollic acid solutions containing rare-earth and other unreacting salts in contact with ion-exchange resins, it became necessary to determine the amount of glycollic acid in these systems. Various published methods were examined and the most suitable modified to meet the present requirements. Since ion-exchange resins are conveniently used to effect the separation of glycollic acid from neutral and cationic substances[1,2], the observations described should have application beyond the systems considered here.

Oxidimetric titration methods employing either manganese(VII)[3], cerium-(IV)[4] or chromium(VI)[5] may be used in this determination. Of these the 'heat of dilution' method using chromium(VI) in strong sulphuric acid was found to be generally satisfactory and the most convenient. Existing methods using the other oxidants are lengthy and the cerium method occasionally gave erratic results in our hands. However 'blank' values were significant for all these methods and depended on the resin with which the glycollic acid had been in contact. It was observed that resin fragments entered into solution and the extent to which this occurred depended markedly on the degree of cross-linking of the resin. For solutions of the acid which had been in contact with 2% or 4.5% cross-linked resins, the blank values were too high and inconsistent to permit the use of any of these methods.

The presence of resinous matter in solutions in contact with ZeoKarb-225 resin was demonstrated by measuring the absorbance of effluent solutions obtained by passing distilled water through columns of resin having 2 or 4.5% cross-linking (DVB). For resin stored for some time the effluent had a golden colour (not due to iron(III)) initially, and absorbed strongly in the near ultraviolet, the absorbance falling off towards the visible without showing the presence of any well-defined peaks or shoulders. Washing the resin reduced the absorbance of the effluent considerably but even after 10 or 20 column volumes had passed it was still appreciable. If the column was permitted to stand unused for several days after such a treatment and then washed with water, the effluent was again coloured initially, suggesting that degradation (probably oxidation) was a continuous process. About a litre of effluent having a golden colour was evaporated down on a water bath to give a dark treacle-like residue which was dried in a vacuum (10^{-3}–10^{-4} mm Hg) at 50°. The spectrum of this dried (brittle) residue in the 2.5 to 16 μ region was compared with that of

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the original resin dried in the same way; Fig. 1 shows that the spectrum of the former possesses many of the features of the latter and leaves little doubt that fragmentation of the resin occurs. Experiment also showed that this fragmentation was much reduced for resins of high cross-linkage (8% DVB or greater). The absorbancy of the effluent was not affected by previous filtration through 'fine' filter papers, and as there was no appreciable scatter of visible light, the light absorbent would appear to be in true solution or dispersed as a very dilute colloid.

Some Dowex and Amberlite resins were also examined and showed similar characteristics to ZeoKarb resins.

An alternative to titrimetry is to utilise the colour produced by treating a mixture of glycollic and chromotropic (1,8-dihydroxynaphthalene-3,6-disulphonic acid) acids with strong sulphuric acid. The use of this organic reagent for the determination of glycollic acid has previously been outlined for systems differing from those under discussion[6,7]. In the reaction giving rise to the colour formation it is likely that glycollic acid is first converted to formaldehyde[8] which then reacts with the chromotropic acid. The more recent method[7], although essentially similar to the earlier one[6], is based on a study of conditions affecting colour development induced by formaldehyde added directly[9]; differences, if any, arising from the preliminary conversion of glycollic acid to this substance were not discussed in either publication. Some features of the reaction relevant to the spectrophotometric determination were therefore examined in the present work. The effect of lactic acid was also investigated.

EXPERIMENTAL

Reagents

Reagents were of 'AnalaR' quality unless otherwise specified.

Chromotropic acid. 'For formaldehyde determination', obtained from B.D.H., Ltd. (Reagent A).

Chromotropic acid, sodium salt (B.D.H.). Laboratory Reagent Grade (Reagent B). A 10% solution was prepared just before use in water de-aerated by boiling. The solution was best protected from light.

Glycollic acid (Judex Laboratory Reagent). The acid was recrystallised from water and dried in vacuum over sulphuric acid. The purity was checked by alkalimetric titration.

Ammonium perchlorate. B.D.H. Laboratory Reagent Grade or prepared by neutralising perchloric acid with ammonia.

Ion exchangers. ZeoKarb-225 series (chromatographic grade, 100–200 mesh) of 2, 4.5, 8 and 20% cross-linking. In the course of the equilibrium studies referred to initially, these resins were carefully freed from fines and then from iron with warm dilute hydrochloric acid and finally converted to the ammonium form.

Lactic acid. Anhydrides were removed by boiling with dilute hydrochloric acid.

N-Phenylanthranilic acid. 0.25 g were dissolved in 12 ml of 0.1 *M* sodium hydroxide and diluted to 250 ml.

Equipment

Spectrophotometric measurements in aqueous solutions were made using a

Unicam 500 spectrophotometer. The infrared spectra were obtained with a Grubb-Parsons GS-2A double beam grating spectrophotometer from *ca.* 1-mg samples in KBr discs.

Procedures

The chromotropic acid procedure of DAGLEY AND RODGERS[7] was used except that the heating time was reduced to 20 min; this permitted more rapid determinations up to 130 μg of glycollic acid, with the system obeying the Beer–Lambert law. By extending the heating time to 45 min, the law was obeyed up to at least 180 μg.

Essentially the general procedure given in the original paper was followed in applying the chromium(VI) oxidation method[5]; a 0.016 *M* potassium dichromate solution was used. However, for 3–8-mg quantities of glycollic acid in 2–5 ml of sample, only 7 ml of concentrated sulphuric acid were added for the initial oxidation (instead of 10) and afterwards a further addition of 10 ml was made (instead of 30). This prevented a tendency towards excessive reduction of chromium(VI). It was found to be more convenient to add an excess of 0.1 *M* iron(II) solution to the chromium(VI) remaining after the oxidation, and to titrate with standard chromium(VI) solution using N-phenylanthranilic acid as indicator, than to titrate the chromium(VI) with iron(II) solution to a potentiometrically determined end-point as previously recommended[5].

RESULTS AND DISCUSSION

Aqueous solutions of chromotropic acid darkened in colour and showed an increase in optical density at 570 mμ with increase in the age of the solution. Solutions prepared from reagent A, the more refined of the two samples, showed a considerably greater increase, particularly if exposed to light, than those prepared from reagent B. The optical density of a solution prepared freshly from B was almost twice that of a similar solution from A. However, when the solutions were mixed and heated with sulphuric acid as in the blank measurements this difference in optical density became

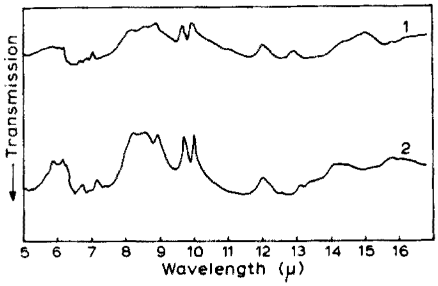

Fig. 1. Infrared spectra of dry ZeoKarb resin, 'chromatographic grade' (SRC 11), 4.5% DVB, 100–200 mesh in the hydrogen form (curve 1) and of 'water soluble' matter washed from a sample of the same resin (curve 2).

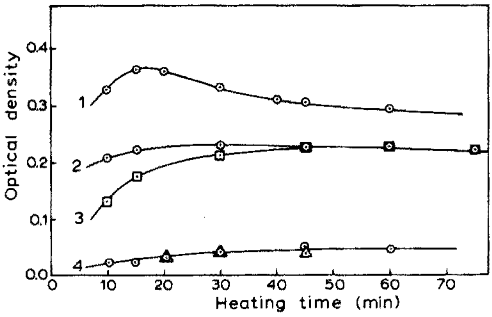

Fig. 2. The effect of heating time on the optical density (at 570 mμ) of the colour developed with chromotropic acid. Curve 1, 90.0-μg amounts of glycollic acid with chromotropic acid, sample A. Curve 2, 60.8-μg amounts of glycollic acid with sample B. Curve 3, 60.8-μg amounts of glycollic acid + 36.0 μg of lactic acid with sample B. Curve 4, blanks run on 0.5 *M* NH_4ClO_4 with sample A (△) and sample B (⊙). All measurements were made with water as the reference.

hardly apparent (Fig. 2). Aged (> *ca.* 10 h) solutions of either sample of reagent did not give such satisfactory colours as freshly prepared solutions. The optical density of the reagent solution in water at 570 mμ therefore is not necessarily a useful guide to the efficiency of a particular reagent sample.

The effect of time of heating of the sulphuric acid solution on colour development was examined for both reagents. Figure 2 shows that with chromotropic acid A a distinct maximum occurred in the optical density measured at 570 mμ after about 15 min whereas with chromotropic acid B the observed behaviour was very similar to that found for the direct formaldehyde reaction. Increase in heating time beyond 15–20 min produced a visible change in the appearance of the solutions. The absorption spectrum, which was the same as that obtained with added formaldehyde[9], underwent a change in the region of 480 mμ.

As might be expected, the strength of the sulphuric acid used in developing the colour was more important than in the direct determination of formaldehyde; the reagent quality also appeared to be significant (Table I).

TABLE I

THE EFFECT OF SULPHURIC ACID CONCENTRATION ON COLOUR DEVELOPMENT

(Glycollic acid in each sample, 90 μg; heating time, 20 min; reference substance, water)

Concn. (M) of H_2SO_4 added (5 ml)	*16*	*17*	*17.5*	*18*
Optical density: reagent A	0.280	0.327	0.338	0.365
reagent B	0.125	0.253	0.298	0.360

TABLE II

GLYCOLLIC ACID DETERMINATION; A COMPARISON OF RESULTS

Resin cross-linkage (%)	*Glycollic acid taken (μg)*	*Glycollic acid found (μg)*	
		Spectroph.	*Titr.*
2	60.8	60.8	—
	121.6	123	—
	182.5	183[a]	—
4.5	60.8	61.6	—
	60.8	60.1	—
	121.6	120	—
	121.6	122	—
8	60.8	61.5	62.0
	60.8	60.1	61.7
	121.6	121	123
	121.6	122	121
20	91.3	90.5	91.2
	152.1	151[a]	150

[a] Heating time 50 min; reagent B. The reference solution was provided by a 'blank' determination run on 0.5 *M* NH_4ClO_4 which had been equilibrated with resin in the same way as the glycollic acid sample.

The only other advantage observed from using the purer chromotropic acid (A) was that the sensitivity was a little higher; for amounts of glycollic acid less than 20 μg more reliable results were possible. For most purposes however reagent B appears to be adequate; Table II gives values obtained with this reagent and by the chromium(VI) method for the determination of known amounts of glycollic acid separated from systems containing ion-exchange resins having different degrees of cross-linking. Blank values for the chromium(VI) oxidation method were about 0.10 ml of 0.1 N chromium(VI) above the indicator blank for solutions from 8 and 20% cross-linked resins. As already pointed out, because of large and variable blank values, this method was unsuitable for solutions from resins of lower cross-linking. The spectrophotometric method was satisfactory for all the resins used and where comparable the results were in agreement with those from the titrimetric method and with the expected values from the amounts of glycollic acid added before equilibration with the resins. Neither ammonium perchlorate nor chloride in concentrations up to 0.5 M in the glycollic acid samples had any effect on the results obtained by either method. (Higher concentrations were not examined.)

Lactic acid, when substituted for glycollic acid, did not give rise to colour formation, nor did it produce an absorption maximum at accessible wavelengths below 570 mμ as it does with 2,7-dihydroxynaphthalene[2]. The colour development with samples of glycollic acid was however retarded when lactic acid was present. This retardation could be overcome by increasing the heating time to 45–50 min provided that the ratio (w/w) of lactic to glycollic acids in the sample did not exceed 3:4 (Table III).

TABLE III

THE EFFECT OF LACTIC ACID ON THE DETERMINATION OF GLYCOLLIC ACID BY THE CHROMOTROPIC ACID METHOD

Glycollic acid taken (μg)	*Latic acid present (μg)*	*Glycollic acid found[a] (μg)*	*Glycollic acid taken (μg)*	*Lactic acid present (μg)*	*Glycollic acid found[a] (μg)*
15.2	—	16	60.8	36	60.8
15.2	5.0	16	60.8	41	61.0
30.4	—	30.5	60.8	46	60.8
30.4	9.0	30.5	60.8	54	57.0
60.8	—	60.8	60.8	72	54.5
60.8	18	61.0	60.8	90	41.5

[a] Heating time for colour development was 45–50 min. Reagent A was used. The reference solution was prepared from a 'blank' run on 0.5 M NH_4ClO_4 previously equilibrated with resin.

2,7-Dihydroxynaphthalene has been recommended[1,2] for the colorimetric determination of glycollic acid. It was found that this reagent was more sensitive than chromotropic acid (by a factor of about 3); however, chromotropic acid is a more versatile and commoner reagent[10], and the reagent solution does not require preparing some 24 h before use as does that of 2,7-dihydroxynaphthalene[1]. For many purposes the additional sensitivity of the latter is unnecessary and the chromotropic acid method may then be regarded as a satisfactory alternative for the determination of glycollic acid.

It seems likely that anion-exchange resins would have somewhat similar effects to cation exchangers on the methods described.

One of us (A.R.S.) acknowledges the support of a Colombo Plan Fellowship and the grant of study leave from the Pakistan Atomic Energy Commission.

SUMMARY

Two methods were examined for the determination of glycollic acid which had been in contact with polystyrene-type cation-exchange resins. For resins with high degrees of cross-linking (8% DVB or greater), a titration based on oxidation with dichromate was satisfactory but for resins with lower cross-linking, variable 'blank' values caused difficulties. A spectrophotometric method with chromotropic acid was shown to be applicable to solutions from any resin irrespective of the cross-linking, and also to the determination of glycollic acid in the presence of lactic acid if the glycollic : lactic ratio (w/w) was not less than 4:3.

RÉSUMÉ

Deux méthodes ont été examinées pour le dosage de l'acide glycollique ayant été en contact avec des résines échangeuses de cations, du type polystyrène: titrage par oxydation au moyen de dichromate et dosage spectrophotométrique, au moyen d'acide chromotropique. Cette dernière méthode permet le dosage de l'acide glycollique, en présence d'acide lactique, à condition que le rapport acide glycollique : acide lactique ne soit pas inférieur à 4:3.

ZUSAMMENFASSUNG

Es wurden 2 Methoden zur Bestimmung von Glykolsäure geprüft, bei denen ein Polystyrol-Kationenaustauscher verwendet wird. Bei Austauscherharzen mit starker Vernetzung war eine Titration, die auf der Oxydation mit Dichromat beruht, befriedigend; bei Harzen mit geringer Vernetzung verursachten unterschiedliche Blindwerte Schwierigkeiten. Eine spektralphotometrische Methode mit Chromotropsäure erwies sich als anwendbar bei Lösungen beliebiger Harze unabhängig von ihrer Vernetzung und ebenso zur Bestimmung von Glykolsäure in Gegenwart von Milchsäure, wenn das Verhältnis Glykolsäure zu Milchsäure nicht kleiner als 4:3 war.

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TRIARYLMETHANE DYESTUFFS AS REDOX INDICATORS

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(Received June 2nd, 1965)

The triarylmethane dyestuffs were first investigated as redox indicators by KNOP[1-4], who made a systematic study of commercially available members of the group. Out of 25 dyes which showed indicator properties, 12 were selected which were sufficiently stable towards permanganate to act as reversible indicators in titrations with this reagent. Their redox potentials were reported to be about 1.0 V. KNOP considered Erioglaucine A (C.I. 42090) and Eriogreen B (C.I. 44025) to be the best indicators of the group.

In spite of the work of KNOP and other investigators[5-17] the indicator properties of a large number of readily available triarylmethane dyestuffs have not previously been examined. Forty-eight further triarylmethane dyestuffs were therefore studied as indicators in a number of redox systems, and their properties were compared with those of 5 previously recommended members of the group.

Eleven of the dyestuffs tested (including the 2 previous recommendations) were found to be satisfactory as reversible indicators in iron(II)–cerium(IV) titrations in 1 *F* sulphuric and perchloric acids, although they were slowly oxidised irreversibly by excess of oxidant and were thus inferior to indicators of the ferroin-type. The transition potentials were measured in both media and were significantly higher in perchloric acid. None of the dyestuffs was found to be suitable for titrations involving dichromate (under normal conditions), hypochlorite or chloramine-T.

For the Andrews' iodate titration 2 irreversible indicators were found. One of them, C.I. 42515 (Regina purple) is considered superior to other indicators available for this titration. The same 2 dyestuffs functioned as irreversible indicators for titrations with bromate in 2 *F* hydrochloric acid, but neither had any advantage over the accepted indicators.

Many of the dyestuffs could be used as indicators in iodine–thiosulphate titrations, and some offered certain advantages over the starch-based indicators.

Eight commercially available phthalocyanine dyestuffs and pigments were also examined in the same systems. None was considered useful for indicator purposes.

The dyestuffs which were examined are listed in Table I. These dyestuffs were subjected to systematic testing for indicator properties in various redox systems.

IRON(II)–CERIUM(IV) TITRATIONS

Cerium(IV) was chosen in preference to permanganate because its colour is less likely to mask the colour changes of the dyestuffs and because indicators have less application in systems involving the self-indicating permanganate except in very

TABLE I

TRIARYLMETHANE DYESTUFFS EXAMINED AS REDOX INDICATORS

C.I. number	*C.I. designation*	*Commercial name*	*Supplier*[a]
42000	Basic Green 4	Malachite Green	C
42040	Basic Green 1	Brilliant Green	C
42050	Acid Green 8	Acilan Fast Green BBF	FBy
42055	Acid Green 7	Guinea Fast Green G	FDN
42095	Acid Green 5	Acid Green A	FDN
42120	Acid Blue 103	Brilliant Indo Blue 5G	FH
42170	Acid Green 22	Acilan Fast Green 10G	FBy
42515*[b]	—	Regina Purple	WSS
42520	Basic Violet 2	Leather Rubine HF conc.	FH
42571	Acid Blue 13	Lissamine Violet 10B;	ICI
		Xylene Fast Blue 10B	S
42580	Acid Violet 21	Acilan Violet 4BL	FBy
42585	Basic Blue 20	Methyl Green	C
42595	Basic Blue 7	Victoria Pure Blue BO	FDN
42600	Basic Violet 4	Ethyl Violet	C
42645	Acid Violet 15	Brilliant Milling Blue FF	YDC
42655	Acid Green 90	Brilliant Acid Blue G	YDC
42660	Acid Blue 83	Benzyl Cyanine 6B	CAC
42675	Acid Blue 100	Supranol Cyanine 7BF	FBy
42685	Acid Violet 19	Fuchsine Acid;	C
		Acid Magenta	CV
42700	Direct Blue 41	Brilliant Pure Blue 8G	FDN
42705	Basic Blue 18	Astra Cyanine B	FH
42710	Acid Violet 38	Alkali Violet 3ROO	BASF
42730	Acid Blue 24	Acilan Brilliant Blue R	FBy
42735	Acid Blue 104	Xylene Brilliant Blue FBR extra	S
42740	Acid Blue 109	Acilan Brilliant Blue FFB	FBy
42750	Acid Blue 110	Alkali Blue	WSS
42755	Acid Blue 22	Soluble Blue;	C
		Soluble Blue 3B	CV
42760	Solvent Blue 23	Opal Blue SS	WSS
42765	Acid Blue 119	Alkali Blue 6B	C
42770	Acid Blue 48	Soluble Methyl Blue	WSS
42775	Solvent Blue 3	Spirit Blue	C, CV
42780	Acid Blue 93	Night Blue	C
43550	Mordant Violet 11	Monochrome Brilliant Violet 5B	FBy
43565	Mordant Violet 1	Brilliant Monochrome Violet 2B	LBH
43570	Mordant Violet 28	Naphthochrome Violet 2B '	CAC
43820	Mordant Blue 3	Eriochrome Cyanine R	C
43825	Mordant Blue 29	Chrome Azurol S	C
43830	Mordant Blue 1	Durochrome Azurol B	YDC
43855	Mordant Blue 47	Diamond Blue FBG	FBy
43865	Mordant Violet 16	Omega Chrome Violet R	S
44040	Basic Blue 11	Victoria Lake Blue R;	ICI
		Victoria Blue R	LBH
44055	Acid Blue 24	Benzyl Violet 5BN	CAC
44060	Acid Blue 88	Basolan Blue R	BASF
44075	Acid Blue 86	Basolan Blue FG	BASF
44085	Basic Blue 15	Night Blue	C
44095	Acid Blue 97	Basolan Blue G	BASF
44510	Acid Blue 123	Wool Fast Blue FBL	FH
44535	Mordant Blue 28	Naphthochrome Azurine B	CAC

TABLE I (continued)

C.I. number	*C.I. designation*	*Commercial name*	*Supplier*[a]
The following dyestuffs, previously recommended by other workers were included for purposes of comparison.			
42051	Acid Blue 3	Patent Blue V	FDN
42090	Acid Blue 9	Erioglaucine	C
42135	Acid Blue 147	Xylene Cyanole FF	C
44025	Acid Green 16	Eriogreen	C
—	Basic Blue 23	Setopalin	C

[a] C Obtained from regular chemical suppliers.
BASF Badische Aniline & Soda Fabrik A.G., Ludwigshafen am Rhein, Germany.
CAC Ciba Clayton Ltd., Clayton, Manchester.
CV The Colne Vale Dye and Chemical Co. Ltd., Milnsbridge, Huddersfield.
FBy Farbenfabriken Bayer A.G., Leverkusen, Germany.
FDN Franken-Donders' n.v., Tilburg, Holland.
FH Hoechst-Cassella Dyestuffs Ltd., Leeds (Farbwerke Hoechst A.G., Frankfurt am Main, Germany).
ICI Imperial Chemical Industries Ltd., Dyestuffs Division, Blackley, Manchester.
LBH L. B. Holliday & Co. Ltd., Huddersfield.
S Sandoz Products Ltd., Horsforth, Leeds.
WSS W. S. Simpson & Co. Ltd., Old Southgate, London.
YDC Yorkshire Dyeware & Chemical Co. Ltd., Leeds.

[b] An asterisk is used in the Colour Index[18] to indicate that a dyestuff, though numbered, is no longer commercially available.

dilute solution. It was found, however, that the results for the titration of iron(II) were the same whether permanganate or cerium(IV) was used.

Sulphuric acid medium

Reagents used. All solutions were made up in distilled water unless otherwise stated.

The 0.01 N ammonium iron(II) sulphate solution used was 1 F in sulphuric acid.

Cerium(IV) sulphate solution (0.01 N) in 1 F sulphuric acid was prepared from pure cerium(IV) hydroxide by the method of SMITH AND DIEHL[19].

Other solutions were prepared by appropriate dilution of those above.

Indicators were used as aqueous 0.1% (w/v) solutions, unless the dyestuff was insufficiently soluble in water, when the minimum quantity of ethanol necessary to dissolve the solid was added.

The dyestuffs were not purified at this stage but were used as obtained. The likely impurities were inorganic diluents such as sodium sulphate.

Preliminary testing. For each test, 1 drop of dyestuff solution was added to 1 ml of 1 F sulphuric acid containing a few drops of iron(II) solution in a small test tube. The colour was noted and oxidant was added dropwise until present in excess. Any colour change was noted. The change was then reversed by addition of reductant.

Most of the dyestuffs gave a colour change on addition of excess of cerium(IV). Most also acted as pH indicators.

The indicators which did not give a reversible colour change in the above test were not later examined under titration conditions.

Above pH 2 most of the dyestuffs were blue or green (except the p-hydroxy derivatives, which were usually red or yellow), but the colour changes on oxidation were too slow for use in titrations. As the pH was lowered, the colours usually changed through green to yellow. In acid concentrations above 4 *F* many of the dyestuffs were orange or red. In 1 *F* acid, the colours generally varied from yellow to green (reduced) and orange to carmine (oxidised).

On the test-tube scale the colour changes were often better in 0.1 *F* than in 1 *F* sulphuric acid, because it was easier to see a colour change from green to red than one from yellow to red. In titrations, however, this effect was more than balanced by the greater speed of the colour change in the more concentrated acid.

The following dyestuffs gave little or no colour change, or their end-point colours were stable for only a few seconds; these were not tested further in this system (only the C.I. numbers are given here):

42120
42515
42520
42655
42685
42700
42740
42750
42755
42760
42765
42770
42775
42780
43565
43570
43820
43825
43830
43865
44075
44085
44535

Trial titrations. The remaining dyestuffs were all tested under titration conditions in 1 *F* sulphuric acid as follows: 10 ml of 0.01 *N* iron(II) solution in 1 *F* sulphuric acid were titrated with 0.01 *N* cerium(IV) solution in 1 *F* sulphuric acid. About 0.5 ml from the end-point, 0.5 ml of dyestuff solution and 0.5 ml of 2 *F* sulphuric acid were added. The titration was then continued to the colour change of the indicator. A potentiometric titration was carried out for comparison. The indicators were then examined in the reverse titration of cerium(IV) with iron(II).

For various reasons — usually irreversibility, sliding end-points, or slowness of colour change — all except 11 dyestuffs were rejected as unsuitable as indicators for the iron(II)–cerium(IV) titration in 1 *F* sulphuric acid.

Redox potentials. Attempts were made to measure the formal redox potentials of the 11 indicators. A mixture of the indicator and iron(II) solution was titrated potentiometrically with 0.1 *N* cerium(IV) sulphate in 1 *F* sulphuric acid, but no suitable curves could be obtained under any conditions. The end-point inflection for the iron(II)–cerium(IV) reaction was normal, but no indicator end-point was obtained because of the irreversible side-reactions which occurred during oxidation. The potential rose sharply on addition of a drop of oxidant, but fell immediately, first rapidly and then gradually over a period of 30 min; this effect occurred with each drop of oxidant until all the indicator was destroyed. Further addition of oxidant then caused the potential to rise normally.

The method of SMITH AND BANICK[20], involving the use of potentiopoised solutions, was then tried. The solutions were prepared starting from ammonium vanadate (SMITH AND BANICK used vanadyl chloride). The transition potentials of the triarylmethane dyestuffs could not be measured by this method because no colour change was observed. The reduced colour, in most cases green or yellow, was masked by the green colour of the solutions. The reversible oxidation product (red) should have been visible if it had been formed, but the irreversible oxidation product (pale yellow-brown) would not have been visible at the concentrations used. These potentiopoised solutions have apparently a limited application in systems which are not completely reversible.

The failure of the 2 previous methods showed that the indicators were too readily oxidised irreversibly for their formal redox potentials to be measured. Also, the practically useful potential of an indicator is that at which its colour change occurs, *i.e.*, the transition potential. The transition potentials were measured under titration conditions in 1 *F* sulphuric acid as follows. A mixture of a small volume of iron(II) solution in 1 *F* sulphuric acid with 0.5 ml of indicator solution and 0.5 ml of 2 *F* sulphuric acid was titrated dropwise with 0.001 *N* cerium(IV) sulphate solution in 1 *F* sulphuric acid. The potential at which the colour transition occurred was noted; 0.001 *N* iron(II) solution was then added to reverse the change and the transition potential again noted. The end-point was traversed several times.

With each indicator the colour change occurred over a range of about 50 mV. This potential range was the same in both directions, however many times the end-point was traversed, except with C.I. 42595. One drop of 0.001 *N* cerium(IV) solution in excess did not destroy any of the indicators during 10 min. The results are given in Table II.

TABLE II

TRANSITION POTENTIALS OF CERTAIN TRIARYLMETHANE INDICATORS IN 1 *F* SULPHURIC AND PERCHLORIC ACIDS

Dyestuff	*Transition range (mV)*	
C.I.	*1 F* H_2SO_4	*1 F* $HClO_4$
42050	945–1005[a]	1145–1185[a]
42051	1105–1145	1120–1170
42090	1095–1155	1120–1190
42135	1085–1145	1125–1195
42571	1090–1150	1075–1140
42595	1065–1110	1110–1180
42705	1075–1115	1090–1130
42735	1125–1165	1145–1165
44025	1115–1155	1135–1195
44040	1040–1085	1060–1125
Basic Blue 23	1105–1150	1120–1180
Potential breaks		
Fe(III)/Ce(IV)	820–1220	900–1450
Ce(IV)/Fe(II)	1260–820	1500–900

[a] These transition ranges are least accurate, because of the poor colour transition of this indicator.

Perchloric acid medium

Reagents. Cerium(IV) perchlorate (0.01 *N* and 0. 001 *N*) in 1 *F* perchloric acid (A.R. grade) was prepared from ammonium cerium(IV) hexanitrate[21].

Iron(II) perchlorate solutions (0.01 *N* and 0.001 *N*) were prepared by dissolving electrolytic iron in 1 *F* perchloric acid.

Results. Tests similar to those described for sulphuric acid media were carried out.

The 11 dyestuffs which were satisfactory as redox indicators in 1 *F* sulphuric acid were also the only ones suitable in 1 *F* perchloric acid.

The transition potential ranges were in all cases higher, and the colour changes occurred more slowly in perchloric acid than in sulphuric acid (Table II). The best colour change in this system was that given by Basic Blue 7 (C.I. 42595).

That the potentials are higher in perchloric acid agrees with the findings of ADAMS AND HAMMAKER[12] for Patent Blue V (C.I. 42051), although the values they found were lower than those obtained in the present work (but see ref. 28).

Nitric acid medium

RAO AND RAO[5] have reported that the 3 triarylmethane dyestuffs, C.I. 42090, C.I. 42135 and C.I. 44025, are unsuitable as indicators for cerium(IV) titrations in nitric acid media.

All 48 dyestuffs were tested for indicator properties in this system. Colour changes similar to those observed by RAO AND RAO were found to occur with all of them, but the changes did not occur anywhere near the region of the end-point. These dyestuffs are considered unsuitable as indicators for titrations with cerium(IV) in nitric acid.

Comparison of results in sulphuric and perchloric acids

Figures 1 and 2 give respectively the titration curves obtained experimentally for the iron(II)–cerium(IV) system in 1 F sulphuric and perchloric acids. The dotted lines indicate the ranges over which the colour transitions of the triarylmethane indicators occur. The formal reduction potentials for the couples Fe(III)/Fe(II) and Ce(IV)/Ce(III) obtained from these curves agree well with their accepted values (Table III) and provide a useful check on the measurements. An exception is the Ce(IV)/Ce(III) potential in 1 F perchloric acid. SMITH AND GETZ[21] have shown that solutions of cerium(IV) perchlorate decompose slowly on standing. Steady potentials were achieved extremely slowly when the oxidant was in excess with the result that the observed potentials might not have been equilibrium values, even although periods of 10 min were allowed between additions of titrant.

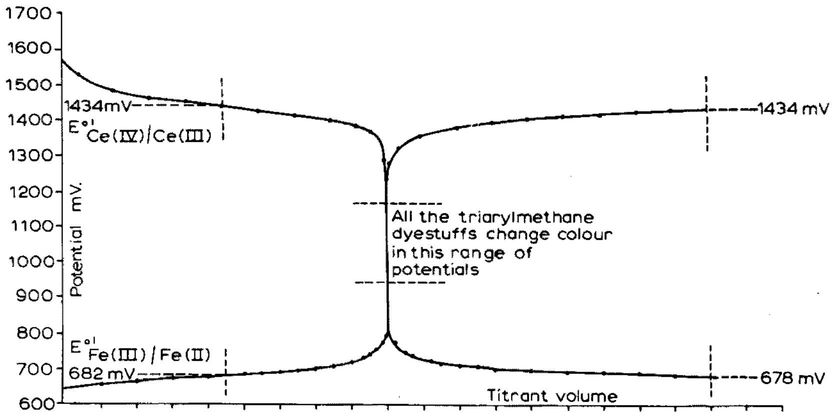


Fig. 1. Titration curves for the system: cerium(IV)–iron(II) in 1 F sulphuric acid.

Table II gives the transition potentials of the indicators in the 2 media. The potential at the end-point of a titration of iron(II) with cerium(IV) is higher than that for the corresponding reverse titration. However, one drop of 0.01 *N* titrant is more than enough to change the potential from one extreme of the potential break to the other, so that discrepancies in the values are unlikely.

Trial titrations were carried out in 1 *F* sulphuric and perchloric acids using 0.01 *N* iron(II) and 0.01 *N* cerium(IV). When aqueous 0.1% solutions of the dyestuffs were used, the optimum volume was found to be 0.5 ml for a titration volume of 50–100 ml (except for C.I. 42595, when 0.15 ml was used). For the titration of cerium(IV) with iron(II), it was necessary to add the indicator about 0.5 ml before the end-point, otherwise irreversible oxidation of the dyestuff occurred. Even for the iron(II) titration with cerium(IV) it was preferable to add the indicator near the end-point to avoid fading of the colour.

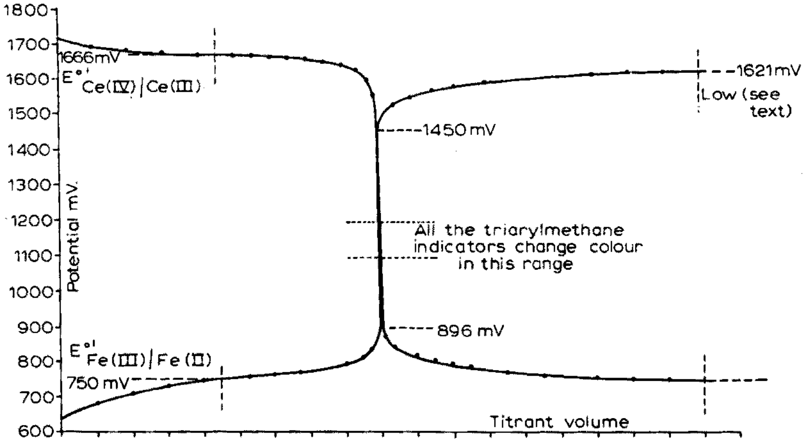


Fig. 2. Titration curves for the system: cerium(IV)–iron(II) in 1 *F* perchloric acid.

TABLE III

FORMAL REDUCTION POTENTIALS FOR THE SYSTEM Fe(II)–Ce(IV) IN 1 *F* SULPHURIC AND PERCHLORIC ACIDS (FROM FIGS. 1 AND 2)

Couple	*Medium*	*Potentials from curves $E^{0\prime}$ (V)*[a]	*Literature value (V)*	*Refs.*
Fe(III)/Fe(II)	1 *F* H_2SO_4	0.678, 0.682	0.68	22
Ce(IV)/Ce(III)	1 *F* H_2SO_4	1.437, 1.434	1.44	23,24
Fe(III)/Fe(II)	1 *F* $HClO_4$	0.750, 0.746	0.735	25
			0.75	23
Ce(IV)/Ce(III)	1 *F* $HClO_4$	1.621, 1.666	1.70	23

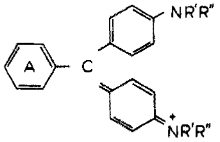
[a] Although potentials are quoted to the nearest mV, an accuracy of only ±10 mV is claimed for these measurements.

The indicators were all reversible. With each, the colour transition point could be traversed at least 8 times without destruction of the dyestuff, provided that the excess of oxidant did not exceed 0.1 ml of 0.01 *N* solution. Duplicate titrations agreed to within 0.02 ml (25-ml aliquots). The indicator blanks were never greater than 0.15 ml of 0.01 *N* cerium(IV). The colour changes were rather slow with 0.01 *N* solutions and these indicators cannot really be recommended for use with such solutions, although a more accurate measurement of indicator blanks was obtained with 0.01 N solutions. The colour changes were all satisfactory with 0.1 N solutions and the indicator blanks were then negligible. The present indicators are, however, inferior to the ferroin-type indicators for these titrations. Errors of up to 1% were obtained by comparison with the potentiometric method.

In 1 F sulphuric acid, the more commonly used triarylmethane dyestuffs, C.I. 42051, C.I. 42090, C.I. 42135, C.I. 44025 and C.I. Basic Blue 23 (Patent Blue V, Erioglaucine, Xylene Cyanole FF, Eriogreen and Setopalin) were superior in indicator action to the other dyestuffs tested. In 1 F perchloric acid, C.I. 42595 (Basic Blue 7) was best. However, all these indicators were irreversibly oxidised by an excess of cerium(IV), and their colour changes occurred over fairly wide potential ranges. Consequently, now that the superior ferroin-type indicators are available for use with cerium(IV) solutions, it is difficult to justify the recommendation of triarylmethane dyestuffs as indicators in titrations with this oxidant.

Relation between structure and indicator properties

A comparison of the chemical structures of the present triarylmethane dyestuffs and the best of those recommended by KNOP shows most of them to have the general structure:



where R' = alkyl, R'' = alkyl, benzyl or H.

In sulphuric acid media the best of the dyestuffs studied were C.I. 42051, C.I. 42090, C.I. 42135, C.I. 44025 and Basic Blue 23, all of which have the above structure. However, not all the dyestuffs with this structure will function satisfactorily as indicators.

In general, simple substituents in the aromatic rings are more likely to result in compounds with acceptable indicator properties. The presence in ring A of a *p*-amino or substituted amino group, generally leads to a decreased resistance to oxidation. KNOP has many such compounds in his list of less satisfactory indicators. The *p*-hydroxytriarylmethane dyestuffs, on the other hand, are useless as indicators.

Although the effects of these variations can be observed, no definite relation between structure and properties is possible in the absence of adequate knowledge of the chemical processes by which these compounds function as indicators. Some investigation into the mechanism of oxidation of the dyestuffs has been made[3,17], but the indicator processes are still uncertain.

DICHROMATE–IRON(II) TITRATIONS

These triarylmethane dyestuffs were also examined for indicator properties with 0.1 N dichromate in 1 F sulphuric acid. None functioned satisfactorily. In view of the transition potentials reported in the previous section, and the reported formal reduction potential of the Cr(VI)/Cr(III) couple in 1 *F* sulphuric acid (0.92[25], 1.09[26], 1.03[27]), this is not surprising. In more concentrated sulphuric acid (4 *F* and above), some of the dyestuffs were found to function as indicators but were of little practical value. These observations accord with the generally higher transition potentials found for the triarylmethane dyestuffs in the present work[28] compared with those obtained by previous workers. The indicators were equally unsatisfactory in 1 *F* perchloric acid.

TITRATIONS WITH HYPOCHLORITE AND CHLORAMINE-T

The only triarylmethane dyestuff previously recommended for use with chloramine-T is C.I. 42510 (rosaniline), which gives an excellent colour change[29].

All 48 dyestuffs were tested for indicator properties with hypochlorite and chloramine-T at pH values from 2 to 12 and 2 to 4 respectively.

Most of them were immediately decolorised by both reagents below pH 4; above pH 4 some were decolorised by hypochlorite. None of the indicator reactions was affected by arsenic(III) solution.

In the presence of bromide, a few of the indicators formed coloured products on the addition of oxidant. This property has been previously noted by GUARESCHI[30] for C.I. 42510 and other related dyestuffs, and was used by BISHOP AND JENNINGS[29] to indicate the end-point of chloramine-T titrations, again with rosaniline. In the present work, the best colour change was obtained with Basic Violet 2 (C.I. 42520) at pH 2–3. This dye is very similar to C.I. 42510. The colour change was from crimson to purple and was irreversible. None of the other dyestuffs can be recommended.

TITRATIONS WITH BROMATE

The best triarylmethane dyestuff which has been recommended for use in direct titrations with bromate is C.I. 42500 (fuchsine)[31,32]. The dyestuffs under study were tested for indicator properties in the arsenic(III)–bromate reaction in 2 *F* hydrochloric acid; 0.5 ml of aqueous 0.1% indicator was used. The dyes which gave reasonable colour changes were then tested under titration conditions and compared with accepted indicators for this titration. All the colour changes were irreversible. The best were:

C.I. 42515 (Regina Purple): colourless→bright purple
C.I. 44085 (Basic Blue 15): orange-yellow→green-yellow

Both colour changes tended to occur early, owing to local excesses of oxidant, and were almost certainly brought about by bromination of the indicator. The indicators had to be added very close to the end-point, to avoid premature oxidation. They were no better than the accepted indicators, Naphthol Blue-Black (C.I. 20470) and Bordeaux (C.I. 16180).

TITRATIONS WITH IODATE

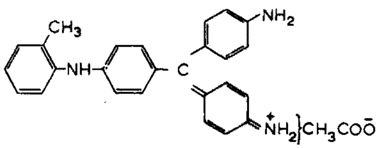
No triarylmethane dyestuff has apparently been recommended for use in iodate titrations.

When the present dyestuffs were examined in the arsenic(III)–iodate titration

in 5 F hydrochloric acid (Andrews' conditions), two of the dyestuffs showed good, though irreversible, indicator properties. These were:
C.I. 42515 (Regina Purple): red-brown→green→purple
C.I. 44085 (Basic Blue 15; Night Blue): yellow→orange→green

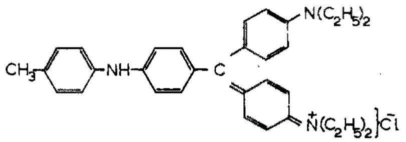
In these tests 25 ml of 0.1 N arsenic(III) solution, 10 ml of water and 30 ml of concentrated hydrochloric acid were titrated with 0.1 N potassium iodate; 0.5 ml of aqueous 0.1% dyestuff was added when the iodine colour had faded appreciably. The precision of duplicate titrations was very good. Regina Purple gave a very vivid colour change; the green colour which appeared immediately before the end-point gave good warning that the change was imminent. This indicator is highly recommended and is considered superior to the other indicators available for the Andrews' titration. It has the advantage of a positive colour change (green→purple) which is not the case with other indicators in this system. C.I. 44085 has a poorer colour change but, with practice, excellent results could be obtained. These dyestuffs were used successfully in the titrations with iodate of iodide, hydroxylamine, arsenic(III), antimony(III) and tin(II).

C.I. 42515 is a mixture, the composition of which depends largely on the process of manufacture. In the present work, the dyestuff used was Regina Purple, supplied by W. S. Simpson and Co. Ltd., who state that it is a low phenolation of C.I. 42510 (magenta), which is itself a mixture. It is listed in the Colour Index as a basic dye, with the typical component:

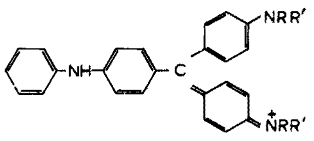


It was not possible to separate the active component from the mixture, but recrystallisation from water and ethanol did not noticeably affect the properties of the dyestuff.

The formula of C.I. 44085 is:



These two indicators have the triarylmethane and the diarylamine structures in common. In view of this, other dyestuffs with these structures were re-examined for indicator properties in the Andrews' titration. All gave colour changes, but these were masked by the yellow colour of the solution. On this basis it seems likely that compounds with the general structure:



can act as indicators in the Andrews' titration.

TITRATIONS WITH IODINE

Qualitative tests showed that a number of the dyestuffs could be used to indicate the end-point of the iodine–thiosulphate titration. Most of the triarylmethane dyestuffs act as pH indicators below pH 2, and so the colour changes in iodine–thiosulphate titrations depend on pH. Tests were carried out at pH 7, pH 4 and in 0.5 *F* and 1 *F* sulphuric acid. The indicators were compared with a commercial starch–urea type indicator.

At pH 4 and pH 7, the best response was given by:

C.I. 44040 (Basic Blue 11): yellow-green→ultramarine
C.I. 44085 (Basic Blue 15): yellow-green→blue
C.I. 42585 (Basic Blue 20): turquoise →blue

C.I. 44040 gave an extremely good colour change which was as sharp as that given by starch–urea. The sensitivities of these dyestuffs to the tri-iodide ion were about the same as starch–urea — $2.5 \cdot 10^{-5}$ *N* iodine in potassium iodide could just be detected. These dyestuffs offer no apparent advantages over the conventional starch indicators for titrations involving iodine in neutral or weakly acidic aqueous solutions, except perhaps in the ease of preparation of the indicator solution. However, MEDITSCH[33] has pointed out the advantages of C.I. 42000 (Basic Green 4; Malachite Green) for iodimetry in aqueous alcoholic solutions or in high salt concentrations in which media starch functions imperfectly. In the presence of 50% alcohol, the response of the above 3 dyes was, if anything, enhanced. The indicator properties of these dyes are considered superior to C.I. 42000. In 0.5 *F* sulphuric acid, the best colour changes were given by:

C.I. 42600 (Basic Violet 4): blue-green →yellow-green
C.I. 44040 (Basic Blue 11): olive-yellow→turquoise

When the acid concentration was reduced to 0.2 *F*, the final colour with C.I. 42600 could be turquoise or violet. In 1.0 *F* sulphuric acid, the colour change of C.I. 42600 was from brown-purple through blue-grey to yellow-green, whereas that of C.I. 44040 was from blue-green to pale apple-green. C.I. 42600 gave a very good colour change but was less sensitive than starch–urea.

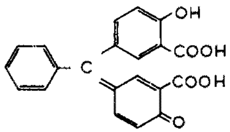
Several of the dyes, and in particular, C.I. 42655 (Acid Green 90), gave distinctive colours with free bromine and iodine. The sensitivities were, however, poor; 1 part in 2000 of bromine or iodine gave a yellow colour with the dye in 1 *F* sulphuric acid. Larger amounts of bromine or iodine gave a green colour.

OTHER INDICATOR PROPERTIES

Most of the present dyestuffs act as pH indicators. In general the colour changes occur below pH 2.5; C.I. 42051 (Patent Blue V) for example has been recommended for the pH range 0.8–3.0[13].

The *p*-hydroxytriarylmethane dyestuffs possess metallochromic properties, which have, for example, been utilised in spot tests for aluminium[34].

These dyestuffs have as their basic structure:



For example, C.I. 43825 (Mordant Blue 49, Chrome Azurol S) has found wide application as a colorimetric reagent and these applications of this class of dyestuffs were not further examined.

PHTHALOCYANINE DYESTUFFS AS INDICATORS

RAO *et al.* have recommended copper[35] and nickel[36] phthalocyaninesulphonic acids as cerimetric indicators. Their work suggested that this group of dyestuffs could provide a source of useful redox indicators.

A number of commercially available phthalocyanine dyestuffs was therefore examined in the systems described in the previous sections. The results were disappointing. The only dyestuff found to function at all satisfactorily as an indicator was C.I. 74140, which is a sulphonated cobalt phthalocyanine. The indicator reactions of the phthalocyanines were found to be less satisfactory than those of the triarylmethane dyestuffs, and in most examples, the reversibility of the indicator was poor. It was not possible to compare the behaviour of the present phthalocyanines with RAO's indicators; the latter are no longer available commercially.

TABLE IV

PHTHALOCYANINE DYESTUFFS TESTED

C.I. number	*C.I. designation*	*Commercial name*	*Source*[a]
74140	Vat Blue 29	Indanthren Brilliant Blue 4G	FBy
74160	Pigment Blue 15	Monastral Fast Blue B	ICI
74180	Direct Blue 86	Durazol Blue 8G	ICI
74200	Direct Blue 87	Paper Blue 10GS	ICI
74240	Ingrain Blue 1	Alcian Blue 8GX	ICI
74250	Pigment Blue 15	Monastral Fast Blue RFS	ICI
74260	Pigment Green 7	Monastral Fast Green GNS	ICI
74350	Solvent Blue 25	Zapon Fast Blue HFL; Methasol Fast Blue 2G	BASF ICI

[a] See footnote to Table I.

The substances shown in Table IV were tested. The transition potential ranges found for C.I. 74140 were 935–990 mV in 1 *F* sulphuric acid and 985–1035 mV in 1 *F* perchloric acid; the measurements were made in the iron(II)–cerium(IV) system. The colour change on oxidation in 1 *F* sulphuric acid was: turquoise→blue→purple. The purple colour soon faded as irreversible oxidation occurred. In 1 *F* perchloric acid the change from turquoise-blue to blue-pink was slow and poor, and the indicator had to be added near the end-point, because of rapid fading of the oxidation colour. Some improvement in the colour change was observed in more concentrated acids, but in general their behaviour was inferior to that of the triarylmethane dyes.

We are grateful to the firms listed in Table I for samples of dyestuffs; without their support this investigation would not have been possible. We also thank Professor R. BELCHER for his interest in and support for this work.

SUMMARY

The redox properties of a number of triarylmethane dyestuffs have been studied in conventional redox titrations and their usefulness as redox indicators has been assessed. None is superior to the established indicators for titrations involving cerium(IV) and chromium(VI) as oxidising titrants. One dyestuff, Regina Purple (C.I. 42515), is strongly recommended for use in the Andrews' iodate titration and another, Basic Blue 11 (C.I. 44040), for the iodine–thiosulphate titration. Certain commercially available phthalocyanine dyestuffs have also been studied as redox indicators and their behaviour is compared with that of the triarylmethane type.

RÉSUMÉ

Les auteurs ont examiné un certain nombre de colorants triarylméthane, comme indicateurs pour des titrages rédox conventionnels. Aucun n'est supérieur aux indicateurs déjà utilisés pour les titrages au moyen de cérium(IV) et de chrome(VI). La "pourpre Regina" (C.I. 42515) est vivement recommandée lors du titrage par l'iodate, selon Andrews et le "bleu basique 11" (C.I. 44040) pour le titrage iode–thiosulfate. Quelques colorants phtalocyanine ont également été examinés comme indicateurs rédox; leur comportement a été comparé à celui des colorants du type triarylméthane.

ZUSAMMENFASSUNG

Die Redoxeigenschaften einer Anzahl Triarylmethanfarbstoffe wurde bei konventionellen Redoxtitrationen untersucht und ihre Brauchbarkeit als Redoxindikator diskutiert. Die angegebenen Indikatoren eignen sich für Titrationen sehr gut, auch für Titrationen mit Cer(IV) und Chrom(VI). Reginapurpur (C.I. 42515) wird sehr für die Andrewssche Jodattitration empfohlen, basisch Blau 11 (C.I. 44040) für die Jodthiosulfattitration. Ferner wurden gewisse kommerziell verfügbare Phthalocyaninfarbstoffe als Redoxindikatoren untersucht und ihr Verhalten mit dem des Triarylmethantyps verglichen.

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A RAPID METHOD FOR THE DETERMINATION OF SUBSTANCES RESOLVED ON THIN-LAYER PLATES

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(Received February 19th, 1965)

The application of spectral reflectance to thin-layer chromatography has made it possible to effect the *in situ* identification and determination of chemical species separated on thin plates. FRODYMA *et al.*[1] succeeded in identifying the components of dye mixtures resolved on chromatoplates by direct examination of the plates by spectral reflectance. The amounts of adsorbed dye were determined at the same time with a precision of approximately ±5%. Subsequently the technique was applied to the analysis of amino acids[2,3] and to the determination of substances which absorb in the ultraviolet[4].

In each of the above instances, it was found that a greater degree of precision was achieved if the reflectance measurements were carried out on spots removed from the plates and packed in an appropriate cell rather than on the plates themselves. Unfortunately the process of scraping a spot off the plate and then preparing an analytical sample of fixed weight by the addition of adsorbent proved to be not only tedious but time-consuming. Approximately 5 min are required for the preparation of a single sample for analysis. Suction techniques for the removal of spots from chromatoplates, which are used widely in conjunction with elution procedures[5,6] were found to be unsuitable for the purpose. Although they are somewhat more expeditious than the manual method, they do not eliminate the weighing operation in the preparation of the analytical sample.

The use of a planchet to remove a fixed amount of material from the plate under examination seemed to offer a means of facilitating the sample preparation provided that a reasonably uniform thickness of adsorbent could be maintained. Accordingly it was decided to determine the uniformity of the distribution of adsorbent on chromatoplates prepared with a commercial applicator and, if necessary, to devise a procedure for the preparation of thin layers of the requisite uniformity. Once this was done, it was proposed to investigate the feasibility of employing the planchet technique in the determination of substances which absorb in the visible and in the ultraviolet.

EXPERIMENTAL

A Desaga-Brinkman Model "SII" applicator was used to coat the 20 x 20 x 0.3 cm plates with Merck silica gel G. Five plates were prepared at one time, and the thickness of the adsorbent layer was varied by setting the height of the applicator gate at either 0.75 mm, 0.50 mm or 0.25 mm. Mixtures of 70, 65 and 35 g, respectively, of silica gel mixed with water in the ratio of 1 to 2 yielded thin layers of acceptably uniform thickness at these 3 settings. The adsorbent–water mixture was prepared by adding the silica gel to the appropriate amount of water contained in a filtering flask which was attached to an aspirator. Following the addition, the flask was stoppered, suction applied, and the mixture was shaken vigorously for 30–45 sec before it was introduced into the applicator chamber. Thin layers prepared in this manner were found to be free of air bubbles and, consequently, more uniform with respect to their thickness. The plates were dried at 120° for 2 h in a mechanical convection oven and then stored in a desiccator over calcium chloride until used.

Analytical samples were removed from chromatoplates with circular aluminum planchets which were manipulated by means of cork stoppers affixed to the planchets. The size of planchet employed was dictated by the thickness of the adsorbent layer and by the area being excised. During the removal, the plates rested on two rectangular wooden blocks to each of which was fastened a 0.5-cm thick L-shaped strip of wood whose function it was to hold the plates in place. The wood blocks were 3.0 cm thick, so as to permit a small agate mortar to be slipped under the chromatoplates, and could be positioned independently, so as to accommodate plates of varying sizes. The assembly employed is depicted in Fig. 1. Once the sample had been cut out of an adsorbent layer by exerting a slight pressure on the inverted planchet,

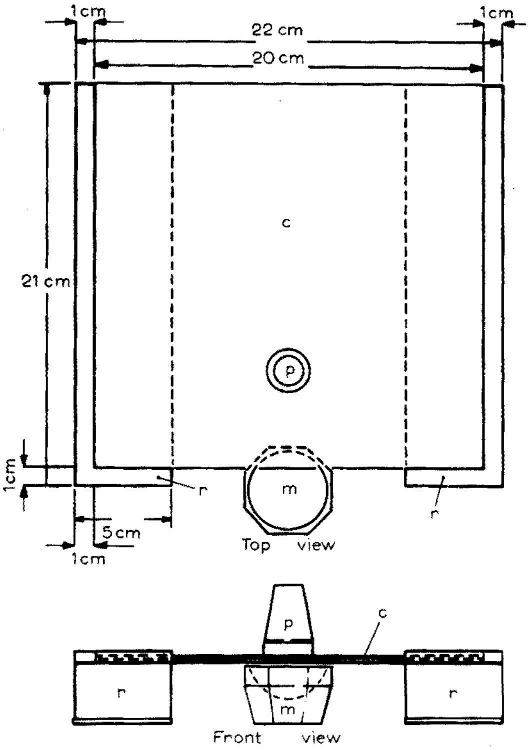

Fig. 1. Assembly employed to excise samples from chromatoplates. c, chromatoplate; m, agate mortar; p, planchet affixed to cork stopper; r, wooden rack.

the most direct path between it and the nearest plate edge was cleared of adsorbent with a brush and the planchet was moved along this path until the sample was deposited in the agate mortar. By means of this procedure, it is possible to remove a spot for analysis in approximately 30 sec.

The practicability of employing this technique to determine substances which absorb in the visible and in the ultraviolet was investigated with the use of an aqueous 0.001 *M* stock solution of eosine B and a 0.1 *M* stock solution of salicylic acid in chloroform. After these stock solutions were applied with a micropipet, the plates were dried in a mechanical convection oven at 110° for 15 min in the case of the eosine B, and at 90° for 2 h in the case of the salicylic acid. All samples were removed from chromatoplates by means of the planchet technique and then ground in a small agate mortar for two periods of 20 sec each to insure homogeneity. Samples used in the preparation of standard dilution curves were also weighed to ±0.4 mg. The reference standard in all cases consisted of adsorbent from the plate under investigation.

Reflectance measurements were made with a Beckman Model DU Spectrophotometer fitted with a standard reflectance attachment. The cells employed with the salicylic acid samples[4] and with the eosine B samples[7] have been described elsewhere by the authors.

RESULTS AND DISCUSSION

Distribution of adsorbent on thin plates

For purposes of identification, chromatoplates were numbered from 1 through 5 in order of their preparation. Similarly each plate was subdivided into 5 equal rectangles, whose long axes were parallel to the direction of movement of the applicator, and the rectangles were numbered from 1 through 5 commencing with the one adjacent to the retaining edge of the mounting board. For the most part, 5 equally-spaced samples were excised from each rectangle by means of the planchet technique and weighed to ±0.2 mg. Occasionally a slight irregularity in the movement of the applicator as it proceeded from one plate to the next resulted in an obvious imperfection in the final surface being laid down on the former plate. In such instances no use was made of the atypical area and only 4 samples were removed from each rectangle. The reproducibility of the weights of the excised samples obtained for different thicknesses of adsorbent is given in Table I, which presents representative data for the various plates. Each tabular entry for the individual plates represents the relative standard deviation of a set consisting of 4 or 5 samples whose weights ranged from 50 to 80 mg.

In general, the relative standard deviation obtained for the weights of samples removed from any one plate was less than that obtained for the weights of samples removed from all 5 of the plates. Reproducibility between pairs of plates was best for those prepared successively and decreased as the number of intervening plates increased. Since the average weight of the samples excised from plates constituting any single series was found to decrease in the order of their preparation, that is from 1 through 5, the above variations are probably due to the gradual decrease in the thickness of the adsorbent layer being laid down by the applicator as the slurry in its chamber is discharged. This effect was diminished by preparing amounts of the water–adsorbent mixture somewhat in excess of that required to coat the plates with the result that the

TABLE I

REPRODUCIBILITY OF WEIGHTS OF EXCISED SAMPLES OBTAINED FOR DIFFERENT THICKNESSES OF ADSORBENT

Gate setting (mm)	*Planchet diameter (cm)*	*Row no.*	*Relative standard deviation (%)*					*Rel. std. dev. for plates 1 and 5 (%)*	*Rel. std. dev. for two intermediate plates (%)*
			Plate 1	*Plate 2*	*Plate 3*	*Plate 4*	*Plate 5*		
0.75	2.0	5	4.0		1.6	0.6	4.5	8.0	2.5
		4	0.7		1.1	1.1	4.2	7.9	1.5
		3	9.1		2.5	1.5	3.7	9.8	2.3
		2	2.5		3.0	4.2	3.5	8.5	3.4
		1	2.6		1.6	0.7	3.3	9.0	1.6
		Ave.	3.8		2.0	1.6	3.8	8.6	2.3
0.50	2.4	5	4.1	0.6	1.9		4.3	3.5	1.3
		4	4.1	2.0	2.4		4.5	6.1	3.2
		3	5.2	1.2	2.5		3.1	7.4	2.5
		2	7.3	3.3	0.9		3.2	3.8	3.3
		1	1.4	1.6	2.3		4.6	8.8	2.9
		Ave.	4.4	1.7	2.0		3.9	5.9	2.6
0.25	3.0	5	6.2	2.3		2.8	5.7	5.2	3.0
		4	2.9	4.3		4.3	1.5	2.1	3.7
		3	1.1	1.4		3.2	0.5	1.7	2.5
		2	7.9	3.4		1.8	9.1	6.4	3.1
		1	7.9	2.1		3.2	6.6	7.9	2.2
		Ave.	5.2	2.7		3.1	4.7	5.3	3.7
Ave. rel. std. dev. for all thicknesses			4.4	2.2	2.0	2.4	4.1	6.6	2.9

reproducibility of the weights of samples excised from different plates recorded in Table I was achieved.

It was also found that the average relative standard deviations for samples excised from plates 1 and 5, considered either separately or together, were significantly greater than those for samples removed from plates 2, 3 and 4, likewise considered either separately or together. This discrepancy might be ascribed, at least in part, to the fact that the applicator was being accelerated and decelerated during the preparation of plates 1 and 5, respectively.

Effect upon reflectance of sample weight variation

The procedure outlined in the experimental section was followed in preparing standard dilution curves for eosine B and salicylic acid, and the data were plotted in the form percent reflectance *versus* concentration, as shown in Fig. 2. Within the indicated concentration ranges, the difference in percent reflectance associated with a given deviation in the concentration can be obtained from the slope, m, of the curve at the appropriate point, or

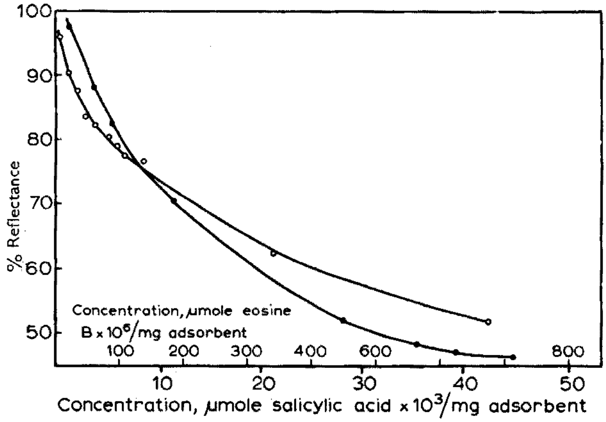

Fig. 2. Reflectance as a function of concentration. ○—○ % reflectance at 520 mμ of eosine B adsorbed on silica gel. ●—● % reflectance at 302 mμ of salicylic acid adsorbed on silica gel.

$$m = \frac{\Delta \text{ in } \% \text{ reflectance (reflectance units)}}{\Delta \text{ in concentration } (\mu\text{mole/mg absorbent})}$$

The difference in concentration resulting from a 1% deviation in the weight of the analytical sample may be estimated as follows,

$$\frac{\Delta \text{ in concentration } (\mu\text{mole/mg adsorbent})}{\text{Unit } \% \ \Delta \text{ in weight}} = -\left(\frac{w}{W} - \frac{w}{W \pm 0.01\,W}\right)$$

where w is the amount of absorbate in μmole and W is the weight of the sample in mg. By combining these two expressions, it becomes possible to estimate the difference in percent reflectance induced by a 1% deviation in the weight of the analytical sample

$$\frac{\Delta \text{ in } \% \text{ reflectance}}{\text{Unit } \% \ \Delta \text{ in weight}} = -\left(\frac{w}{W} - \frac{w}{W \pm 0.01\,W}\right) m$$

When this equation was applied to data obtained with a series of 70-mg samples, at points corresponding to 5, 30, 60, 100, 150, 200, 300, 500 and 600 · 10^6 μmoles of adsorbed eosine B differences in the percent reflectance amounting to 0.03, 0.06, 0.08, 0.10, 0.12, 0.16, 0.16 and 0.20, respectively, were indicated for a 1% deviation in the sample weight. Similarly, at points corresponding to 2.5, 10, 20, 30, 35 and 45 · 10^3 μmoles of adsorbed salicylic acid it was indicated that differences in the percent reflectance amounting to 0.07, 0.18, 0.20, 0.16, 0.17 and 0.04, respectively, were to be expected for a 1% deviation in the sample weight.

Employing these data in conjunction with the data set forth in Table I, one can approximate the average relative standard deviation provided by the planchet technique within the concentration range studied. For example, the maximum deviation that may be anticipated with any individual plate or combination of plates can be arrived at by using 0.20, the maximum observed deviation in the percent reflectance of both eosine B and salicylic acid caused by a one percent sample weight deviation, as the basis for an approximation. Reflectance measurements carried out on samples excised from a single plate would then have an estimated average relative standard deviation of 0.9 reflectance unit for plates 1 and 5, which exhibited an overall average relative standard deviation in weight of 4.3% for all thicknesses of an individual plate, and of 0.4 reflectance unit for plates 2, 3 and 4, where the corresponding weight deviation only amounted to 2.2%. Similarly measurements involving samples excised from various combinations of plates would have an average relative standard deviation of 1.3 reflectance units for plates 1 and 5, where the overall average relative standard deviation in weight was 6.6% for all thicknesses of series of both plates, and of 0.6 reflectance unit for plates 2, 3 and 4, which manifested a weight derivation of only 2.8%.

On the basis of these calculations it would appear that plates 1 and 5 are unsuitable for use with the planchet technique if the precision of which the reflectance technique is capable is to be fully realized. For analyses dealing with stable systems and involving no chromogenesis this has been found to be limited by variations associated with the packing of the sample cell[1] and amounts to an average relative standard deviation of ±0.3 reflectance unit. Plates 2, 3 and 4, therefore, would seem to be suited to the purpose at hand, since the actual percent reflectance deviation resulting from a variation in the sample weight would most likely be smaller than the maximum value used as the basis for the above approximations.

TABLE II

RELATION BETWEEN RELATIVE STANDARD DEVIATION OF PERCENT REFLECTANCE AND RELATIVE STANDARD DEVIATION OF SAMPLE WEIGHT

(3.2 · 10^{-10} mole eosine B added in sets 1 and 4, 4.5 · 10^{-10} mole eosine B added in sets 2 and 3)

Set	*Members in set*	*Range of sample weights (mg)*	*Mean weight (mg)*	*Rel. std. dev. of weights (%)*	*Range of reflectance readings (%R)*	*Mean of reflectance readings (%R)*	*Rel. std. dev. of reflectance (%)*
1	5	46.0–58.3	51.0	10.4	80.6–82.7	81.9	1.1
2	4	74.4–82.3	79.0	4.9	82.2–83.0	82.5	0.5
3	4	72.1–78.5	75.8	4.2	82.1–83.0	82.6	0.5
4	5	64.2–68.0	65.4	2.5	84.1–84.7	84.4	0.3

To substantiate this conclusion, the relation between the relative standard deviation of the percent reflectance and the relative standard deviation of the sample weight was determined directly. This was accomplished by preparing 4 sets of silica gel samples representing 4 different degrees of deviation of the sample weight, adding identical amounts of eosine B to the members of each set, and then determining the reflectance of the resulting mixtures. The data obtained, which are summarized in Table II, revealed that a relative standard deviation in weight amounting to 2.5% produced a relative standard deviation in the reflectance of the sample identical with that caused by variations associated with the packing of the cell. It is also worth noting that it is possible to come by data having a relative standard deviation of only 0.5 reflectance unit with samples whose weights deviate by as much as 4.9%.

Precision of planchet technique

The suitability of the planchet technique as a means of expediting the analyses of substances resolved on chromatoplates and absorbing in the visible or in the ultraviolet was tested by determining the deviation in the percent reflectance of samples of eosine B and salicylic acid prepared from plates 2, 3 and 4. Table III gives the precision attained with different thicknesses of these plates for 4- and 5-membered sets of samples. For individual plates of all thicknesses, average relative standard deviations of 0.3 and 0.4 reflectance unit were obtained for eosine B and salicylic acid, respectively. A value of 0.5 reflectance unit was obtained for both compounds when the precision was computed for all plates of all thicknesses. The first values represent the level of precision inherent in the application of the reflectance technique to thin-layer chromatography while the latter exceeds this level only slightly.

CONCLUSIONS

When the procedure recommended by the maker for the preparation of thin layers is appropriately modified, a commercial applicator is capable of laying down adsorbent of a uniform enough thickness to justify the use of the planchet technique in the determination of substances resolved on chromatoplates by means of reflectance spectrophotometry. With other than the first and last plates of a series, the technique is capable of providing quantitative data of a precision consistent with the maximum precision afforded by the reflectance technique. An average relative standard deviation ranging from 0.3 to 0.4 reflectance unit was obtained for measurements carried out on samples excised from single plates, and a value of 0.5 reflectance unit was arrived at using samples removed from more than one plate. Within the limitations set for the investigation, there appeared to be no relationship between the precision attained and the thickness of the adsorbent layer. Where the precision achieved with the reflectance technique is limited by elements associated with the color development process and not by deviations arising from the preparation of the analytical sample, as in the analysis of amino acids[2,3], the errors introduced by the employment of the planchet technique would be negligible.

The authors wish to acknowledge the helpful suggestions made by Mr. WEBSTER R. HUDGINS, and the generous support provided Mrs. IRIS T. FUKUI by the National Science Foundation, Grant GE-3107.

TABLE III

RELATIVE STANDARD DEVIATION OF PERCENT REFLECTANCE OF SAMPLES OF EOSINE B AND SALICYLIC ACID ADSORBED ON SILICA GEL AND PREPARED BY MEANS OF THE PLANCHET TECHNIQUE

Gate setting (mm)	*Mean reflectance (%R)*			*Rel. std. dev. (%R)*			*Mean reflectance (%R) All plates*	*Rel. std. dev. (%R) All plates*
	Plate 2	*Plate 3*	*Plate 4*	*Plate 2*	*Plate 3*	*Plate 4*		
Eosine B								
0.75	84.5	83.2	83.8	0.3	0.5	0.6	83.5	0.6
0.50	83.1	82.6	82.5	0.4	0.2	0.2	82.7	0.5
0.25	84.6	84.4	84.1	0.2	0.2	0.3	84.3	0.4
				Ave. rel. std. dev. for individual plates		0.3		Ave. rel. std. dev. for all plates 0.5
Salicylic acid								
0.75	78.2	78.8	78.0	0.4	0.3	0.5	78.3	0.5
0.50	78.8	78.2	78.0	0.3	0.5	0.3	78.3	0.5
0.25	77.3	77.5	76.8	0.3	0.3	0.4	77.5	0.5
				Ave. rel. std. dev. for individual plates		0.4		Ave. rel. std. dev. for all plates 0.5

SUMMARY

A method is described for the removal of spots from thin-layer plates, which, when used in conjunction with spectral reflectance, makes possible the rapid analysis of substances resolved on chromatoplates. Data are provided which indicate that the surfaces laid down by a commercial applicator are, with certain limitations, satisfactory for use with this technique.

RÉSUMÉ

Les auteurs décrivent une méthode de déplacement des taches de chromatogrammes en couches minces, qui appliquée en connection avec la spectroscopie de réflexion permet une analyse rapide des substances fixées sur couches chromatographiques. Les valeurs obtenues indiquent que les couches préparées avec un applicateur commercial sont satisfaisantes pour cette technique, malgré certaines restrictions.

ZUSAMMENFASSUNG

Eine Methode zur quantitativen Gewinnung von auf Dünnschichtchromatogrammen aufgetrennten Substanzflecken wird beschrieben, die im Zusammenhang mit Reflektionsspektrophotometrie die schnelle Analyse von Gemischen ermöglicht. Die aufgeführten Daten zeigen, dass die Reproduzierbarkeit von Schichtdicken, wie sie mit einem kommerziellen Beschichtungsapparat erzielt werden kann, für eine Anwendung dieser Methode genügt.

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SOLUTION OF ROCKS AND REFRACTORY MINERALS BY ACIDS AT HIGH TEMPERATURES AND PRESSURES

DETERMINATION OF SILICA AFTER DECOMPOSITION WITH HYDROFLUORIC ACID*

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(Received April 23rd, 1965)

The decomposition of minerals by acids is advantageous to the analytical chemist because such decompositions do not result in the introduction of foreign cations other than hydrogen ion. Many refractory minerals however, are not dissolved even after protracted treatments with acids.

If acid attacks are made in sealed vessels at temperatures above the normal boiling points of the acids, the speed and extent of decomposition can be increased considerably. Thus, nearly all refractory minerals can be decomposed with appropriate acids at temperatures in excess of 200°. Such decompositions are advantageous if non-oxidizing atmospheres are required and they also eliminate the possibility of volatilization losses as may occur in open-dish decomposition with acids or fluxes.

High-temperature high-pressure decompositions were done first in platinum vessels sealed in glass[1] or directly in sealed glass tubes which were heated in steel bombs[2]. Temperatures achieved were 400° by JANNASCH[1] and 250–300° by WICHERS *et al.*[2]. These decomposition techniques are very effective in dissolving refractory oxides and some silicates. Disadvantages of the use of glass are the introduction of silica into samples and the inability to use hydrofluoric acid.

ITO[3] successfully decomposed a large number of refractory minerals using a Teflon-lined steel bomb. This liner permitted the use of sulfuric acid plus hydrofluoric acid, as well as hydrofluoric acid alone, but maximum temperatures were limited to about 240° because of the Teflon. Slight leakage of vapor occurred at the Teflon seals at pressures above 300 p.s.i. A Teflon-lined aluminum autoclave was used by WAHLER[4] for the decomposition of minerals and rocks with hydrofluoric plus perchloric acids at 200°**.

Platinum liners are resistant to attack by hydrofluoric acid and are not limited to use at relatively low temperatures. Such liners can be used at temperatures and pressures as high as the design of the bomb and its seals will permit.

A platinum-lined bomb, shown in Fig. 1, has been used by us[6] for the decomposition of small mineral samples. Representative samples of refractory minerals can be

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* Publication authorized by the Director, U.S. Geological Survey.

** Subsequent to the preparation of this paper, LANGMYHR AND SVEEN[5] published a report on the decomposability of 28 minerals by a mixture of hydrofluoric and perchloric acids. They studied decompositions in plastic beakers at steam bath temperatures and in Teflon-lined bombs at 250°.

decomposed successfully in the bomb using either hydrofluoric acid, a mixture of hydrofluoric and sulfuric acids, or hydrochloric acid.

A novel feature of the bomb is the construction of the reaction vessel which is a platinum-lined nichrome crucible having an outside taper to facilitate its removal from the bomb body. The crucible can be removed from the bomb while still sealed, thereby minimizing the danger of contaminating the sample solution while transferring it from the crucible. As the crucible weighs less than 200 g, it can be weighed with its contents on an analytical balance.

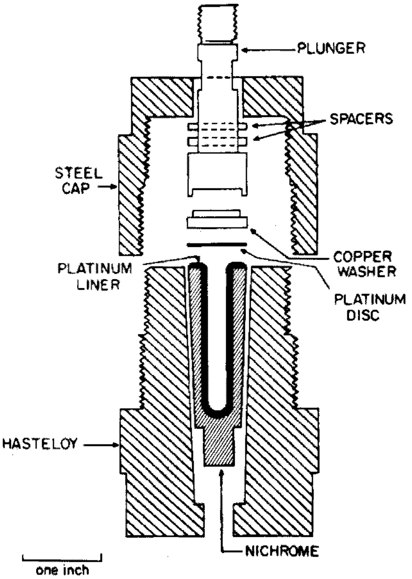

Fig. 1. Morey-type bomb with platinum-lined crucible.

Removal of the crucible at the termination of a run is aided not only by its taper, but by the projection of the crucible through a hole in the bottom of the bomb. This enables the direct application of pressure with a press for releasing the crucible.

The crucible, when being handled outside the bomb, is supported conveniently in a circular aluminum holder with a center bore to fit the lower portion of the crucible.

The platinum seals are discs of pure platinum, 0.72 in. in diameter and 0.006 in. thick. These seals adhere strongly after a run and occasionally must be punctured in order to be pried off. Coating the surfaces with Aquadag, a colloidal suspension of graphite, enables the seal to be removed cleanly, with only gentle prying required. The Aquadag is applied lightly, before loading the bomb, to the lip of the crucible and to the contacting surfaces of the seal and the copper washer. After drying, the coated surfaces are burnished by rubbing with filter paper.

The volume of the crucible is 3.5 ml, which permits the use of sample weights up to 100 mg and acid volumes of 1–2 ml. Temperatures as high as 425° and pressures as high as 6,000 p.s.i. were used in mineral decomposition studies. Pressures were estimated from the temperatures and degrees of filling, complete volatilization of the acids being assumed.

The bomb was also tested successfully with water alone, using a 75% fill at 525° and an estimated pressure of 30,000 p.s.i.

The bomb has proven to be very reliable. It has been used for more than 30 runs for periods of 16–24 h each. The only maintenance required has been an occasional refacing of the lip and a reboring of the mouth of the crucible. A newly constructed crucible using 80% platinum–20% iridium alloy should require less frequent refacing than the pure platinum liner.

Because there are no losses of vapor during the decomposition in the bomb, it is possible to determine silica spectrophotometrically on an aliquot of the solution, even though the decomposition is effected by hydrofluoric acid. The interference of fluoride ion can be eliminated by the formation of a complex ion with aluminum. SHELL[7] and CZECH *et al.*[8] demonstrated that aluminum is effective for complexing fluoride and thereby preventing loss of silica during dehydration. GRAFF AND LANGMYHR[9] used aluminum successfully to eliminate the interference of fluoride in the yellow α-silicomolybdic acid procedure for silica.

A procedure is described below for determining silica after decomposition of the sample with hydrofluoric acid in the bomb. Silica is determined spectrophotometrically by the molybdenum-blue method on 0.1–0.25 mg aliquots of sample in fluoride solution, after adding aluminum to complex the fluoride. Excellent results for silica were obtained on replicates of standard samples.

EXPERIMENTAL

Decomposition of samples

The crucible is prepared for a run by scrubbing it thoroughly with a soft brush or a stiff felt and a nonscratching cleanser. The crucible is then nearly filled with hydrofluoric acid and after a few minutes the acid is carefully poured out and the crucible is rinsed with distilled water and dried in the oven.

Samples can be weighed directly into the crucible on an analytical balance. When greater accuracy is necessary, samples are weighed from a vial by difference on a semimicro balance. Acids are introduced carefully using appropriate pipets to measure the volumes. The crucible is covered with a platinum seal and, after weighing, is placed in the bomb. The bomb threads are lubricated with Molykote (a molybdenum disulfide lubricant) and the bomb is then sealed. The temperature of the reaction is monitored by a thermocouple inserted in a well in the bomb.

The bomb is permitted to cool to room temperature before being opened. After removal from the bomb the crucible is reweighed to check for possible leakage. The weight should agree within a few milligrams with the initial weight. Small differences in weight may be caused by the transfer of metal between the seal and the copper washer. The seal is then removed and the contents of the crucible are carefully transferred to a platinum dish with the aid of a fine stream of water. A salt cake which forms sometimes at the bottom of the crucible is broken up with a platinum rod. The interior of the crucible is policed thoroughly during the washing operation.

Reagents

Ammonium molybdate reagent. Dissolve 7.5 g of ammonium molybdate in 75 ml of water. Add 10 ml of 1 : 1 sulfuric acid and dilute to 100 ml. Store in a plastic bottle.

Tartaric acid solution, 10% (w/v). Store in a plastic bottle. Discard and prepare fresh reagent when an appreciable sediment forms.

Reducing solution. Dissolve 0.7 g of anhydrous sodium sulfite in 10 ml of water. Add 0.15 g of 1-amino-2-naphthol-4-sulfonic acid and stir until dissolved. Dissolve 9 g of sodium bisulfite in 90 ml of water and add this solution to the above solution and mix. Store in a plastic bottle.

Aluminum chloride solution. Dissolve 65 g of $AlCl_3 \cdot 6H_2O$ in water and dilute to 250 ml.

Procedure for the determination of silica

Add water to the crucible after removing seal. Transfer the contents to a platinum dish, 125 ml or larger. Wash the crucible and the seal, policing thoroughly. Add 25 ml of the aluminum chloride solution to the diluted sample solution. Transfer to a 1-l volumetric flask and dilute to volume with water. Transfer to polyethylene if the analysis is not done immediately. Pipet an aliquot containing 100–200 μg SiO_2 into a 100-ml volumetric flask. Prepare a standard stock solution of silica by fusing 100.00 mg of quartz with 3.0 g of sodium carbonate in a platinum crucible. Dissolve the melt in water and pour the solution into a beaker containing a large volume of water and sufficient hydrochloric acid to yield a final pH of 1.7 on dilution to one liter. Prepare a blank solution by adding 3.0 g of sodium carbonate to 400 ml of water containing 24 ml of 1 : 1 hydrochloric acid and diluting to 1 l. Prepare dilutions of the stock solution using blank solution as diluent. Take aliquots of sample solutions and of standard solutions not exceeding 300 μg SiO_2. Add appropriate volumes of blank solution to give an equivalent of 10 ml in each in order to equalize salt effects and to adjust the pH to the range 1.5 to 2.0. Add 1.0 ml of ammonium molybdate reagent. Mix and wait 10 min. Add 4.0 ml of 10% tartaric acid, mix, and add 1.0 ml of reducing reagent while swirling the flasks. Dilute to volume with distilled water and allow to stand for about 30 min. Determine the absorbance with a spectrophotometer in 2-cm cells at 640 mμ using the blank as reference.

DISCUSSION

Table I summarizes the experimental data for the decomposition studies for a representative number of refractory minerals and also for the rocks G-1 and W-1. Overnight treatments sufficed for the complete decomposition of all the samples. The garnet was decomposed in 5 h and zircon was 70% decomposed after 4 h. No attempt was made with the other minerals to arrive at a minimum time for complete decomposition.

Difficultly soluble residues were obtained with samples with high aluminum content. The residues from staurolite, beryl, and chrysoberyl were identified as AlF_3 by X-ray analysis. In the residue from chrysoberyl a compound was also found having a structure similar to $KAlF_4$, possibly being H_3OAlF_4. A large, difficultly soluble, green precipitate was obtained with the hydrofluoric acid decomposition of chrome refractory. A hydrochloric acid decomposition gave a clear green solution with a small precipitate of silica which spectrographic analysis showed was free of chromium.

The procedure for the silica determination was tested on samples decomposed with hydrofluoric acid in the bomb although mixed acids such as hydrofluoric plus

TABLE I

SUMMARY OF DECOMPOSITION STUDIES

Sample	*Sample weight (mg)*	*Acid*	*Time (h)*	*Temperature (°)*	*Comments*
Garnet	20	1 ml HF	5	425	Complete decomposition; small precipitate
Zircon ($ZrSiO_4$)	20	1 ml HF	3½	400	Incomplete decomposition
	25	1 ml HF	4	400	Incomplete decomposition; 30% unattacked
	25	1.5 ml HF	20	425	Complete decomposition; clear solution
Staurolite ($HFeAl_5Si_2O_{13}$)	100	1 ml HF + 0.5 ml (1 + 1 H_2SO_4)	19	420	Complete decomposition; fine precipitate
	100	1.5 ml HF	19	375	Complete decomposition; precipitate of AlF_3[a]
Diabase, W-1	102	1 ml HF + 0.5 ml (1 + 1 H_2SO_4)	20	375	Complete decomposition; small precipitate
Beryl ($Be_3Al_2(SiO_3)_6$)	102	1.5 ml HF	18	400	Complete decomposition; precipitate of AlF_3[a]
Phenacite (Be_2SiO_4)	97	1.5 ml HF	18	400	Complete decomposition; clear solution
Chrysoberyl ($BeAl_2O_4$)	100	1.5 ml HF	20	400	Complete decomposition; large precipitate[b]
	100	1.5 ml HCl	19	400	Sample largely undecomposed
Kyanite (Al_2SiO_5)	99	1.5 ml HF	18	400	Complete decomposition; small precipitate
Granite, G-1	27	1.5 ml HF	17	400	Complete decomposition; very small precipitate
Sapphirine ($Mg_5Al_{12}Si_2O_{27}$)	28	1.5 ml HF	17	400	Complete decomposition, small precipitate
Chrome Refractory NBS-103a	50	1.5 ml HF	17	425	Complete decomposition; large green precipitate
	50	1.5 ml HCl	17	425	Complete decomposition; small gelatinous precipitate[c]

[a] Identification by X-ray.

[b] X-ray showed AlF_3 + unknown similar to $KAlF_4$ (H_3OAlF_4?).

[c] Spectrographic analysis showed chromium absent.

TABLE II

DETERMINATION OF SILICA IN GRANITE G-1 AND DIABASE W-1

Granite G-1		*Diabase W-1*	
Wt. of sample (mg)	*Silica found (%)*	*Wt. of sample (mg)*	*Silica found (%)*
50.24	72.4_5	51.10	52.2_1
50.84	72.7_8	56.43	52.3_0
52.56	72.8_3	33.36	53.0_0
46.45	73.4_8	45.64	53.5_9
42.05	72.0_4	48.50	52.6_6
Mean	72.7_2	Mean	52.5_5
Standard deviation	0.53	Standard deviation	0.31
Relative deviation	0.73	Relative deviation	0.59

sulfuric acids could also be used. Five decompositions each were made of granite, G-1, and diabase, W-1, using sample weights of approximately 30–50 mg. The decompositions were complete in all cases although small aluminum fluoride precipitates were obtained. The precipitates which were carried along with the solutions dissolved in the diluted solutions on standing. Aluminum chloride was added equal to twice the equivalent of 1.5 ml of hydrofluoric acid. In an analysis where other constituents are sought, the aluminum could be added to an aliquot of the solution if its presence would complicate the analytical scheme.

The results obtained for silica are given in Table II. The average value found for G-1 is 72.72% with a standard deviation of 0.53%. This compares well with the mean of 72.35%, standard deviation = 0.48% (STEVENS AND NILES[10]) and the recommended value 72.65% (STEVENS AND CHODOS[11]). The mean of the silica determinations found on W-1 is 52.55%, standard deviation = 0.31%, which also is in good agreement with the reported values of 52.40%, standard deviation = 0.33% and the recommended value of 52.77%.

SUMMARY

A modified Morey bomb was designed which contains a removable nichrome-cased 3.5-ml platinum crucible. This bomb is particularly useful for decompositions of refractory samples for micro- and semimicro-analysis. Temperatures of 400–450° and pressures estimated as great as 6000 p.s.i. were maintained in the bomb for periods as long as 24 h. Complete decompositions of rocks, garnet, beryl, chrysoberyl, phenacite, sapphirine, and kyanite were obtained with hydrofluoric acid or a mixture of hydrofluoric and sulfuric acids; the decomposition of chrome refractory was made with hydrochloric acid. Aluminum-rich samples formed difficultly soluble aluminum fluoride precipitates. Because no volatilization losses occur, silica can be determined on sample solutions by a molybdenum-blue procedure using aluminum(III) to complex interfering fluoride.

RÉSUMÉ

Les auteurs proposent une modification de la bombe de Morey, utilisée en particulier pour les décompositions de substances réfractaires, en vue de leur analyse à l'échelle micro et semimicro. Une décomposition complète de diverses roches est possible, au moyen d'acide fluorhydrique ou avec un mélange acide fluorhydrique–acide sulfurique. Les échantillons riches en aluminium donnent des précipités de fluorure d'aluminium difficilement solubles. La silice peut être dosée par la méthode au bleu de molybdène, en utilisant l'aluminium pour complexer les fluorures gênants (aucune perte par volatilisation ne pouvant se produire).

ZUSAMMENFASSUNG

Es wurde eine modifizierte Morey-Bombe entworfen, die einen mit Nickel-Chrom überzogene 3.5-ml grossen Platintiegel enthält. Diese Bombe ist besonders für Zersetzungen für die Mikro- und Halbmikroanalyse von widerstandsfähigen Proben geeignet. Es wurden in der Bombe Temperaturen von 400–450° und Drucke von

schätzungsweise 6000 p.s.i. für eine Dauer von 24 Stunden erreicht. Die völlige Zersetzung verschiedenster Gesteine wurde mit Flusssäure oder einer Mischung aus Flusssäure und Schwefelsäure erzielt. Die Zersetzung von Chromeisensteinen wurde mit Salzsäure durchgeführt. Aluminiumreiche Proben bilden schwer lösbare Aluminiumfluoridniederschläge. Da keine Verdampfungsverluste auftreten, kann Siliciumdioxid in den Probelösungen durch das Molybdänblauverfahren bestimmt werden, wobei Aluminium(III) störende Fluoride komplex bindet.

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PROOF OF ULTRAPURITY IN ZONE-REFINED NAPHTHALENE*

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(Received April 12th, 1965)

The zone-melting of organic substances for purposes of achieving ultrapurity has only recently come under intensive investigation[1,2]. Studies on a large variety of organic pharmaceuticals in particular have established the properties that a substance must possess to qualify for the zone-melting process[3]. The need for ultrapure medicinal agents and the technology of zone-melting of organic materials have been treated elsewhere[4]. Theoretical considerations necessary to zone-melt organic substances for optimum efficiency have also recently received much attention[5–7]. Although hundreds of pharmaceuticals have been zone-melted, rigorous proof of ultrapurity of these substances has been lacking. Thus, the purpose here is to establish a rationale for proof of ultrapurity of zone-melted organic substances and to describe one series of investigations based on this technique.

Analysis for ultrapurity after an organic sample has been zone-melted, at first may not appear more difficult than the extension of the analytical techniques usually employed. It is of interest to illustrate one of the current modes of thinking expressed in the literature relative to ultrapurity analysis of zone-melted materials. A method often employed consists of adding an impurity (*e.g.* a dye) *before* the sample has been zone-melted and analyzing the sample for traces of that impurity *after* the ultrapurification process is complete. This technique has also been used as a measure of the zone-refining process. In one study[8] when 0.2% of anthracene was added as an impurity to naphthalene and the mixture zone-melted with seven passes, analysis for anthracene by fluorescence under U.V. light indicated an impurity concentration of 0.00002%. No further details were given in this report.

What are the assumptions and principles of ultrapurity analysis being employed here? This "relative approach"[1] assumes that the impurity added acts as the standard. That is to say, when the impurity that has been added can no longer be detected, the sample is assumed to be at a maximum ultrapurity.

Unfortunately, this approach suffers from severe disadvantages. Perhaps, the strongest criticism of the method is that it does not measure the ultrapurity of the sample at all. Aside from the impurity added, the contaminants in the sample before

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* This work is abstracted from a dissertation submitted to the Graduate School, University of Connecticut in partial fulfilment of the requirements for the Ph.D. degree.

and after ultrapurification have not been assayed, nor in any way identified. No relationship has been established between the impurity added and the contaminants originally present, nor between the rate of removal of anthracene and the other contaminants. The method of assay itself gives no evidence of constancy of physical properties of the major component. In general, such an approach offers at best only a rough estimate of efficiency of the zone-melting apparatus with a single impurity or other impurities that are similar to anthracene.

This example should not mislead one to believe that highly reliable ultrapurity measurements on organics are not available. On the contrary the works of HERINGTON[9], BENYON AND SAUNDERS[10], SCHWAB AND WICHERS[11], to name only a few, have done much to validate highly precise and accurate methods and results for impurities in the micro-region. Yet a criterion or rationale for such measurements has never been explicitly stated.

In order to establish a rationale for assaying impurities in the micro-region, it is necessary to consider definitions and concepts delineated by the terms "purity" and "ultrapurity". No attempt will be made to survey this vast field of theory and practice. Excellent summaries are available[12]. Suffice it to say that "absolute methods" (as distinguished from "relative methods" based on a comparison with a chemical standard) which rely upon the measurement of unchanging physical characteristics of a substance may be used reliably to assay for ultrapurity. However, the use of this classification is not unambiguous. For example, a supposedly ultrapure compound gives specific spectra by U.V or I.R. measurements. Nevertheless, U.V. peaks are usually too broad and too readily influenced by extraneous materials to make the technique applicable in critical impurity analysis. Absorption maxima in the infrared range, on the other hand, are sharper and better defined. The position and height of the peaks are functions of the nature and amount of the substance present and this leads to quantitative estimation. But what part of the spectrum is contributed by impurities in parts per million is not known. Comparison with a less pure sample *may* or *may not* indicate a change in the impurity peaks of the ultrapure compound. Such spectra should *not* be regarded as an "absolute method" of ultrapurity analysis. The methods most suitable for these determinations would include (*a*) mass spectrographic analysis, (*b*) thermal and differential thermal analysis, (*c*) phase solubility analysis, (*d*) gas–liquid chromatography and (*e*) radioactive tracer techniques (when labeling the major component). These methods have the characteristics of measuring *total impurities* based on an "internal standard", namely the constancy of a physical property of the major component. In this investigation, methods (*b*), and (*c*) and (*d*) were utilized considering the following rationale:

(*A*) The primary ultrapurification process (zone-melting, in this case) must theoretically predict the extent of ultrapurity of the sample under specified conditions.

(*B*) More than one method of ultrapurification should be utilized to corroborate results.

(*C*) More than one "absolute method" of assay should be utilized to determine *total impurities*.

(*D*) Assays should be made on starting materials as well as on ultrapure products in each ultrapurification technique employed.

Even a limited treatment of zone-melted organics from this point of view is not possible at this time. Originally this study was planned to include 4 organic samples thought to be representative of the difficulties one might encounter in the zone-melting process, and their concomitant ultrapurity analyses. The 4 samples so chosen were (*1*) naphthalene, (*2*) anthracene, (*3*) thymol and (*4*) benzoic acid. The reasons for this choice were the simplicity of the chemical structures, their known phase diagrams in binary mixtures, and their being representative types of aromatic hydrocarbons, alcohols and acids yet simple enough that comprehensive studies had already been made on their physical properties. The advantages attending the selection of simple organic materials allow for a reduced number of factors influencing both the zone-melting process and the ultrapurity assays. However, as the investigation proceeded it was clear that the problems associated with ultrapurity methods of assay presented more than enough challenge for a thorough study with one sample. Thus, in this investigation *naphthalene* was selected as the subject for intensive study. It must be emphasized that the methods used in these experiments are applicable to many kinds of organic materials and may also be extended to pharmaceuticals that meet the necessary requirements of the zone-refining process.

EXPERIMENTAL

Ultrapurification methods

(*1*) *Zone-melting procedures.* The general procedures for zone-melting were carried out according to the findings of WALTER[3]. The zone velocities tested ranged from 10.0 cm/h through 0.37 cm/h, the latter being the lower limit of the Fisher Zone Refiner used. An analysis treating segregation properties as a function of zone velocity based on findings from this investigation has been published separately[6]. Details and corroboration of the procedures of WALTER including sizes of glass tubes, prevention of fracture, direction of zone-melting, zone length, etc. are given in the original thesis[1]. In accordance with theory outlined previously[5], the cooling attachment for the freezing interface was disconnected and the freezing interface was allowed to cool at ambient temperature. Although the conditions under which these zone-melting experiments were conducted were far from being ideal, the equipment did not allow for more rigorous treatment without a complete rebuilding of the zone refiner. It was considered more pertinent in this investigation to emphasize the ultrapurity analysis and to allow another investigation to be concerned with establishing ideal conditions for the zone-melting process. The theoretical analysis for ideal conditions based on this investigation has also been published separately[5].

Preliminary experiments were focused on determining optimum conditions for the instrumentation available. Optimum conditions included the following:

(*1*) a zone velocity of 0.37 cm/h.

(*2*) 30-cm thin-walled pyrex tubes (8 mm I.D. by 10 mm O.D.; 10 mm I.D. by 12 mm O.D.).

(*3*) the use of a "rubber policeman" and glass wool to seal the bottom of the tube.

(*4*) zone length kept as large as practical (*ca.* 1.5 in.).

(*5*) zone-melting in a vertical position in an upward direction.

Zone-melting experiments were performed on two commercial grades of naphthalene. Since WILCOX[13] had found it possible to ultrapurify naphthalene by zone-melting starting from the commercial product his work was repeated to verify and extend his data. Average values of impurities were obtained for a large section of

..ne zone-melted charge, with 1 zone pass, under the conditions specified. A much larger sample of naphthalene zone-melted with 1 zone pass was also analyzed at different fractions of the charge. Finally a zone-melted sample with 30 zone passes was analyzed to obtain an average value for the purified material.

(*2*) *Other ultrapurification procedures.* A number of methods are cited in the literature for ultrapurifying naphthalene. Three were chosen for comparison with zone-melted samples: (*a*) formation of the picrate[15]; (*b*) fractional distillation[16]; (*c*) recrystallization from alcohol[14].

(*a*) Stoichiometric quantities of picric acid were added to commercial naphthalene samples dissolved in purified ethanol. The crude picrate was removed by filtration and naphthalene regenerated by addition of 1 *M* sodium hydroxide. The material so obtained was analyzed after one and two recrystallizations from ethanol by the Soxhlet extraction phase solubility method.

(*b*) A sample of commercial naphthalene was distilled under reduced pressure and the distillate was divided into 4 fractions. No temperature difference could be distinguished among the 4 fractions collected. Each of the fractions was subjected to the Soxhlet extraction method of analysis.

(*c*) Commercial samples of naphthalene were recrystallized from purified ethanol 3 consecutive times by standard procedures. Each of the recrystallized products was analyzed as above.

Analytical methods

The versatility of the methods of assay chosen allows for measurements of impurities at both high and low concentrations of impurities. Analytical methods were applied to (*a*) 2 commercial grades of naphthalene, (*b*) zone-melted samples of naphthalene, (*c*) samples of naphthalene ultrapurified by the 3 other methods listed above, and (*d*) a zone-melted naphthalene sample supplied by the Fisher Scientific Company.

In order to validate the methods used, the commercial products, both technical and reagent grade, were analyzed by 4 different methods: (*1*) thermal analysis and differential thermal analysis (DTA), (*2*) phase solubility methods, (*3*) gas–liquid chromatography and (*4*) thin-layer chromatography. In addition, thermal analysis and DTA measurements were applied to zone-melted samples with 1 and 30 zone passes respectively, to obtain average values of total impurities in each of the ultrapure charges. Two methods of phase solubility analysis were applied to zone-melted naphthalene with 1 zone pass as well as to the crude and chemically purified samples. Difficulties encountered with gas–liquid chromatography in obtaining a separation of impurities did not allow more than an evaluation of the crude commercial products. Thin-layer chromatography was used as an adjunct to the gas–liquid method, but only on the commercial samples. An additional sample of zone-melted naphthalene supplied by the Fisher Scientific Company was used for a comparison with commercial samples zone-melted in this laboratory.

A description of the analytical methods utilized follows. Only those details relevant to proof of ultrapurity or which involve a distinct departure from accepted procedures are included. (Further details may be found in reference 1 or sources listed under each method.)

(*1*) *Phase solubility methods.* The "principal procedure" for phase solubility analysis and its theoretical basis have been amply described elsewhere[17]. The phase solubility Soxhlet extraction method of STENGER, CRUMMETT AND KRAMER[18] was modified in this laboratory in several ways. The original procedure calls for 70 ml of solvent with large (125 ml) Soxhlet extraction flasks and condensers. In preliminary experiments, parallel determinations were run involving 3 samples in large Soxhlets and 3 samples in micro Soxhlets. It was found that greater precision was obtained with the micro method and all further determinations were carried out using reduced quantities of both solvent and sample. The solvent chosen for analyzing zone-melted samples of naphthalene was the *tert.*-butanol–water azeotrope. A brief description of the modified procedure follows: a 1-g sample of naphthalene (accurately weighed to 6 significant figures) contained in a sealed extraction thimble, which had been cleaned with the purified azeotrope, dried and weighed beforehand, was placed in a micro-extraction apparatus. Exactly 15 ml of the solvent were measured into the flask and the temperature of the Glas-col heating mantle was adjusted so that gentle boiling of the azeotrope ensued. After 30 min, the solution was allowed to cool, whereupon the solvent was recovered by filtration and its volume was carefully measured. Using specially adapted volumetric flasks, the original volume was restored with naphthalene-saturated azeotrope, known as the wash solution. The recovered azeotrope was used in the assay of soluble impurities. Six such extractions were run simultaneously, under identical conditions.

Naphthalene, being a highly volatile compound, created several problems in applying this method. All weighings were made on a constant weight basis, throughout which time the sample containers were tightly wrapped in aluminum foil. Studies of weight loss by sublimation were performed to determine the loss of naphthalene if allowed to stand with a maximum surface area exposed to the air for the length of time necessary to complete an analysis. These time–weight studies were completed on different days so that a random sampling of barometric pressures and temperatures was obtained. The 1-h period that is required for the analysis showed a negligible loss for the sublimation conditions of this experiment. Since the greatest care was taken to avoid losses due to the volatility of the sample, this factor can be neglected.

The problem of weighing the thimble after the extraction process to determine the insoluble impurities involved a means of drying the thimbles of all residual solvent and bringing them to constant weight. By using desiccators filled with sulfuric acid and allowing the thimbles to remain in the desiccators for as long as two weeks, no insoluble impurities could be detected. Since the *tert.*-butanol–water azeotrope is an excellent solvent for naphthalene at higher temperatures, it is assumed that it and all impurities were dissolved by the solvent. The entire sample appeared to dissolve in the solvent within 15 min after the extraction process began. An additional 15 min of extracting was allowed to render the thimble free of all partially soluble components. Repeated checks indicated that the thimbles were free of insoluble impurities and that only soluble impurities were to be determined.

The method of assay first used to determine the soluble impurities in the azeotrope involved the weighing of known volumes of the azeotrope extraction. Inconsistencies in values from one run to another indicated the difficulties attendant to very accurate weighings of small quantities of liquid. An alternative method of assay by use of refractive indices was developed. This method is based on the principle that soluble impurities will alter the refractive index of the solvent in a manner very similar to their effect on a saturated solution. Thus, extrapolating a plot of concentration of material in the solvent against refractive index into the supersaturated region gives a measure of impurities that would be closely related to naphthalene (see Fig. 1). This plot assumes linearity of the concentration function and all evidence gathered in this laboratory indicates that this is true. Thus,

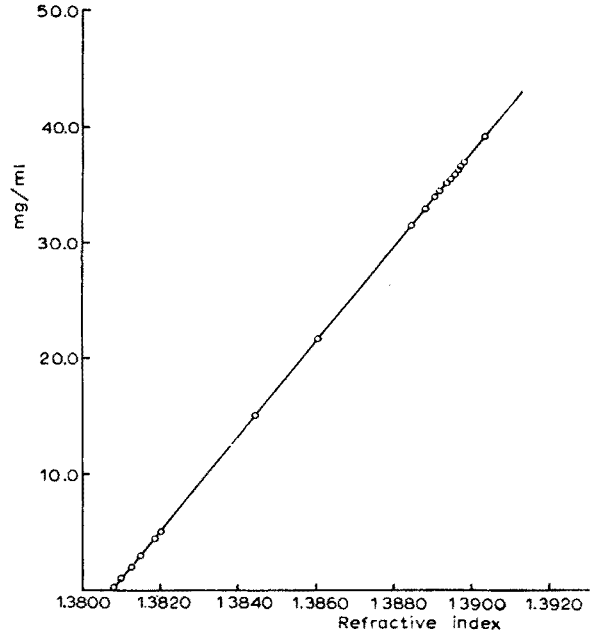

Fig. 1. Standard curve, naphthalene; Abbé refractometer; 30°. Reduced scale graph 4: 1.

after filtration, a few drops of the azeotropic extract were examined on the Abbé refractometer and the exact concentration of soluble impurities was read off the graph.

A further series of experiments was conducted to determine the relation between the weight method of assay and the refractive index method. Since a small percentage error was difficult to determine at low concentrations of impurities, an approximately 10% impure material (naphthalene) was used as a test sample. Carefully weighed quantities of naphthalene were dissolved and diluted to volume at constant temperature in Weld-type pycnometers and reweighed after dilution. These solutions were then measured for refractive index and the soluble impurities taken off the standard curve. A comparison of values indicated that the refractive index method gave the correct values and that an approximate 2% error in the weight values was due to volume and temperature corrections during the weighing process. At low concentrations of impurities, this was indeed a small error, and these findings were used mainly to corroborate the accuracy of the refractive index method.

The wash solution (previously defined) is significant in the calculations of impurities in the Soxhlet extraction method. Several techniques were employed in the filtering of naphthalene samples to obtain a saturated solution: (*1*) suction filtration, (*2*) pressure filtration, and (*3*) gravity filtration. The refractive indices of these solutions were (*1*) 1.3850, (*2*) 1.3860 and (*3*) 1.3840 respectively. Experiments with the

Weld pycnometer and the principal phase solubility method corroborated the saturated solution to be 0.0150 g-% with a refractive index of 1.3850. Therefore, the suction filtration method was adopted. The wash solution was always prepared by adding excess naphthalene to the azeotrope and allowing it to stand for 1 h with stirring.

During the extraction process, the tendency of naphthalene to crystallize in the side arm was overcome by wrapping the apparatus in aluminum foil.

(2) *Gas–liquid chromatography.* The gas–liquid chromatography unit used in this investigation was an Aerograph Hifi-A600B with a hydrogen flame ionization attachment. The sensitivity of the detector in this unit is controlled by an input and output impedance used in combination with one another. Four combinations are possible involving maximum sensitivity in the parts per thousand, per ten thousand, per hundred thousand and per million range. An automatically adjusted integrator attachment was installed in the recording device enabling the total area to be given in the prescribed sensitivity range.

The choice of solvent for the naphthalene samples was made on the basis of detection characteristics and carbon disulfide was generally used. However, several experiments were conducted with *tert.*-butanol–water azeotrope, *tert.*-butanol, acetone and methanol.

The following columns were used in order to obtain separations: (all columns were 5 ft. long, stainless steel columns with Chromosorb W as the inert support unless otherwise specified)

Se 30, 1.5% (on glass beads)
Se 30, 5%
Se 30, 15%
Se 30, 30% (10 ft. long)
Apiezon 20%
Carbowax 400, 20%
Dodecyl phthalate 20%

Of the columns used, the Se 30 columns were highly recommended by the Aerograph Company for the separation of hydrocarbons, and an extensive series of experiments was run with this stationary phase. Solvent studies were run with all columns to note the behavior of the solvent alone, with different volumes, sensitivities and temperature. Initial experiments were conducted at constant temperature, and runs at 50°, 85°, 100°, 125°, 175° and 210° were standard procedure. Temperatures below 80° were questionable since the melting point of naphthalene was above this. However, several runs below this temperature were made since no definitive answer could be given to what was taking place inside the column at these temperatures. The Se 30 experiments formed a self-consistent group since the concentration of the stationary phase was varied (1.5% to 30%) as well as the temperature and the length of the column. Other experiments with other columns involved temperature programming and a more rigorous control of the flow rate. Since the flow rate could not be measured while the apparatus was in operation, a special flow meter was attached to the carrier gas cylinder (which was either purified helium or nitrogen). This flow meter was calibrated in arbitrary units and 4 different flow rates (0.4, 0.3, 0.2, 0.1) could be specified. It was found that only the 0.2 setting gave symmetrical peaks and was therefore used for most of the later experiments. Since the inlet and outlet pressures were fixed in this instrument, no attempt was made to change these variables.

Three types of experiments were conducted with each column or variation of conditions. For each sensitivity range used, both a low and a high concentration in a small volume, plus a high concentration in a large volume were run. For example, in a 1 g-% solution of naphthalene, if a 1-μl sample were injected, the instrument would be detecting in the parts per thousand range, 1-μg quantities of naphthalene or its impurities. If 1 μl of a 100 g-% solution were used, the minimum sensitivity of the instrument would be detecting units of 100-μg quantities of naphthalene or its impurities, thus increasing 100-fold the chances of impurities being detected in the naphthalene sample chosen. Another method of doing this is to increase the volume 100-fold by taking 100 μl of a 1 g-% solution. However, a 10-μl sample was the largest volume a column could hold without flooding, and it was apparent that the sensitivity of the instrument decreased with the larger volumes. Most of the experiments were run in p.p.m. (parts per million range), so that 1 μl of a 1 g-% solution involved 0.0001-μg quantities while a 100 g-% solution involved 0.01-μg quantities. To verify these facts, decreasing concentrations of naphthalene were run to determine the minimum concentration of naphthalene that the instrument would detect at the various sensitivities. It was found that these values were fully substantiated and all further experiments were geared to altering the column or conditions to bring about a separation of impurities using both a high and low concentration of naphthalene for each experiment.

Temperature programming was performed by allowing the column to equilibrate at ambient temperature or some predesignated temperature and then increase at a set non-linear rate. Usually a slow and fast rate of heating was utilized with each column. If a run indicated a possible separation, additional heating rates were used as well as additional isothermal runs at the significant temperatures.

A final series of experiments was performed by adding known impurities to the naphthalene solutions. These combined solutions were subjected to many of the standard procedures described in this section. Solutions (1 and 10%) of benzoic acid, β-naphthol, and anthracene were run independently and with standard amounts of naphthalene. These were tested on several columns (particularly Apiezon 20%) and under several specified conditions.

(*3*) *Thin-layer chromatographic procedures.* Silica gel and aluminum oxide plates prepared in the standard manner were used. The sample was introduced on the plate quantitatively by a microliter syringe calibrated in tenths of a microliter. Two common solvent systems were used: chloroform, benzene (1:3); and ethyl acetate, benzene (1:2); and one dimensional plates were run at ambient temperature. The plates were stained with the standard dichromate–sulfuric acid solution[19,20] and upon drying were placed in a 120° oven for 10 min. Before the application of this method to naphthalene, preliminary standards were prepared to test the sensitivity of the method.

One microliter of commercial naphthalene samples dissolved in carbon disulfide in concentrations of 1, 5, 10, 50 and 100 μg/μl were spotted on silica gel and aluminum oxide plates and subjected to the procedure indicated.

(*4*) *Thermal analysis and DTA methods.* Detailed descriptions of these methods used in this investigation have been published separately[21,22]. Thermal analysis was performed on samples of zone-melted naphthalene ultrapurified by 1 pass and by 30 passes. The dynamic method used was an extension and refinement of HERINGTON's procedure[9] to allow temperature measurement of 6 significant figures in line with adiabatic calorimetric sensitivity and accuracy. The DTA method employed was a new quantitative procedure devised for its simplicity (completely automatic), sensitivity (*cf.* thermal analysis method above) and accuracy. Both thermal analysis and DTA equipment are economical and may be found in any well equipped analytical laboratory. Standardization of the DTA method was performed on two kinds of commercial naphthalene (reagent and technical grade). The DTA procedures were performed parallel to the thermal analysis method on zone-melted naphthalene with 1 zone pass and 30 zone passes.

RESULTS

Phase solubility analysis

The solubility data (not given here) for the "Principal Method"[17] of phase solubility analysis for the two commercial samples of naphthalene indicated approximate impurity concentrations of 12.5% and 7.5% (see Table I). This method is considered accurate to *ca.* 2%. The purpose here was only to establish the range of impurity concentration.

The modified phase solubility method using micro-Soxhlet extractors was applied to reagent-grade naphthalene samples in two ways: (*1*) by the weight method of assay, and (*2*) the refractive index method. The first data obtained by the weight

TABLE I

ANALYSIS OF NAPHTHALENE BY PRINCIPAL PHASE SOLUBILITY METHOD

Sample	*Impurities (%)*	*Number of determinations*
Commercial reagent-grade	12.6	2
Commercial technical-grade	7.45	8
Zone-melted (1 pass)	4.7	2

TABLE II

SOLUBILITY OF NAPHTHALENE IN *tert.*-BUTANOL–WATER AZEOTROPE[a]

Weight method at 30°[b]			
Wt. of wash solution	(1) 61.22040	(2) 61.55865	(3) 61.25405
Wt. of azeotrope	61.12050	61.48630	61.15990
Wt. of naphthalene (g/25 ml)	0.09990	0.07235	0.09415
Corrections for volume			
$d_{30} = 0.99567$ *tert.*-butanol azeotrope	25.94693	25.44647	25.38121
Refractive index method at 30°[b]			
Identical wash solutions gave Refractive Indices:			
	1.3851	1.3850	1.3850

[a] By weight method of assay and refractive index method of assay using Weld pycnometers.

[b] When increasing amounts of naphthalene were added to the 25-ml pycnometer, the weighed quantity of naphthalene corresponding to the above refractive index and the weight of naphthalene by difference was 0.0150 g/ml.

TABLE III

PURITY OF NAPHTHALENE DETERMINED BY PHASE SOLUBILITY METHOD

Modified micro-Soxhlet extraction procedures		
Sample	*Refractive index assay*[a]	*Weight method of assay*[a]
Commercia naphthalene,	11.660	10.66
reagent-grade[b]	11.689	10.76
	11.662	10.90
Commercial naphthalene,	7.216	
technical-grade[b]	7.260	
	7.262	
Zone-melted naphthalene	1.849	
(Fisher Scientific Co.)	1.863	1.821
Zone-melted sample, 1 pass, refractive index assay		
Average values of charge[b]		
	3.956%	
	3.837%	
Segments of charge, sample 1[a]		
(whole charge, 2-cm segments)		
	(1)	2.265%
	(2)	9.534%
	(3)	9.536%
	(4)	12.534%
	(5)	12.561%
Segments of charge, sample 2[a]		
(lower half of charge, 1-cm segments)		
	(1)	1.924%
	(2)	3.040%
	(3)	3.956%
	(4)	5.186%

[a] Impurities g-%.
[b] Representing 2 different sources of supply.

method of assay are given in Table II along with data obtained from weight–volume–temperature experiments with the Weld pycnometer. The results by the refractive index method of assay on commercial samples of naphthalene are given in Table III. These samples include two different lots of reagent-grade naphthalene and one of technical grade. Table III also lists the average values from an analysis of a 15-cm tube, 10-mm O.D., with 1 zone pass where 2 cm at both ends were discarded. In this Table are also the assay values for 2-cm segments of a 15-cm zone-melted charge with 1 zone pass, by the refractive index method. A comparison can be made with an analysis of a Fisher zone-melted sample with 1 zone pass which is also given in this Table. The results from the chemical methods of purification analyzed also by this modified procedure are given in Table IV.

Gas–liquid chromatography

Over 200 individual chromatograms were obtained in runs analyzing the commercial samples of naphthalene as described in the experimental section. Reproductions of these chromatograms along with their detailed analysis may be found in the original thesis[1]. A collation of the most successful results is given in Table V along with the impurity concentrations determined.

TABLE IV

PURITY OF NAPHTHALENE DETERMINED BY PHASE SOLUBILITY ANALYSIS

Modified micro-Soxhlet extraction procedures using naphthalene purified by other means	
Distillation under vacuum[a]	
Fraction #1	7.851%
#2	2.433%
#3	0.861%
#4	1.179%
Purification through the picrate[a]	
#1, Crude product	6.329%
#2, One recrystallization from ethanol	3.842%
Recrystallization from ethanol[a]	
#1, Recrystallized once	4.643%
#2, twice	2.398%
#3, three times	1.956%

[a] Impurities g-%.

TABLE V

GAS-CHROMATOGRAPHIC ANALYSIS OF NAPHTHALENE

No.	*Substances*	*Approx. imp. (%)*	*Analysis (%)*	*Sensitivity*	*Column*	*Conditions*
1	Naphthalene	11	0.027278	$1 \cdot 10^9$	Se 30, 30%	1 µl CS$_2$, 200 µg Nap., 200°
2	Naphthalene	11	0.078761	$10 \cdot 10^9$	Se 30, 30%	2 µl CS$_2$, 10 µg Nap., 200°
3	Naphthalene	11	0.488822	$10 \cdot 10^9$	Se 30, 30%	3 µl CS$_2$, 15 µg Nap., 175°
4	Naphthalene	11	0.02062	$10 \cdot 10^9$	Se 30, 30%	1 µl CS$_2$, 5 µg Nap., 175°
5	Naphthalene	11	8.50592	$10 \cdot 10^9$	Apiezon 20%	1 µl CS$_2$, 5 µg Nap., 150°
6	Naphthalene	11	10.12081	$10 \cdot 10^9$	Apiezon 20%	1 µl CS$_2$, 5 µg Nap., 175°
7	Naphthalene	11	7.969227	$10 \cdot 10^9$	Carbowax 400, 20%	1 µl CS$_2$, 5 µg Nap., 175°

The results indicate that it is possible to obtain quantitative results on a component by GLC when an approximate value is available for total impurities from another absolute method. That is to say, the difficulty lies in making separations and knowing whether all the impurities have come off the column. Theoretically, if an approximate impurity value is known, it is only a matter of trying enough columns and conditions until the necessary separations are obtained.

The problems confronting the use of the Aerograph HiFi GLC instrument in this exacting work involved the lack of rigorous control of the following conditions: (*1*) inlet and outlet pressures, (*2*) precision temperature readings, (*3*) heat transfer properties of the oven, (*4*) control of flow rate while the instrument is operating. Deviations in any of these factors would account for discrepancies in results.

On the basis of the experimental data obtained, the Apiezon 20% column appeared most promising in determining the impurities in naphthalene. At a low sensitivity range, naphthalene was separated from other hydrocarbons. On several columns, the number of impurity peaks corresponded to the findings of thin-layer chromatography. With better control of conditions, it is possible that routine analysis of ultrapure naphthalene could be performed. The fact that polar impurities are present is evidenced by the separations obtained with the Carbowax 400 and diethylene glycol succinate columns. It is also possible that further variation of the silicone columns (higher concentration of stationary phase and longer columns) may yield more precise separations.

The chief advantage of this method lies in the rapidity of assay and accuracy in determining the quantities present. However, the validity of assuming complete separation of impurities can only be verified by another absolute method of analysis giving total impurities.

Thin-layer chromatography

Reproductions of both silica gel and aluminum oxide plates of commercial, reagent-grade naphthalene samples may be found in the original thesis[1]. These data indicate that 3 major impurities were present. The standardization procedure used to indicate sensitivity also pointed to an estimated 10% impurity concentration level.

Thermal analysis and DTA

The calculated values in mole-% of impurities for (*a*) commercial reagent-grade, (*b*) commercial technical-grade, (*c*) 1-pass zone-melted, and (*d*) 30-passes zone-melted naphthalene samples are given in Table VI. Details of measurements and calculations may be found elsewhere[1,21,22].

TABLE VI

THERMAL ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS OF NAPHTHALENE

Sample	*Thermal analysis (mole-%)*	*DTA (mole-%)*
Commercial reagent-grade	2.69936	2.77991
Commercial technical-grade		1.32665
Zone-melted (1 pass)	0.060403 0.063352	0.060381 0.045572 0.095813
Zone-melted (30 passes)	0.000947 0.000562	0.000786

Purity of naphthalene by sample type

The various naphthalene samples studied in this investigation are compared in Table VII as regards their impurity concentration. The methods of assay are indicated for each value listed, the value chosen for this Table being that one which allows the

TABLE VII

PURITY OF NAPHTHALENE BY SAMPLE AND METHOD (%)

Sample	*Principal phase solubility*	*Modified*[a] *Soxhlet*	*Thermal analysis*[b]	*Differential thermal analysis*[b]
Commercial naphthalene reagent-grade	12.6	11.662	2.69936	2.7791
Commercial naphthalene technical-grade	7.45	7.262		1.32665
Zone-melted naphthalene (1 pass) (purest segment)		1.924	0.063352	0.060381
Zone-melted sample (furnished by Fisher Scientific Co.)		1.863		
Zone-melted naphthalene (30 passes)			0.000947	0.000788
Distilled (purest fraction)		0.861		
Via picrate		3.842		
3 Recrystal. from alcohol		1.956		

[a] Impurity g-%.
[b] Impurity mole-%.

greatest confidence or represents an average value from a series of the measurements previously described.

A relationship can be observed between the values obtained by thermal analysis and DTA measurements and phase solubility results. The following calculation from the data corroborates the accuracy of these methods:

Approximate molecular weight of impurity in zone-melted naphthalene

$$\text{Mole fraction} = \frac{\text{moles of impurity}}{\text{moles of impurity} + \text{moles of major component}}$$

Mole fraction of zone-melted naphthalene, 1 pass = 0.00063352
Moles of major component = 0.075120 g
Calculated moles of impurity = $4.5397 \cdot 10^{-5}$
g-% of zone-melted naphthalene *ca.* 1%
Average molecular weight of impurity *ca.* 220.

DISCUSSION

The National Bureau of Standards expresses ultrapurity in mole-% by thermal analysis measurements. It offers an ultrapure standard of naphthalene of 0.04 mole-%. However, it has been shown in this article that in terms of other methods of assay this value represents approximately 1.0 g-% impurities (assuming the molecular weight of the impurity to be close to that of naphthalene). Wide variation of this value is possible since the kinds of impurities are unknown.

The use of mole-% value as a means of identifying ultrapure organic substances has been shown to be deceptive[4]. In a similar manner, gas–liquid chromatographic studies may prove to be inadequate if used alone. Studies[23] made on crude naphthalene manufactured in England have indicated similar difficulties with the gas–liquid chromatographic technique because substantial quantities of the impurities remained on the columns. Thus, proof of ultrapurity must be based on critical analysis beginning with the impure product and carrying through the ultra-refined material, employing more than one method of assay.

This work was supported by research grant GM 07967 U.S. Public Health Service, Bethesda, Maryland.

SUMMARY

Zone-melting as an ultrapurification technique for organic substances has recently received much attention but *proof* of ultrapurity in final measurements has often been lacking. The numerous difficulties encountered in *proof* of ultrapurity narrowed the present study to only one compound, naphthalene. The use of only one analytical procedure has serious disadvantages. It was shown that gas–liquid chromatographic analysis and thermal analysis measurements can be deceptive. However, a combination of "absolute methods" of ultrapurity analysis (thermal analysis, gas–liquid chromatography, phase solubility methods) that measure *total* impurities can yield a reliable picture of the sample.

Whether the zone-melted naphthalene sample used is 100.00000 mole-% pure, or 99.9999 mole-% pure as given by the thermal analysis data, is uncertain. The thermal analysis and DTA method were capable of detecting 0.00008 mole-% of impurities. However proof of ultrapurity is dependent upon a combination of measurements *via* several ultrapurification processes and several methods of assay.

RÉSUMÉ

Les auteurs ont effectué un examen d'ultrapureté du naphtalène, purifié par zone de fusion. L'utilisation d'une seule méthode d'analyse présente de gros inconvénients (analyse chromatographique gaz–liquide et mesures d'analyse thermique). Cependant une combinaison de "méthodes absolues": analyse thermique, chromatographie gaz–liquide, méthodes de solubilités en phase, donnant une mesure des impuretés totales peut fournir une image réelle de l'échantillon. La méthode par analyse thermique et la méthode par analyse thermique différentielle permettent de détecter 0.00008 mole-% d'impuretés.

ZUSAMMENFASSUNG

Dem Zonenschmelzen als eine Technik zur Ultrareinigung für organische Substanzen ist in jüngster Zeit viel Aufmerksamkeit gewidmet worden, jedoch wurde eine Prüfung der Ultrareinheit durch anschliessende Messungen oft versäumt. Die zahlreichen Schwierigkeiten, die bei der Prüfung der Ultrareinheit auftreten, beschränken die Untersuchung dieser Arbeit auf das Naphthalin. Die Anwendung nur eines analytischen Verfahrens hat ernsthafte Nachteile. Es wurde gezeigt, dass chromatographische und thermische Messungen trügen können. Jedoch kann eine

Kombination von Methoden, die die gesamten Verunreinigungen messen, zu einem sinnvollen Bild der Probe führen. Ob die benutzten zonengeschmolzenen Naphthalinproben eine Reinheit von 99.9999 Mol-% oder mehr besitzen, wie es die thermische Analyse ergab, ist ungewiss. Die thermische Analyse und die DTA-Methode sind im Stande 0.00008 Mol-% Verunreinigungen anzuzeigen.

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SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM(III) WITH AZIDE

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(Received March 12th, 1965)

The azide ion, a pseudo-halogenoid, has found application for the colorimetric determination of iron(III)[1], copper(II)[2], uranium(VI)[3] and chromium(III)[4]. In a recent communication[5], palladium has been reported to form 1:1 and 1:4 complexes with the azide in 80% acetone solution, having absorption maxima in the regions 430 and 480 mμ. In the absence of acetone, however, neither the palladium nor the platinum complex shows any peak between 370 and 520 mμ. In aqueous solution at pH 5.0–8.0, rhodium forms with an excess of azide a stable rose-red colour; two absorption maxima were found, one at 405 mμ and the other at 480 mμ. At 405 mμ, the sensitivity of the reaction was quite good, though all those metals which give coloured ions in solution showed absorption in this region and should be removed before the rhodium determination. At 480 mμ the reaction was less sensitive but more selective. The coloured system measured at either wavelength obeyed Beer's law from 2 to 40 p.p.m. of rhodium with an optimum range from 6 to 40 p.p.m.

For the separation of ions which interfered in the determination of rhodium with azide, a scheme involving ion-exchange and solvent-extraction procedures was worked out.

EXPERIMENTAL

Apparatus

All optical density measurements were made with a Unicam SP 600 spectrophotometer provided with 10-mm corex glass cells. The pH of the solutions was determined with a Cambridge pH meter.

Standard solutions

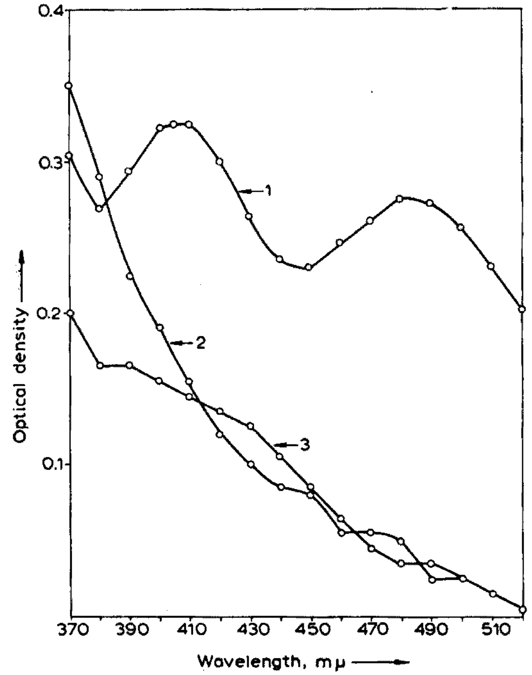
A solution of rhodium(III) chloride was prepared by dissolving about 0.1 g of rhodium chloride trihydrate (Johnson, Matthey and Co.) in water containing 1 ml of 60% perchloric acid and diluting to the mark in a 100-ml volumetric flask. The solution was standardized by the tin(II) iodide method[6].

An aqueous 1 *M* stock solution of sodium azide was prepared and standardized by direct titration with a standard silver nitrate solution, using potassium chromate as the indicator[7].

All other reagents were of analytical grade and were used as indicated.

Absorbance curves

For absorbance studies, different quantities of rhodium(III) solution were taken in separate 25-ml flasks, each of which contained 10 ml of 1 *M* reagent solution. These were then heated on a steam bath for 15 min, cooled to room temperature and the volume of each was made up after the adjustment of the pH to 5.0–8.0. The optical densities were then measured against a reagent blank. The results are shown in Fig. 1; it can be seen that the rhodium–azide system had maxima at 405 mμ and 480 mμ, whereas under the same experimental conditions, the palladium(II) and platinum(IV) complexes had no maxima though they would obviously interfere with the rhodium determination.



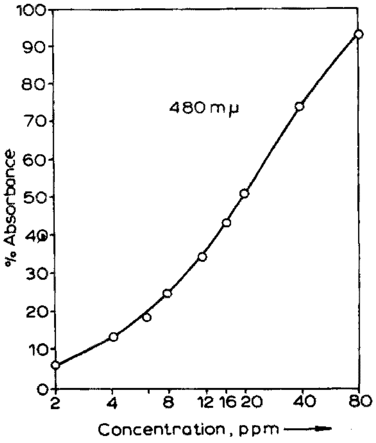


Fig. 1. Spectral transmittancy curves. (1) Rh(III)–azide complex, (2) Pt(IV)–azide complex, (3) Pd(II)–azide complex.

Fig. 2. Standard curves. Rh(III)–azide complex at 480 mμ.

Effects of reagents, pH and time

Solutions containing a known amount of rhodium(III) and 10 ml of the reagent, were adjusted to different pH values with perchloric acid and sodium hydroxide. The optical densities of these solutions were measured both at 405 and 480 mμ against a reagent blank, as described above. It was found that the optical density increased up to pH 5.0 and then remained constant in the range 5.0–8.0. For full colour development, with 2 to 40 p.p.m. of rhodium, 10 ml of the reagent solution sufficed, but the addition of up to 20 ml did not affect the colour intensity.

The maximum intensity of colour was obtained only on standing overnight or on heating for 15 min on a steam bath. Once developed, the system was stable for at least 24 h.

Beer's law, optimum range and relative error

The colour complex obeyed Beer's law over the range 2–40 p.p.m. of rhodium. Measurements were carried out at pH 7.0 against a reagent blank. Ringbom's curve[9], obtained by plotting percent absorbance against log concentration, showed that the optimum concentration range was 6–40 p.p.m. of rhodium. Figure 2 shows the graph obtained at 480 mμ; essentially the same line was obtained at 405 mμ.

As suggested by AYRES[8], the percent relative errors per 1% photometric error were plotted against transmittance to show how the analysis error varied (Fig. 3). The percent relative error per 1% absolute photometric error for this optimum range was 2.73 (Fig. 3). The reproducibility of the results is shown in Table I.

Effect of diverse ions

In order to study the effect of diverse ions, solutions containing 4 p.p.m. of rhodium were mixed with solutions of different ions and the pH was adjusted to 7 after the addition of 10 ml of 1 *M* azide. The colour was then developed as described above and the absorbance was measured at 480 mμ. It was found that no interference was caused by Mg^{2+}(100 μg), Ca^{2+}(100 μg), Sr^{2+}(100 μg), Ba^{2+}(100 μg), Al^{3+}(100 μg), Zn^{2+}(100 μg), Cd^{2+}(100 μg), Hg^{2+}(100 μg), Co^{2+}(20 μg), Ni^{2+}(20 μg), Mn^{2+}(40 μg), Cr^{3+}(40 μg), Os^{8+}(20 μg), Ru^{3+}(16 μg), Au^{3+}(10 μg) and Ir^{4+}(4 μg). Aqueous solutions of chromium, thorium, titanium and zirconium azide undergo hydrolysis with the precipitation of hydroxide and hence can be removed by filtration, as can silver and lead which form insoluble precipitates.

Other interfering ions and the ions mentioned above, if necessary, can be removed before the rhodium determination by the application of ion-exchange and solvent-extraction procedures, as described below. Some of the ions were separated in an ion-exchange column as chlorides and those which formed anionic complexes were separated by extraction with organic solvents (tributyl phosphate and ethyl acetate) after complexation, as needed, with N-benzoyl-*o*-tolyl hydroxylamine (BTH)[10], benzoylthiouridobenzoic acid (BTBA)[11] or thiocyanate[12].

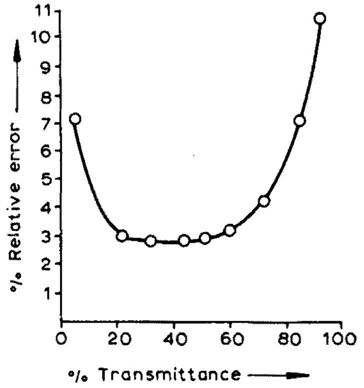
TABLE I

ANALYSIS OF KNOWN CONCENTRATIONS OF RHODIUM

Rh taken (p.p.m.)	20.00	15.00	10.00	8.00
Rh found (p.p.m.) (av.)	20.03	15.01	10.04	8.05
Range	20.01–20.05	14.99–15.03	10.02–10.06	8.03–8.07
No. of samples	5	5	5	5

Separation procedure

Rhodium along with other ions as chlorides was treated with an excess of potassium chloride solution and passed through Amberlite IR-120 (Na^+) resin. The scheme was then as follows:



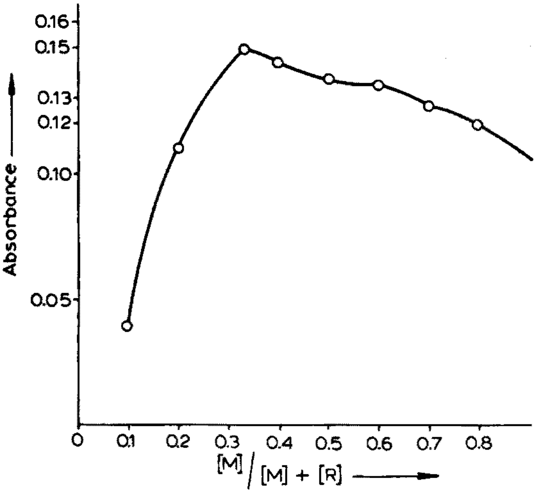
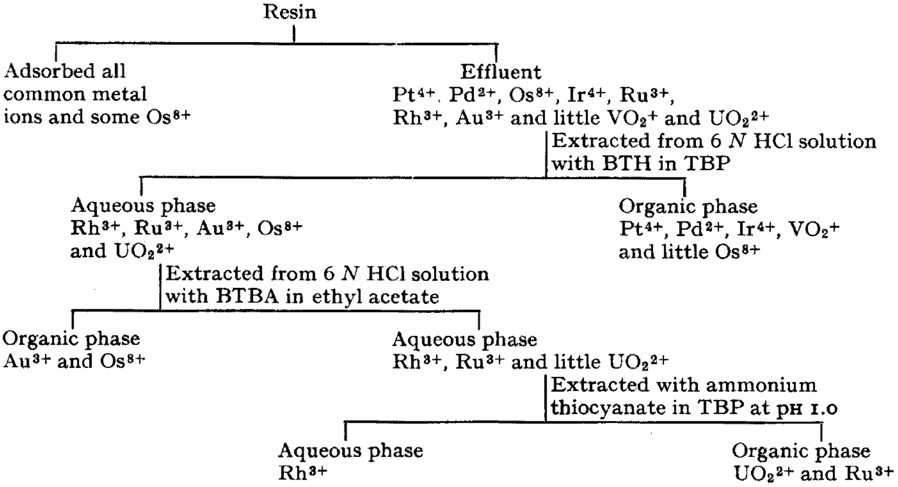


Fig. 3. Percent relative error curve for Rh(III) complex at 405 mμ.

Fig. 4. Job's method. Rh(III), 0.9 · 10^{-2} *M*; azide, 0.9 · 10^{-2} *M*.



The solution containing rhodium and the other ions as chlorides was treated with 25 ml of 1.0 *M* potassium chloride solution and passed through Amberlite IR-120 (Na^+) in a 13-mm i.d. glass column with a resin height of 16 cm, at a flow rate of 1–2 ml per min. The column was washed with another 25-ml portion of 0.1 *M* potassium chloride solution.

For solvent extraction, 25 ml each of 0.5% solutions of BTH in tributyl phosphate and of BTBA in ethyl acetate were used, and in each case the aqueous layer was washed only once with the respective solvent.

The aqueous layer containing ions of ruthenium, rhodium and uranyl was evaporated to dryness and then dissolved in 25 ml of 1.0% ammonium thiocyanate solution at pH 1.0. This was heated on a water bath for 5 min and extracted with three 10-ml portions of tributyl phosphate. After each extraction, the organic layer was washed with 10 ml of a 0.1% solution of ammonium thiocyanate at pH 1.0. These washings were added to the main aqueous phase for the determination of rhodium.

The aqueous phase which contained the entire quantity of rhodium as thiocyanate was fumed with nitric–perchloric acid mixture to decompose the complex before the element was determined as azide (*cf.* Table II).

TABLE II

Ions (mg) taken along with rhodium were: Pt^{4+}(2.0), Pd^{2+}(2.5), Ir^{4+}(1.0), Ru^{3+}(1.0), Os^{8+}(1.0), Au^{3+}(1.5), Hg^{2+}(4.0), Cu^{2+}(2.0), Cd^{2+}(3.0), Sn^{4+}(2.0), Bi^{3+}(1.8), Al^{3+}(3.2), Fe^{3+}(2.0), Cr^{3+}(2.0), Ti^{4+}(1.8), Th^{4+}(2.1), Zr^{4+}(3.0), Mn^{2+}(3.3), Zn^{2+}(2.0), Co^{2+}(3.0), Ni^{2+}(3.5), Ca^{2+}(2.5), Sr^{2+}(2.0), Ba^{2+}(2.0), Mg^{2+}(2.2), VO_2^+(2.5) and UO_2^{2+} (3.2).

Rh added (p.p.m.)	100[a]	40	20	10
Rh found (p.p.m.)	97.8	38.6	18.5	8.5

[a] Volume was made up to 100 ml and an aliquot portion (25 ml) was taken for absorption measurement.

Composition of the rhodium–azide complexes

During the study of the absorption at different pH values, it was observed that at pH 2.0 two plateaux, one in the region 400–410 mμ and the other in the region 470–480 mμ, were formed and that with rise of pH these extended to humps with peaks at 405 and 480 mμ at the optimum pH range, 5 to 8.

The composition of the complex formed in the optimum pH range could not be determined by JOB's method[13], because when the metal concentration was high and the azide concentration was low, the rhodium salt invariably hydrolysed; an attempt was therefore made to determine the composition of the complex formed at pH 2.0 by JOB's method. Accordingly, the absorption mixtures (keeping the total volume constant) were prepared by taking different volumes of rhodium solution in separate beakers, evaporating just to dryness with 2 drops of perchloric acid and mixing with an appropriate volume of equimolar azide solution. The pH of the mixtures was then adjusted with sodium hydroxide and perchloric acid to a constant value of 2.0. The colour intensities of the solutions were then measured at 410 mμ after heating for 15 min on a steam-bath (*cf.* Fig. 4). The curve shows that in dilute aqueous solution a mixture of complexes is formed depending on the concentration of the azide; a 1:2 complex predominates under the conditions of the experiment, and a 1:1 complex is probably also formed, as indicated by the shoulder in that region. The complexes formed in the dilute azide solution (10^{-2} *M*) were found to be cationic and not anionic; they were retained by a cation exchanger, Amberlite IR-120 (Na^+), but not by an anion exchanger, Amberlite IRA-400 (ClO_4^-).

When pyridine (10 ml) was added to a solution of rhodium(III) chloride trihydrate (25 mg) and sodium azide (100 mg), a precipitate, which was insoluble in most organic solvents, excepting pyridine and dimethyl formamide, separated on cooling for about 24 h. The visible absorption spectrum of the compound in the latter two solvents showed no maxima. The compound was filtered and washed twice with absolute ethanol. The results for elemental analysis were as follows: found Rh 27.98, C 16.40, N 15.20, H 3.50, Cl 19.60; calc. for $[Rh(N_3)\,Py(H_2O)_4]Cl_2$: Rh 28.06, C 16.30, N 15.20, H 3.50, Cl 19.30%. When a pyridine solution of this compound was passed through a column of Amberlite IRA-400 (ClO_4^-), rhodium was found in the effluent, but after similar treatment with Amberlite IR-120 (Na^+) no rhodium could be detected in the effluent; this proved the compound to be cationic.

SUMMARY

Sodium azide was shown to be a sensitive reagent for the spectrophotometric determination of rhodium(III). The coloured complex showed absorption maxima at 405 mμ and at 480 mμ. At both wavelengths, the system obeyed Beer's law from 2 to 40 p.p.m. of rhodium. The percent relative error for the optimum range (6 to 40 p.p.m.) was 2.73. Both 1:1 and 1:2 complexes appear to be formed in solution, but in pyridine only one complex is formed. A scheme for the separation of rhodium from all other ions, involving ion-exchange and solvent-extraction processes, is proposed.

RÉSUMÉ

L'azoture de sodium constitue un réactif sensible pour le dosage spectrophotométrique du rhodium. Maxima d'absorption à 405 mμ et 480 mμ. A ces deux longueurs d'onde la loi de Beer s'applique entre 2 et 40 p.p.m. de rhodium. Les deux complexes 1:1 et 1:2 peuvent se former en solution. On propose une méthode de séparation du rhodium d'avec d'autres ions, comprenant échange d'ions et extraction dans un solvant.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass Natriumazid ein empfindliches Reagenz für die spektralphotometrische Bestimmung von Rhodium(III) ist. Der gefärbte Komplex zeigt Absorptionsmaxima bei 405 mμ und 480 mμ. Bei beiden Wellenlängen gehorcht das System dem Beerschen Gesetz für Konzentrationen von 2–40 p.p.m. Rhodium. Der prozentuale relative Fehler für den optimalen Bereich (6–40 p.p.m.) beträgt 2.73%. In der Lösung werden anscheinend sowohl 1:1 als auch 1:2-Komplexe gebildet, in Pyridin jedoch nur ein Komplex. Es wird ein Schema für die Trennung des Rhodiums von allen anderen Ionen unter Anwendung von Ionenaustauscher- und Extraktionsverfahren vorgeschlagen.

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SHORT COMMUNICATIONS

Spectrophotometric determination of ruthenium with 2-amino-8-naphthol-6-sulphonic acid

Various organic reagents, including derivatives of thiourea[1], *o*-phenanthroline[2], *p*-aminosalicylic acid[3], and salicylic and 5-sulpho-salicylic acids[4], have been recommended for the spectrophotometric determination of ruthenium.

The reactions of certain phenols and naphthol derivatives with ruthenium are cited in a recent study by KONEČNÝ[5]. Simultaneously, MANNING AND MENIS[6] used 2-nitroso-1-naphthol for the spectrophotometric determination of ruthenium. This reaction was later studied spectrophotometrically in the presence of the citrate ion[7].

In the present paper, the use of 2-amino-8-naphthol-6-sulphonic acid (γ-acid) is proposed for the spectrophotometric determination of ruthenium.

Apparatus

Spectrophotometric measurements were made by means of a Carl Zeiss Jena V.S.U.-1 spectrophotometer with a MQVS photocell, using the glass prism. The absorption spectra were registered by a Beckman DB spectrophotometer. The pH of the solutions was determined by means of a pH meter MV-11, with a glass electrode.

Reagents

Standard ruthenium solution. This was prepared from $RuCl_3$ (insoluble black modification, "Fluka" product) by fusion with sodium hydroxide and sodium nitrate; the product from the fusion was distilled in the presence of perchloric acid and oxygenated water, in a glass apparatus as described by BANKS AND O'LAUGHLIN[2]. The ruthenium tetroxide liberated was absorbed in a solution of 0.2 *M* sodium hydroxide. The titre of the ruthenium solution was determined by reduction with alcohol in a stream of hydrogen and by direct weighing of the obtained metallic ruthenium. In this way, a stock solution containing 280 μg Ru/ml was obtained, and working solutions containing 80 μg Ru/ml were prepared by suitable dilution.

Reagent solution. A 0.1% solution of 2-amino-8-naphthol-6-sulphonic acid was prepared in 0.2 *M* sodium hydroxide.

For the study of the effects of diverse elements, the solutions used were prepared from OsO_4 (B.D.H.; 300 μg Os/ml), $PdCl_2$ (Fluka; 3000 μg Pd/ml), H_2PtCl_6 (B.D.H.; 1500 μg Pt/ml) and uranyl nitrate solution (Riedel de Haen; 1000 μg U/ml).

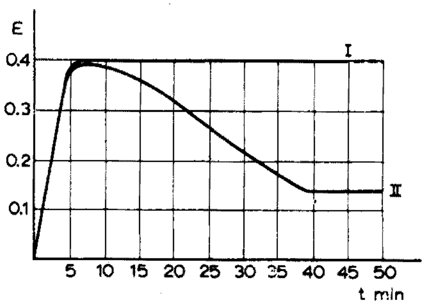
Procedure

The ruthenium solution, 2 ml of reagent solution and 0.5 ml of 20% (v/v) sulphuric acid were introduced in this order into 10-ml volumetric flasks. The mixtures were diluted to the mark with distilled water. Under these conditions a sharp blue colour appeared which turned green in basic medium.

When the test was prepared in the same manner, but without adding sulphuric acid and with 0.2 *M* sodium hydroxide for dilution, the colour of the compound formed was green; this green compound became blue in acidic medium. For each determination a blank test was prepared in the same manner, except for the ruthenium solution. The readings were effected in 1-cm cells.

Results

Effect of time. In order to determine the influence of time on the extinction, tests were made both in acidic and basic media, as discussed in the *Procedure.* The determinations were performed with tests containing 8 μg Ru/ml at wavelengths of 585 mμ (for the acidic test) and at 660 mμ (for the basic test). The results obtained are given in Fig. 1, from which it can be seen that the blue compound formed in acidic medium was very stable with time, whereas the green compound formed in basic medium was much less stable.



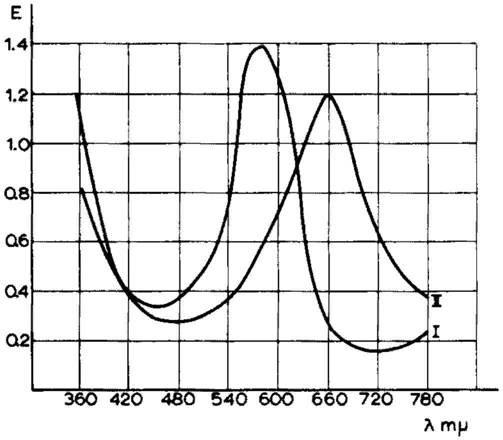


Fig. 1. The influence of time on the ruthenium–γ acid reactions (c = 8 μg Ru/ml). I, pH 0.85; II, pH 13.0.

Fig. 2. The influence of pH on the absorption spectra of the ruthenium–γ acid complexes (c = 24 μg Ru/ml). I, pH 0.85; II, pH 13.0.

Effect of acidity. As shown above, a change in the pH of the solution caused considerable modifications in the equilibria established. The strongly acidic medium created by addition of 20% sulphuric acid (pH 1) favoured the formation of the blue, stable compound. Varying the amounts of 20% sulphuric acid added had little effect on the system. An increase in the pH of the solution to give a strongly basic medium (pH 13) modified the original equilibrium and transformed the blue stable compound to a green labile compound. This transition was readily reversed when the pH of the solution was changed, and a closer study of the system was therefore made.

The absorption spectra of the compounds at pH values of 0.85 and 13 were determined for solutions containing 24 μg Ru/ml finally. The results are plotted in Fig. 2, from which it can be seen that the absorption maximum of the blue compound formed in acidic medium appeared at 585 mμ whereas the maximum for the green compound in basic medium lay at 660 mμ. Several tests, which were made to find an isosbestic point (of equal absorption) where the two forms would be in equilibrium, were unsuccessful. The absorption maximum occurred at the same wavelength despite changes in acidity, although the colour intensity increased or decreased as a function of the amount of acid added.

Method of determination. The study of the absorption spectra showed that two distinct bands were obtained depending on the pH of the solution; accordingly, a wavelength of 585 mμ was chosen for actual determinations.

The results of further measurements showed that the Bouguer–Beer–Lambert law was followed, the extinction being directly proportional to the ruthenium concentration. Thus 2-amino-8-naphthol-6-sulphonic acid could be applied for the spectrophotometric determination of ruthenium between the limits 0.8 μg Ru/ml and 27.2 μg Ru/ml.

Effect of diverse ions. It is well-known that ruthenium can be separated from most elements by distillation of RuO_4. Accordingly, only the effects of osmium, palladium, platinum and uranium on the reaction were studied; it was found that osmium and palladium interfered strongly, making the determination of ruthenium impossible. However, ruthenium could be determined in the presence of 22-fold amounts of platinum and 31-fold amounts of uranium. Common anions did not interfere; nitric, hydrochloric and perchloric acids could be used instead of sulphuric acid without effect on the results.

Conclusions

The reaction of ruthenium with 2-amino-8-naphthol-6-sulphonic acid (γ-acid) can be utilized for spectrophotometric determination of ruthenium at a wavelength of 585 mμ in the presence of sulphuric acid. This method allows the determination of ruthenium between the limits 0.8 μg Ru/ml and 27.2 μg Ru/ml, and is thus one of the most sensitive available for the element.

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(Received March 5th, 1965)

Spectrophotometric determination of chloropicrin in water

Recently chloropicrin has been widely used as a nematicide, fungicide, bactericide and herbicide. It is also frequently used in soil treatment and as a warning agent in mixtures with hydrocyanic acid and cyanogen chloride or with methyl bromide in fumigants[1-3]. It has been used to prevent fermentation in wine, in concentrations of 1 μg/ml[4]. Because of the great toxicity of this compound, its detection and sensitive determination are essential. Several methods have been published for this purpose[1,5-9] but the most sensitive method of determination in aqueous solution is that of FOURNIER AND PERSON[7], by which concentrations as low as 4 μg/ml can be determined.

The need for a method with a lower detection limit led to the development of the new procedure described below. The method is based on the formation of cyanogen chloride from chloropicrin and cyanide; cyanogen chloride then reacts with pyridine and 1-phenyl-3-methyl-5-pyrazolone to give a highly colored compound, as in EPSTEIN's procedure for cyanide[10].

Apparatus

All absorbances were measured with a Beckman DU Spectrophotometer equipped with 1.00-cm cells.

Chemicals and reagents

1-Phenyl-3-methyl-5-pyrazolone. This was prepared as described in the literature[11].

Bis-(1-phenyl-3-methyl-5-pyrazolone). This was prepared as described by JØRGENSEN[12] from ethyl acetoacetate and phenylhydrazine. It can also be prepared from phenylmethylpyrazolone and phenylhydrazine[10].

Potassium cyanide. The purity of this reagent (Merck) was very important. A freshly prepared 3% (w/v) solution in distilled water was used.

Pyridine. Colorless; freshly distilled (b.p. 113–115°).

Pyridine–pyrazolone solution. A mixture of the mono- and bis-pyrazolone derivatives was prepared as described by JØRGENSEN[12]. One part of the bis derivative was mixed with 5 parts of the mono derivative. This mixture was indefinitely stable. To prepare the reagent solution, 150 mg of the pyrazolone mixture was dissolved in 25 ml of pyridine. The solution was stable for only one week in the refrigerator.

Chloropicrin stock solution. Chloropicrin was obtained from H. STOLZENBERG, sealed in neutral glass ($N_D^{23} = 1.4608$). About 50 mg of chloropicrin was weighed into a 50-ml volumetric flask containing 10 ml of a 1:1 ethanol–water mixture. The solution was diluted to the mark and from this solution standard solutions containing 0.5–4 μg of chloropicrin/ml were prepared. This procedure prevented evaporation and accelerated dissolution.

Recommended procedure

Add successively to each test tube 2 ml of the pyrazolone reagent solution, 0.30 ml (exactly measured) of the potassium cyanide solution and 4 ml of the chloropicrin test solution. Simultaneously prepare a colorimetric blank without chloropicrin and apply the same procedure to the chloropicrin standard solutions.

Allow the color to develop at constant temperature for the time needed to obtain stability. The time depends on the temperature employed. The operator can select the working temperature or the time according the desired sensitivity and accuracy or the available time (see Table I). The accuracy and reproducibility of the method decrease with increasing temperature; at 50° or more the operator must use test tubes of the same thickness and measure the time exactly. Finally, cool under running water and read in the spectrophotometer at 632 mμ.

Results

When the recommended procedure was followed, the color produced obeyed Beer's law up to 4 μg of chloropicrin/ml. At higher concentrations deviations occurred, probably because better yields of cyanogen chloride were obtained. At normal laboratory temperatures and below 50°, the reproducibility was good (in the 3–5% range). At higher temperatures, the errors increased to ±5–10%, because of partial decomposition of the colored species. These factors had a smaller effect when the test tubes were of uniform thickness and the heating time was measured exactly; the values quoted were obtained in this way.

Table II shows the results obtained for various concentrations of chloropicrin;

TABLE I

EFFECT OF TIME AND TEMPERATURE

Temperature (°)	*Time needed for color stability*	*Absorbance for 1 μg/ml*
15	5 h	0.130
20	4 h	
26	2.5 h	0.100
40	1 h	
50	20 min	
60	15 min	
80	10 min	
100	2.5 min	0.085

TABLE II

RECOVERY OF CHLOROPICRIN

Chloropicrin (μg/ml)					
Added	*Found*	*Error(%)*	*Added*	*Found*	*Error(%)*
1.19[a]	1.15	− 3.3	1.68[a]	1.60	− 5.0
2.39[a]	2.47	+ 3.3	2.30[a]	2.52	+ 9.5
3.48[a]	3.62	+ 4.0	2.57[b]	2.44	− 5.1
3.52[a]	3.70	+ 5.1	2.68[b]	2.77	+ 3.7
3.58[a]	3.86	+ 7.3	3.38[b]	3.85	+13.8
0.84[a]	0.72	−14.2	4.02[b]	4.32	+ 7.4
1.34[a]	1.40	+ 4.5	4.52[b]	4.86	+ 7.5

[a] Temperature 26°.
[b] Temperature 100°.

at 100° the results were variable, but the error was never greater than 14%. At concentrations higher than those shown, the errors were large.

It was observed that several salts interfered in the procedure by affecting the color intensities. It is therefore advisable to apply the method to steam-distillates of the sample. Chlorine and organic chloramines interfered by forming cyanogen chloride. Sulfur dioxide destroyed the color formed.

Discussion

Several critical factors of the procedure were studied. It was found that when the volume of the pyridine–pyrazolone reagent was increased, the absorbance rose to a maximum and then decreased. The sensitivity was inversely proportional to the working temperature, and the time necessary to attain color stability diminished as the temperature increased. When the amount of cyanide added was increased, the color intensity increased to a maximum and then decreased. Table III shows how small variations in the amount of cyanide added could produce large variations in the absorbance measurements; the cyanide must therefore be measured accurately.

The following observations may clarify some aspects of the reaction.

TABLE III

EFFECTS OF AMOUNT OF CYANIDE AND pH ON SENSITIVITY

Tube	*1*	*2*	*3*	*4*	*5*	*6*	*7*
ml 3% KCN	0.1	0.2	0.3	0.5	0.6	0.8	1.0
pH	8.4	9.2	9.5	9.8	9.9	10.0	10.1
Absorbance	0.145	0.465	0.487	0.425	0.399	0.337	0.226

(*a*) The color formed was partially destroyed by excess of cyanide; a smaller effect was produced by an equivalent amount of alkali. When chloramine T was used instead of chloropicrin, identical behavior was observed. Thus the effect was not related specifically to the reaction between chloropicrin and cyanide.

(*b*) When EPSTEIN's procedure for the formation of cyanogen chloride was followed, and the pyridine–pyrazolone reagent and cyanide (or sodium hydroxide) were added in that order, the color intensity was less than in the normal procedure; the size of this effect depended on the time of development before the addition of cyanide or sodium hydroxide, an increase in time giving an increase in color intensity. When ethyl acetoacetate was used instead of phenylmethylpyrazolone, the color obtained no longer changed with the volume of cyanide added.

(*c*) When chloramine T was added to a mixture of pyridine and potassium cyanide, followed, a few minutes later, by phenylmethylpyrazolone, no color was obtained; but when the phenylmethylpyrazolone was added immediately after chloramine T, a color was obtained, though it was feeble compared with that formed with the pyridine–pyrazolone mixture. This observation indicated the existence of an irreversible transformation of glutaconic aldehyde, produced by the excess of cyanide, but it is uncertain, if the action was related to an effect of the ion itself (*e.g.* cyanohydrin formation or addition to a double bond) or to the alkaline pH produced.

Observations (*b*) and (*c*) proved that the action of cyanide on glutaconic aldehyde was very fast, and much faster than the condensation of glutaconic aldehyde with phenylmethylpyrazolone. Ethyl acetoacetate reacted more quickly with the aldehyde, so that the reaction was not affected by high concentrations of cyanide. Obviously, the processes involved in the reaction are very complex.

The sensitivity was affected when the order of addition of the reagents was altered, and it was important not to allow contact between chloropicrin and cyanide in the absence of the pyridine–pyrazolone reagent, because no color was produced; possibly, the cyanogen chloride formed was destroyed by a change in pH. When chloropicrin was mixed with the pyridine–pyrazolone reagent before the addition of cyanide, the color produced was much less than that obtained when chloropicrin was added last.

Owing to the slight solubility of potassium cyanide in pyridine, the previous preparation of a mixture of the two reagents is not recommended. The order of addition given in the *Procedure* produced the most satisfactory results.

Other pyridine derivatives such as 4-(4′-nitrobenzyl-pyridine) also produce the reaction, and might be useful for air pollution analysis.

SCHOLL AND BRENNEISEN[13], working with bromopicrin and potassium cyanide, found that cyanogen bromide, potassium bromide, potassium nitrite, etc. were formed. BASSET[14] isolated cyanogen chloride in the reaction between chloropicrin and sodium cyanide.

In the present work, it was proved that the color formed had an absorption spectrum (Fig. 1) the same as that obtained in EPSTEIN's procedure for hydrocyanic acid. Thus it seems likely that the reaction proceeds as follows:

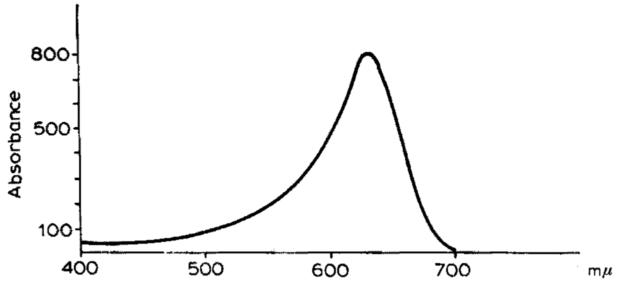

Fig. 1. Absorption spectrum of reaction product.

$$2\,CCl_3NO_2 + KCN \rightarrow KCl + CNCl + (CCl_2NO_2)_2$$

The subsequent reactions are those of the EPSTEIN's procedure[9]. Other secondary reactions are also involved and these lead to an increased yield of cyanogen chloride.

We are grateful to Mr. C. LANGE for German translations, and to Dr. M. A. RÚVEDA and Mr. J. VANETTA for reading of this manuscript.

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(Received March 22nd, 1965)

Determination of micro quantities of niobium in uranium

Difficulties were encountered in the determination of niobium in alloys of uranium containing very low amounts of niobium (about 0.05% or less). Several methods have been reported[1–6] for the analysis of uranium–niobium alloys containing higher amounts of niobium (1–25% Nb), but there is no satisfactory chemical method for the determination of small amounts of niobium in uranium. The extraction of niobium with a chloroform solution of oxine and subsequent spectrophotometric determination as described by MOTOJIMA AND HASHITANI[7] entails a rather involved procedure of washing the chloroform extract with different complexing agents and buffers to remove interfering ions; even then, corrections have to be made for iron and molybdenum and the authors do not recommend the method for samples containing 10 times as much molybdenum as niobium.

Various methods are available for the colorimetric determination of niobium[8]; but they are all subject to a series of interferences. A prior separation of niobium from uranium and other interfering elements is therefore essential. Quantitative separation of niobium by fuming with perchloric acid, as is used for uranium alloys containing high amounts of niobium[1] is not possible because of the appreciable solubility of niobium in perchloric acid. The solubility of tantalum under similar conditions is, however, negligible. The possibility of recovering micro quantities of niobium by fuming with perchloric acid using tantalum as carrier was, therefore, investigated. The results recorded in this paper show that as little as 5 p.p.m. of niobium in uranium can be recovered by this method.

BUKSH AND HUME[9] have described the thiocyanate method for the spectrophotometric determination of niobium in the presence of 20 times as much tantalum, and have suggested that it should be applicable even with a 100-fold excess. The method described below gives good recoveries in the presence of even a 400-fold excess of tantalum. Further, it was found that interference from molybdenum and tungsten can be eliminated by treating the precipitate of earth acids with ammoniacal ammonium carbonate solution. Although it is likely that vanadium is also eliminated in this step, the procedure recommended by WARD AND MARRANZINO[10] was followed, *i.e.*, the ether extraction was carried out in the absence of tin(II) chloride and iron and titanium was subsequently removed by shaking the ether phase with a solution of tin(II) chloride. Under these conditions vanadium is not extracted since it is not reduced to the trivalent state. The method is thus applicable for the determination of niobium in uranium metal and alloys in the presence of comparatively large amounts of the interfering elements.

Procedure

Dissolve the uranium metal (or alloy) in a mixture of nitric acid and hydrofluoric acid in a platinum dish. Add tantalum solution (= 2 mg Ta_2O_5) and 15 ml of perchloric acid. Evaporate to strong fumes of perchloric acid, cool, rinse the sides of the dish with water and fume again. Transfer the contents to a beaker, dilute to about 200 ml with water and heat to boiling. Allow the precipitate to settle after addition of a little filter paper pulp, filter and wash well with water. Transfer the precipitate back into the beaker and treat with excess of ammoniacal ammonium carbonate solution (1%). Filter and wash first with the carbonate solution and then several times with water. Ignite the precipitate, fuse with potassium bisulphate, dissolve in 10% tartaric acid solution and make up in a volumetric flask with the same solution.

Development of colour. As soon as possible after making up the sample solution, transfer an aliquot containing 5–50 μg Nb to a 50-ml separating funnel and *immediately* add 5 ml of 20% potassium thiocyanate solution and 5 ml of 9 *M* hydrochloric acid (which is also 1 *M* with respect to tartaric acid). Shake thoroughly after the addition of each reagent and allow to stand for 5 min.

Add 5 ml of ether (which has been freshly washed with a solution containing 10 g $SnCl_2 \cdot 2\,H_2O$ per 100 ml of 2 *N* HCl). Shake the funnel vigorously and allow the phases to separate.

Run the lower (aqueous) portion into another separating funnel and add 1 ml of 9 *M* hydrochloric acid and 0.7 ml of 50% potassium thiocyanate solution. Re-extract with 5 ml of ether and combine the ether extracts.

Shake the combined extracts with a mixture of 2 ml of 10% tin(II) chloride solution and 0.5 ml of 20% potassium thiocyanate solution for 10 sec. Allow the phases to separate.

Transfer the ether layer to a 25-ml volumetric flask. Rinse the separating funnel with 2.5 ml of ether and add to the flask. Make up to the mark with acetone.

Measure the optical density on a spectrophotometer at 385 mμ against a blank carried through the entire procedure. Compare with standards prepared by following the procedure for development of color.

Results

Table I shows results on synthetic samples prepared by adding varying quantities of niobium to 1 g of pure uranium metal to which were also added 250 μg each of the interfering metals, titanium, tungsten, molybdenum and vanadium.

TABLE I

Sr no.	*Nb added (μg)*	*Nb found (μg)*
1	5	4.9
2	5	5.0
3	25	25.2
4	100	99.2
5	200	202
6	500	500

TABLE II

DETERMINATION OF Nb IN Nb–U ALLOYS

Nominal composition % Nb	*Nb found (%)*
0.100	0.097, 0.095, 0.102 (Av. 0.098)
0.050	0.047, 0.047, 0.046 (Av. 0.047)
0.025	0.033, 0.032, 0.030 (Av. 0.032)

As a further check on the reproducibility of the proposed method, three samples of a niobium–uranium were prepared and analysed. The results (Table II) indicate that the precision is good; the accuracy appears to be less satisfactory, but this is not considered to be significant because the final composition of the alloys is unlikely to be exactly the same as the nominal composition in view of the small amounts which were prepared.

The authors wish to thank Dr. V. T. ATHAVALE, Head of Analytical Division, for his encouragement and helpful discussions during the progress of the work.

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(Received March 4th, 1965)

BOOK REVIEWS

O. G. KOCH UND G. A. KOCH-DERIC, *Handbuch der Spurenanalyse*, Springer-Verlag, Berlin–Göttingen–Heidelberg, 1964, xvi + 1232 S., Ganzleinen DM 226.—.

Cet ouvrage de 1230 pages est l'un des plus complets du moment, en ce qui concerne les méthodes de séparation par extraction et les méthodes spectrophotométriques. Il comprend une première partie assez courte (124 pages) subdivisée en 7 chapitres parmi lesquels citons: les méthodes utilisées pour le dosage de traces, les méthodes de séparation, un exposé très succint sur la sensibilité, les techniques de travail fort bien décrites et illustrées, et un excellent exposé sur les erreurs, la précision et l'exactitude dans l'analyse de traces.

La deuxième partie intitulée partie spéciale est beaucoup plus importante puisqu'elle compte plus de 1000 pages. Elle comprend 7 chapitres parmi lesquels: la préparation de l'échantillon, la technique de l'extraction et la détermination des éléments. Dans ce dernier, le plus vaste, les auteurs étudient 51 éléments classés par ordre alphabétique. Pour chacun d'eux sont donnés les réactifs utilisés avec leur formule, leurs propriétés, le spectre d'absorption (ou de transmission), la limite de sensibilité, etc. Les méthodes d'analyse sont décrites minutieusement si bien qu'il est possible de les mettre en pratique le plus souvent sans avoir recours aux articles originaux dont les auteurs donnent la référence. On y trouve aussi une description du dosage de l'élément considéré dans divers échantillons.

Le chapitre suivant a pour objet la détermination des groupes d'éléments et le dernier de cet ouvrage traite de l'analyse microbiologique. Rarement on trouve rassemblé autant de renseignements sur ce sujet. Les techniques de dosages microbiologiques de plusieurs éléments dans divers milieux terminent cette présentation.

En fait, on trouve dans cet ouvrage une foule de renseignements indispensables à l'analyste qui se spécialise dans ce domaine. Pourtant nous regrettons que les auteurs n'aient développé que la spectrophotométrie. C'est une remarquable méthode de dosage pour des quantités de l'ordre du microgramme mais qui peut rarement être utilisée à la détermination de submicro-quantités. Une préface du livre indique bien qu'il ne sera question, sinon de façon très succinte, ni de spectrométrie de masse, ni de méthodes par activation, ni même de spectrophotométrie de flamme qui sont pourtant parmi les méthodes les plus sensibles. Mais pourquoi n'avoir pas développé davantage l'électroanalyse? La polarographie est parfois citée mais il y a aussi la coulométrie, l'ampérométrie et la méthode à la goutte suspendue qui sont de remarquables moyens pour la détermination de traces d'éléments. En outre la spectrométrie d'absorption atomique n'est pas mentionnée bien que très sensible et remarquablement sélective. Mais ceci n'enlève rien à la valeur de cet ouvrage. Il est l'oeuvre de spécialistes, les méthodes préconisées ont été choisies en connaissance de cause, leur valeur est indiscutable. On peut donc leur faire toute confiance; dans cet ouvrage tout est sérieux, bien étudié. Ceux qui auront recours à lui ne seront pas déçus.

D. MONNIER (Genève)

Treatise on Analytical Chemistry, Edité par I. M. KOLTHOFF ET P. J. ELVING avec l'aide de E. B. SANDELL, *Part II, Analytical Chemistry of the Elements, Vol. 6, Be-Pb- Nb- Ta- Te- Ac- At- Fr- Po- Pa,* J. Wiley, New York, 1964, xxii + 627 pp., price 173 s.

Dans ce Volume 6, section A, chaque chapitre a été confié, comme pour les autres fascicules, à des spécialistes. On en compte 7 et non des moindres: J. W. COBBLE, T. W. GILBERT, S. KALLMANN, B. R. F. KJELLGREN, E. S. MELICK, C. W. SCHWENZFEIER, J. SEDLET. C'est dire la confiance qu'on peut leur accorder, particulièrement en ce qui concerne le choix des méthodes, pour le dosage des macroquantités comme pour celui des traces. Evidemment l'équilibre entre les divers paragraphes varie d'un élément à l'autre. C'est ainsi que les complexes du plomb sont minutieusement étudiés; on y trouve dans un tableau très complet des constantes d'instabilité, l'auteur donne même plusieurs valeurs pour un même complexe, avec les références correspondantes. Par contre pour les autres éléments cette partie est beaucoup moins développée. On peut faire la même remarque pour les méthodes radiochimiques largement traitées dans le cas du niobium et du tantale, à peine cîtées dans celui du plomb.

Le premier chapitre de cet ouvrage a pour objet le béryllium; il comprend, entre autre, les procédés industriels d'obtention, la toxicologie, les produits industriels et leurs usages, les composés et leurs propriétés, l'échantillonnage, les méthodes de séparation, la détection par colorimétrie, par précipitation, par spectrographie et par radiochimie. Suivent les dosages classiques puis photométriques, fluorimétriques, spectrographiques et photochimiques. Enfin, une des originalités de cet ouvrage, le dernier chapitre est consacré aux méthodes recommandées par l'auteur et on peut lui faire confiance.

Le chapitre suivant, qui traite du plomb, est bien ordonné et renferme de nombreux tableaux; l'un d'eux résume de façon fort suggestive les méthodes de séparation de cet élément; un autre la stabilité thermique d'un certain nombre de composés.

On a confié à S. KALLMANN le chapitre concernant le niobium et le tantale, qui compte 229 pages. On y trouve une foule de renseignements, particulièrement en ce qui concerne les spectres d'absorption des complexes de cet élément, les méthodes d'extraction, d'échangeurs d'ions et les schémas de décroissance des isotopes de ces deux éléments. En résumé, un grand nombre de documents précieux, souvent inédits.

L'actinium, l'astatine, le francium, le polonium et le protoactinium sont traités dans un même chapitre. La partie radiochimique entre autre est remarquablement présentée. Des tables et des schémas donnent les propriétés nucléaires de ces éléments et de leurs isotopes: période, énergie des radiations émises, schémas de décroissance, spectres gamma, etc.

A la fin de chaque chapitre de cet ouvrage on trouve un choix important de références bibliographiques (arrêtées en 1961 ou 1962).

D. MONNIER (Genève)

Analysis of Essential Nuclear Reactor Materials, contributing editor CLEMENT J. RODDEN, Division of Technical Information, U.S. Atomic Energy Commission, 1964, xiii+1280 pp., Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402, price (paper cover) $4.25.

This book is a collection of papers encompassing the analyses of nuclear fuels, moderators, reactor construction materials and the impurities in them. It supersedes Dr. RODDEN's earlier book *Analytical Chemistry of the Manhattan Project*. Contents of the chapters are: (*1*) Uranium, (*2*) Plutonium, (*3*) Thorium, (*4*) Beryllium, (*5*) Alloys and Ceramics, (*6*) Expended Reactor Fuels, (*7*) Graphite, (*8*) Boron, (*9*) Heavy Water, (*10*) Reactor Coolants, (*11*) Trace Elements, (*12*) Spectrochemical Methods, (*13*) Mass Spectrometry, (*14*) Radiochemical and Nuclear Methods, (*15*) Electrometric Methods, (*16*) X-Ray Spectroscopy, and Index.

The above arrangement leads to some difficulty in locating the desired information as well as some duplication in information. However, familiarity with the arrangement and use of the index easily overcome any such difficulty which is greatly overshadowed by the wealth of information available. Each chapter is very well documented by references to recent literature, USAEC reports, books and even the sources of unpublished data. Anyone working with nuclear materials should find this book worth many times its small cost. Almost anyone dealing with inorganic analyses will find some information of value: either methodology or literature guide-posts.

As with any such comprehensive work, some details escape notice and obsolescence begins to grow on the day the first final draft is cast. Atomic absorption spectroscopy has escaped unnoticed and activation analysis drew only 4 pages. These and other faults are small compared to the amount of information available in this compact, concise, and inexpensive collection of analytical methods for nuclear reactor materials.

FRANK A. IDDINGS (Baton Rouge)

JÁNOS INCZÉDY, *Analytische Anwendungen von Ionenaustauschern*, Akadémiai Kiadó, Budapest, 1964, 365 pp., price $8.40.

Books on the analytical applications of ion-exchangers are few and far between, and an addition to their number is always welcome. This book seems to be fairly comprehensive and reasonably up-to-date (the translation was finished about a year after the latest references given). The most useful part is undoubtedly the 21-page table of inorganic applications, which gives a good start to a literature search. There is adequate coverage of theory and interesting sections on applications rather outside the domain of analysis. It is debatable whether the so-called liquid ion-exchangers should be treated in a work of this kind or in a book on solvent extraction methods. In view of the amount of useful information given, it is a pity that the original Hungarian was not translated into English, which would have considerably enlarged the potential market.

R. A. CHALMERS (Aberdeen)

ANNOUNCEMENTS

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY, DIVISION OF ANALYTICAL CHEMISTRY, COMMISSION ON MICROCHEMICAL TECHNIQUES

International Investigation Into Errors in Elementary Organic Microanalysis*

Approximately one year ago, a questionnaire (see *e.g.*, *Anal. Chim. Acta*, 30 (1964) 597) was sent to microanalysts throughout the world for the purpose of collecting data in regard to the errors encountered in elementary organic microanalysis. Although the response seemed favorable, only a small percentage of the microanalysts throughout the world actually co-operated. The following table shows the number of participants and the number of reports from each country:

United States	6 Authors	7 Reports	Japan	4 Authors	6 Reports
France	5 Authors	17 Reports	Netherlands	1 Author	7 Reports
United Kingdom	4 Authors	12 Reports	Switzerland	5 Authors	7 Reports
Italy	1 Author	1 Report	U.S.S.R.	20 Authors	34 Reports

If the Commission's report is to be of the greatest possible value, it is necessary to have information from those countries from which there was no response. It is also obvious that from certain countries the response was poor. Consequently, the Commission is making another appeal to all microanalysts. Each person should list the problems with which he has had difficulty, and if possible, he should describe the manner in which these problems were solved. However, as much information as possible should be included, since this might yield clues which are insignificant to the analysts but valuable to the Commission.

The deadline for this information will be January 1, 1966, and it should be sent to one of the following people:

Reports in ENGLISH to: Al Steyermark, Head Microchemical Department, Hoffmann-La Roche Inc., Nutley, New Jersey, U.S.A.

Reports in FRENCH to: Dr. Roger Lévy, Directeur Service Central de Microanalyse, Laboratoire Municipal, 39 bis, rue de Dantzig, Paris ,France.

Reports in GERMAN to: Dr. Wolfgang Schöniger, Microanalytical Laboratory, Department of Pharmaceutical Chemistry, Sandoz Limited, Basle 13, Switzerland.

Reports in RUSSIAN to: Dr. N. E. Gel'man, Institute of Elemental Organic Compounds, Academy of Sciences, Moscow, RUSSIA.

Reports in SLAVIC LANGUAGES and in HUNGARIAN to: Mr. Jiři Körbl, Analytical Laboratory, Research Institute for Pharmacy and Biochemistry, Czechoslovakian Academy of Science, Kourimska 17, Prague, Czechoslovakia.

Reports in LANGUAGES OTHER THAN THE ABOVE to: Dr. Roger Lévy (see above address).

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* The present investigation does not include trace analysis.

Anal. Chim. Acta, 33 (1965) 689

SIXTH INTERNATIONAL SYMPOSIUM ON GAS CHROMATOGRAPHY AND ASSOCIATED TECHNIQUES, ROME 1966

The Sixth International Symposium on gas chromatography organised by the Gas Chromatography Discussion Group of the Institute of Petroleum will be held at the Catholic University, Rome, from September 20–23rd, 1966 (inclusive). The Group invites the submission of papers for consideration for inclusion in the proceedings. Papers on the following groups of subjects will be considered:

(a) Principles, Techniques, or Novel Applications of Gas Chromatography.
(b) The use of gas chromatography together with other techniques for the solution of analytical problems.
(c) Novel principles and techniques in connection with liquid chromatography or other kinds of chromatography.
(d) Theoretical or experimental studies involving use of or comparison of more than one kind of chromatography.

Abstracts not more than 500 words long of proposed papers should be sent not later than January 1st, 1966, to the Editor: Dr. A. B. Littlewood, School of Chemistry, The University, Newcastle upon Tyne, 1, England.

Anal. Chim. Acta, 33 (1965) 689

ANALYTICA CHIMICA ACTA, VOL. 33 (1965)
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SUBJECT INDEX

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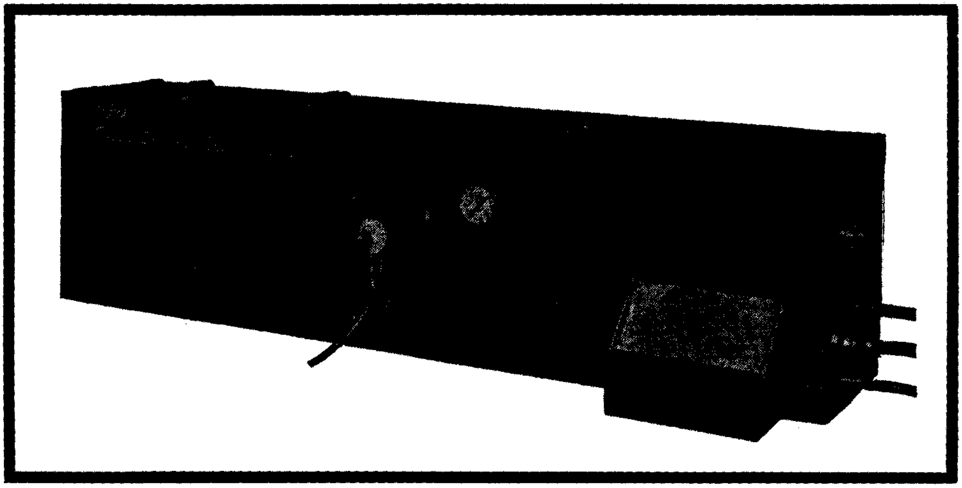

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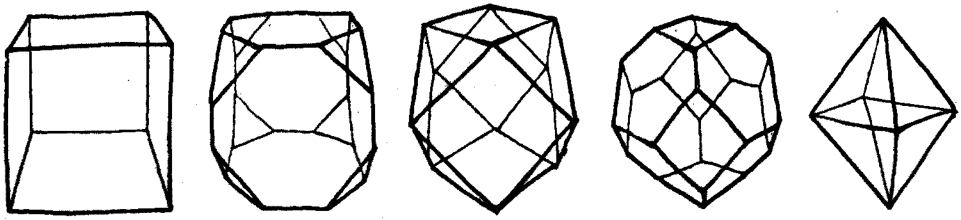

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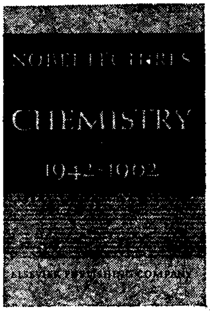
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