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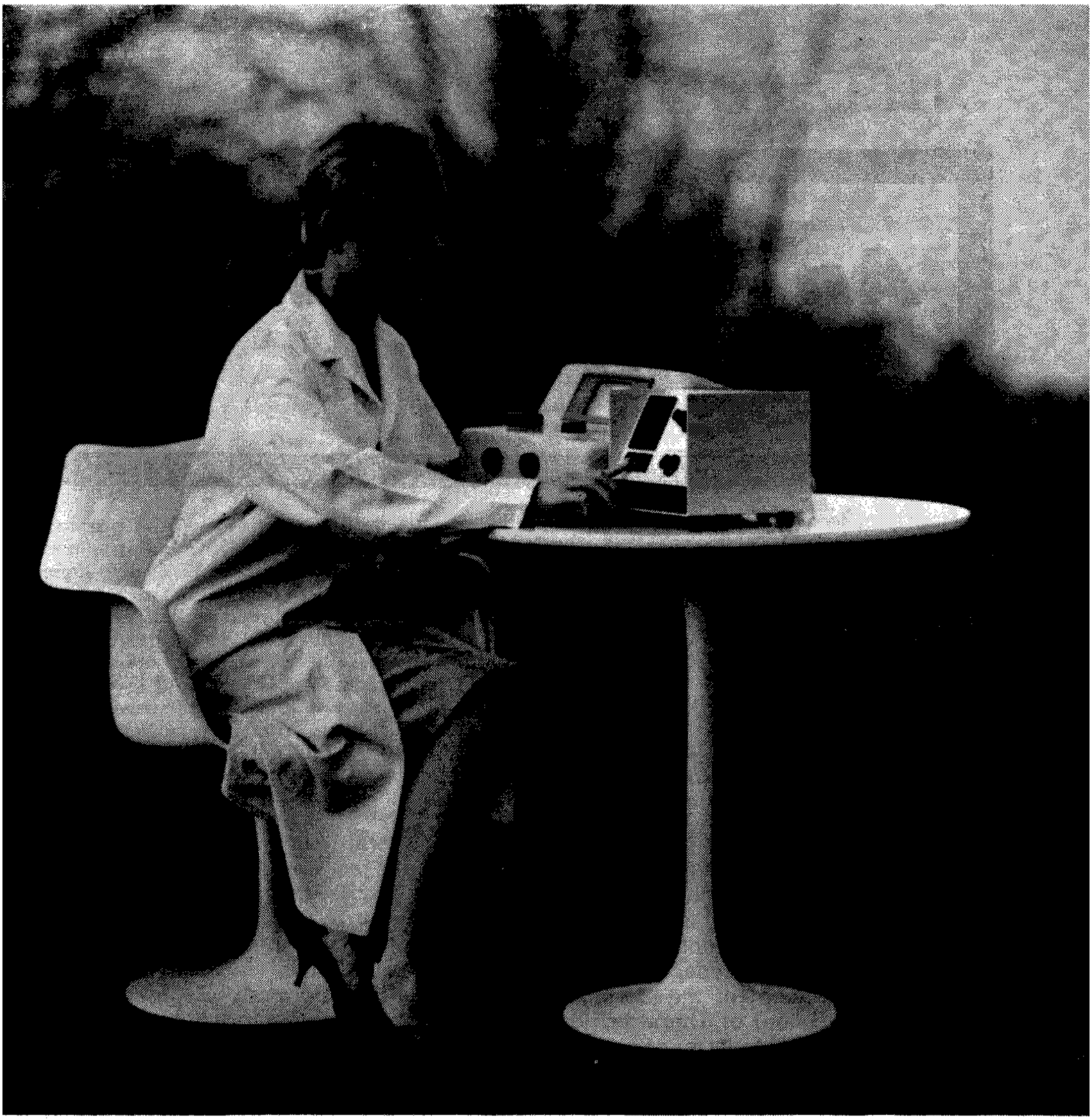

An Introduction to Fuel Cells

edited by **KEITH R. WILLIAMS**
Head of Surface Reactions Division, 'Shell' Research Ltd.,
Thornton Research Centre, Chester, England

6 x 9", xiv + 329 pages, 15 tables, 112 illus., 468 lit. refs., 1966, 90s., Dfl. 45.00 or U.S.$15.00

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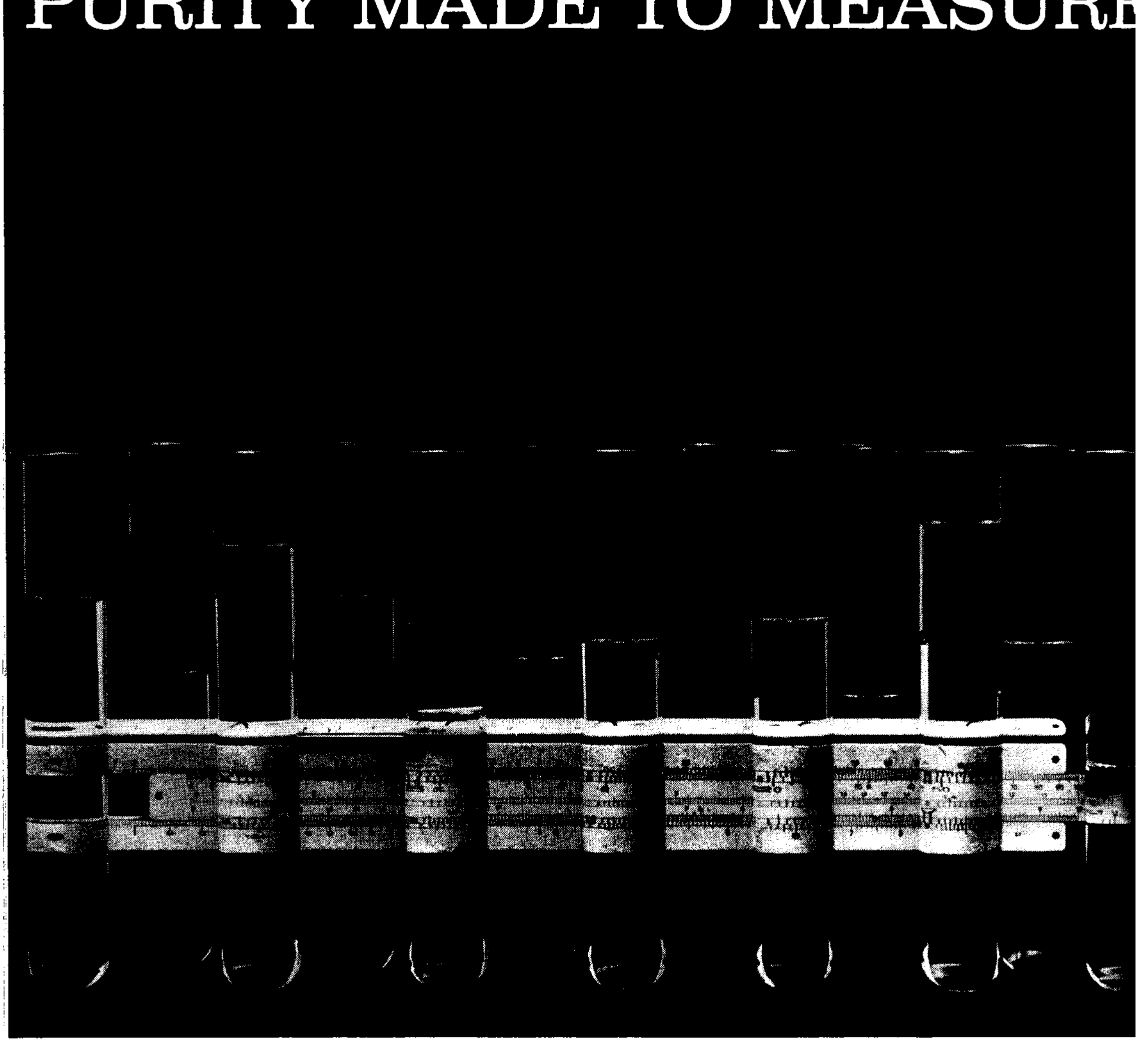

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 38, No. 3, July 1967

COLORIMETRIC DETERMINATION OF FURFURAL AND ITS PRECURSORS WITH AZULENE

APPLICATION TO AIR POLLUTION

Two procedures in which azulene is used as the reagent for the determination of furfurals and furfurals and their carbohydrate precursors are described. Aliphatic aldehydes, alcohols, and 2-deoxy sugars and their derivatives gave weak to negative reactions. The methods have been applied to the estimation of furfurals and furfural-precursor carbohydrates in effluent from a coffee-roasting industrial plant.

E. SAWICKI AND C. R. ENGEL,
Anal. Chim. Acta, 38 (1967) 315–320

DETERMINATION OF COPPER IN SALINE WATERS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY COMBINED WITH APDC–MIBK EXTRACTION

A technique has been developed for the determination of copper in saline waters by extraction of its complex with ammonium pyrollidine dithiocarbamate into methyl isobutyl ketone and subsequent analysis by atomic absorption spectrophotometry. The method is self-compensating for any incomplete extraction of copper. With a 15:510 solvent–aqueous phase ratio, a sensitivity of 0.2 p.p.b. and a precision of ±10% were achieved. The method was used to determine copper in a number of sea water and other saline water samples.

R. R. BROOKS, B. J. PRESLEY AND I. R. KAPLAN,
Anal. Chim. Acta, 38 (1967) 321–326

NEUTRON ACTIVATION ANALYSIS BY STANDARD ADDITION AND SOLVENT EXTRACTION

DETERMINATION OF TRACES OF THORIUM IN ALUMINIUM BY EXTRACTION OF PROTACTINIUM-233

A rapid and selective radiochemical separation for protactinium-233 is suggested. The method is based on extraction of protactinium with 0.3 *M* tridodecylamine from 4.5 *M* HCl–1.5 *M* $AlCl_3$ solution, stripping with 1.35 *M* HCl followed by another extraction with 0.5 *M* 2-thenoyltrifluoroacetone. The separation, coupled with the application of the standard addition technique, is applied to the determination of traces of thorium in aluminium by neutron activation.

A. ALIAN AND W. SANAD,
Anal. Chim. Acta, 38 (1967) 327–332

DETERMINATION OF TRACE ELEMENTS IN STANDARD REFERENCE MATERIALS BY NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis with its high sensitivity and accuracy in trace analysis, is being used at the NBS for analysis of Standard Reference Materials. Four problems affecting precision and accuracy are discussed. First, the positive bias introduced by induced radioactivity of similar γ-ray energy was found in the determination of interstitial argon in ultra-pure silicon; a decay-curve resolution technique was used to compensate for the error. Secondly, errors due to differences in geometrical location between sample and standard during irradiation were observed; flux gradients were determined by copper foil flux monitoring to give necessary means of correction. Thirdly, errors are caused by differences in neutron self-shielding between sample and standard during irradiation; an empirical correction method was used and a computer program written for calculation. Finally, the problem of γ-ray attenuation during counting of sample and standard has been explored; a theoretical and experimental study gives the necessary corrections.

G. W. Smith, D. A. Becker, G. J. Lutz, L. A. Currie and J. R. DeVoe,
Anal. Chim. Acta, 38 (1967) 333–340

NEUTRON ACTIVATION ANALYSIS FOR SODIUM TRACES IN MAGNESIUM

When sodium traces are determined in magnesium matrices by neutron activation analysis, the reaction ^{24}Mg(n,p)^{24}Na interferes by simulating spurious sodium concentrations (about 400–500 p.p.m. for usual irradiation positions in the RS 1 water-pool reactor). A preliminary separation of the sodium traces from the bulk of the matrix by electrodeposition on a mercury cathode and recovery in water by amalgam decomposition, prevented the fast-neutron effects. Electrolysis for 4 h gave almost quantitative recovery of sodium $(93\pm5\%)$ and satisfactory decontamination factors for magnesium $(1.5$ to $5\cdot10^3)$. The method is limited by the blank correction (14 μg Na with a glass electrolysis cell). Some results for magnesium samples with both destructive and non-destructive techniques are reported.

R. Malvano,
Anal. Chim. Acta, 38 (1967) 341–347

A SPECTRUM STRIPPING METHOD FOR THE COMPUTER-COUPLED ACTIVATION ANALYSIS OF UNKNOWN SAMPLES BY γ-RAY SPECTROMETRY

A spectrum stripping method for the computer-coupled activation analysis of unknown samples using γ-ray spectrometry is discussed. Before the unscrambling of the γ-ray is performed using standard spectra of the components, each spectrum is smoothed, statistically weighted and corrected for background. The photopeaks of the standard spectra are then aligned with the respective peaks of the sample spectrum, one at a time after correcting for gain drift if necessary, and the undesired components are stripped out. After successive subtraction, the characteristic spectrum of the desired element is compared with that of the standard to determine its weight. The results obtained using the present method are as good as those obtained from least-squares analysis in ideal cases, but appear to be better when assumptions inherent in the least-squares method are no longer valid.

M. P. Menon and D. W. Berry,
Anal. Chim. Acta, 38 (1967) 349–356

THE OSCILLOMETRIC TITRATION OF ALKALI METALS BY PRECIPITATION IN NON-AQUEOUS SOLUTION

(in German)

Various alkali metal salts are insoluble in ketones, acetonitrile, ethanol, etc., depending on the nature of the anion present; this can be utilized for the determination of some alkali metals by precipitation titration with oscillometric end-point detection. Sodium or potassium iodide in ketonic or acetonitrile media can be titrated with lithium chloride in ethanolic or ketonic solutions. The average error is 0.6%. Calcium does not interfere but barium does.

G. HENRION AND E. PUNGOR,
Anal. Chim. Acta, 38 (1967) 357–362

HIGH-PRECISION ANALYSIS OF NUCLEAR MATERIALS BY CONSTANT-CURRENT COULOMETRY

PART II. DETERMINATION OF THORIUM

A constant-current coulometric method is described for the precise determination of thorium by titration with EDTA, electrogenerated from its mercury complex in acetate-buffered solution at pH 4.5. With polarised mercury electrodes for end-point detection, relative standard deviations of 0.02 and 0.3% for 30 mg and 30 μg respectively were obtained; the method was applied to the analysis of zone-refined thorium of high purity.

G. C. GOODE AND W. T. JONES,
Anal. Chim. Acta, 38 (1967) 363–368

DIFFERENTIAL CONTROLLED-POTENTIAL COULOMETRY: APPLICATION TO THE DETERMINATION OF URANIUM

Differential controlled-potential coulometry has been investigated as a high-precision analytical technique using the reduction of uranium(VI) in 0.5 *M* sulphuric acid at a mercury cathode. A relative standard deviation of 0.009% was obtained with 30–120 mg samples of uranium and the method was applied to the comparison of uranium standards.

G. C. GOODE AND J. HERRINGTON,
Anal. Chim. Acta, 38 (1967) 369–375

COUNTERCURRENT EXTRACTION SEPARATION OF SOME PLATINUM GROUP METALS: PART III

The bromo complexes of platinum(IV), palladium(II), rhodium(III), and iridium(IV) were prepared and studies were made on their distribution between hydrobromic acid solutions and various common solvents. The solvents employed were *n*-tributyl phosphate (TBP), methyl isobutyl ketone, amyl acetate, and various TBP–benzene mixtures. Distribution coefficients as a function of HBr concentration are given for each metal for each solvent system. A careful study of the measured distribution coefficients clearly showed that a number of binary and ternary mixtures of the metals can be resolved with a Craig countercurrent distribution apparatus. Rh–Pt and Rh–Pd mixtures in 4.38 *M* HBr solutions were quantitatively separated on a 10-stage Craig apparatus using a 90% TBP–10% benzene solvent. Rh–Ir mixtures in 4.38 *M* HBr were resolved by 3 consecutive batch extractions with 90% TBP–10% benzene. Mixtures of Pd, Rh, and Ir in 4.38 *M* HBr were resolved in 90 stages using methyl isobutyl ketone as the solvent. Pd, Rh and Ir were recovered in 97.0, 87.6 and 94.5% yields, respectively. Mixtures of Pd, Rh and Pt in 4.38 *M* HBr were resolved in 90 stages using amyl acetate and methyl isobutyl ketone as solvents. Pd, Rh and Pt were recovered in 96.0, 96.0 and 94.0% yields, respectively. Two computer programs for the IBM 1620 Computer are given; these facilitate the comparison of theoretical and actual solute distributions.

E. W. BERG AND J. R. SANDERS,
Anal. Chim. Acta, 38 (1967) 377–384

DETERMINATION OF OXYGEN AND HYDROGEN IN TUNGSTEN AND OTHER METALS BY A VACUUM-FUSION GAS-CHROMATOGRAPHIC METHOD

A gas-chromatographic method has been developed for the analysis of gas evolved from tungsten and tungsten-base alloys in the vacuum-fusion process. The method is suitable for determining 5–3,000 p.p.m. of oxygen and 0.2–300 p.p.m. of hydrogen, and can be applied to other metals. Above 50 p.p.m. of oxygen and 3 p.p.m. of hydrogen, the values found compare favourably with those obtained by alternative methods; below these levels, no reliable alternative procedures are readily available. In the proposed method, the sample is submitted to vacuum fusion in a molten platinum bath in a graphite crucible, and an aliquot of the evolved gas is transferred by means of a specially modified Drallim valve, to a stream of high-purity helium. The components are separated on a column of molecular-sieve 5A at 100° and detected with a radioactive-type ionization detector. Calibration and operation of the system are described in detail, and the effects of variables are discussed. Evidence was obtained that hydrogen recoveries by the conventional vacuum-fusion method are sometimes slightly low, because of methane formation. An important advantage of the method is that the evolved gases are positively identified by their retention volumes.

D. F. Wood and G. Wolfenden,
Anal. Chim. Acta, 38 (1967) 385–402

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF SILICON BY AN EXTRACTION METHOD

A general method is presented for the spectrophotometric determination of silicon at trace levels. It involves the extraction of the yellow silicomolybdate with isoamyl alcohol and subsequent reduction to silicomolybdate blue. The method covers the range 0.2–15 μg of silicon. A comprehensive study of interferences using standard additions of 5 and 10 μg of silicon was carried out and many modifications are incorporated to permit the determination of silicon in a wide variety of metals and salts.

P. Pakalns and W. W. Flynn,
Anal. Chim. Acta, 38 (1966) 403–414

PRELIMINARY STUDIES OF PRECIPITATION TITRATIONS OF ORGANIC COMPOUNDS USING POLAROVOLTRIC END-POINT INDICATION

PART III. TITRATION OF NITROGEN BASES WITH IODINE

Precipitation titrations of a number of organic bases have been carried out in acid solution with iodine. The influence of several factors, principally the pH value, on the stoichiometry of the reaction has been examined.

M. R. F. Ashworth and U. Hartmann,
Anal. Chim. Acta, 38 (1967) 415–420

REACTION OF TELLURIUM(IV) WITH DITHIZONE

With an excess of dithizone over tellurium, the extraction of Te(IV) from 1 *M* perchloric acid solutions into a carbon tetrachloride solution (o) of dithizone follows the relation

$$\frac{[\mathrm{Te(HDz)_2}]_o}{[\mathrm{TeO(OH)^+}]} = 1.5 \cdot 10^5\ [\mathrm{H_2Dz}]_o^2[\mathrm{TeO(OH)^+}]^{-\frac{1}{2}}\,.$$

When the acidity is varied, again with a sufficiently large excess of dithizone, the following relation seems to be approached:

$$\frac{[\mathrm{Te(HDz)_2}]_o}{[\mathrm{TeO(OH)^+}]} = 1.5 \cdot 10^5\ [\mathrm{H_2Dz}]_o^2[\mathrm{TeO(OH)^+}]^{-\frac{1}{2}}[\mathrm{H^+}]^{-\frac{1}{2}}\ (\mu = 1.0).$$

K. MARHENKE AND E. B. SANDELL,
Anal. Chim. Acta, 38 (1967) 421–434

SUBMICRO METHODS FOR THE ANALYSIS OF ORGANIC COMPOUNDS

THE DETERMINATION OF HYDROXYL GROUPS

Various procedures were examined for the determination of organic hydroxyl groups. Conventional acetylation methods could not be used on the submicro scale, but the spectrophotometric method based on esterification with 3,5-dinitrobenzoyl chloride followed by extraction of the ester and colour development with alkaline acetone proved reasonably satisfactory for aliphatic alcohols. Acidic hydroxyl groups, *e.g.* in phenolic compounds, were titrated accurately with 0.01 *M* tetrabutylammonium hydroxide in benzene–methanol solution in a pyridine medium; visual end-points or potentiometric end-points with glass–silver or glass–in-stream platinum electrode pairs were used depending on the strength of the acidic group. Some differentiating titrations were possible. A general submicro bromination method for phenols was not feasible.

R. BELCHER, G. DRYHURST AND A. M. G. MACDONALD,
Anal. Chim. Acta, 38 (1967) 435–445

TRACE ELEMENTS IN MARINE WATERS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Trace elements of interest in sea water fall into two well-defined categories. Strontium, lithium, and rubidium are ideally suited to determination by atomic absorption spectrophotometry since minimal sample preparation is required and standard equipment may by utilized; standardization of techniques by which large batches of samples may be rapidly and accurately processed, is important. The transition elements are present in significantly lower concentrations and in complex, and largely unknown, chemical forms; pre-concentration is vital. Solvent extraction can also provide a crude differentiation between total and extractable fractions.

D. C. BURRELL,
Anal. Chim. Acta, 38 (1967) 447–455

A RAPID COLORIMETRIC METHOD FOR THE DETERMINATION OF THORIUM IN HUMAN URINE

(Short Communication)

E. BAZZANO AND G. GHERSINI,
Anal. Chim. Acta, 38 (1967) 457–460

INDIRECT DETERMINATION OF CAESIUM BY COMPLEXIMETRIC TITRATION OF CALCIUM AFTER EXTRACTION WITH CALCIUM DIPICRYLAMINATE IN NITROBENZENE

(Short Communication)

M. KYRŠ AND P. SELUCKÝ,
Anal. Chim. Acta, 38 (1967) 460–463

ON THE USE OF THE SODIUM ELECTRODE

(Short Communication)

P. C. TOWNSING, A. M. POSNER AND J. P. QUIRK,
Anal. Chim. Acta, 38 (1967) 464–467

INTERNAL ELECTROLYSIS FOR THE SEPARATION OF IONS PART III. SEPARATION AND DETERMINATION OF SELENIUM AND TELLURIUM

(Short Communication)

A. K. MAJUMDAR AND SM. GOURI BHOWAL,
Anal. Chim. Acta, 38 (1967) 468–469

A STUDY OF GALLIUM AND GERMANIUM DITHIZONATES

(Short Communication, in German)

G. IWANTSCHEFF AND C. JÖRRENS,
Anal. Chim. Acta, 38 (1967) 470–473

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COLORIMETRIC DETERMINATION OF FURFURAL AND ITS PRECURSORS WITH AZULENE

APPLICATION TO AIR POLLUTION

E. SAWICKI AND C. R. ENGEL

Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Robert A. Taft Sanitary Engineering Center, Public Health Service, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio 45226 (U.S.A.)

(Received October 11th, 1966)

Three major health problems that appear to be induced or aggravated by airborne material are allergy, asthma, and virus epidemics. Asthmatic attacks in the New Orleans[1] and Tokyo–Yokohama[2] areas are believed to be caused or aggravated by some types of air pollutants. An association between acute allergic asthma and exposure to grains or grain products[3] or to the dust of dried vegetation[4] has been known for many years. The difficulty with research projects in this field is that very little is known about the chemical structure of allergens, especially atmospheric allergens. Preliminary evidence has been obtained that some of the allergens are glycopeptide or polyhydroxy organic compounds[5].

Compounds containing polyhydroxy organic compounds may also be of some importance in flu epidemics. As with allergy–asthma studies, research on this subject entails much controversy and conjecture. The flu epidemics are believed to be caused by viruses and virus-like materials. Since these materials contain nucleic acids, of which ribose or deoxyribose are essential backbone components, research on the composition of the atmosphere in terms of the polyhydroxy organic compounds would appear to have some merit in this case also.

In this Laboratory, an investigation of the composition of polluted airs in terms of polyhydroxy organic compounds has been initiated by studying various colorimetric methods for determining ribose and other sugars that can form furfural derivatives in acid solution.

EXPERIMENTAL

Reagents

Azulene was obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin. It was purified by chromatography on the alumina column with pentane as the developer and eluant. The carbohydrates were obtained from Calbiochem and Sigma.

Apparatus

A Cary Model 11 Quartz Recording Spectrophotometer with 1-cm cells was used for all absorption spectral work.

Procedure 1: for furfural and its derivatives

To 2 ml of aqueous test solution containing 0.2–5 μg of furfural or derivative was added, with mixing, 3 ml of reagent (0.1% azulene in glacial acetic acid) followed by 3 ml of concentrated sulfuric acid. The solutions were mixed, allowed to stand for 5 min, and then cooled under the tap. The absorbance was read against a blank at the wavelength maximum, 492 nm for furfural. The color was stable for 24 h. In the analysis for furfurals in a mixture the baseline method of procedure 2 was used.

Procedure 2: for ribose and other furfural precursors

To 2 ml of aqueous test solution was added 3 ml of reagent (0.05% azulene in concentrated sulfuric acid). The solutions were mixed, allowed to stand for 5 min, and cooled under the tap. The spectrum from 400–600 nm was obtained for this mixture run against the blank. The baseline method with wavelengths 413, 488, and 550 nm was used to determine the sugars.

DISCUSSION

Principles of the methods

Furfural derivatives reacted readily with azulene in sulfuric acid solution. Sugars, such as ribose, fructose, and dextrose, which in hot acid solution are dehydrated to furfural and its 5-methyl and 5-hydroxymethyl derivatives, respectively, react also with azulene in acid solution. Sugars that were expected to form furfural on dehydration, *e.g.* ribose, gave the same spectrum as was obtained with furfural; sugars expected to form 5-methylfurfural, *e.g.* rhamnose and fucose, gave the same spectrum as that obtained with 5-methylfurfural (Table II). The equation for the determination of ribose is shown in Fig. 1. The postulated chromogen fits in with the wavelength shift obtained with vinyl-containing test substances. Thus, benzaldehyde and cinnamaldehyde gave long-wavelength bands at 437 and 507 nm, respectively, whereas furfural and 3-α-furilacrolein gave bands at 492 and 560 nm.

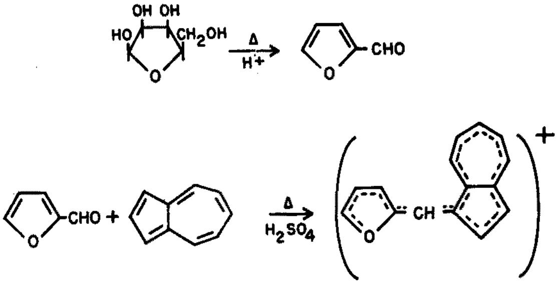

Fig. 1. Reaction of ribose.

Variables

The variables in procedure 1 were investigated with furfural as the test substance. The amount of azulene in the reagent could be varied from 0.02 to 1% with no loss in sensitivity. A concentration of 0.1% gave a low blank and optimum sensitivity in the procedure. The volume of sulfuric acid was not critical in that

2, 3, or 4 ml could be used. With the recommended method the color was stable for 24 h. Twelve determinations of furfural gave a percent deviation of ±1.02. Beer's law was obeyed from 0.17 ($A = 0.1$) to 4.8 µg. Sugars and aliphatic aldehydes reacted weakly (Table I).

The variables in procedure 2 were investigated with ribose as the test substance. The amount of azulene in the reagent could be varied from 0.01 to 0.4% with little loss in intensity; an intermediate concentration of 0.2% was selected. The heat of mixing was a vital part of the reaction. The heated acid dehydrated the sugars to the appropriate furfural, which then condensed with the azulene. The azulene must be purified, otherwise a pink chromogen is formed from the impurities in the hot acid solution. Because the color intensity of the blank can vary it is necessary, after obtaining the spectrum of the final solution *versus* the blank, to use a baseline method of analysis to subtract the contribution of the impurities in the azulene from the absorbance of the chromogen. Without the baseline method of analysis a 15% deviation was obtained for 10 analyses. With the baseline method the deviation was reduced to 6.0%. The blank obtained with purified azulene gave a triplet at 480, 512, and 543 nm with an absorbance of 0.28 at all 3 wavelengths. The color obtained in the analytical procedure was stable for 12 h. Beer's law was obeyed from about 0.7 to 12 µg of ribose.

TABLE I

DETERMINATION OF FURFURALS BY PROCEDURE 1[a]

Compound	*λ max (nm)*	$\varepsilon \cdot 10^{-3}$	*Relative intensity at 492 nm*
Furfural	492	42	100
5-Hydroxymethylfurfural	500	42	100
5-Methylfurfural	535	64	75
3-α-Furilacrolein	560 br[b]	46	46
1,1,3,3-Tetramethoxypropane	472	12	19
1,3,3-Trimethoxy-1-propane	472	11	17
Rhamnose	533	5	7
Ribose	500	2	4
Galactose	500	0.4	1

[a] Formaldehyde, pyruvaldehyde, crotonaldehyde, and acrolein give molar absorptivities less than 2000 in the 450 to 800 nm region.
[b] br = broad band composed of two component bands.

Comparison of methods

Procedure 1 was used for the determination of furfural and its derivatives. The wavelength maximum shifted to the red in the order furfural < 5-hydroxymethylfurfural < 5-methylfurfural. Malonaldehyde precursors also reacted, but they gave a weaker band at 472 nm (Table I). Sugars and aliphatic aldehydes gave weak reactions. 5-Methylfurfural could be readily differentiated from the other furfurals by the one sharp band it gives at 535 nm.

Various colorimetric methods for the determination of furfural are compared in Table II[6–10]. The azulene method was the most sensitive.

TABLE II

COMPARISON OF COLORIMETRIC METHODS FOR DETERMINATION OF FURFURAL

Reagent	*Ref.*[a]	*λ max (nm)*	*ε·10⁻³*	*Detm. limit (μg)*	*Molar sens.*[b]	*Anal. time (min)*
Azulene		492	42	1.7	11.5	15
Pyrogallol	6	496	30	1.6	6.0	29
Anthrone	7	610	14	7.6	1.3	44
Orcinol	8	598	10	4.8	2.0	34
Orcinol	9	668	3.3	11.5	1.65	42
Phloroglucinol[c]		622	2.7	14.	1.4	4
Phloroglucinol	10	526	2.3	230.	0.2	15

[a] References refer to the procedure used to obtain reported results.

[b] Equivalent to millimolar absorptivity divided by the dilution factor, where the dilution factor equals final volume divided by test solution volume.

[c] Procedure was: 2 ml of test solution and 2 ml of saturated solution of phloroglucinol in concentrated hydrochloric acid and read.

TABLE III

DETERMINATION OF ALDOSES, KETOSES, AND RELATED COMPOUNDS BY PROCEDURE 2

Compound[a]	*λ max (nm)*	*Relative molar intensity at λ max*	*Compound*[a]	*λ max (nm)*	*Relative molar intensity at λ max*
5-Methylfurfural	535	100[b]	D-Arabinose	490	40
Furfural	489	60		504	40
	506	60	Adenosine	489	40
Rhamnose	535	60		506	40
			Guanosine	489	30
				506	40
L-Xylose	492	60	Maltose	492	30
	504	60		504i	30
L-Fucose	535	50	β-D-Fructose	495	30
				538s	20
Melezitose	492	50	β-Dextrose pentaacetate	483	20
	514s	49		507i	20
3-α-Furilacrolein	549	50	Galactose	492	20
	575s	50		506i	20
Cinnamaldehyde	507	50	Dextrose	487	20
				514i	20
D-Ribose	490	50	Glucuronic acid lactone	485	8
	506	50			
Sucrose	490	44	D-Glucuronic acid	487	8
	506s	43			
Trehalose	487	40	L-Ascorbic acid	506	6
	514s	37			
Raffinose	493	40	2-Deoxy-D-glucose	500	5
	514s	40	2-Deoxy-D-ribose	480	5

[a] The following compounds gave relative intensities of about 2 in the 450–550 nm region: deoxyadenosine, deoxycytidine, deoxycytidylic acid, deoxyguanosine, deoxyguanosine-5′-monophosphate, thymidine, and thymidylic acid. The following compounds gave essentially negative results, relative intensities less than 0.8 in the visible region: acetone, N-acetylglucosamine, 2-aminopyrimidine, deoxyribosenucleic acid, dulcitol, ethanol, gluconolactone, D-glucosamine, and glycerol. s = shoulder; i = inflection.

[b] $\varepsilon = 63{,}000$.

The reaction of sugars and other compounds with azulene was investigated by procedure 2 (Table III). 5-Methylfurfural and its sugar precursors gave the most sensitive reactions. A variety of mono- and polysaccharides were tested. Most of these compounds are precursors of furfural, 5-hydroxymethylfurfural, and 5-methylfurfural. Other sugars such as 2-deoxy-D-glucose and 2-deoxy-D-ribose gave weak reactions. The deoxynucleosides, the deoxynucleotides, and deoxyribosenucleic acid gave essentially negative results as did alcohol, glycerol, acetone, and a variety of other compounds. It is believed that with the help of procedures 1 and 2, furfurals and their carbohydrate precursors could be estimated in complex mixtures.

Application

Because of the interest in the relation of air pollution to asthmatic incidents in New Orleans a preliminary investigation was begun on one of the major New Orleans industrial effluents—airborne byproducts of coffee roasting. An effluent was obtained from an industrial coffee-roasting operation in New Orleans. This particulate material contained a large amount of caffeine. Caffeine gave negative results in both procedures. To determine whether furfurals and their carbohydrate precursors were present, the material was extracted with boiling water. This solution was then analyzed by the two procedures. Since the test solution was dark yellow-brown, a blank containing the test solution and other solutions (minus azulene) was used. In both cases the baseline method of analysis was necessary. Absorbance readings were obtained at wavelength 488 nm from a baseline drawn from the points at which the spectra intersect at wavelengths 413 and 550 nm. In this way it was estimated that 1 g of the effluent particulates contained *ca.* 11 mg of furfural precursors in terms of ribose and *ca.* 2.1 mg of furfurals in terms of furfural. These results indicated that this type of sample should be amenable to chromatographic analysis for sugars and furfurals.

SUMMARY

Two procedures in which azulene is used as the reagent for the determination of furfurals and furfurals and their carbohydrate precursors are described. Aliphatic aldehydes, alcohols, and 2-deoxy sugars and their derivatives gave weak to negative reactions. The methods have been applied to the estimation of furfurals and furfural-precursor carbohydrates in effluent from a coffee-roasting industrial plant.

RÉSUMÉ

On décrit deux procédés de dosage colorimétrique de furfurals au moyen d'azulène. Les aldéhydes aliphatiques, les alcools, les sucres 2-deoxy et leurs dérivés ne donnent qu'une faible ou pas de réaction. Ces méthodes sont appliquées à l'analyse d'effluents dans une installation industrielle de torréfaction de café.

ZUSAMMENFASSUNG

Es werden zwei Verfahren beschrieben, bei denen Azulen als kolorimetrisches Reagenz für die Bestimmung von Furfurolen und ihrer Abkömmlinge verwendet

wird. Aliphatische Aldehyde, Alkohole und 2-Deoxy-Zucker und ihre Derivate gaben schwache bis negative Reaktionen. Die Methoden wurden zur Abschätzung von Furfurolen in den Abgasen von Kaffeeröstereien angewendet.

REFERENCES

1 H. WEILL, M. M. ZISKIND, R. C. DICKERSON AND V. J. DERBES, *J. Air Pollution Control Assoc.*, 15 (1965) 467.
2 R. B. W. SMITH, E. J. KOLB, H. W. PHELPS, H. A. WEISS AND A. B. HOLLINDEN, *Arch. Environ. Health*, 8 (1964) 805.
3 D. W. COWAN, H. J. THOMPSON, H. J. PAULUS AND P. W. MIELKE, JR., *J. Air Pollution Control Assoc.*, 13 (1963) 546.
4 D. E. VAN WORMER, *Arch. Environ. Health*, 10 (1965) 71.
5 J. H. MORRIS, L. BERRENS AND E. YOUNG, *Clin. Chim. Acta*, 12 (1965) 407.
6 M. TOMADA, *Chem. Pharm. Bull. (Tokyo)*, 11 (1963) 806.
7 R. SAWAMURA AND T. KOYAMA, *Yakugaku Zasshi*, 81 (1961) 1689.
8 M. TOMADA, *Chem. Pharm. Bull. (Tokyo)*, 11 (1963) 809.
9 R. L. THOMAS AND D. L. LYNCH, *Soil Sci.*, 91 (1961) 312.
10 L. BOLOGNANI, G. COPPI AND V. ZAMBOTTI, *Experientia*, 17 (1961) 67.

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DETERMINATION OF COPPER IN SALINE WATERS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY COMBINED WITH APDC–MIBK EXTRACTION*

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RILEY[1] has summarized the available data for the determination of copper in sea water and has concluded that much of the early classical work is unreliable because of faulty analytical techniques and contamination. At present, atomic absorption spectrophotometry and neutron activation analysis would appear to offer the best promise for the determination of trace elements in sea water. Although many of these elements exist in sea water at concentrations below their detection limits by atomic absorption techniques, they can often readily be concentrated by extraction into a suitable solvent with an increase in sensitivity which is due not only to a favorable aqueous phase/solvent ratio but also to the existence of the "solvent effect"[2] which results in enhanced sensitivity. Clearly, a combination of solvent extraction and atomic absorption spectrophotometry should be useful for the determination of trace elements in saline waters particularly as it is often possible to insure that the alkali metals and alkaline earths are not simultaneously extracted. Direct aspiration of sea water usually results in difficulties associated with clogging of the burner and scattering effects because of the high solid content.

It is well known that ammonium pyrollidine dithiocarbamate (APDC) is a useful chelating agent for a number of transition metals and furthermore will extract over a very wide pH range[3,4]. Recently, SPRAGUE AND SLAVIN[5] have shown that it may be used with methyl isobutyl ketone (MIBK) to separate trace elements from 25% potassium chloride solutions and have suggested its use for sea water. MAGEE AND RAHAMAN[6] have used the system APDC–ethyl acetate to determine copper in sea water. Ethyl acetate is, however, not a good solvent to use because of its appreciable solubility (9%) in water and because it shows a relatively poor solvent effect[2]. MULFORD[7] has recently reviewed solvent extraction systems for use with atomic absorption spectrophotometry and has pointed out the advantages of the APDC–MIBK system.

The following work was carried out in order to investigate further the potentialities of the APDC–MIBK system and to apply it to the analysis of copper and other elements in sea water, interstitial waters of ocean sediments and other saline waters.

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EXPERIMENTAL

Apparatus

Atomic absorption measurements were carried out on a Perkin Elmer 303 Atomic Absorption Spectrophotometer equipped with a conventional burner for use with air–acetylene. The output of the instrument was connected to a Sargent Model MR Recorder via a Perkin Elmer Recorder Readout Accessory.

Reagents

Redistilled commercial-grade methyl isobutyl ketone, ammonium pyrollidine dithiocarbamate supplied by Eastman Organic Chemicals and reagent-grade hydrochloric acid. The latter two reagents were sufficiently free of copper to render purification unnecessary. A standard copper solution containing 200 p.p.m. in distilled water was used and was diluted as required to give a solution containing 0.4 p.p.m. This latter solution was used immediately after preparation.

The distribution coefficient of copper between sea water and MIBK

When large sea water/solvent ratios are used, the percentage extraction of the copper will decrease as this ratio increases since the relationship between the distribution coefficient (D), the percentage extraction (E) and the volume of the organic phase (V_o) and aqueous phase (V_a) is given by the expression:

$$E = \frac{100D}{D + V_a/V_o}$$

Neglect of this relationship can often lead to significant errors in this type of work and the technique which has been developed, is designed to correct for incomplete extraction whatever its magnitude. The distribution coefficient for copper was determined by successive extraction of an aqueous solution containing 5 p.p.m. of copper at a pH of 3.0. Provided that extraction is reasonably complete, the ratio of the amounts in the two extracts is an approximate measure of D. A value of 620 was obtained for the distribution coefficient which corresponds to 95.0% extraction for a 15:500 solvent/water ratio.

The stability of the copper complex

The stability of the copper complex was tested by making an extract of the APDC complex into MIBK. This extract was divided into 3 portions, one of which was kept at room temperature and its absorbance measured at regular intervals. Another fraction was kept frozen in liquid nitrogen and thawed temporarily for absorbance measurements. The third portion was frozen in liquid nitrogen and warmed slightly until only the solvent had melted. A small amount of water remained in the vessel as ice and the solvent was removed by decantation. The absorbance of each sample was compared with that of a stable copper solution prepared from a mixture of hydrochloric acid, MIBK and acetic acid.

In all cases there was no appreciable lessening of the absorbance of the copper complex over a period of 8 h. This was in marked contrast to the stability of complexes of other elements which were examined simultaneously. For example, the stability of the manganese complex was greater in the frozen and dehydrated samples than in the "wet" portion maintained at room temperature.

The rate of uptake of copper

Samples of sea water containing added copper were extracted for varying periods and it was determined that a period of 10 min was necessary to insure that the copper extraction had reached its maximum.

The determination of copper in sea water and natural waters

The following technique was developed to compensate for any incomplete extraction of copper with high sea water/solvent ratios. The technique also allowed for simultaneous determination of both "soluble" and particulate copper.

Samples (500 ml) of freshly collected sea water which had been stored in polythene bottles, were filtered through a 0.45-μ membrane filter. The filtrate contained the "soluble" copper. The millipore filters were dissolved in 1 ml of concentrated hydrochloric acid and 25 ml of MIBK. On gentle warming, complete dissolution was achieved and no further treatment was required. A blank was carried out simultaneously.

The pH of the filtrate was adjusted to 3.0 by addition of 2 *N* hydrochloric acid and the samples were placed in 1-l Erlenmeyer flasks. MIBK (25 ml) was then added to each flask followed by 5 ml of an aqueous 1% solution of APDC. At equilibrium, 10 ml of solvent entered the aqueous phase owing to its solubility. This resulted in a 15:510 phase ratio. The samples were then shaken for 10 min on an automatic shaker and the phases were separated via a separatory funnel. Clean separations were easily achieved and since concentrations only were involved, there was no need for a quantitative recovery of the solvent.

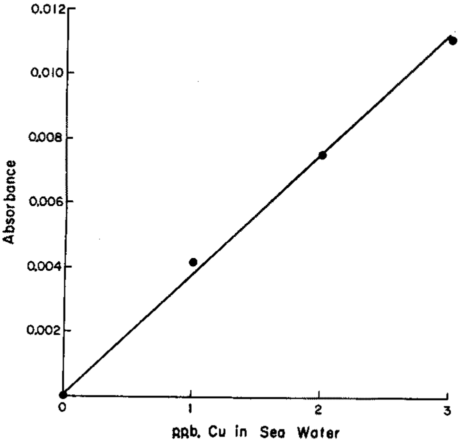

Fig. 1. Working curve for copper in sea water.

In order to prepare the working curve, the extracted sea water samples were combined and reextracted to insure that they were free of copper. Aliquots (500 ml) were then placed in clean Erlenmeyer flasks and sufficient copper was added from the freshly-prepared 0.4-p.p.m. solution to give concentrations of 0, 1, 2, and 3 p.p.b. in the sea water. MIBK (15 ml) and 5 ml of the APDC solution were then added, and shaking and phase separation were carried out as before. It will be noted that 15 ml of solvent were used for the standards instead of 25 ml. This is because the sea water used for the standards had already been equilibrated with MIBK. A typical working curve is shown in Fig. 1.

The zero of the working curve was not satisfactory as a blank since it did not include the acid added to adjust the pH of the sea water or the amount of copper impurity in the 10 ml of solvent represented by the different amounts used for the samples and standards. The blank was carried out as follows. Sufficient hydrochloric acid corresponding to the amounts needed to adjust the pH of 10 samples was taken almost to dryness in a teflon beaker heated by an infrared lamp. MIBK (250 ml) was then added to the residue and heated until its volume had decreased to 150 ml. Fifteen ml of this "prepared" solvent was then added to a 500-ml quantity of twice-extracted sea water. This was followed by addition of 5 ml of APDC solution, equilibration for 10 min and phase separation.

All samples including the particulate specimens were then aspirated into a lean air–acetylene flame. A × 10 scale expansion and noise suppression 3 were used. The hollow cathode was a conventional Perkin Elmer lamp run at 15 mA for the analysis line at 3247 Å.

The oxidation state of copper in sea water

The experiments were carried out with copper(II). In case the existence of copper(I) in sea water could have affected the results, one of two identical samples of sea water was treated with a small quantity of bromine water to insure that all copper was in the divalent state. When this sample and the untreated sample were extracted in the normal manner, no noticeable difference in absorption was noted. There is therefore no need to oxidize sea water before these determinations of copper.

The precision of the method

The precision of the method was tested by carrying out determinations on 16 identical samples of sea water. The coefficient of variation was ±10%. Considering the fact that this was for a copper content of around 1 p.p.b., this degree of precision must be considered satisfactory.

RESULTS AND DISCUSSION

Copper determinations were carried out on a number of sea water samples, interstitial waters and samples (3.6% solids) from the Salton Sea of California. The sea water samples were all taken from surface waters off the coast of S. California. The results are presented in Table I. All duplicates agreed well within experimental error. Three of the samples were repeated in duplicate at a later data and gave good agreement with earlier values. These are shown in parentheses in the Table. Where copper values were high, as in the Red Sea sample, phase ratios closer to unity were used to insure that values fell within the range of the working curve.

The sea water values are at the lower end of the suggested range of 1–20 p.p.b.[1]. This may be due to the fact that they were taken off the coast of S. California at the end of the dry season when there is little runoff from the land. The average of 0.9 p.p.b. compares with a value of 1.85 p.p.b. obtained by other workers for

TABLE I

COPPER IN NATURAL WATERS

(All results in p.p.b.)

Type of water	*Location*	*Lat.*	*Long.*	*Dissol. copper*	*Particulate copper*
Sea water	Santa Barbara Basin	34°13′	120°62′W	1.31(1.49)	<0.10
Sea water	Santa Cruz Basin	33°42′	119°36′W	0.85	0.34
Sea water	Continental Rise	33°34′	120°41′W	0.64(0.74)	<0.10
Sea water	Tanner Basin	32°57′	119°45′W	0.60(0.57)	<0.10
Sea water	Catalina Basin	33°23′	118°48′W	0.78	<0.10
Lake water	Salton Sea	33°20′	115°47′W	1.35	0.25
Lake water	Salton Sea	33°30′	115°56′W	1.28	<0.10
Marine marsh	Newport, California	33°48′	117°54′W	4.58	—
Interstitial	Ocean sediment	33°46′	118°32′W	2.08	—
Interstitial	Ocean sediment (Red Sea, Atlantis Deep)	21°20′	38°3′E	167.0	—

Belfast Lough. There was little or no particulate copper except in the region of the Santa Cruz Basin.

The sensitivity of the method appears to be about 0.1 p.p.b. and is comparable to that of neutron activation which would be about 3 p.p.b. for raw sea water or about 0.1 p.p.b. for analyses on the solid matter. The method also appears to have the dual advantages of speed and adequate precision.

It is concluded that a particular advantage of the method lies in the self-compensation afforded by preparing a working curve by adding and extracting fixed amounts of copper to and from sea water. In this way, incomplete extraction of copper from the samples is corrected for. For this reason also, it has not been necessary to carry out the usual addition and recovery tests which are conventionally applied to a new technique.

Preliminary work has indicated that the copper extracts will probably be suitable for simultaneous determinations of nickel, cobalt, iron and possible manganese. It is hoped to apply the combined technique to the analysis of further samples of saline waters.

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SUMMARY

A technique has been developed for the determination of copper in saline waters by extraction of its complex with ammonium pyrollidine dithiocarbamate into methyl isobutyl ketone and subsequent analysis by atomic absorption spectrophotometry. The method is self-compensating for any incomplete extraction of copper. With a 15:510 solvent–aqueous phase ratio, a sensitivity of 0.2 p.p.b. and a precision of ±10% were achieved. The method was used to determine copper in a number of sea water and other saline water samples.

RÉSUMÉ

On a développé une méthode pour le dosage du cuivre en eaux salinaires. On a extrait le complexe avec du pyrollidine-dithiocarbamate d'ammonium en solution de méthylisobutylcétone et effectué la détermination finale par spectrophotométrie par absorption atomique. La méthode possède une compensation interne pour l'extraction incomplète du cuivre. La précision obtenue est de ±10% et la sensibilité est d'environ 0.2 p.p.b. On a utilisé la méthode pour le dosage du cuivre dans l'eau de mer et autres échantillons salinaires.

ZUSAMMENFASSUNG

Ein Verfahren wurde für die Bestimmung von Kupfer in salzhaltigen Wassern entwickelt. Es bestand aus der Extraktion des Komplexes mit Ammoniumpyrollidindithiocarbamat im Methylisobutylketon mit anschliessender Bestimmung mit Flammenabsorptionsspektroskopie. Das Verfahren enthält Selbstkompensation für unvollständige Kupferextraktion. Eine Genauigkeit von ±10% und eine Empfindlichkeit von etwa $2 \cdot 10^{-8}\%$ wurde erreicht. Die Methode wurde verwendet um Kupfer in verschiedenen Seewasser- und Naturwasserproben zu bestimmen.

REFERENCES

1 J. P. Riley, in *Chemical Oceanography*, Vol. 2, Academic Press, New York, 1965, p. 295–424.
2 J. W. Robinson, *Anal. Chim. Acta*, 23 (1960) 479.
3 H. Malissa and E. Schoffmann, *Mikrochim. Ichnochim. Acta*, 1 (1955) 187.
4 J. E. Allan, *Spectrochim. Acta*, 17 (1961) 459.
5 S. Sprague and W. Slavin, *Perkin-Elmer Atomic Absorption Newsletter*, 3 (1964) 11.
6 R. J. Magee and A. K. M. Rahaman, *Talanta*, 12 (1965) 409.
7 C. E. Mulford, *Perkin-Elmer Atomic Absorption Newsletter*, 5 (1966) 88.

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NEUTRON ACTIVATION ANALYSIS BY STANDARD ADDITION AND SOLVENT EXTRACTION

DETERMINATION OF TRACES OF THORIUM IN ALUMINIUM BY EXTRACTION OF PROTACTINIUM-233

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Neutron activation analysis for thorium is very sensitive because of the favourable features of the natural isotope thorium-232 (100% isotopic abundance, neutron activation cross-section 7.3 barns). Neutron irradiation of thorium leads to the following reaction:

$$^{232}\text{Th}\,(\text{n},\gamma)^{233}\text{Th} \xrightarrow[23.3\ \text{min}]{} {}^{233}\text{Pa}\,(27.4\text{d}) \qquad (1)$$

JENKINS[1] has described a lengthy radiochemical procedure for the purification of thorium-233, with a chemical yield of only 35%. Protactinium-233 with a more convenient half-life has no stable isotope which can be applied as an isotopic carrier. LEDDICOTTE AND MAHLMAN[2] have described a method in which the ^{233}Pa produced is quantitatively separated from other elements by extraction from dilute acid solution with diisobutylcarbinol, so that the chemical yield need not be determined. The authors reported, however, that any serious interferences from other radionuclides must be eliminated by the use of scavenging or holdback carriers in the basic separation procedures.

BATE *et al.*[3] have described another method for the determination of thorium, in which protactinium was separated by two different radiochemical procedures, involving extraction with diisopropyl ketone and 2-thenoyltrifluoroacetone; the time of separation is 12–14 h for two samples.

In the present paper a new method is described for the determination of traces of thorium in aluminium by the "standard addition and solvent extraction" technique. The principle of this type of analysis and its application for the determination of uranium in rocks and aluminium have been reported in previous studies[4,5]. In the method presented the time of separation is about 15 min. The method also obviates the need for a strictly quantitative separation procedure; this makes possible the separation of the induced radioisotope (^{233}Pa) in a purer state.

EXPERIMENTAL

Apparatus

An ECKO scintillation counter connected to a well-type 2.5 × 2.5″ NaI(Tl) crystal and a phototube was used for gross activity measurements. A single-channel "Nuclear Chicago" Model 132 B spectrometer connected to a scintillation head of a $3 \times 3''$ NaI(Tl) crystal and a photomultiplier tube was applied to measure the γ-ray spectrum of ^{233}Pa.

Reagents

Tridodecylamine (TDA, a high-purity product of Rhone-Poulenc, France) and thenoyltrifluoroacetone (TTA, Fisher certified Reagent, m.p. 41.8–44.1°) were used without further purification. The solutions of the two solvents were prepared by dissolving the appropriate weights in "reagent grade" xylene. Other reagents were prepared from analytical-grade chemicals.

Irradiations

The thorium standard was prepared by carefully wrapping an amount of thorium nitrate tetrahydrate containing 6 mg of thorium in a small piece of thin aluminium foil. About 3 g of aluminium pieces, cut from cans used for pile irradiation, were etched with dilute nitric acid, washed with water and dried; a known weight (about 1 g) was enclosed in aluminium foil. Two standards and two aluminium samples were placed in an aluminium can and irradiated in the UAR-RRI-Research Reactor at Inshas for 48 h at a flux of about $1 \cdot 10^{13}$ n cm^{-2} sec^{-1}. After irradiation, the can was cooled for 10 days to allow for decay of the short-lived unwanted activities.

Selectivity

In an investigation[6] on the determination of trace elements in aluminium, it was found that the elements which give rise to long-lived radioisotopes on irradiation of aluminium are mainly scandium, zinc, chromium, iron, cobalt, silver and mercury, together with smaller proportions of tin and rubidium; TDA was used to extract these elements. The separation of ^{233}Pa from the isotopes induced from these elements was, therefore considered. The optimum acidity for the selective isolation of ^{233}Pa with TDA and TTA was first investigated; it is well-known that protactinium can be extracted with TTA from acidic solution[7]. To a series of separating funnels, containing 10 ml of hydrochloric acid of different concentrations, 50 μl of ^{233}Pa in 6 M hydrochloric acid was added. After extraction with 10 ml of 0.3 M TDA or 0.5 M TTA solution for 5 min, the activities of equal volumes (3.0 ml) of the organic

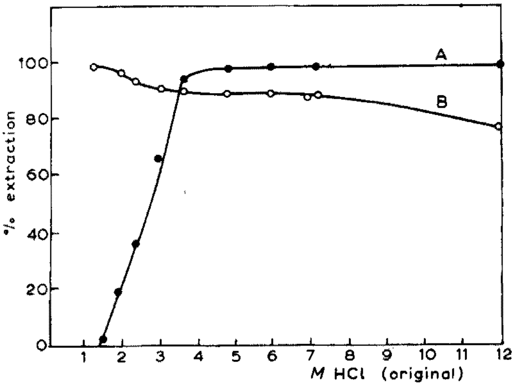

Fig. 1. Effect of acidity on extraction of ^{233}Pa with 0.3 M TDA (A) and 0.5 M TTA (B) in xylene.

and aqueous phases were measured in the scintillation counter; the percentage extraction was plotted against the original acidity in the aqueous solution (Fig.1). From the data obtained it was evident that quantitative extraction with TDA was achieved from 5–12 *M* hydrochloric acid solutions, while more than 80% of the ^{233}Pa could be stripped from the organic phase with 1.5–2 *M* acid solutions; also more than 95% of the ^{233}Pa was extracted with TTA from 1.5–2 *M* hydrochloric acid.

The percentage extraction of ^{233}Pa and the other long-lived radioisotopes with 0.3 *M* TDA and 0.5 *M* TTA from the media selected for separation is shown in Table I. It can be seen that iron, tin, zinc, cobalt, mercury, antimony and partly silver and zirconium are co-extracted with protactinium by TDA from 4.5 *M* HCl–1.5 *M* $AlCl_3$ solution. Cobalt, zirconium, about 70% antimony and some iron are stripped with protactinium from the TDA extract by 1.7 *M* hydrochloric acid. Extraction with TTA will clearly separate ^{233}Pa in a radiochemically pure state, since the amount of zirconium, the only other element that is extracted with TTA, in aluminium is negligible.

TABLE I

EXTRACTION OF ^{233}Pa AND OTHER ISOTOPES WITH 0.3 *M* TDA AND 0.5 *M* TTA

Isotope[a]	*% Extraction*[b]		
	0.3 M TDA; 4.5 M HCl–1.5 M AlCl₃	*0.3 M TDA; 1.7 M HCl*	*0.5 M TTA; 1.7 M HCl*
^{233}Pa	>99	6.5	97
^{59}Fe	97	96	35
^{113}Sn	98	98	0
^{65}Zn	98	>99	0
^{60}Co	96	1	<1
^{203}Hg	>99	>99	0
^{124}Sb(V)	95	29.5	<1
^{110}Ag	35	89	0
^{95}Zr	21	5	38
^{51}Cr	21	—	—
^{46}Sc	1	—	—

[a] Prepared by irradiating the pure metal, oxide, chloride or nitrate and then dissolving in HCl (or HNO_3 in the cases of mercury and silver). [b] Average of 2 parallel experiments.

Reproducibility

The time required to reach extraction equilibrium was determined by extraction of ^{233}Pa with 0.3 *M* TDA from 4.5 *M* HCl–1.5 *M* $AlCl_3$ and with 0.5 *M* TTA from 1.7 *M* hydrochloric acid. With vigorous shaking by hand, equilibrium was attained within 30 sec for TDA extraction and within 4–5 min for TTA extraction.

The reproducibility of separation by the standard addition and solvent extraction technique was evaluated as follows. Two series of solutions which were respectively 4.5 *M* HCl–1.5 *M* $AlCl_3$ and 1.7 *M* HCl and contained increasing amounts of ^{233}Pa solution, were extracted with equal volumes of 0.3 *M* TDA and 0.5 *M* TTA, respectively. The percentage extraction was then calculated from the radioactivity in the two phases. The experimental results are shown in Table II, from which it can be seen that very good reproducibility was achieved, and that equal yields were obtained from the sample solution and from the mixture of the sample and standard solution.

Adsorption of ^{233}Pa on glass

Losses due to adsorption of ^{233}Pa on glass were estimated as follows: 50 μl of ^{233}Pa solution were transferred to 5 ml of 2 *M* hydrochloric acid solution in a test tube and the activity was measured. The solution was then transferred to a separating funnel, shaken for about 10 min and then returned to the test tube and the activity was measured again. Losses due to adsorption of ^{233}Pa on the glass of the funnel were found to be less than 1%.

TABLE II

REPRODUCIBILITY OF ^{233}Pa EXTRACTION WITH TDA AND TTA

Original activity (counts/min)	*% Extraction*	
	0.3 M TDA; 4.5 M HCl–1.5 M AlCl$_3$	*0.5 M TTA; 1.7 M HCl*
1356	>99	96.5
2720	>99	96.5
2140	>99	97.0
5420	>99	97.0
8030	>99	96.0

Processing of irradiated standard and sample

Each aluminium foil containing the thorium standard was transferred to a 100-ml beaker, and treated with 6 *M* hydrochloric acid until complete dissolution. The solution was then quantitatively transferred to a 50-ml measuring flask and diluted to the mark with 6 *M* hydrochloric acid. One ml of this solution was diluted to 10 ml with the same acid; 50 μl of the resulting solution contained 0.6 μg Th.

Each aluminium sample was removed from the foil, dissolved in 9 *M* hydrochloric acid in a covered 200-ml beaker and diluted to 25 ml with this acid. The resulting solution was about 4.5 *M* in hydrochloric acid about 1.5 *M* in aluminium chloride. This dissolution procedure was done with a non-irradiated aluminium sample and with a known amount of ^{233}Pa solution; losses of ^{233}Pa as a result of dissolution were found to be negligible.

Procedure

Take 4 equal aliquots (5 ml) of each sample solution into 4 separating funnels. Transfer the following solutions to the respective funnels: 150 μl 6 *M* HCl; 100 μl 6 *M* HCl + 50 μl Th standard solution; 50 μl 6 *M* HCl + 100 μl Th standard solution; and 150 μl Th standard solution. The acidity of the 4 solutions is thus equal. Transfer 5 ml of 0.3 *M* TDA in xylene to each funnel, shake vigorously for 1 min and allow the phases to separate. Drain off the aqueous phases and discard. Transfer 5 ml of 1.35 *M* hydrochloric acid to each funnel, shake for 2 min and allow the phases to separate; after equilibrium the acidity in the aqueous phase is 1.7 *M*. Withdraw the aqueous phases to another 4 separating funnels (previously rinsed with dilute hydrochloric acid solution in order to minimize protactinium adsorption on glass).

Transfer 5 ml of 0.5 *M* TTA to the funnels, shake for 6 min, allow the phases to separate and discard the aqueous fractions. Transfer the organic phases to 4 similar stoppered glass counting vials.

The above procedure was tested on a synthetic sample solution having the same composition as the sample solutions (4.5 *M* HCl and 1.5 *M* $AlCl_3$) and prepared from non-irradiated aluminium. To this solution (250 ml), 1 ml of irradiated thorium solution containing 120 μg Th was added and the whole procedure reported above was repeated on aliquots of this solution.

Measurement of radioactivity and calculation of the results

The γ-spectra of the 4 extracts were measured at constant geometry. The photopeak activities at 0.31 MeV of ^{233}Pa were measured for the sample and for mixtures of sample and standards.

The amount of thorium in the sample (x) was calculated by means of the relationship:

$$x = x_s A/(A_m - A)$$

where x_s is the weight of thorium in the added amount of thorium standard, A is the activity of the TTA extract obtained from the sample and A_m is the activity obtained from the mixture of the sample and standard.

RESULTS AND DISCUSSION

The γ-spectra of the isolated ^{233}Pa isotope showed that the purification of

TABLE III

DETERMINATION OF THORIUM IN THE SYNTHETIC SOLUTION

Volume of solution	*Th taken (μg)*	*Th found (μg)*
5	2.4	2.33
10	4.8	4.69
15	7.2	7.6

TABLE IV

DETERMINATION OF THORIUM IN ALUMINIUM BY THE STANDARD ADDITION AND SOLVENT EXTRACTION TECHNIQUE

Sample	*Weight (in 5 ml)*	*Amount of standard added (μg)*	*Activity[a] in the TTA extract (counts/min)*	*Th found (p.p.m.)*
1	0.2021	—	1480[b]	—
		0.6	2937[c]	3.01
		1.2	4715[c]	2.73
		1.8	6340[c]	2.71
2	0.1986	—	1532	—
		0.6	3094	2.92
		1.2	4620	2.96
		1.8	6245	2.89

[a] Activity between 5 and 10 channels. [b] A. [c] A_m.

protactinium was complete, so that protactinium could be determined by either a γ- or β-counter.

The results obtained in the analysis of the synthetic sample solution and the aluminium samples are presented in Tables III and IV. The reported data show that the method is precise and sensitive for determining small amounts of thorium.

The proposed method should also be applicable for the determination of traces of thorium in a variety of substances, including ferrous materials, rocks, soil, waters, some mineral acids, etc., with no or very slight modifications. The determination of thorium and some other elements in the above materials by the standard addition and solvent extraction technique is being investigated.

SUMMARY

A rapid and selective radiochemical separation for protactinium-233 is suggested. The method is based on extraction of protactinium with 0.3 *M* tridodecylamine from 4.5 *M* HCl–1.5 *M* $AlCl_3$ solution, stripping with 1.35 *M* HCl followed by another extraction with 0.5 *M* 2-thenoyltrifluoroacetone. The separation, coupled with the application of the standard addition technique, is applied to the determination of traces of thorium in aluminium by neutron activation.

RÉSUMÉ

On propose une méthode de séparation radiochimique rapide et sélective pour le protactinium-233. Elle consiste en une extraction du protactinium avec la tridodécylamine 0.3 *M* en milieu HCl 4.5 *M*–$AlCl_3$ 1.5 *M*, suivie d'une autre extraction à l'aide de 2-thénoyltrifluoroacétone 0.5 *M*. Cette séparation, combinée avec la technique par addition d'étalon est appliquée au dosage de traces de thorium dans l'aluminium par activation au moyen de neutrons.

ZUSAMMENFASSUNG

Die Bestimmung von Spuren Thorium in Aluminium mit der Neutronenaktivierungsanalyse geschah durch schnelle und selektive radiochemische Abtrennung des Protactiniums-233. Die Methode beruht auf der Extraktion des Protactiniums mit 0.3 *M* Tridodecylamin aus einer Lösung mit 4.5 *M* HCl und 1.5 *M* $AlCl_3$, Rückextraktion mit 1.35 *M* HCl und erneuter Extraktion mit 0.5 *M* 2-Thenoyltrifluoroaceton.

REFERENCES

1 E. N. JENKINS, *Analyst*, 80 (1955) 301.
2 G. W. LEDDICOTTE AND H. A. MAHLMAN, *Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, Vol. 8, 1956, p. 250.
3 G. L. BATE, J. R. HUIZENGA AND H. A. ROTRATZ, *Geochim. Cosmochim. Acta*, 16 (1949) 88.
4 A. ALIAN, *AEET/217*, 1965.
5 A. ALIAN AND R. PARTHASARATHY, *Anal. Chim. Acta*, 35 (1966) 69.
6 A. ALIAN AND A. HAGGAG, *Talanta*, 9 (1967) in press.
7 E. K. HYDE, *Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, p. 728.

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DETERMINATION OF TRACE ELEMENTS IN STANDARD REFERENCE MATERIALS BY NEUTRON ACTIVATION ANALYSIS

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Neutron activation analysis has a high sensitivity for the majority of elements, together with an intrinsic high degree of accuracy. The method has been used widely for elemental trace analysis in a variety of inorganic, organic and biological media. Standard Reference Materials as issued by the National Bureau of Standards, which may contain many elements at minor constituent and trace levels, are being analyzed by this technique.

Problems affecting precision and accuracy have been encountered in the use of activation analysis for this purpose. Commonly observed are bias, and/or lack of reproducibility due to (*a*) sample contamination, (*b*) interfering nuclear reactions, (*c*) changes in neutron flux level, (*d*) lack of carrier exchange, (*e*) insufficient purity of separated radioactivity, (*f*) errors in separation yield determination, (*g*) induced radioactivity of similar γ-ray energy, (*h*) geometry differences between sample *vs.* standard, (*i*) neutron self-shielding during irradiation and (*j*) γ-ray attenuation during counting. The last 4 types of error above will be discussed in this paper. Of these, types (*i*) and (*j*) are most frequently neglected by those using activation analysis.

Bias due to induced radioactivity of similar γ-ray energy

When radioactive isotopes are induced by nuclear reactions in samples of materials, it is commonly observed that γ-rays of almost identical or overlapping energy may be present, either from matrix or impurity elements. If the analysis is to be performed nondestructively, some means of differentiating between the nuclides must be found, to eliminate a positive bias.

One approach to the correction of this type of error was exemplified by the determination of argon in single crystal, ultra-pure silicon[1]. Single crystals had been grown in an argon atmosphere and were to be used in a density determination having a standard deviation of 2 parts in 10^6. Electrical resistivity or other analytical techniques would not detect interstitial argon, so activation analysis was used to establish an upper limit of argon contamination.

The neutron activation analysis for argon utilizes the nuclear reaction ^{40}Ar(n,γ)^{41}Ar, with the argon-41 decaying with a 1.82-h half-life and having a 1.29-MeV γ-ray of about 100% abundance. The nuclear reaction ^{30}Si(n,γ)^{31}Si causes an interference because the product, silicon-31, has a half-life of 2.62 h, though the 1.27-MeV γ-ray has only 0.07% abundance.

Carefully etched and cleaned samples were irradiated in snap-cap polyethylene vials for 10 min at the Naval Research Laboratory reactor at a flux of 10^{12} n·cm^{-2}

sec^{-1}. A known volume of air [(0.934±0.001)% argon by volume] was used as an argon standard. After irradiation, each silicon crystal was removed from the vial and placed in a second clean snap-cap vial which had not been irradiated. The sample and argon standard were then counted with a sodium iodide detector by γ-ray spectrometry. The half-lives were followed by counting over a period of 20 h and decay curves were plotted.

If all of the 1.25–1.30-MeV γ-ray radioactivity in the sample was assumed to be from an argon impurity in the crystal, the actual count rate found would give an argon content of 4.8 p.p.m. However, the radioactivity of the sample was found to have a 2.78-h half-life, which is in substantial agreement with the silicon-31 half-life of 2.62 h, but not with the experimentally-determined argon-41 half-life of 1.60 h (literature value, 1.82 h). To demonstrate this, Fig. 1 shows 4 decay curves. Curve (1) shows the experimentally-determined silicon crystal decay curve. Curve (2) is a decay curve showing 60% of the total crystal radioactivity as pure silicon radioactivity (^{31}Si), taken at zero time. Curve (3) is a decay curve of pure ^{41}Ar (which is equivalent to 40% of the total silicon crystal radioactivity taken at zero time). Curve (4) shows the sum of the second and third curves, or a hypothetical decay curve of 60% silicon radioactivity (^{31}Si) and 40% argon radioactivity (^{41}Ar). This 4th curve definitely shows curvature and has an average half-life of 2.4 h. Thus, it may be safely stated that if an argon impurity of 2 p.p.m. were present in the silicon crystal (or approximately 40% of the total silicon crystal activity), it could definitely be seen in the decay curve. Therefore, there is less than 2 p.p.m. of argon in the silicon crystal.

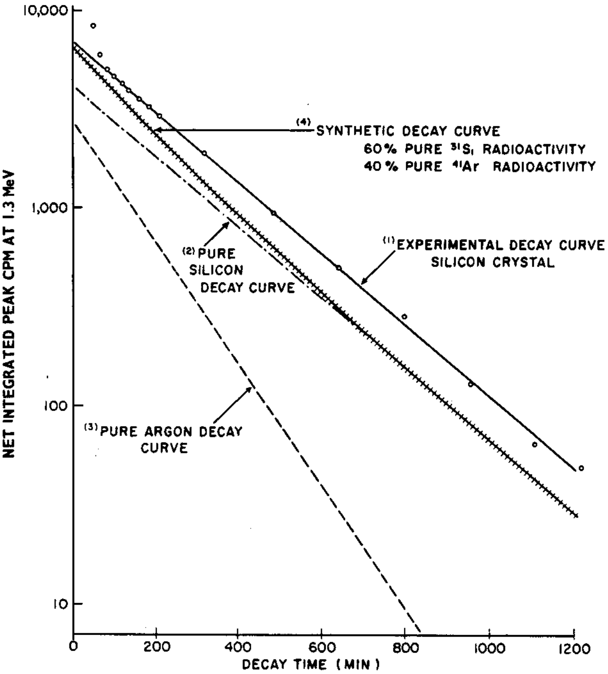

Fig. 1. Decay curves of argon–silicon mixture.

Effect of difference in geometrical location during irradiation of sample and standard

It is well known that neutron fluxes can vary markedly at different positions within and adjacent to a nuclear reactor core. Such flux variations can cause serious biases and lack of reproducibility in activation analysis if not corrected.

Neutron flux gradients have been observed[1] in both vertical and horizontal rabbit axes by the use of copper foil flux monitors in the north pneumatic tube of the Naval Research Laboratory pool-type reactor. The relatively large gradients to be discussed are caused by the location of the north rabbit terminal on a graphite ledge just above the reactor core, giving an approximate inverse square dropoff, which would be much less if the rabbit were surrounded by neutron-emitting fuel elements.

The copper foil flux monitors utilize the nuclear reaction ^{63}Cu(n,γ)^{64}Cu. Copper-64 decays with a 1.34-MeV γ-ray and 0.51-MeV annihilation radiation from positron emission. To determine the flux gradients, 5-mil thick copper foils (3/16" diameter) were attached to a thin cylinder of polyethylene at various vertical and horizontal locations in the rabbit. After irradiation and decay of the 5.1-min half-life ^{66}Cu (induced by (n,γ) reaction on ^{65}Cu), the 0.51-MeV annihilation radiation was counted by γ-ray spectrometry, correcting to "time zero".

A plot of the relative neutron flux *vs.* distance from the bottom of the rabbit showed a linear vertical dropoff in flux of 0.68% per mm. By a similar plot, the side-to-side gradient was found to be 0.37% per mm over the 12-mm diameter of the rabbit.

Because a linear relationship was found in vertical flux dropoff, an accurate correction may be made for sample position. However, it is usually simpler to control the irradiation conditions so that all samples and standards are at the same level in the polyethylene rabbit, using flux monitors each time a sample or standard is irradiated.

A numerical correction for side-to-side flux variations is difficult, since the rabbit turns while moving. Therefore efforts must be made to keep the sample as close to the center line of the rabbit as possible. However, by affixing the flux monitor to the base of the sample container, the need for side-to-side corrections may be avoided for samples of small diameter.

Neutron self-shielding errors

Neutron self-shielding is caused by elements in a sample which have high cross-sections in the thermal and resonance energy regions. This effect, though known, is frequently ignored and can cause large errors if there are significant differences in neutron absorption between sample and standard. A number of mathematical expressions correcting for this source of error have been proposed, both rigorously theoretical and empirical. One empirical method, which has been used in analysis for tellurium[2] in Standard Reference Material cast irons and cartridge brasses*, will be described. The method used follows in detail that proposed by REYNOLDS AND MULLINS[3].

The authors[3] proposed an empirical method of correcting for neutron flux perturbation in activation analysis which took into account thermal and resonance neutron self-shielding, as well as enhancement of thermal neutron flux by moderation within aqueous samples. Experimental verification of calculated values was obtained

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* Corrections of 8 and 18%, respectively.

by them with a mean deviation of ±3%, using weights or thicknesses of metals (or compounds) commonly used in activation analysis. In the case of solutions, volumes of 1.5 and 30 ml were taken.

Thermal neutron self-shielding was calculated by the method of ZWEIFEL[4]. The equations used were:

For a foil, $f = 1 - \tau/2(0.923 + \ln 1/\tau)$

For a sphere, $f = 1 - 9\tau/8$

For a wire, $f = 1 - 4\tau/3$

where f = "attenuation factor" = average flux within sample divided by flux if sample were absent

τ = shape parameter = $n\sigma t$ for foil, $n\sigma r$ for wire, $2n\sigma r/3$ for sphere

n = atom density (atoms cm^{-3})

σ = thermal neutron cross-section (cm^2)

t = thickness (cm)

r = radius (cm)

When τ is larger than *ca.* 0.05, the corresponding value of f is read from a family of curves[4].

Because of the lack of rigorous calculations for resonance neutrons and the laborious nature of the approximate computations required, the empirical approach of EASTWOOD AND WERNER[5] was used[3]. By fitting empirical data on self-shielding of epicadmium neutrons in cobalt, they calculated the resonance neutron attenuation factor by

$$f_r = -0.29 \log t_{\text{eff}} = -0.29 \log \frac{tI_x n_x}{I_{\text{Co}} n_{\text{Co}}}$$

where f_r = average resonance flux within sample divided by value if sample were absent

I_x = resonance integral for element x (barns)

t = thickness (cm) of foil, radius of wire, $2\tau/3$ for sphere

I_{Co} = resonance integral for cobalt (barns)

n_x = atom density of element x (atoms cm^{-3})

n_{Co} = atom density of cobalt (atoms cm^{-3})

Enhancement of thermal activation by moderation of neutrons was studied experimentally[3], irradiating wires of various materials with and without water in 1.5-ml vials and 30-ml bottles. By calculations based on the specific activity at the wire center, the enhancement was found to be 5% for the small volume and 12% for the large volume.

An over-all self-shielding factor (f') is calculated[3] from the relationship:

$$f' = f_{\text{th}} R_{\text{th}}/R + f_r R_r/R$$

where R_{th} = thermal neutron reaction rate = $\phi_{\text{th}}\sigma$

ϕ_{th} = thermal neutron flux (n·cm^{-2}sec^{-1})

R_r = resonance neutron reaction rate = $\phi_r I$

Values of f for thermal (f_{th}) and resonance (f_r) activation are calculated separately, weighting values for the amount of each component in a sample by multiplying the fractional component of each in a dilute sample and summing.

A typical calculation for correction of neutron self-shielding was made on a Standard Reference steel chip (No. 82b) containing 0.75% manganese, 2.6% carbon, 1.2% nickel, 2.1% silicon, 0.33% chromium and 5 other minor constituents (0.022% P, 0.007% S, 0.036% Cu, 0.023% V and 0.024% Ti). Copper was to be determined by neutron activation analysis. Only the constituents which have relatively high thermal and/or resonance cross-sections were used in the calculation which was performed by computer[6]. Data on thermal and resonance neutron flux, irradiation and decay time, weight (g) and atomic weight of relatively high cross-section elements, density of sample, sample configuration, and cross-sections were put into the program. At flux levels of $8 \cdot 10^{11}\text{n} \cdot \text{cm}^{-2}\text{sec}^{-1}$ thermal and $1 \cdot 10^{10}\text{n} \cdot \text{cm}^{-2}\text{sec}^{-1}$ resonance, and assuming a 1-g sphere of iron, an f' value of 0.967 was found. When a 100-mg foil sample was assumed for the same flux levels, f' calculated to be 0.9815. Respective f_{th} values were 0.970 and 0.982, whereas f_{r} values were 0.707 and 0.909, indicating the small influence of the resonance neutron absorbing components in the neutron spectrum used.

γ-Ray attenuation difference between sample and standard

An exact mathematical treatment of external- and self-absorption of γ-radiation would require detailed consideration of the initial spectrum as well as the effects of scattering and absorption within the sample itself and external absorbing material, geometrical (solid angle) effects, and inherent peak efficiencies in the radiation detector. An alternative approach is to treat the problem in a semi-empirical manner, deducing average values for peak efficiency, external absorption and self-absorption as a function of sample configuration and absorption coefficient, and normalizing this approximate treatment by means of experimental observations. Calculations have been carried out in which detailed consideration has been given to the effects of geometrical configuration upon external- and self-absorption of γ-radiation. The effects of geometry on absorption and peak-detection efficiency have been related, in turn, to a "mean" sample thickness, and all 3 factors — peak efficiency, external absorption, and self-absorption — have been combined to give a more accurate estimate of detection efficiency. External absorption is given by the factor, $f_{\text{a}} = e^{-\nu\mu' L'}$; self-absorption, by $f_{\text{s}} = \{(1 - e^{-\nu\mu L}/\nu\mu L)\}$. L and L' represent the sample and absorber thicknesses, respectively; μ and μ', the respective absorption coefficients, and ν represents a calculated geometrical correction factor which depends upon μL, and $\mu' L'$ and the sample-detector configuration.

External- and self-absorption corrections may be readily approximated when the sample is distant from the detector, for then the parameter ν approaches unity. If, in addition, the sample is relatively "thin" (with respect to $1/\mu$), the exponent in the self-absorption factor may be expanded leading to the simplified expression,

$$f_{\text{s}} = \frac{1 - e^{-\nu\mu L}}{\nu\mu L} \approx \frac{1 - e^{-\mu L}}{\mu L} \approx \frac{1}{\mu L}\left(1 - 1 + \mu L - \frac{(\mu L)^2}{2!} + \ldots\right) \tag{1}$$

$$f_{\text{s}} \approx 1 - \frac{\mu L}{2} \approx e^{-\mu(L/2)} \tag{2}$$

That is, the self-absorption correction produced by the sample is approximately equivalent to the absorption correction due to an external absorber one half as thick as the sample. The approximation is 4% in error if $\mu L = 1$, and it is only 0.35% in error when $\mu L = 0.30$. The validity of the approximation is due to the fact that for a "thin" sample, the mean point of origin of an escaping γ-ray is approximately the midpoint of the sample.

In order to illustrate the approach to the problem, the parameter, ν, has been calculated, using a computer, for a range of sample configurations and thicknesses. The exact expressions for f_s and f_a have been specifically evaluated for hypothetical aluminum and lead samples, each 4 mm thick, and located 2.5 cm and 11.5 cm above a 7.6×7.6 cm diameter NaI(Tl) detector with a 4-mm thick aluminum absorber. For each location and each element two γ-ray energies were considered, 0.20 MeV and 1.00 MeV. The results are listed in Tables I and II. To make the illustration more concrete, one may estimate the resulting detection efficiencies by including published values for total and peak/total efficiencies[7]. For example:

TABLE I

EXTERNAL ABSORPTION FACTORS, f_a

(4 mm of aluminum)

	h = 11.5 cm	*h = 2.5 cm*
0.20 MeV	0.874	0.844
1.00 MeV	0.934	0.918

TABLE II

SELF-ABSORPTION FACTORS, f_s

	Aluminum		*Lead*	
	11.5 cm	*2.5 cm*	*11.5 cm*	*2.5 cm*
0.20 MeV	0.933	0.920	0.225	0.184
1.00 MeV	0.970	0.958	0.852	0.820

Al(1.00 MeV, 2.5 cm): $\text{Eff.} = \varepsilon_{\text{pk}} \cdot f_a \cdot f_s = (0.0403)(0.918)(0.958) = 0.0354$

Pb(0.20 MeV, 11.5 cm): $\text{Eff.} = \varepsilon_{\text{pk}} \cdot f_a \cdot f_s = (0.0230)(0.874)(0.225) = 0.00452$

The relative importance of the absorption effects and their dependence upon energy and absorber are readily seen from the Tables. The effect of distance on the parameter, ν, manifests itself through the decreased absorption (larger f_s and f_a) for the more distant location. This arises because the path is more "vertical" and the effective thickness of the sample more nearly approximates its actual thickness.

For highest accuracy, the best experimental approach is to fix the conditions for counting of the standard (system calibration) so that they are identical to those for counting the sample. Generally this may best be accomplished by dissolving the samples and counting the solution in a container which is as similar as possible to that used for the standard. For the special case of the activation analysis of a standard steel sample for selenium, this experimental approach was taken. In order to correct accurately for self-absorption of the 160-keV γ-ray from ^{77m}Se, the "unknown"* steel sample was dissolved in perchloric acid and the solution was counted in a specific position. A solution of the same chemical composition was then prepared for calibration purposes, with a known amount of selenium as the activation analysis "standard". In the more general case, however, varying configurations and sample matrices may be encountered and it may be difficult to achieve exact replication of sample and standard counting conditions. For this reason, the semi-empirical approach referred to above, is being pursued.

Connection between experiment and theory will be made by introducing an experimental normalization factor—normalization taking place with a convenient sample-type and reference energy. Probably the most reasonable choice for the sample is a dilute aqueous solution of specified volume and configuration. Small deviations from the theoretical formalism with variations in sample nature (thickness, absorption coefficient) or γ-ray energy are being determined experimentally for variations about the reference point. In order to test the validity of the approach a series of aqueous solutions were prepared, each containing a fixed amount of ^{44}Ti, emitting 78-keV γ-rays. Different concentrations of lead nitrate were used to vary the effective absorption coefficient. The locations and thicknesses of the solutions were identical, so that self-absorption changes were due entirely to μ-variations. Values for μ were calculated from the solution compositions, and the relationship of eqn. (2) was tested by plotting the common logarithm of the counting rate *vs.* μ. As may be seen from Fig. 2, a linear relationship was obtained in agreement with eqn. (2). Such empirical plots may be utilized for correcting future samples for self-absorption, simply by interpolating to the correct value of μ.

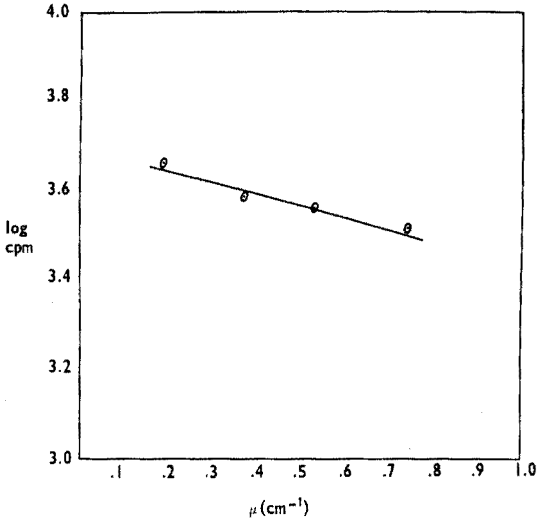

Fig. 2. Plot of log counting rate of ^{44}Ti (78-keV γ-ray) *vs.* μ.

Conclusion

Among the possible causes of bias and lack of precision in neutron activation analysis, the effects of, and methods of correction for, 4 different types of error have been examined in some detail. It is believed that careful study of sources of error in activation analysis will reveal in many cases simple means for their avoidance. In most other situations, corrections may be experimentally determined or calculated by semi-empirical techniques. Laborious and impractical computations will thus be unnecessary and maximum precision and accuracy be obtained in trace analysis of materials by activation analysis.

SUMMARY

Neutron activation analysis with its high sensitivity and accuracy in trace analysis, is being used at the NBS for analysis of Standard Reference Materials. Four problems affecting precision and accuracy are discussed. First, the positive bias introduced by induced radioactivity of similar γ-ray energy was found in the determination of interstitial argon in ultra-pure silicon; a decay-curve resolution technique was used to compensate for the error. Secondly, errors due to differences in geometrical location between sample and standard during irradiation were observed; flux gradients were determined by copper foil flux monitoring to give necessary means of correction. Thirdly, errors are caused by differences in neutron self-shielding between sample and standard during irradiation; an empirical correction method was used and a computer program written for calculation. Finally, the problem of γ-ray attenuation during counting of sample and standard has been explored; a theoretical and experimental study gave the necessary corrections.

RÉSUMÉ

L'analyse par activation au moyen de neutrons, grâce à sa grande sensibilité et son exactitude lors de l'analyse de traces, est utilisée par le "National Bureau of Standards" pour l'analyse d'étalons de référence. On examine quatre problèmes affectant précision et exactitude. Une étude théorique et expérimentale indique les corrections nécessaires.

ZUSAMMENFASSUNG

Folgende vier Probleme, die die Genauigkeit und Richtigkeit der Neutronenaktivierungsanalyse beeinflussen, werden diskutiert. 1. Der positive Einfluss der durch induzierte Radioaktivität ähnlicher γ-Strahlenenergien hervorgerufen wird. 2. Fehler, die zu Unterschieden gehören, die durch geometrische Anordnung der Proben beim Bestrahlen hervorgerufen werden. 3. Fehler, die durch Unterschiede in der Neutronen-Selbstabschirmung verursacht werden. 4. Das Abklingen der γ-Strahlung während des Zählens.

REFERENCES

1 J. R. DeVoe (Editor), *Radiochemical Analysis: Activation Analysis, Instrumentation, Radiation Techniques, and Radioisotope Techniques*, NBS Technical Note 276, July 1964 to June 1965.
2 D. A. Becker and G. W. Smith, *Proc. 1965 Intern. Conf. Modern Trends in Activation Analysis*, Texas A & M University, College Station, Texas, pp. 230–235.
3 S. A. Reynolds and W. T. Mullins, *Intern. J. Appl. Radiation Isotopes*, 14 (1963) 421.
4 P. F. Zweifel, *Nucleonics*, 18 (11) (1960) 174; J. C. Stewart and P. F. Zweifel, *Proc. Second Intern. Conf. Peaceful Uses At. Energy, Geneva*, Vol. 16, United Nations, New York, 1958, p. 650.
5 T. A. Eastwood and R. D. Werner, *Nucl. Sci. Eng.*, 13 (1962) 385.
6 Activation Analysis Section (310.08), National Bureau of Standards, Gaithersburg, Md., *Symbolic instruction code (BASIC)* designed by Dartmouth College (unpublished).
7 R. L. Heath, *Phillips Petroleum Report: U.S. At. Energy Comm. Rept.*, IDO-16408, 1957.

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NEUTRON ACTIVATION ANALYSIS FOR SODIUM TRACES IN MAGNESIUM*

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Neutron activation methods are widely applied to the determination of sodium traces in various substances[1]; in most cases extremely small amounts of sodium can be determined without any special difficulty because of the favourable nuclear features of this element. However, in the special case of magnesium (and aluminium) materials, the analytical process is complicated by the spurious contributions from the matrix itself, which interact with the reactor fast-neutron flux. Some techniques that take into account the fast-neutron contributions can be used, but generally the analytical sensitivity is lowered.

A relatively simple method for the determination of sodium in magnesium samples has been developed at the SORIN laboratories in which the traces of sodium are separated from the bulk of the matrix before the irradiation. Although a blank correction is necessary in this case, the preliminary separation method seems to offer some remarkable advantages compared with other techniques.

Spurious contribution from the matrix

The simulated sodium amounts in magnesium matrices were experimentally evaluated by irradiating cadmium-lined samples of pure magnesium in various irradiation positions. The value found for the mean cross-section for the reactor fast-neutron spectrum, 1.28 ± 0.09 mb, for the reaction $^{24}Mg(n,p)^{24}Na$, is very close to the mean cross-section data for a fission spectrum as reported in the literature (1.2 mb)[2,3]. The experimental results were obtained by using the value of 0.61 mb for the reaction $^{27}Al(n,\alpha)^{24}Na$ as a reference.

In Table I the simulated sodium concentrations are reported for some irradiation positions.

TABLE I

SPURIOUS CONTRIBUTIONS OF SODIUM FROM MAGNESIUM SAMPLES

Irradiation position	*Spurious Na contribution (p.p.m.)*
A (rabbit)	550 ± 10
B (pool)	410
C (pool)	370

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NON-DESTRUCTIVE METHODS

Since the values of the thermal-to-fast flux ratio are low in the usual irradiation positions of the RS 1 pool-reactor(3–5), in most cases the effect of the interfering reaction on the magnesium matrix cannot be neglected. Sodium concentrations of the order of 1% can be determined without any special difficulty and with a sufficient accuracy, but the concentration range of greater interest in activation analysis is much lower.

The spurious contributions can be subtracted, when evaluated for an individual irradiation position. Since sodium-free magnesium was not available, the correction was made by employing duplicate samples successively irradiated in the bare and Cd-covered states in the same position. The epithermal activation of sodium can be neglected because of the high cadmium ratios (79–55).

This technique has been applied for similar problems: BOCK-WERTHMANN AND SHULZE[4] analyzed aluminium samples for sodium; in our laboratories traces of manganese and chromium were determined in iron matrices[5], as well as manganese and vanadium in cobalt and chromium samples respectively[6]. However, for the determination of sodium in magnesium (as well as in aluminium), the duplicate-irradiation method fails in several cases because of its poor sensitivity. For the usual irradiation positions of the RS 1 reactor, for instance, an approximate sensitivity of 40 μg of sodium can be achieved, if 10% of the spurious contribution is taken as the minimum count that can be measured with a sufficient accuracy.

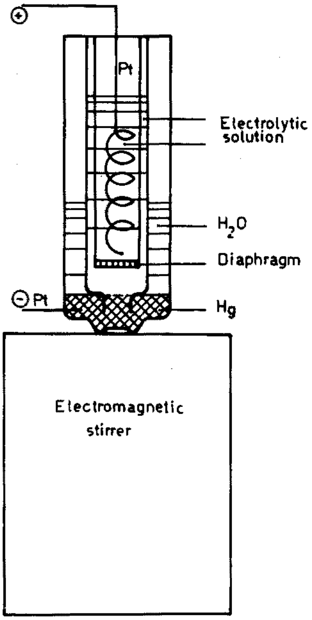
Irradiations in the graphite-thermalized fluxes of the reactor thermal column can be useful when fast-neutron activation must be avoided. This method was used, for instance, in the determination of manganese traces in iron[5], sodium in aluminium, and copper in zinc samples[6]. In the case of the RS 1 reactor a thermal-to-fast flux ratio higher than $3 \cdot 10^3$ was measured, so that no appreciable fast-neutron interference could be expected. However, the available thermal flux in the column is low ($5 \cdot 10^8$ n/cm^2/sec), and prolonged irradiations of large samples must be carried out to attain a satisfactory activation (a sensitivity of about 3 μg Na for saturation irradiation).

PRELIMINARY SEPARATION METHOD

The problem set by a preliminary separation of sodium traces from the bulk of the magnesium matrix is somewhat difficult, owing to the probable occurrence of sodium contaminations. Manipulations must be kept to a minimum, and the reagents and materials must be as sodium-free as possible, in order to reduce the blank correction. Moreover, a quantitative sodium recovery and a sufficient decontamination from magnesium is required.

An electrochemical method was found to be adequate. The method is basically that proposed by CHEMLA AND PAULY[7] who separated carrier-free sodium-22 from a cyclotron-irradiated magnesium target (0.2 g) dissolved in hydrochloric acid, by a 10-h electrolysis; the ^{22}Na activity was recovered by electrodeposition on a mercury cathode and simultaneous amalgam decomposition by water outside the cell. Some improvements were made, mainly by the use of a sintered-glass diaphragm in order to prevent any interference from the evolved chlorine on the mercury surface. By using the glass cell shown in Fig. 1, larger magnesium samples can be processed in shorter times: almost quantitative recoveries of sodium traces in water were obtained for 4-h electrolysis on 0.5-g samples of magnesium (93 ± 5 %, for 20 experiments).

Several experiments were carried out in order to establish the optimal conditions for separation by employing carrier-free sodium-22 and pure magnesium to simulate the matrix. Since hydrochloric acid is first electrolyzed, the minimum amount of acid should be used for the dissolution of the matrix (about 3.6 ml of concentrated hydrochloric acid for 0.5-g Mg), in order to reduce the overall procedure time. In the 30-ml electrolytic solution some citric acid must be present to prevent hydroxide precipitation; a citric acid concentration of 11–12% (w/v) was found to be suitable for 0.5-g samples. When more diluted citric acid solutions were used, precipitation occurred in the cathode compartment (due to the increase in the pH value near the cathode), which lowered the deposition rate of sodium; higher citric acid concentrations reduced the deposition rate by buffering the solution at low pH values. In Fig. 2 a typical sodium electrodeposition experiment is illustrated, for standard conditions (0.5 g Mg, 3.6 ml HCl, 3.5 g citric acid, 30 ml of solution).



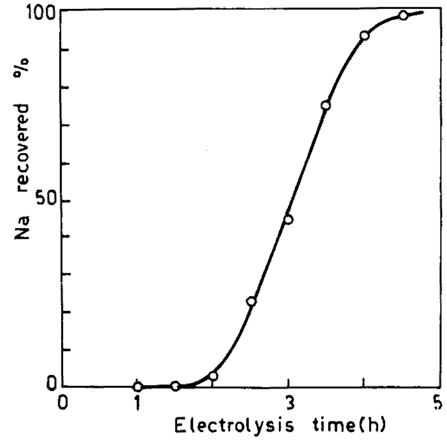


Fig. 1. Electrolysis cell.

Fig. 2. Recovery rate of traces of sodium into water.

For amounts of magnesium less than 0.5 g, the concentrations of both hydrochloric acid and citric acid could be reduced, and the electrolysis time needed for complete separation of sodium was shorter (3 h for 0.2 g Mg).

The electrolysis was carried out by applying a 30-V voltage, resulting in an initial current of about 400 mA; when chlorine had been completely evolved, the current fell to lower values (200–250 mA).

Quite satisfactory decontamination factors for the magnesium matrix were achieved, as tested by means of a number of independent measurements ($\geqslant 1.5 \cdot 10^3$), employing activation analysis for magnesium on aliquots of the recovered aqueous solution. Activation methods were also used for the determination of the sodium content of materials and reagents in order to check the potential sodium contamination sources. No particular difficulty was encountered in these analyses. In both cases direct γ-spectrometry measurements were carried out. Decay measurements were performed in order to resolve the 9.45-min ^{27}Mg activity from the longer-lived ^{24}Na and ^{22}Na (used as yield monitor); for determination of sodium the 2.76-MeV photopeak of ^{24}Na was measured to avoid interferences from the added carrier-free ^{22}Na tracer. In the case of samples of hydrochloric acid, ^{24}Na was measured after some hours to allow the decay of 37.5-min ^{38}Cl. The sodium contribution from the glass cell was evaluated by analysing the recovered solution after 4-h electrolysis of diluted solutions of hydrochloric acid, whose sodium content had been previously determined.

Table II shows the decontamination factors of magnesium, and Table III the sodium contributions from the selected reagents and from the cell. The total blank correction was found to be about 14 μg of sodium for the standard conditions; since the contribution from the reagents was sufficiently low (6 μg), no attempt was made to purify the reagents further.

TABLE II

DECONTAMINATION FROM MAGNESIUM MATRIX

Run	*Electrolysis time (h)*	*Decontamination factor $\cdot 10^3$*
1	3	1.8
2	3	1.4
3	4	4.3
4	4	3.7
5	4.5	3.3
6	4.5	5.0
7	6	4.0

TABLE III

EVALUATION OF SODIUM FOR BLANK CORRECTION[a]

Contamination source	*Na (μg)*	*No. of independent measurements*
H_2O, deionized (40 ml[b])	0.8 ± 0.00	2
HCl, reagent grade (3.6 ml)	2.1 ± 0.1	4
Citric acid, reagent grade (3.5 g)	3.1 ± 0.3	5
Glass cell	7.7 ± 1.3	4
Total contribution	13.7 ± 1.3	—

[a] For standard conditions, suitable for 0.5-g Mg samples.
[b] Both electrolytic solution and recovery water are taken into account.

As other trace impurities which may be present in magnesium samples (such as Cu, Mn and Zn) were found to be partially recovered into the water together with the sodium traces during the electrolysis procedure, a further purification step was necessary after the activation. Two simple and fast decontamination methods were therefore developed. The former is based on the solvent-extraction of the interfering activities from the irradiated aqueous solution adjusted to pH 7, with a solution of 1% oxine and 0.05% dithizone in chloroform (two 2-min extractions, 1:1 volume ratio). The second method consists of an anion-exchange procedure, after adjustment of the solution to pH 8 with dilute ammonia and addition of EDTA to give a 0.5% (w/v) solution, on a Dowex 1-X10 column (100–200 mesh, 5 × 50 mm) at an elution rate of about 0.2 ml/min. The contaminating activities are fixed on the resin, while sodium is completely washed out from the column. Tracer experiments with ^{54}Mn, ^{64}Cu and ^{65}Zn showed that suitable decontamination factors were obtained by both methods (Mn 230 and 85, Cu 165 and 80, Zn 55 and 50, for the solvent-extraction and the ion-exchange procedure respectively).

The destructive method could also be applied to the determination of sodium in aluminium matrices (about 300 p.p.m. Na simulated for irradiation in the pneumatic facility): in this case, smaller samples must be treated, and precipitation occurs during the electrolysis, lowering the separation rate (probably owing to the amphoteric nature of aluminium). When a 0.25-g sample of aluminium (1.5-g citric acid) is treated, a 5-h electrolysis leads to a quantitative recovery and the decontamination factors for aluminium are of the same order as those for magnesium.

DETERMINATION OF SODIUM IN MAGNESIUM MATRICES

Two types of magnesium were analyzed by both the non-destructive and destructive method (99.5% reagent-grade, C. Erba; 99.99% spectrographic-grade, Johnson & Matthey). All the ^{24}Na measurements were carried out with a 200-channel pulse-analyzer (Laben C-31) equipped with a 3 × 3″ NaI (Tl) detector, well-type (Harshaw).

In the case of thermal-column activation, 3–5 g samples were irradiated for 50 h together with sodium standards. For the duplicate-irradiation method only the less pure magnesium type was tested; 0.2-g samples were irradiated, both bare and Cd-covered, for 5 min in the pneumatic facility of the reactor (thermal flux $5 \cdot 10^{12}$, fast flux $1.5 \cdot 10^{12}$ n/cm^2/sec).

TABLE IV

DETERMINATION OF SODIUM IN MAGNESIUM SAMPLES

Mg type	*Na concentration (p.p.m.)*		
	Duplicate irradiation	*Thermal column irradiation*	*Preliminary separation*
Mg 99.5%	77 111 73 } 87	93 107 } 100	108 90 108 88 96 } 98
Mg 99.99%	—	44 42 } 43	44 34 47 } 42

For the preliminary separation method, 0.5-g samples were easily dissolved in 3.6 ml of concentrated hydrochloric acid, the solution was diluted to 30 ml with 13% citric acid, some carrier-free ^{22}Na was added as yield monitor, and the electrolysis was carried out for 4 h; 10-ml aliquots of the recovered water were then irradiated during 10 min in the pneumatic facility. No further radiochemical purification was necessary in the cases considered.

Table IV shows the analytical results obtained.

CONCLUSIONS

The problem of determining traces of sodium in magnesium samples can be advantageously resolved by employing a separation method before the activation. Electrodeposition on a mercury cathode proved to be quite adequate as far as the chemical yields, the decontamination from the matrix and the simplicity of the procedure were concerned. The blank correction, unusual for normal activation methods, sets a limitation to the analytical sensitivity, but improvements can be expected if other materials than glass are used for the construction of the electrolysis cell (*e.g.* pure quartz) and higher-purity reagents are used. The reproducibility of the method was sufficiently good (~15%), and the agreement with the results of comparative methods quite satisfactory. In Table V the characteristics of the destructive method, as well as those of non-destructive techniques, are collected for the sake of comparison.

TABLE V

CHARACTERISTICS OF ACTIVATION METHODS FOR DETERMINATION OF SODIUM IN MAGNESIUM

Method	*Spurious contribution (p.p.m.)*	*Sensitivity (p.p.m.)*	*Overall time (h)*
Duplicate-irradiation (bare and Cd-lined samples)	~400 (matrix activation)	40	0.5
Thermal column irradiation[a]	< 0.5 (matrix activation)	3	90
Preliminary Na separation[b]	26.4 ± 2.6 (blank correction)	5	4.5

[a] 1-g sample.
[b] 0.5-g sample.

SUMMARY

When sodium traces are determined in magnesium matrices by neutron activation analysis, the reaction ^{24}Mg(n,p)^{24}Na interferes by simulating spurious sodium concentrations (about 400–500 p.p.m. for usual irradiation positions in the RS 1 water-pool reactor). A preliminary separation of the sodium traces from the bulk of the matrix by electrodeposition on a mercury cathode and recovery in water by amalgam decomposition, prevented the fast-neutron effects. Electrolysis for 4 h gave almost quantitative recovery of sodium (93 ± 5%) and satisfactory decontamination factors for magnesium (1.5 to $5 \cdot 10^3$). The method is limited by the blank correction (14 μg Na with a glass electrolysis cell). Some results for magnesium samples with both destructive and non-destructive techniques are reported.

RÉSUMÉ

Lors du dosage de traces de sodium dans des matrices en magnésium par activation au moyen de neutrons, la réaction $^{24}Mg(n,p)^{24}Na$ gêne. Une séparation préliminaire de traces de sodium de la masse de la matrice par électrodéposition permet d'éviter l'influence des neutrons rapides. Une électrolyse de 4 heures donne des rendements presque quantitatifs en sodium (93±5%). Quelques résultats sont donnés pour des échantillons de magnésium avec des techniques soit destructives, soit non-destructives.

ZUSAMMENFASSUNG

Bei der Bestimmung von Natriumspuren in Magnesium mit der Neutronenaktivierungsanalyse stört die Reaktion $^{24}Mg(n,p)^{24}Na$. Durch vorhergehende vierstündige Abscheidung des Natriums an einer Quecksilberkathode konnten 93±5% des Natriums vom Magnesium abgetrennt werden und sowohl der Einfluss schneller Neutronen verhindert als auch ein Dekontaminationsfaktor für das Magneisum von $1.5–5 \cdot 10^3$ erzielt werden. Die Methode wird durch die Blindwerte begrenzt. Über einige Ergebnisse für Magnesiumproben, sowohl mit der zerstörenden als auch nichtzerstörenden Technik wird berichtet.

REFERENCES

1 See, *e.g.*, *Report EUR 1886.f*, 1964.
2 J. MOTEFF, *Nucleonics*, 20 (12) (1962) 56.
3 J. C. ROY AND J. J. HOWTON, *Canad. Rep. AECL 1181*, 1960.
4 W. BOCK-WERTHMANN AND W. SHULZE, *Proc. 1961 Intern. Conf. Modern Trends in Activation Analysis, College Station, Texas*, p. 145.
5 R. MALVANO AND P. GROSSO, *Anal. Chim. Acta*, 34 (1966) 253.
6 R. MALVANO, unpublished data.
7 M. CHEMLA AND J. PAULY, *Bull. Soc. Chim. France*, (1953) 432.

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A SPECTRUM STRIPPING METHOD FOR THE COMPUTER-COUPLED ACTIVATION ANALYSIS OF UNKNOWN SAMPLES BY γ-RAY SPECTROMETRY

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Rapid instrumental activation analysis of a large number of unknown samples by γ-ray spectrometry can be practical only if reliable data reduction techniques are available. Measurement of the elemental concentration in an unknown activated sample consists of two parts: (*1*) computer analysis of the multicomponent γ-ray spectrum of the activated sample using the library spectra of the components and one of the several methods available[1-5]; (*2*) determination of the weight of the elements present in the sample using the weights of the elements chosen as comparators and the parameters selected for activation, cooling and counting. The first part, namely the measurement of the spectral contributions from each of the components of the mixed spectrum, is the more difficult to achieve.

Of the several methods suggested by many authors, the least-squares curve-fitting technique is the one which is more often used[1,2]. It has been shown that if certain assumptions are valid, the least-squares analysis of the γ-ray spectra will yield results which are quite comparable with the actual values, especially in the case of synthetic mixtures. The least-squares method, however, often breaks down because of gain and base-line shifts, the presence of unsuspected isotopes or the absence of expected ones when a large number of samples of completely unknown nature are analyzed by γ-ray spectrometry. It is not uncommon that gain shifts occur when a large number of samples with varying levels of activities are counted with a γ-ray spectrometer and at least a few of them including the vials contain unsuspected isotopes. EMERY *et al.*[6] have recently reviewed both the linear and non-linear least-squares methods and discussed some of the problems associated with these methods.

Several spectrum stripping procedures[7-10] have been used in the past for the analysis of multicomponent spectra but with varying degrees of success. In most of these cases, however, the stringent conditions for an ideal stripping have not always been met. For instance, ANDERS AND BEAMER[7] have reported that a "shadow peak" results when a major photopeak is peeled off from a complex spectrum if the spectrum is recorded with considerable gain shifts. Equally true is the fact that unscrambling of the complex spectrum is likely to be affected by large statistical scatter in the sample and the library data which are neither smoothed nor weighted properly. The present method, although based on the "peeling technique" used by previous authors, incorporates several provisions to correct for gain shifts, counting statistics, background etc. which could yield better results.

ANALYTICAL METHODS

Spectrum stripping procedures

The following procedures are employed for the computer analysis of the multicomponent γ-ray spectrum of the activated sample.

(*1*) For any given counting system, obtain pure spectra of a number of radionuclides (library spectra) which are of interest. Natural background should also be taken for the same length of time as these radionuclides were counted.

(*2*) The samples and the standards (with known weights) of the elements being measured are activated for a known time and counted in the same counting system for any t_{live}. A natural background spectrum of the same length of time is also taken.

(*3*) Each of the spectra, including the natural background spectrum, is then smoothed by fitting a third order polynomial through a series of 5 data points using the method of least squares[8,11].

(*4*) Each spectrum is then statistically weighted using a weighting factor, W_i, based on the percent of standard deviation for each channel count, as given by the relation:

$$W_i = 1 + 1/[(\sigma_i/C_i)100]^2 \tag{1}$$

where C_i is the counts in channel i and $\sigma_i = \sqrt{C_i}$.

(*5*) The respective natural background is then subtracted from each of the above scaled spectra.

(*6*) The highest-energy peak in the composite spectrum is identified and an identical peak of the library spectrum is aligned with this peak by a peak shifting program as described later. From the shifted standard spectrum C_i/C_p ratios are measured, where C_i is the counts in the ith channel and C_p is that in the peak channel. From these ratios and the counts in the respective peak channel of the sample spectrum, a γ-ray spectrum of that component is generated and then subtracted from the composite spectrum. This generation and successive subtraction of the spectra is continued until the characteristic spectrum of the desired element is peeled off.

Determination of the weight of the element in the sample

The γ-ray spectrum of the activated standard of the element is smoothed, scaled up by multiplication with the weighting factor and corrected for the background as described above. If, by visual examination, an impurity, either from the sample container or due to the presence of other contaminants such as ^{41}Ar, was observed in this spectrum, a pure spectrum of the standard is simulated from its library after proper correction as described before. The spectrum characteristic of the desired element in the sample, after peeling, is then compared with the pure spectrum of the respective standard, minimizing the difference between the two by the following least-squares formula for a single component:

$$\Sigma_i (Y_{ik} - \beta_k x_{ik})\, x_{ik} = 0 \tag{2}$$

where Y_{ik} represents the counts in the ith channel of the standard, x_{ik} those due to element k in the sample and β_k is the proportion of the standard spectrum of the element k in the sample. From this proportion, the weight of the element in the standard and the parameters used for activation and counting, the weight of the element in the sample is computed.

Outline of the computer program

The complete computer program used for the activation analysis of the unknown sample by the spectrum stripping method is described elsewhere[12]. The main program, coded in Fortran IV for an IBM 7094 computer, consists of a group of subroutines which may be called in the proper sequence to perform the various operations such as smoothing, weighting, spectrum stripping, etc., necessary for the determination of the elemental concentration in the sample. Only the "Subroutine SIM" which is used to simulate the pure spectrum of each component is described in this section.

In generating the pure spectrum, if the actual peak channels of the sample spectrum are not the same as those of the library spectra, it is necessary to correct for the gain drift by shifting, one at a time, each library spectrum in such a way that the prominent photopeaks of the desired element in the library and the sample are aligned. This is accomplished by forming an array (A) of pseudo channel numbers of the standard spectrum using the relation:

$$A_i = \frac{P_u}{P_s} \cdot i \tag{3}$$

where P_u is the desired peak channel in the sample spectrum, P_s the respective peak channel and i the channel number of the library spectrum. The assumptions inherent in this procedure are: (*1*) there is no relative drift in the first channels of the library and sample spectra, and (*2*) the drift relationship is linear. With the computed channel numbers A_i, an array of counts Y_i is formed by assuming a linear relationship between the counts for two adjacent pseudo channel numbers in the array A. Since the array A is in the form of fractional channel numbers, a unit channel number k is defined as $A_i < k < A_{i+1}$ and the number of counts Y_k for channel k is obtained from the relation:

$$Y_k = C_i + \frac{(k - A_i)(C_{i+1} - C_i)}{(A_{i+1} - A_i)} \tag{4}$$

where C_i and C_{i+1} represent the counts for the pseudo channels A_i and A_{i+1}, respectively.

RESULTS

Analysis of synthetic mixtures

Mixtures with known amounts of the components were prepared and irradiated in the Texas A &M Research Reactor together with the pure standards, for 1 h. The activated mixtures and the standards were counted, after sufficient cooling, with a dual 3″ × 3″ NaI(Tl) crystal assembly connected to an RIDL 400-channel pulse-height analyzer. The spectra of all the standards were checked and in a few cases the impure spectra were stripped of the impurity as described above. One spectrum of each standard was used as a library spectrum and the other as a comparator standard for weight determination. Figure 1 illustrates how the spectrum of the desired component is obtained from the mixed spectra by successive stripping. It is interesting to see from this Fig. that the residual bremsstrahlung spectrum from the mixture overlaps the pure spectrum of phosphorus which is a β-emitter. The results of the analysis of the synthetic mixtures using the stripping method are given in Table I and compared with the values obtained by the least-squares method. Except in the case of potassium and mercury there is good agreement between the values obtained using both methods. The large difference between the results for potassium obtained from least squares and those from the stripping method is probably due to an error in the weight of potassium in the standard. However, this does not affect the basic method, because the results of potassium analysis of replicate hay samples seem to be consistent within experimental errors (see Table II). It is obvious from Table I that the stripping method apparently yields better results for the analysis of mercury, which produces a weak γ-emitter upon activation with thermal neutrons, than the least-squares method.

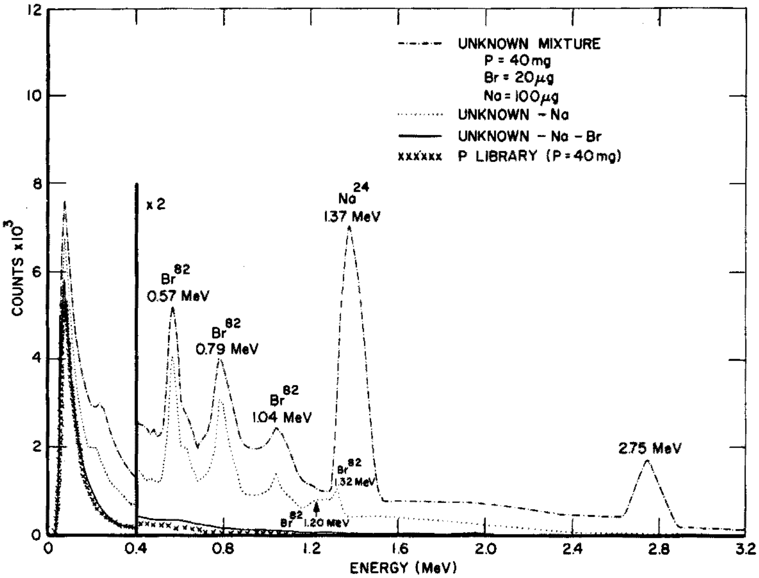

Fig. 1. Effect of bremsstrahlung on the activation analysis of unknown samples by γ-ray spectrometry.

Analysis of unknown samples

One of the problems encountered in the activation analysis of bromine pesticide residues in plant materials[13] was that the bromine content obtained for some of the samples using the AA-6 least-squares program[1] was found to be larger for the earlier countings than the values obtained later in the decay. This behavior was not, however, reflected in the values obtained for sodium and potassium. Since the amount of bromine in these samples was in the range of 5–20 p.p.m., it is probable that vial impurities such as sodium and copper which produce relatively shorter-lived activities than ^{82}Br, can make the bromine values appear larger in the early

TABLE I

COMPARISON OF THE RESULTS OBTAINED FOR THE ANALYSIS OF SYNTHETIC MIXTURES USING THE LEAST-SQUARES PROCEDURE AND THE STRIPPING METHOD

Components of the mixture	*Known weights of the components (mg)*	*Results obtained using the least-squares method*[a] *(mg)*	*Results obtained using the stripping method (mg)*
P	40.00	—	—
Na	0.100	0.0934	0.1053
Br	0.020	0.0193	0.0203
P	40.00	—	—
Na	0.050	0.0487	0.0489
Br	0.010	0 0097	0 0096
Na	0.100	0.0954	0.1004
K	1.496	1.5601	1.9336
Br	0.0020	0.00195	0.00223
Na	0.100	0.0973	0.0979
K	1.496	1.5745	2.0311
Br	0.0020	0.00194	0.00253
Na	0.100	0.1031	0.109
K	1.496	1.3035	1.5260
Cr	0.500	0.4894	0.5483
Na	0.100	0.0947	0.1019
K	1.496	1.4146	1.660
Hg	0.010	0.0056	0.0107

[a] The spectral data for channels 25–200 were used for the comparison of mass in all cases except for Cr and Hg in which cases data for channels 15–200 and 2–200, respectively, were used.

TABLE II

COMPARISON OF THE RESULTS OBTAINED FOR THE ANALYSIS OF REPLICATE HAY SAMPLES USING THE LEAST-SQUARES PROCEDURES AND THE STRIPPING METHOD[a]

Sample number	*Weight of sample (g)*	*Elements measured*					
		Sodium (µg/g)		*Potassium (mg/g)*		*Bromine (µg/g)*	
		Least squares	*Stripping method*	*Least squares*	*Stripping method*	*Least squares*	*Stripping method*
1	0.3651	366.5	386.8	19.51	15.24	15.15	14.27
2	0.4057	322.4	345.8	19.06	15.91	13.97	11.96
3	0.3693	334.5	359.2	19.14	15.61	14.66	13.15
4	0.3840	275.1	298.1	20.60	18.75	16.00	17.50
5	0.3636	319.0	341.4	17.63	15.84	15.00	14.30
6	0.3726	277.4	307.1	18.45	16.40	15.20	15.00
7	0.3642	312.5	361.2	18.05	16.22	15.30	13.90
	Average	315.3±32	342.8±34	18.92±1	16.28±1.2	15.04±0.6	14.30±0.9

[a] In all cases the spectral data for channels 25–200 were used for the computation of the weights.

runs when these impurities are not properly accounted for in the least-squares method. It should be pointed out that the 0.51-MeV peak of ^{64}Cu can hardly be distinguished from the 0.55-MeV γ-ray peak of ^{82}Br for a visual identification of the traces of copper in the sample. Since the 0.78-MeV peak of ^{82}Br may be used to simulate its γ-ray spectrum in the successive stripping procedure, any contribution from ^{64}Cu to the measurement of ^{82}Br activity may be avoided.

Seven replicates of one of the hay samples received from the U.S.D.A., Gulfport, were irradiated, together with duplicates of sodium, potassium and bromine standards, in the reactor for about 8 h at a neutron flux of about 10^{11} n cm^{-2} sec^{-1}. These samples and the standards were counted, after sufficient cooling, in the same counting system as described before. Analysis of the data was performed using both the least-squares and the spectrum stripping computer programs. Figure 2 shows the residual spectrum after successive stripping of each of the components, including that of the bromine standard. It appears from this Fig. that there are some impurities which can hardly be identified in the composite spectrum of the sample. The results of the analyses of these samples for sodium, potassium and bromine obtained using the spectrum stripping method are compared in Table II with the respective values from the least-squares program.

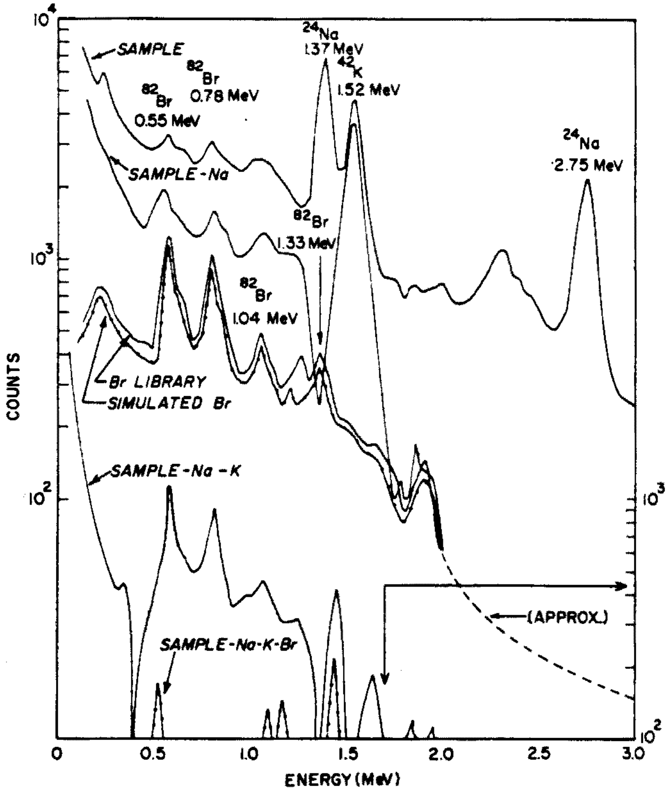

Fig. 2. The analysis of the γ-ray spectrum of an activated unknown sample for bromine using the stripping method.

DISCUSSION

It can be seen from Tables I and II that the spectrum stripping method is as good as the least-squares method in ideal cases. However, the former seems to be better than the latter if the sample contains unobservable impurities for which no library data can be furnished for the least-squares analysis. One need not even use the entire spectrum for comparison, but instead measure the area under the prominent photopeak of the stripped spectrum much more precisely than from the complex spectrum and compare this with the peak area of the standard (see Fig. 2). Furthermore, if the activation product of the element of interest happens to be a weak γ-emitter ($E_\gamma < 0.25$ MeV) the effect of bremsstrahlung produced by the β-emitters in the sample can be considerably reduced on the analysis of this element by resorting to the spectrum stripping method. An added advantage of this method is that there is no need for activating and counting the standards of the unwanted impurities along with the sample if a catalogue of the library spectra is available. The spectrum stripping method will be particularly useful for the analysis of an element in the "limit-of-sensitivity" range in the presence of matrix interference. The activation analysis of bromine pesticides in plant materials shows that the stripping method yields results with better precision than the least squares, especially in the "limit-of-sensitivity" range, and compares favorably with those obtained using other instrumental techniques. These results will be reported in a later communication.

The arbitrarily chosen weighting factor in the present method should be mentioned. The weighting factor generally used in the least-squares method[1-3] corrects for the statistical fluctuations in the counting of the sample only and not of the standards. The weighting factor which is more often used, is a function of the channel counts and is represented by $W_i = 1/C_i$ where C_i is the counts in the channel i. Thus W_i used for the background region, for instance when $C_i = 100$, will be 100 times higher than W_i for the peak region registering 10,000 counts per channel. Also it is not quite conceivable that no statistical fluctuations in the counting of the standards can be expected when the activity levels of the standards are lower than that of the sample. The weighting factor chosen in the present method gives less weight to the background region than to the peak of each spectrum which gives more importance to the analysis. Besides, the same weighting factor is used to take into account the statistical fluctuations in the counting of the samples and the libraries alike.

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SUMMARY

A spectrum stripping method for the computer-coupled activation analysis of unknown samples using γ-ray spectrometry is discussed. Before the unscrambling of the γ-ray is performed using standard spectra of the components, each spectrum is smoothed, statistically weighted and corrected for background. The photopeaks of the standard spectra are then aligned with the respective peaks of the sample spectrum, one at a time after correcting for gain drift if necessary, and the undesired components are stripped out. After successive subtraction, the characteristic spectrum of the desired element is compared with that of the standard to determine its weight. The results obtained using the present method are as good as those obtained from least-squares analysis in ideal cases, but appear to be better when assumptions inherent in the least-squares method are no longer valid.

RÉSUMÉ

On décrit une méthode ("spectrum stripping") par spectrométrie gamma pour l'analyse d'échantillons inconnus par activation. Après soustraction successive, le spectre caractéristique de l'élément est comparé à celui d'un étalon pour déterminer son poids. Les résultats sont aussi bons que ceux obtenus par la méthode des moindres carrés.

ZUSAMMENFASSUNG

Es wird eine aktivierungsanalytische Methode diskutiert, bei der unbekannte Proben unter Verwendung eines γ-Spektrometers, das mit einem Rechner gekoppelt ist, analysiert werden. Dazu werden vorher γ-Spektren der einzelnen Bestandteile näher untersucht und dann mit dem Spektrum der Probe verglichen. Durch aufeinanderfolgende Subtraktionen der Spektren einzelner Elemente von denen der Probe mittels des Rechners, lässt sich der Gehalt bestimmen. Das Verfahren wird mit der Methode der letzten Quadrate verglichen.

REFERENCES

1 R. E. Wainerdi, M. P. Menon and L. E. Fite, *Investigations in Automated Activation Analysis*, Report TEES 2671-4, TID-4500, January, 1965, Available from the Clearing House for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Dept. of Commerce, Springfield, Va.
2 L. Salmon, *Application of Computers to Nuclear and Radiochemistry*, Nuclear Science Series, National Academy of Sciences, NAS-NS-3107, National Research Council, 1962, edited by G. D. O'Kelley, p. 165.
3 J. I. Trombka, Ref. 2, p. 183.
4 L. H. Smith, *Ph.D. Dissertation*, Texas A&M University, August, 1964.
5 M. Putnam, R. G. Helmer, D. M. Cripson and R. L. Heath, *Report IDO-17016*, August, 1965.
6 J. F. Emery, F. F. Dyer, T. Alexander and E. Schonfeld, *Oak Ridge Nat. Lab. Rept.*, ORNL-P-1127, 1964.
7 O. U. Anders and W. H. Beamer, *Anal. Chem.*, 33 (1961) 226.
8 D. Gibbons, L. E. Fite and R. E. Wainerdi, *Report TID-7629*, Texas Agricultural and Mechanical College, College Station, Texas, 1962, p. 221.
9 N. E. Scofield, *Application of Computers to Nuclear and Radiochemistry*, Nuclear Science Series, National Academy of Sciences, NAS-NS-3107, National Research Council, 1962, edited by G. D. O'Kelley, p. 108.
10 W. R. Burrus and D. Bogert, Ref. 9, p. 127.
11 H. P. Yule, *Anal. Chem.*, 38 (1966) 103.
12 Activation Analysis Research Laboratory, Texas A&M University, College Station, Texas, Investigations in Automated Activation Analysis, *Report TEES 2671-5, TID-4500*, August 31, 1966.
13 M. P. Menon and R. E. Wainerdi, *The Automated Activation Analysis of Plant Materials for Bromine Pesticides*, Proc. 11th Pacific Science Congr., Tokyo, Japan, 6 (Aug. 1966) 29.

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DIE QUANTITATIVE BESTIMMUNG DER ALKALIIONEN DURCH OSZILLOMETRISCH INDIZIERTE FÄLLUNGSTITRATION IN NICHTWÄSSRIGEN LÖSUNGEN

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(Eingegangen den 5. Dezember 1966)

Die im Vergleich zu Wasser oft völlig veränderten Löslichkeitsverhältnisse vieler Salze in organischen Medien lassen sich zu Fällungsreaktionen ausnutzen, die in wässriger Lösung nicht denkbar sind. So sind z.B. die Löslichkeiten der Chloride der Alkalimetalle Natrium, Kalium, Rubidium und Cäsium in Azeton[1] und auch in Azetonitril[2] sehr gering (siehe Tabelle I). Das ermöglicht die quantitative Ausführung der Reaktion:

$$Me^+ + Cl^- = MeCl$$

Es wurde versucht, diese Umsetzung zur Grundlage einer Fällungstitration der Alkalimetalle zu machen.

TABELLE I

LÖSLICHKEITEN DER ALKALICHLORIDE

in Azeton	*Gewichts %*	*M*	*(M)²*
LiCl	0.9	*0.176	$3\cdot10^{-2}$
NaCl	$4\cdot10^{-5}$	*$0.5\cdot10^{-5}$	$0.3\cdot10^{-10}$
KCl	$8\cdot10^{-5}$	*$0.9\cdot10^{-5}$	$0.8\cdot10^{-10}$
RbCl	$2\cdot10^{-4}$	*$1.4\cdot10^{-5}$	$2\cdot10^{-10}$
CsCl	$4\cdot10^{-4}$	*$1.9\cdot10^{-5}$	$3.6\cdot10^{-10}$
in Azetonitril			
LiCl	*$1.5\cdot10^{-1}$	$2.8\cdot10^{-2}$	$8\cdot10^{-4}$
NaCl	*$1.5\cdot10^{-4}$	$2\cdot10^{-5}$	$4\cdot10^{-10}$
KCl	*$2.4\cdot10^{-3}$	$3\cdot10^{-4}$	$7\cdot10^{-8}$
RbCl	*$3.4\cdot10^{-3}$	$2\cdot10^{-4}$	$5\cdot10^{-8}$
CsCl	*$8\cdot10^{-3}$	$4\cdot10^{-4}$	$14\cdot10^{-8}$

* Literaturwerte, die anderen wurden daraus berechnet.

Zur Indikation des Endpunktes der Reaktion ist die Leitfähigkeitsmessung geeignet. Ihre Anwendbarkeit ist allerdings an das Auftreten einer elektrolytischen Dissoziation gebunden. Zur Leitfähigkeitsbestimmung können konduktometrische oder oszillometrische Verfahren benutzt werden. Ein Vorzug der oszillometrischen Messung liegt darin, dass die Abscheidung des Niederschlages die Untersuchung nicht stört, weil (z.B. bei Anwendung einer kapazitiven Zelle) die Elektroden ausserhalb des Becherglases, das die Lösung enthält, angeordnet sind[3]. Weiter besitzt die Oszillometrie den Vorteil, dass die Elektroden durch das Lösungsmittel und durch

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eventuelle Elektrolyseprodukte nicht angegriffen werden können[4]. Schliesslich wird bei der oszillometrischen Titration die Änderung der Messgrösse über den gesamten Leitfähigkeitsbereich mit Abnahme der DK des Lösungsmittels grösser. Werden also gleiche Leitfähigkeiten in verschiedenen Lösungsmitteln miteinander verglichen, so stellt man fest, dass die Empfindlichkeit der Messanzeige mit abnehmender DK wächst. Der Ausnutzung dieses Zusammenhanges sind allerdings Grenzen gesetzt, da mit abnehmender DK in der Regel auch der Dissoziationsgrad der Elektrolyte sinkt und die erzielbare Empfindlichkeitssteigerung durch eine Leitfähigkeitsminderung häufig eliminiert, wenn nicht sogar übertroffen wird[5]. Die Erfahrung bei den untersuchten Systemen zeigte, dass die Oszillometrie erheblich empfindlicher ansprach als die Konduktometrie.

EXPERIMENTELLER TEIL

Masslösung

Als chloridhaltiges Massreagenz dienten Lösungen von Lithiumchlorid. Wasserfreies Lithiumchlorid wurde in absolutem Äthanol bis fast zur Sättigung (2–3 *M*) aufgelöst. Wenn erforderlich musste diese Stammlösung filtriert werden. Ihr Titer wurde gegen Silbernitrat eingestellt. Durch Verdünnen entweder mit Äthanol oder mit dem jeweiligen Lösungsmittel, in dem die Titration ausgeführt werden sollte, erhielten wir aus ihr Masslösungen geeigneter Konzentration (ungefähr 0.2 *M*). Dabei kann im Falle von Azetonitril oder auch Methyl-iso-butylketon wegen der hier gegenüber Äthanol recht geringen Löslichkeit des Lithiumchlorides eine Trübung auftreten. Sie wurde durch Zugabe von wenig absolutem Äthanol beseitigt. Der geringe Alkoholgehalt der nichtalkoholischen Masslösungen (unter 10%) war ohne Bedeutung, weil keine theoretischen Untersuchungen der Systeme beabsichtigt waren, sondern eine praktische Vorschrift für die Bestimmung der Alkalien erarbeitet werden sollte.

Weitere Reagenzien

Folgende Lösungsmittel kamen zur Anwendung: Absoluter Äthanol, Azetonitril, Azeton, Azetophenon, Cyclohexanon, Methyl-äthylketon (alle von Reanal Budapest) und Methyl-iso-butylketon (Schuchardt, München). Ausserdem benutzten wir die p.A. Salze Natriumjodid, Kaliumjodid, Rubidiumjodid und Kalziumjodid. Aus diesen Jodiden wurden durch Auflösen in Äthanol oder in den genannten Lösungsmitteln ebenfalls Stammlösungen (ungefähr 0.1 *M*) hergestellt und ihr Faktor gegen Silbernitrat ermittelt. Aus den Stammlösungen wurden später die jeweiligen Analysenproben entnommen.

Messinstrumente

Zu den konduktometrischen Messungen wurde ein Konduktometer (hergestellt von Radelkis, Budapest) mit direkter Anzeige benutzt. Die Messelektrode bestand aus einem Dreielektrodensystem, bei dem die beiden äusseren Elektroden geerdet waren.

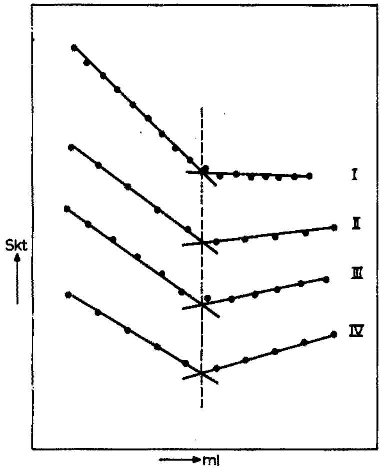
Bei den oszillometrischen Messungen verwendeten wir den Oszillotitrator (System E. PUNGOR, hergestellt von Radelkis, Budapest) und eine kapazitive Messzelle mit einem 100 ml Becherglas. Es wurde meist bei der Maximalempfindlichkeit des

Oszillotitrators gearbeitet. Die Reagenzzugabe erfolgte in Stufen mit einer von Hand geregelten Bürette unter ständigem Rühren der vorgelegten Lösung.

ERGEBNISSE

Die Einzelbestimmung der Alkalimetalle

Bild 1 zeigt Ergebnisse, die bei der Titration von Natriumjodid in Azeton mit Lithiumchlorid in Äthanol erhalten wurden. Auf der Ordinate sind Skalenteile Instrumentenausschlag abgetragen, auf der Abszisse ml Reagenzzugabe. Dabei ist allerdings zur besseren Übersicht der Abszissenmasstab entsprechend den veränderten Natriumjodidkonzentrationen so variiert, dass gleiche Lage der Äquivalenzpunkte (gestrichelte Linie) erhalten wurde.



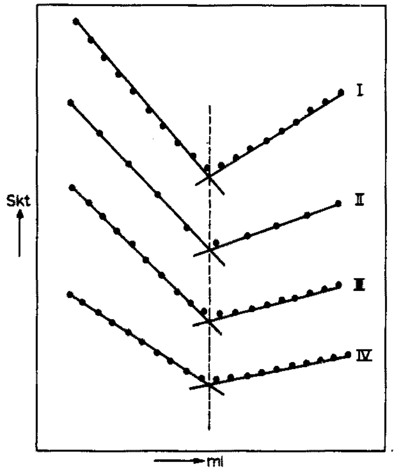


Bild 1. Titration von NaI in 100 ml Azeton mit LiCl in Äthanol (0.2550 *N*). I, 0.00236 Mol NaI; II, 0.00118 Mol NaI; III, 0.00059 Mol NaI; IV, 0.000236 Mol NaI.

Bild 2. Titration von NaI in 100 ml Azetophenon mit LiCl in Äthanol (0.2550 *N*). I, 0.001180 Mol NaI; II, 0.000590 Mol NaI; III, 0.000470 Mol NaI; IV, 0.000236 Mol NaI.

Bereits nach wenigen Tropfen Masslösung trübt sich die vorgelegte Lösung durch den ausfallenden Niederschlag. Die Einstellung des Endwertes der Anzeige auf dem Instrument erfolgt nach einigen Sekunden und scheint im Wesentlichen durch die Rührgeschwindigkeit bestimmt zu sein. Eine Serie von 17 Titrationen mit variierten Natriumjodidmengen in der Vorlage ($236 \cdot 10^{-5}$ bis $236 \cdot 10^{-6}$ Mol) ermöglichte die Errechnung des mittleren (quadratischen) Fehlers zu 0.6%. Der in der Messerie aufgetretene Maximalfehler betrug 1%.

Die Titration der schwereren Alkaliionen erfolgt analog, liefert jedoch entsprechend den grösseren Ionenbeweglichkeiten im ersten Ast der Diagramme steileres Absinken der Anzeige. Die betreffenden Diagramme werden wegen der Geringfügigkeit der Unterschiede nicht abgebildet.

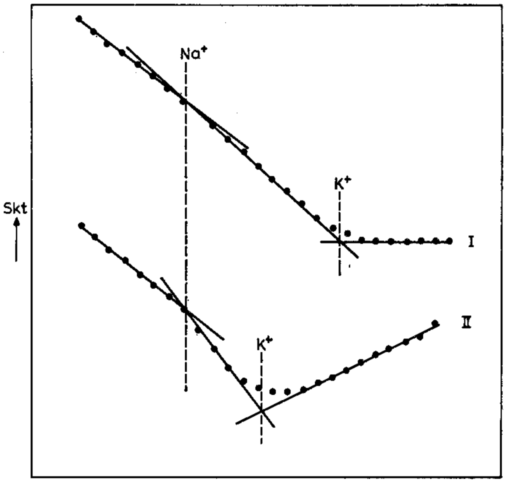
Unter analogen Bedingungen wurden Titrationsserien in Methyl-äthylketon, Methyl-iso-butylketon, Cyclohexanon und Azetophenon durchgeführt. Dabei erhielten wir Ergebnisse, die den am Azeton gewonnenen glichen, wie Bild 2 mit einigen

Beispielen aus einer Serie von 10 Bestimmungen für den Fall des Azetophenons zeigt.

Zu bemerken ist, dass die grössere Viskosität dieser Lösungsmittel die Rührung und die Gleichgewichtseinstellung etwas verlangsamt. Beim Beispiel des Azetophenons wurde sogar eine erhebliche Verzögerung der Niederschlagsbildung beobachtet, was aber ohne merklichen Einfluss auf die Anzeige des Instruments war. Der grosse Vorzug der letzteren Lösungsmittel gegenüber dem Azeton liegt in ihrer geringeren Flüchtigkeit. Als am geeignetsten erwies sich Methyl-iso-butylketon. Es vermag nur 1% Wasser aufzunehmen. So braucht man hier keine Beeinflussung der Resultate durch die Luftfeuchtigkeit zu befürchten. Sie wurde allerdings auch in den anderen Fällen nicht beobachtet. Ein weiterer Vorzug des Methyl-iso-butylketons liegt in seiner leichten Regenerierbarkeit durch Extraktion mit Wasser, Trocknen mit Natriumsulfat und anschliessende Destillation.

Die Bestimmung von Natriumjodid neben Kaliumjodid

Versuche, Natriumjodid und Kaliumjodid in den Ketonen nebeneinander zu titrieren, waren nicht erfolgreich und lieferten nur die Summe beider Komponenten, wie nach Lage der Löslichkeiten (Tabelle I) auch zu erwarten war. Die Diagramme werden deshalb nicht abgebildet. Dagegen liessen die etwas grösseren Differenzen in Azetonitril den Versuch einer selektiven Titration aussichtsreicher erscheinen. Bild 3



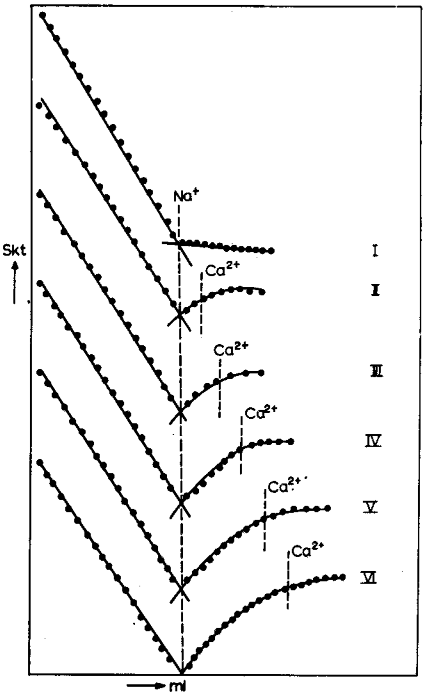


Bild 3. Titration von $NaI + KI$ in 100 ml Azetonitril mit LiCl in Azetonitril (0.2080 *N*). I, 0.0003875 Mol NaI + 0.0005250 Mol KI; II, 0.0003875 Mol NaI + 0.0002625 Mol KI.

Bild 4. Titration von $NaI + CaI_2$ in 100 ml Methyl-iso-butylketon mit LiCl in Methyl-iso-butylketon (0.2573 *N*). I, 0.001180 Mol NaI; II, 0.001180 Mol NaI + 0.000195 Val CaI_2; III, 0.001180 Mol NaI + 0.000370 Val CaI_2; IV, 0.001180 Mol NaI + 0.000585 Val CaI_2; V, 0.001180 Mol NaI + 0.000740 Val CaI_2; VI, 0.001180 Mol NaI + 0.000975 Val CaI_2.

zeigt die erhaltenen Resultate. Allerdings wurden zwei besonders günstige Beispiele ausgewählt. Bei allen anderen Konzentrationen und Mischungsverhältnissen wurde keine brauchbare Übereinstimmung erzielt. Auch waren die Einzelbestimmungen der Alkalien in diesem Medium mit einem grösseren Fehler als in den Ketonen behaftet. Das liegt möglicherweise an einer Mitfällung von Lithiumchlorid, dessen Löslichkeit in Azetonitril relativ gering ist (siehe Tabelle). Deshalb muss die selektive Titration der Alkalimetalle als noch nicht gelungen angesehen werden.

Die Bestimmung der Alkalijodide neben Kalziumjodid

Bild 4 zeigt Titrationsdiagramme aus einer Versuchsserie, die die Bestimmung der Alkalijodide neben Kalziumjodid zum Ziel hatte. Die Fällung wurde in Methyl-iso-butylketon ausgeführt. Lithiumchlorid in Äthanol war hier als Masslösung weniger geeignet als die in dem gezeigten Beispiel zur Anwendung gebrachte Masslösung von Lithiumchlorid in Methyl-iso-butylketon. Unter letzteren Bedingungen ist die Ermittlung des Alkalis innerhalb einer Fehlergrenze von ±1%, also trotz wachsender Mengen Kalziumjodid praktisch ungestört, möglich. Unter den gleichen Bedingungen stören jedoch Bariumionen, da Bariumchlorid neben Alkalichlorid ausgefällt wird.

Zusammenfassung der Ergebnisse

In den Lösungsmittel Azeton, Methyl-äthylketon, Cyclohexanon, Azetophenon und Methyl-iso-butylketon kann der Alkaligehalt der in diesen Lösungsmitteln löslichen Alkalijodide mit einer alkoholischen Masslösung von Lithiumchlorid titriert werden. Der Äquivalenzpunkt der dabei ablaufenden Fällungsreaktion lässt sich oszillometrisch indizieren. Der Fehler liegt allgemein innerhalb der Grenzen von ±1%. Aus grösseren Messerien wurden bei Azeton und bei Azetophenon ein mittlerer Fehler von 0.6% errechnet. Die selektive Titration ist in den Ketonen nicht, in Azetonitril nur ungenau möglich. Die Alkalien können in Methyl-iso-butylketon auch bei Anwesenheit von Kalziumionen titriert werden. Zu diesem Zweck erwies sich eine Masslösung von Lithiumchlorid in Methyl-iso-butylketon als vorteilhaft. Die Ausfällung des Kalziumchlorids beginnt erst nach der Beendigung der Ausfällung der Alkalichloride. Anders verhält sich das Barium. Es fällt mit den Alkalien gemeinsam und stört so deren Bestimmung. Über die Titration von anderen Alkalisalzen (hier wurden nur die Jodide betrachtet) und der Erdalkalien werden weitere Untersuchungen Aufschluss geben. Es wird angenommen, dass die beschriebene Methode auch auf andere Lösungsmittel und Ionenpaare geeigneter Wahl übertragbar ist.

ZUSAMMENFASSUNG

Die Alkalisalze zeigen in Abhängigkeit vom Typ des Anions in verschiedenen Ketonen, Azetonitril, Äthanol usw. geringe Löslichkeit. Die Autoren untersuchten auf dieser Grundlage die Fällungstitration der Alkalien. Die in Ketonen und Azetonitril lösbaren Alkalijodide wurden mit in Äthanol oder in den anderen genannten Lösungsmitteln gelöstem Lithiumchlorid titriert. Die Alkalichloride—ausgenommen das Lithiumchlorid—fallen aus. Zur Indikation der Reaktion wurde die oszillometrische Methode gewählt. Der mittlere Fehler der Bestimmungen betrug 0.6%. Kalzium störte die Bestimmung von Natrium und Kalium nicht, dagegen ist aber eine Mitfällung des Bariums zu beobachten.

SUMMARY

Various alkali metal salts are insoluble in ketones, acetonitrile, ethanol, etc., depending on the nature of the anion present; this can be utilized for the determination of some alkali metals by precipitation titration with oscillometric end-point detection. Sodium or potassium iodide in ketonic or acetonitrile media can be titrated with lithium chloride in ethanolic or ketonic solutions. The average error is 0.6%. Calcium does not interfere but barium does.

RÉSUMÉ

Plusieurs sels de métaux alcalins sont insolubles dans les cétones, l'acétonitrile, l'éthanol, etc. suivant la nature de l'anion présent; ceci permet le dosage de quelques métaux alcalins par titrage par précipitation avec détection oscillométrique du point final. L'iodure de sodium ou de potassium, en milieu cétonique ou acétonitrile peut être titré à l'aide de chlorure de lithium, en solution alcoolique (éthanol) ou cétonique. Erreur moyenne 0.6%. Le calcium ne gène pas, mais le baryum gène.

LITERATURVERZEICHNIS

1 A. Lannung, *Z. Physik. Chem.* A 161 (1932) 255.
2 H. Stephen und T. Stephen, *Solubilities of Inorganic Compounds*, Pergamon Press, Oxford, 1963, Vol. I, S. 739.
3 N. Van Meurs, *Chem. Weekblad*, 54 (1958) 298.
4 E. Pungor, *Oscillometry and Conductometry*, Pergamon Press, Oxford, 1965.
5 K. Cruse und R. Huber, *Hochfrequenztitration*, Verlag Chemie, Weinheim/Bergstr., 1957.

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HIGH-PRECISION ANALYSIS OF NUCLEAR MATERIALS BY CONSTANT-CURRENT COULOMETRY

PART II. DETERMINATION OF THORIUM

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In continuation of the work on the application of constant-current coulometry to high-precision analysis of nuclear materials[1], the determination of thorium has been investigated by titration with electrogenerated EDTA. This technique, in which EDTA is electrogenerated from its mercury(II) chelate, was first described by REILLEY AND PORTERFIELD[2] and later applied to microgram quantities of a number of elements by MONK AND STEED[3]. In the titration of milligram quantities of calcium, lead, zinc and copper at pH 8.5 by REILLEY AND PORTERFIELD[2], average errors of less than 1% were obtained. These were due in part to the relatively poor sensitivity of the Hg–S.C.E. electrode system and this can be improved by using differential electrolytic potentiometry (D.E.P.) with mercury electrodes[3]. The purpose of the present work was to investigate the application of this method for high-precision analysis of thorium, both for the assay of standard materials and for the determination of microgram quantities on nuclear targets.

For titration of thorium with EDTA, a low pH is necessary owing to its hydrolytic behaviour and under these conditions the sensitivity of the D.E.P. end-point is considerably reduced, becoming inadequate below about pH 4.5. Direct titration at this pH is likely to give low results and alternative procedures involving either back-titration, or electrogeneration of a near-stoichiometric amount of EDTA before addition of thorium have been examined.

At the present time no entirely satisfactory high-purity thorium standard is available in quantity, the metal most suitable for this purpose being generally less than 99.5% purity. Recently, however, small quantities of zone-refined metal, estimated to contain less than 120 p.p.m. of impurities, have become available as a research material[4] and this was used for this investigation.

EXPERIMENTAL

Apparatus

Coulometric cells. Two types of cell were used.

(*1*) For titration of microgram quantities of thorium(IV) the perspex cell described by MONK AND STEED[3] was constructed.

(*2*) For milligram titrations, the cell consisted of a flat-bottomed glass vessel, 70 mm in height and 30 mm in diameter, 7 ml of mercury being used as cathode. It was fitted with a polythene lid, drilled to accommodate a pair of mercury indicator electrodes, a ¼″ diameter unfired Corning 7930 Vycor tube containing a platinum wire anode immersed in 0.1 *M* ammonium nitrate solution, a glass paddle stirrer, and nitrogen inlet tube. Since constant stirring conditions improve the reproducibility of potentials in the D.E.P. method a paddle stirrer driven by a 1500 rev./min synchronous motor was used. Indicator electrodes were constructed from 25 S.W.G. platinum wire by electroplating, first with gold and finally with mercury as described by MONK AND STEED[3]. A polarising current of 1 μA was supplied from a 120-V dry battery in series with a 120-Mohm resistor.

Constant-current coulometer. A brief description was given in a previous paper[1].

Auto-titration switching unit. This has been described by STEED AND FRANSMAN[5].

Reagents

Stock mercury(II)–EDTA solution. 13.3 g of A.R. mercury(II) oxide, dissolved in 150 ml of 1 *M* nitric acid were added to a solution containing 22.61 g of disodium ethylenediaminetetraacetate in 600 ml of water. The pH was adjusted to 7.0 with ammonium hydroxide, and the solution diluted to 900 ml and stored in a polythene bottle.

Working electrolytes. These were prepared by addition of stock mercury(II)–EDTA solution to 0.5 *M* sodium acetate at pH 4.5, diluting with water to give the following concentrations.

(*a*) For titrations at 50 mA: 0.016 *M* mercury(II)–EDTA–0.15 *M* sodium acetate.

(*b*) For titrations below 500 μA: 0.008 *M* mercury(II)–EDTA–0.15 *M* sodium acetate.

Standard thorium solutions (approx. 40 mg per g). Prepared from zone-refined thorium crystal bar (Metal Hydrides Incorporated, Beverley, Mass., U.S.A.) by refluxing with 60% perchloric acid containing a few drops of 0.002 *M* hydrofluoric acid, evaporating several times to perchloric acid fumes, and diluting appropriately.

Mercury. Triple distilled metal was washed first with 6 *M* nitric acid and then with distilled water.

Preliminary experiments

The method used was in general similar to that described by MONK AND STEED[3], suitably modified to improve precision. Titration curves for the thorium(IV) ion in acetate-buffered electrolyte at pH 4.5 using both micro and macro titration assemblies are shown in Fig. 1; end-points were taken at a definite fixed potential on the steep portion of the curve. To ensure that the curves for both pre-titration of uncomplexed mercury(II) and for sample are parallel a small quantity of thorium(IV) solution is introduced before pre-titration. An automated technique is particularly suitable for this type of titration, where termination at a fixed potential is required, and for which approach to the end-points at a constant rate is advantageous; the instrument described by STEED AND FRANSMAN[5] was used. This follows the potential across the polarised mercury electrodes and, by suitable choice of potentials based on a preliminary manual titration, enables the electrolysis current to be switched off at a suitable point (40 mV) just before the end-point and to proceed by short pulses until the end-point potential (80 mV) is finally reached.

Three alternative methods for the titration of thorium(IV) were briefly investigated.

(*1*) Direct titration with electrogenerated EDTA at pH 4.5.

(*2*) Electrogeneration of less than the stoichiometric amount of EDTA required (>99%) before addition of thorium(IV) solution.

(*3*) Electrogeneration of excess EDTA, addition of thorium(IV) solution, followed by back-titration using current reversal.

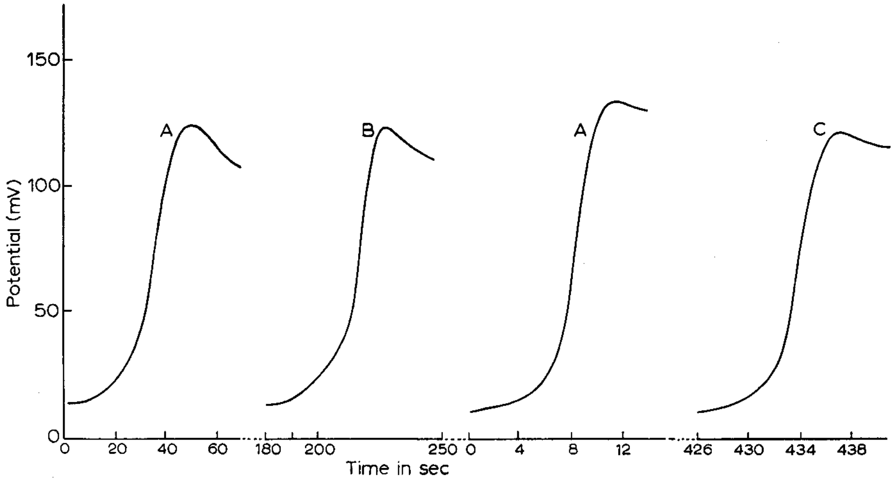


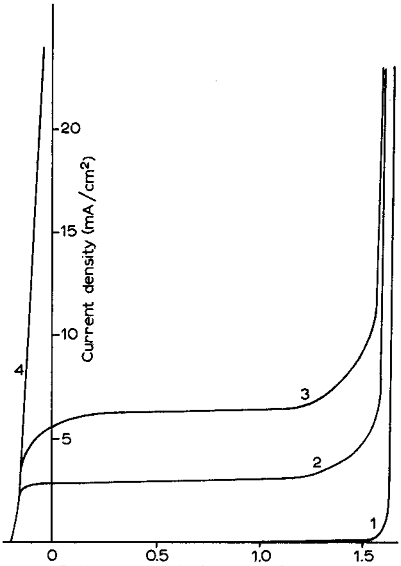
Fig. 1. Titration curves for thorium at pH 4.5. (A) pre-titrations; (B) 10.16 μg Th at 248.0 μA; (C) 25.196 mg Th at 49.150 mA.

Results obtained by method (*1*) were of poor precision and at least 0.5% low because of hydrolysis. Methods (*2*) and (*3*) gave relative standard deviations of 0.03 and 0.14% respectively for titration of 30 mg of thorium(IV) and method (*2*) was therefore used.

Current efficiency for electrogeneration of EDTA from its mercuric complex

Conditions for the electrogeneration of EDTA at 100% efficiency were established by REILLEY AND PORTERFIELD[2] by following the change in mercury cathode potential with respect to the S.C.E. when concentrated mercury(II)–EDTA was added to buffered electrolyte. This potential changes sharply to a more positive value at a critical mercury(II)–EDTA concentration and a solution containing a threefold excess was chosen by these authors. To define the conditions more precisely for high-precision work, current–voltage curves were determined using a mercury cathode of known area; these are shown in Fig. 2. Figure 3 shows current efficiency plotted as a function of current density; these figures were calculated from the data of Fig. 2. It can be seen that for titrations at 50 mA (current density 4.1 mA per cm^2) an efficiency of only 95.5% would be obtained using a 0.004 *M* mercury(II)–EDTA solution and, although a concentration of 0.006 *M* would give essentially 100% efficiency, the drop in mercury(II) ion concentration during titration would give an overall value well below this. A 0.016 M solution was actually used which contained sufficient mercury(II) to maintain 100% efficiency throughout the titration.

For titrations involving microgram quantities of thorium(IV) using current densities below 1.2 mA per cm² a 6 mM mercury(II)–EDTA solution was satisfactory.



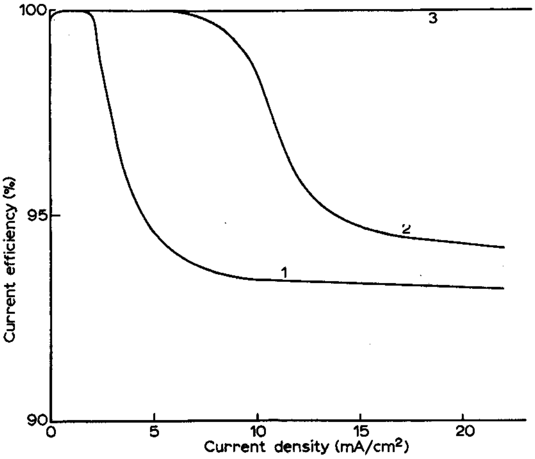


Fig. 2. Current density, cathode potential curves for electrolysis of Hg–EDTA. (1) 0.15 M sodium acetate; (2) 0.004 M Hg–EDTA, 0.15 M sodium acetate; (3) 0.006 M Hg–EDTA, 0.15 M sodium acetate; (4) 0.016 M Hg–EDTA, 0.15 M sodium acetate.

Fig. 3. Current efficiency as a function of current density and electrolyte composition. (1) 0.004 M Hg–EDTA, 0.15 M sodium acetate; (2) 0.006 M Hg–EDTA, 0.15 M sodium acetate; (3) 0.016 M Hg–EDTA, 0.15 M sodium acetate.

Procedure

(a) Milligram quantities of thorium. Place 7 ml of clean mercury in the cell and add 20 ml of 0.016 M mercury(II)–EDTA–0.15 M sodium acetate electrolyte. Fit the cell cap and deoxygenate by passing nitrogen through the solution for 10 min. Add 1 drop of the standard thorium solution, continue deoxygenation for 1 min and then raise the nitrogen inlet tube so that gas flows over the liquid surface.

Set the automatic switching unit to provide 0.1-sec pulses every 20 sec at a potential of 40 mV and to terminate the titration when the indicator electrodes reach a potential of 80 mV. Pretitrate the solution to the end-point using the automated technique and then reset to the manual mode of operation. Using a current of 50 mA, electrogenerate EDTA for approximately 600 sec, and then add the thorium solution from a weighed polythene ampoule until a slight excess is indicated by a drop in the indicator electrode potential. Reweigh the ampoule. Reset the instrument to the automatic mode and continue the titration after allowing a further 10 min for deoxygenation. Determine the electrolysis current several times during the titration by measuring the voltage across a standard resistor in series with the cell using a precise potentiometer.

(b) Microgram quantities of thorium. Follow a similar procedure using 0.8 ml of 0.006 *M* mercury(II)–EDTA–0.15 *M* sodium acetate electrolyte using the 1-ml perspex cell described by MONK AND STEED[3]. Switch off the 1-μA polarising current during the electrogeneration of the EDTA before addition of thorium.

RESULTS

The results for a number of analyses of thorium solutions in the range 20 μg to 30 mg are shown in Table I.

TABLE I

SUMMARY OF RESULTS

Solution	*Th taken*	*Current*	*Assay %*		*Standard deviation*
			Results	*Mean*	
1	20–30 μg	248.4 μA	99.9, 100.2, 100.4, 99.7, 99.7	100.0	0.3
2	20–30 μg	248.4 μA	99.6, 99.9, 100.4, 100.2, 99.9	99.9	0.3
1	300–400 μg	465.84 μA	100.07, 99.94, 99.92, 99.87, 99.98	99.96	0.07
2	300–400 μg	465.84 μA	99.89, 99.98, 99.95, 100.03, 100.02	99.97	0.06
1	30–40 mg	49.055 mA	99.98, 99.96, 99.98, 99.93, 99.94, 100.01, 99.97, 99.98	99.98	0.03
2	30–40 mg	49.055 mA	99.98, 99.99, 99.97	99.98	0.01

DISCUSSION

The constant-current coulometric method has given results of high accuracy for the zone-refined metal which contains less than 30 p.p.m. of impurities titratable with EDTA under the conditions described. The precision, which is considerably poorer than that for the analysis of uranium, is limited by the end-point sensitivity.

This work furnishes another illustration of the applicability of the constant-current coulometric technique in high-precision analysis and the method, although lacking specificity, is useful for the assay of standard thorium materials.

We thank Dr. K. F. LAUER of the Central Bureau of Nuclear Measurements, Euratom, Geel, Belgium, for supplying the zone-refined thorium.

SUMMARY

A constant-current coulometric method is described for the precise determination of thorium by titration with EDTA, electrogenerated from its mercury complex in acetate-buffered solution at pH 4.5. With polarised mercury electrodes for end-point detection, relative standard deviations of 0.02 and 0.3% for 30 mg and 30 µg respectively were obtained; the method was applied to the analysis of zone-refined thorium of high purity.

RÉSUMÉ

Une méthode coulométrique à courant constant est décrite pour le dosage précis du thorium par titrage au moyen d'EDTA, formé électrochimiquement à partir de son complexe mercurique en solution tampon acétique (pH 4.5). On a obtenu des déviations standard relatives de 0.02 et 0.3% pour 30 mg et 3 µg respectivement en utilisant des électrodes de mercure polarisées pour la détection du point final. On a appliqué cette méthode à l'analyse de thorium de grande pureté.

ZUSAMMENFASSUNG

Eine coulometrische Methode mit konstantem Strom wird für die genaue Bestimmung von Thorium beschrieben. Es wird mit AeDTE, das auf elektrolytischem Wege aus seinem Quecksilberkomplex in azetatgepufferter Lösung beim pH 4.5 erzeugt wird, titriert. Mit polarisierten Quecksilberelektroden zur Endpunktsbestimmung wurden relative Standardabweichungen von 0.02 und 0.3% bei 30 mg bzw. 30 µg erhalten. Die Methode wurde für die Analyse von hochreinem Thorium verwendet, das durch Zonenschmelzen gereinigt worden war.

REFERENCES

1 G. C. Goode, J. Herrington and W. T. Jones, *Anal. Chim. Acta*, 37 (1967) 445.
2 C. N. Reilley and W. W. Porterfield, *Anal. Chem.*, 28 (1956) 443.
3 R. G. Monk and K. C. Steed, *Anal. Chim. Acta*, 26 (1962) 305.
4 *Bulletin No. 18-A*, Metal Hydrides Incorporated, Beverley, Mass., U.S.A.
5 K. C. Steed and F. Fransman, *Anal. Chim. Acta*, 32 (1965) 472.

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DIFFERENTIAL CONTROLLED-POTENTIAL COULOMETRY: APPLICATION TO THE DETERMINATION OF URANIUM

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In a previous paper[1], differential constant-current coulometry was established as a high-precision analytical technique by the titration of dichromate with electrogenerated iron(II). It was suggested that extension of the differential principle to the controlled-potential method would be worthwhile and this has been investigated by RECHNITZ AND SCRINIVASAN[2]. Although this work established its feasibility and confirmed that a higher precision was attainable than with controlled-potential coulometry alone, the choice of system, *viz.* the reduction of dichromate to chromium(III) was unfortunate since the method appears to give a considerable negative bias and suffers from lack of selectivity.

The advantages of specificity offered by the controlled-potential technique are often over-emphasised, since in practice the irreversibility of many electrode processes necessitates working at a more negative potential than that predicted by theory.

The above system provides a good example of this since a potential some 940 mV more negative than the standard potential is required for the reduction of dichromate. In fact, in this particular case, direct titration with iron(II) would offer greater selectivity than controlled-potential coulometry. In general, differential controlled-potential coulometry is unlikely to be as precise as the constant-current technique since it requires relatively large corrections for the background faradaic current component rather than the termination of a titration at a well-defined end-point. A high electrolysis rate together with a low background current is therefore desirable for highest precision to be attained and ideal systems for investigation would be, for example, the oxidation of iron(II) or plutonium(III) at a large solid electrode.

The present work on the application of the differential technique to the reduction of uranium(VI) in 0.5 *M* sulphuric acid was undertaken primarily because of an interest in the high-precision analysis of uranium standards but also to enable the potentialities of the technique to be investigated using a well-established reaction at a mercury electrode.

EXPERIMENTAL

Preliminary work

The method used was essentially that described by SHULTS AND THOMASON[3] in which uranium(VI) is reduced to uranium(IV) in 0.5 M sulphuric acid after pre-reduction of more electropositive ions, including iron(III), at a suitable potential.

Experience with this method showed that errors up to 2% are obtained when less than 100 μg of uranium is used and therefore in the differential experiments, sample weights greater than 30 mg were considered necessary for an overall precision of 0.01% to be attainable.

To establish identical stirring conditions in both cells, and minimise current fluctuations caused by break-up of the mercury surface, precise stirring assemblies were constructed using synchronous electric motors driving glass disc stirrers through a pair of ball-races. Even under the smoothest stirring conditions very small quantities of electrolyte splashed on to the upper parts of the cell walls and it was found that gentle swirling of the cell and contents near the end of the electrolysis produced a significant increase in current. This effect was eliminated by swirling the cell repeatedly.

Diffusion of small amounts of oxygenated anolyte into the cell during electrolysis also led to erroneous results but considerable improvement resulted from covering all but the tip of the Vycor tube with tightly fitting PVC.

The experimental arrangement for the differential method was similar to that described by RECHNITZ AND SCRINIVASAN[2] in which the two identical electrolysis cells were connected in series, the first (cell A) containing the standard and the second (cell B) a slightly larger concentration of sample. The electrical circuit was arranged so that the potentiostat initially controlled cell A with both cells in series and then after electrolysing to a constant background current, controlled cell B for the differential determination, cell A being shorted out. Constant background current conditions were most conveniently detected by measuring the readout voltage from the integrator at equal increments of time (usually 1 min) on a sensitive integrator range.

To avoid switching off the potentiostat when the integrator was zeroed, a suitable switching circuit was provided.

It was confirmed that in order to maintain favourable mass-transport conditions in both cells, it was necessary to keep the volume of electrolyte in cell A slightly in excess of cell B, a 2-ml difference being satisfactory.

Apparatus

Controlled-potential coulometer. This has been described previously[4].

Electrolysis cells. A diagram of the cell and stirring assembly is shown in Fig. 1. The stirrer consists of a glass disc 15 mm in diameter made by flattening the end of a 3-mm diameter glass rod. A number of small glass spikes are drawn out perpendicular to the base of the disc and are immersed in the mercury, the base of the disc being located at the mercury–electrolyte interface. The stirrer is driven through a pair of ball-races by a 35-V synchronous motor (2500 rev./min supplied by Vactric Control Equipment Ltd.) mounted in a drilled-out perspex block. Reference and auxiliary electrodes are separated from the working electrolyte by unfired Corning 7930 Vycor tubes.

Reference electrodes. Mercury–mercury(I) sulphate electrodes, immersed in 0.5 M sulphuric acid, were used in preference to the standard calomel to avoid diffusion of small quantities of chloride into the electrolyte.

Reagents

Mercury. Thrice-distilled metal was washed, first with 6 *M* nitric acid and then with water and stored under 0.5 *M* sulphuric acid.

Nitrogen. Oxygen was removed from the nitrogen gas by passage through 2 gas washing-bottles containing 0.5 *M* chromium(II) chloride in 1 *M* hydrochloric acid, stored over zinc amalgam.

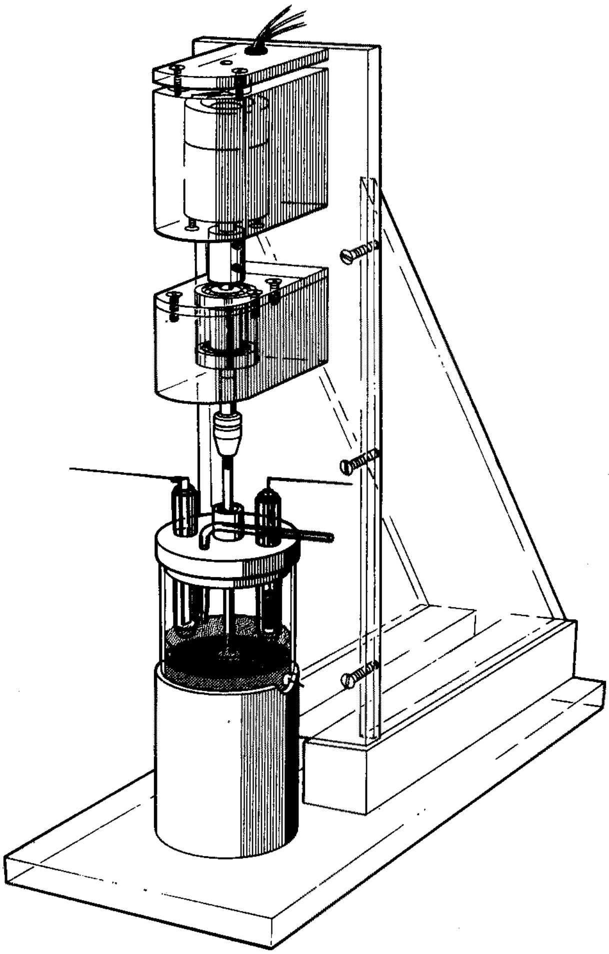

Fig. 1. Electrolysis cell and stirring assembly.

Preparation of standard uranium solutions

Two samples of natural uranium metal were used for the preparation of standards.

(*1*) Dingot metal, supplied by the New Brunswick laboratory of the USAEC. This has been analysed by a number of US laboratories and it is believed that the assay value of 99.97% is accurate to within 0.01%. The purity assumed in this work was 99.972 ± 0.004% for 95% confidence, a value obtained by constant-current coulometry at the National Bureau of Standards[5].

(2) A metal of lower purity, used as a secondary uranium standard by the UKAEA Production Group Laboratories, Springfields. This gave an assay of 99.75 ± 0.01% by the method of DUCKITT AND GOODE[6] which correlates well with a result of 99.74% which was obtained by difference from 100%, after the determination of impurities. Solutions containing at least 20 mg of uranium per g were prepared from standard metal, after cleaning with 6 *M* nitric acid, washing with water and drying with acetone.

At least 2 g of metal, weighed to ±0.02 mg, was transferred to a 50-ml conical flask, fitted with a B19 air condenser. For low-purity metal, dissolution in 6 *M* nitric acid was satisfactory; high-purity material however, dissolves only very slowly so hydrochloric acid was used, followed by oxidation of uranium to the hexavalent state by 6 *M* nitric acid. In either case, the solutions were then treated with 20 ml of 9 *M* sulphuric acid, evaporated to fumes, transferred to a weighed 100-ml stoppered flask, diluted to approximately 100 ml, and re-weighed.

Procedure

Add a suitable quantity of mercury to the 2 clean dry electrolysis cells; from weighed polythene ampoules, introduce not less than 2 g of uranium solution into each cell so that the weight of uranium in cell B does not exceed that in cell A by more than 1%. Adjust the total volume of electrolyte to 9 and 7 ml for cells A and B respectively with 0.5 *M* sulphuric acid.

Carefully attach the cells to the stirring assemblies and pass nitrogen over the surface of the solutions for 15 min. With the cells connected in series and cell A controlled, electrolyse at −0.40 V until a current of less than 5 μA is obtained, indicating complete removal of oxygen. Repeat the electrolysis at −0.79 V until the current falls to less than 50 μA and then gently swirl cell A and contents a number of times until no increase in current is observed. Zero the integrator without switching off the potentiostat, reset to a suitable range (400 mV per coulomb) and record the voltage readout at 1-min intervals until constant values are obtained over a 5-min period. Zero the integrator, transfer potentiostatic control to cell B (cell A shorted out) and determine the differential concentration of uranium remaining in cell B by integrating the current to background, again swirling the cell and contents several times near the end of the electrolysis. Determine the concentration of uranium from the readout, extrapolated to zero time.

RESULTS

Two main sources of error arise in the differential determination: (a) if insufficient time is allowed for the initial electrolysis to reach a constant background current, and (b) if the differential electrolysis itself is not allowed to go to completion. Although the first of these would not be expected to result in significant errors provided that cell B was electrolysed to the same background current as cell A, in practice satisfactory results were only obtained if the electrolysis in cell A was allowed to proceed to completion. Such errors must presumably be due to the different rates of electrolysis in the 2 cells. The effect of relatively small changes in faradaic background current on the extrapolation of the differential readout to zero time was investigated using approximately 40 mg of a "Dingot" uranium solution in both cells. The results are shown in Table I. These results clearly illustrate the necessity of continuing the electrolysis to a constant faradaic background current and show that an overall error of less than 0.01% can be achieved if this is done. To evaluate the overall errors involved in the application of the differential procedure, a series of determinations was made using the same uranium solution in each cell, the differential concentration being in each case less than 1%. Results are given in Table II.

TABLE I

TYPICAL DATA FOR A DIFFERENTIAL DETERMINATION

(Cell A was controlled for 50 min until a background current, equivalent to a change in readout of 1.4 mV per min (400 mV per coulomb range) was obtained. Electrolysis was continued with cell B controlled)

Time (min)	*Readout (V)*	*Diff. in readout per min (mV)*	*Readout extrapolated to zero time (V)*	*Mean background current over 1 min period (μA)*	*Calculated purity of U in cell B*
20	0.5328		0.4808	18.3	99.953
21	0.5354	2.6			
25	0.5440		0.4990	12.7	99.976
26	0.5458	1.8			
30	0.5526		0.5046	11.3	99.982
31	0.5542	1.6			
35	0.5602		0.5077	10.6	99.986
36	0.5617	1.5			
40	0.5676		0.5116	9.8	99.992
41	0.5690	1.4			
45	0.5746		0.5116	9.8	99.992
46	0.5760	1.4			
50	0.5816		0.5116	9.8	99.992
51	0.5830	1.4			

TABLE II

DIFFERENTIAL CONTROLLED-POTENTIAL DETERMINATION WITH THE SAME URANIUM SOLUTION IN BOTH CELLS

(Relative standard deviation calculated on difference=2.8%; relative standard deviation calculated on whole=0.009%)

Wt. of U(mg)				*Error*		
Cell 1	*Cell 2*	*Difference*	*Difference found*	*mg*	*% on difference*	*% on whole*
114.8837	115.1016	0.2179	0.2088	−0.0091	−4.2	−0.008
115.0870	115.5356	0.4486	0.4245	−0.0241	−5.4	−0.020
35.1949	35.3509	0.1560	0.1537	−0.0023	−1.5	−0.007
35.1375	35.3040	0.1665	0.1505	−0.0160	−6.6	−0.016
35.1022	35.3115	0.2093	0.2079	−0.0014	−0.7	−0.004
42.0131	42.0687	0.0556	0.0559	+0.0003	+0.5	+0.001
42.0774	42.1292	0.0518	0.0499	−0.0019	−3.8	−0.005
41.9220	42.1934	0.2714	0.2679	−0.0035	−1.3	−0.008
33.8436	34.0493	0.2057	0.2092	+0.0035	+1.7	+0.010

The procedure was also applied to the comparison of the 2 different uranium metal standards. A solution of Dingot metal (99.972%) was used in cell A as standard and a solution of the lower purity metal (99.75%) in cell B as sample. Results are shown in Table III.

TABLE III

COMPARISON OF TWO DIFFERENT URANIUM SOLUTIONS

Wt. of U(mg)			*% purity of sample in cell B*
Cell A Dingot metal standard	*Cell B sample*	*Difference found*	
90.1087	90.6019	0.5331	99.744
89.1547	89.7518	0.3684	99.745
89.4065	89.7792	0.1414	99.742
79.1169	79.7038	0.3876	99.750
79.1518	79.8772	0.5181	99.738
78.7586	79.3233	0.3537	99.734
		Mean	99.742
		Relative standard deviation	0.006%

DISCUSSION

The results obtained clearly show that considerable improvement in precision results from the application of the differential technique, a relative standard deviation of 0.009% being attained, compared with 0.08% by single-cell measurement with the same apparatus.

The relative standard deviation of 0.009% corresponds to 2.8% calculated on the differential amount of uranium (56–425 µg) which is considerably higher than would be obtained by a single-cell determination at these levels. Individual errors are not related to the differential amounts of uranium and it therefore appears that the loss of precision arises from factors involved in the differential mode of operation. This is a general observation in differential procedures but the effect is particularly marked in this case. The applicability of the method to the comparison of uranium standards has been clearly demonstrated, the results in Table II for the lower purity standard being in excellent agreement with those of other methods[7].

Whilst this work has confirmed the practicability of differential controlled-potential coulometry as a high-precision technique, it has also illustrated its limitations and the extreme care required for its successful operation. The precision attained is somewhat lower than that by the constant-current method and although control of the working electrode potential offers some advantages in selectivity, the latter method would appear more suitable as a general high-precision technique only when a precise constant-current coulometer is not available.

SUMMARY

Differential controlled-potential coulometry has been investigated as a high-precision analytical technique using the reduction of uranium(VI) in 0.5 *M* sulphuric acid at a mercury cathode. A relative standard deviation of 0.009% was obtained with 30–120 mg samples of uranium and the method was applied to the comparison of uranium standards.

RÉSUMÉ

La coulométrie différentielle à potentiel contrôlé est appliquée au dosage de l'uranium. La méthode décrite est basée sur la réduction de l'uranium(VI) dans l'acide sulfurique 0.5 *M*, à une cathode de mercure. La déviation standard relative est de 0.009% pour des échantillons d'uranium de 30–120 mg. Ce procédé a pu être appliqué à la comparaison d'étalons d'uranium.

ZUSAMMENFASSUNG

Die differentielle, potentialkontrollierte Coulometrie wurde als sehr genaue analytische Technik zur Reduktion von Uran(VI) in 0.5 *M* Schwefelsäure an einer Quecksilberkathode verwendet. Die relative Standardabweichung von 0.009% wurde mit 30–120 mg Uran erhalten. Die Methode wurde zum Vergleich von Uranstandards verwendet.

REFERENCES

1 R. G. Monk and G. C. Goode, *Talanta*, 10 (1963) 51.
2 G. A. Rechnitz and K. Scrinivasan, *Anal. Chem.*, 36 (1964) 2417.
3 W. D. Shults and P. F. Thomason, *Anal. Chem.*, 31 (1959) 492.
4 G. C. Goode, J. Herrington and G. Hall, *Anal. Chim. Acta*, 30 (1964) 109.
5 J. K. Taylor and G. Marinenko, *Round Table on High Precision Chemical Analysis of Substances of Interest to Nuclear Energy*, Report EANDC 42S, Euratom, Brussels, 1965.
6 J. A. Duckitt and G. C. Goode, *Analyst*, 87 (1962) 121.
7 G. C. Goode, J. Herrington and W. T. Jones, *Anal. Chim. Acta*, 37 (1967) 445.

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COUNTERCURRENT EXTRACTION SEPARATION OF SOME PLATINUM GROUP METALS: PART III

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(Received December 4th, 1966)

Separations of the platinum group metals by countercurrent extraction were first reported by BERG AND SENN[1,2] and BERG AND LAU[3]. The earlier work reported on studies carried out with the chloro[1,2] and thiocyanato[3] complexes of the platinum metals partitioned between *n*-tributyl phosphate and hydrochloric acid solutions. Numerous binary mixtures of the metals were completely resolved in no more than 5 to 10 stages on a Craig countercurrent extractor. This early success clearly demonstrated the feasibility of using countercurrent extraction as a tool for the separation of the noble metals.

The present investigation was undertaken to extend the previous extraction studies to include the behavior of the bromo complexes of the platinum group metals as they were partitioned between hydrobromic acid solutions and various organic solvents.

Experience had shown that much time and effort could be saved in the laboratory if one could predict from the measured distribution coefficients the number of stages required to effect a good separation. The Craig equation can predict, reliably in many instances, the distribution of solutes after multiple extractions in a countercurrent extractor, therefore 2 computer programs were written which permitted the theoretical distribution of solutes to be calculated quickly and easily from the measured distribution coefficients for any number of equilibrium stages.

EXPERIMENTAL

Apparatus

A Beckman model DU spectrophotometer with matching silica cells was used for the analysis of the platinum, palladium, rhodium and iridium solutions. Separatory funnels were used to obtain the distribution coefficients. The countercurrent distribution apparatus was a 100-stage extractor based on the design of CRAIG AND POST[4]. An IBM 1620 computer was employed for all theoretical calculations.

Reagents

The bromo complexes of the 4 platinum group metals considered were prepared in the following manner. A 100-ml aliquot of standard metal chloride solution was

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transferred to a beaker and heated to dryness. The residue was dissolved in 25 ml of 48% hydrobromic acid and the solution was again taken to dryness. This was done 2 more times to ensure complete conversion of the chloro complexes to the bromo form. The bromides thus formed were then dissolved in dilute hydrobromic acid, quantitatively transferred to a 100-ml volumetric flask and diluted to volume. This procedure maintained the original metal concentration of the stock solutions. The concentration of the stock solutions was as follows: platinum—2.150 mg/ml, palladium—1.960 mg/ml, rhodium—2.240 mg/ml and iridium—3.040 mg/ml. All had been standardized previously by the method of GILCHRIST[5].

Measurement of distribution coefficients

Bromo complexes of the noble metals in 1.05, 2.19, 4.38 and 6.57 M hydrobromic acid solutions were equilibrated with various organic solvents. The extractants used were *n*-tributyl phosphate (TBP), amyl acetate, methyl isobutyl ketone and various volume ratios of benzene and TBP. The procedure was as follows. A measured aliquot of the stock metal solution was evaporated to dryness on a steam bath and the residue was dissolved in 15 ml of hydrobromic acid of the desired molar concentration. This sample was saturated with sodium bromide and equilibrated with 100 ml of the appropriate solvent in a separatory funnel. The two phases were mixed for 1 min and allowed to settle before being separated and analyzed. It was necessary to analyze only the raffinate because aliquots of standard solutions were used in the distribution studies. The concentration of metal in the extractant was determined by difference.

The distribution coefficient, K_d, was defined as

$$K_d = \frac{\text{mg of metal/ml of extractant}}{\text{mg of metal/ml of raffinate}}$$

Plots of K_d as a function of hydrobromic acid concentration for the various solvents are given in Figs. 1–4.

Separation technique

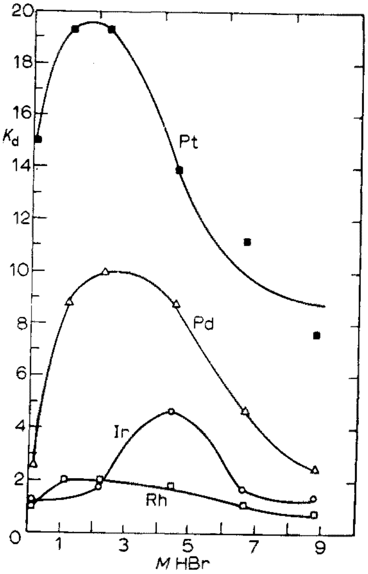
Equal volumes of the raffinate and extractant phases selected for a given separation study were equilibrated with each other twice before use in the separations, by shaking together in a large separatory funnel containing an excess of sodium bromide. Thus each phase was saturated with the other phase and sodium bromide before being used.

Appropriate aliquots of the stock solutions of the metals to be separated were mixed and taken to dryness on the steam bath. The sample was then dissolved in 4.38 M hydrobromic acid which had been previously equilibrated with the extractant to be used. It was then transferred to the first tube of the Craig extractor. The other tubes in the extractor were filled with an equal volume of the 4.38 M hydrobromic acid which previously had been equilibrated with the extractant. A given volume of the extractant was then added to the first tube of the extractor. The system was equilibrated by inverting the extractor 50 times before allowing the two phases to settle. The extractant phase was then transferred to the second tube of the extractor and fresh extractant was added to the first tube. This procedure was repeated until the desired number of transfers had been accomplished.

Analytical procedures

The metal content of both raffinate and extractant phases was determined in the separation studies. First, the metal was stripped from the extractant phase with 25% nitric acid solution saturated with sodium nitrate. This nitric acid solution

1



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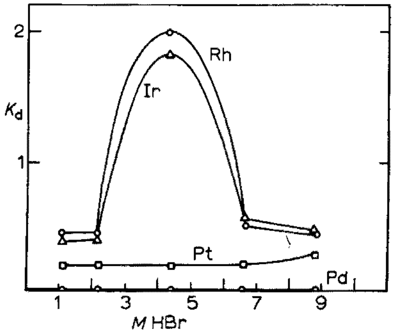

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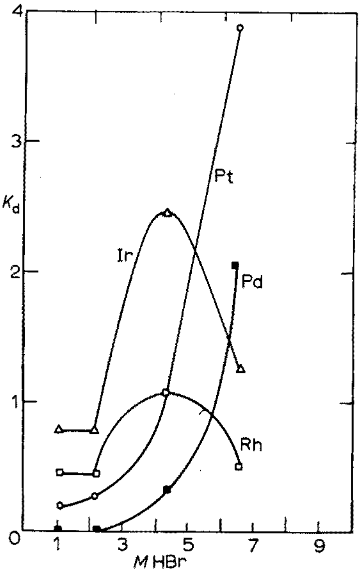

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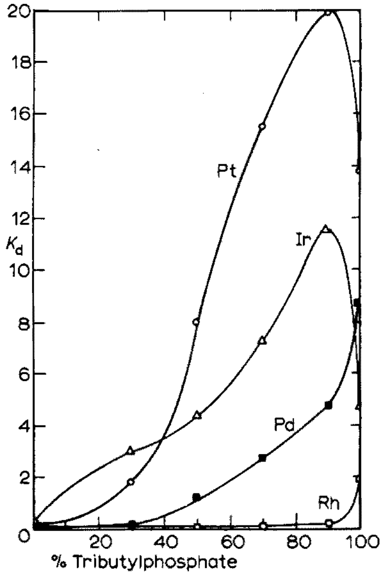


Figs. 1–3. Distribution coefficients *versus* HBr concentration for platinum–bromo complexes distributed between hydrobromic acid solutions and (1) tributyl phosphate, (2) amyl acetate, (3) methyl isobutyl ketone.

Fig. 4. Distribution coefficients *versus* percent tributyl phosphate for platinum–bromo complexes distributed between tributyl phosphate–benzene mixtures and 4.38 M hydrobromic acid.

TABLE I

COMPUTER PROGRAM FOR THE CRAIG EQUATION

```
C C COUNTERCURRENT DISTRIBUTION
    READ 1, EN, EK, X, RATIO
  1 FORMAT(4F6.3)
    EK=EK*RATIO
 16 FACN=1.
  2 FACN=FACN*EN
    IF(EN-1.)3,3,4
  4 EN=EN-1.
    GO TO 2
  3 R=O.
    Y=O
 13 ANS=X-R
    FCANS=1.
  5 FCANS=FCANS*ANS
    IF(ANS-1.)8,8,6
  6 ANS=ANS-1.
    GO TO 5
  8 FACR=1.
    IF(R-1.)15,7,7
  7 FACR=FACR*R
    IF(R-1.)9,9,11
 11 R=R-1.
    GO TO 7
 15 FACR=1.
  9 T=(FACN/FACR*FCANS) )*((1./(EK+1.))**X)*(EK**Y)
    PUNCH 10,X,Y,T
 10 FORMAT(3F18.8)
    Y=Y+1.
    R=Y.
    IF(X-R)20,12,13
 12 Z=((1./(EK+1.))**X)*(EK**X)
    PUNCH 10,X,Y,Z
 20 X=X+5
    EN=X
    IF(EN-40.)16,16,17
 17 STOP
    END
```

Definition of terms

EN–number of transfers

EK–distribution coefficient

RATIO–volume ratio of extractant to raffinate

FACN–*n* factorial

FCANS–(*n*–*R*) factorial

FACR–*R* factorial

T–fraction of solute in tube *R* after *n* transfers

TABLE II

COMPUTER PROGRAM FOR THE GAUSSIAN APPROXIMATION OF THE CRAIG EQUATION

```
C C COUNTERCURRENT DISTRIBUTION N GREATER FORTY
    READ 1, EN, EK, RATIO
  1 FORMAT(3F6.3)
    EK=EK*RATIO
    RMAX=(EN*EK)/(EK+1.)
    R=O.
    A=2.
    PI=3.1417
  7 TPART=1./SQRT(A*PI*EN*EK/(EK+1.)**2)
    EPART=EXP(-(RMAX-R)**2/(A*EN*EK/(EK+1.)**2))
    T=TPART*EPART
    PUNCH 5, EN,R,T
  5 FORMAT(3F18.8)
    R=R+1
    IF(R-EN)7,7,11
 10 STOP
    END
```

Definition of terms

EN–total number of transfers

EK–distribution coefficient

RATIO–volume ratio of extractant to raffinate

T–fraction of solute in tube *R* after *n* transfers was evaporated to a moist residue and taken up in aqua regia and again taken to dryness. A second fuming to dryness in aqua regia was followed by taking the sample up in 1.2 M hydrochloric acid.

The raffinate phases were subjected to a preliminary oxidation with concentrated nitric acid, evaporated to dryness twice with aqua regia, and taken up in 1.2 M hydrochloric acid. From this point on, the raffinate and extractant fractions were analyzed by identical procedures. Platinum was determined by the method of AYRES AND MEYER[6], palladium by the method of AYRES AND TUFFLEY[7], rhodium by the method of AYRES AND YOUNG[8] and iridium by the method of AYRES AND QUICK[9].

Computer programs for the Craig equation

The fraction of solute, $T_{n,R}$ remaining in tube R of the countercurrent extractor after n transfers of extractant is given by the Craig equation.

$$T_{n,R} = \frac{n!}{R!\,(n-R)!}\left(\frac{1}{K+1}\right)^n K^R$$

where

$$K = (K_d)(\text{volume ratio of extractant to raffinate phases})$$

and

$$K_d = \frac{\text{mg of metal/ml of extractant}}{\text{mg of metal/ml of raffinate}}$$

The computer program for this form of the Craig equation is given in Table I.

Because of the limitations of the IBM 1620 computer to calculate factorials greater than forty factorial, a computer program was written also for the Gaussian form of the Craig equation which does not involve factorials. The Gaussian approximation of the Craig equation is

$$T_{n,R} = \frac{1}{[2\pi nK/(K+1)^2]^{\frac{1}{2}}}\exp\left(\frac{-(R_{\max}-R)^2}{2nK/(K+1)^2}\right)$$

where

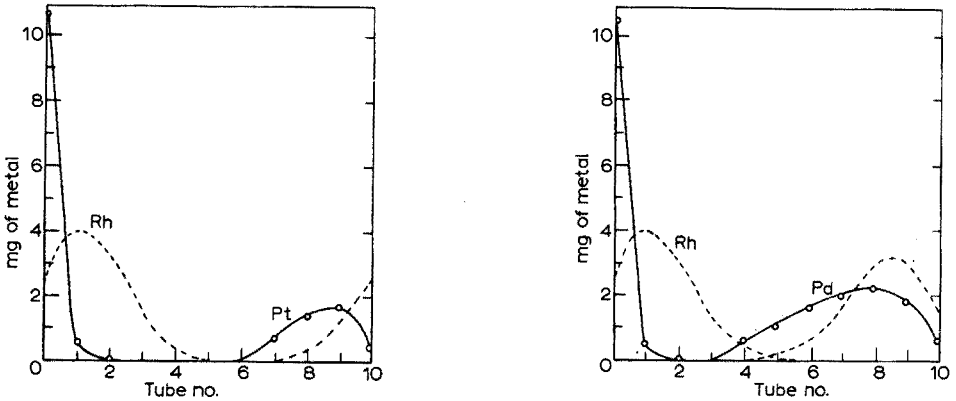
$$R_{\max} = nK/(K+1).$$

The computer program written for the Gaussian approximation of the Craig equation was used for all calculations involving values of n greater than forty and is given in Table II.

RESULTS AND DISCUSSION

A critical evaluation of Figs. 1–4 reveals that there are several solvents which can be used to effect a separation of various mixtures of the platinum group metals. Certainly one would expect to be able to separate Pd, Ir, and Pt from Rh using an extractant which is 90% tributyl phosphate (TBP)–10% benzene if the platinum metals are extracted from 4.38 M hydrobromic acid. Rh–Pt and Rh–Pd mixtures were resolved in 10 stages on the Craig apparatus. The distribution of solutes in the Craig apparatus after 10 equilibrations is shown graphically in Figs. 5 and 6. The percentage recovery of the metals were: Pt 98.5%, Rh 99.5% and Pd 98.5%, Rh 98.2%. The results were well within experimental error for quantitative recoveries.

Attempts to separate mixtures of Rh and Ir on the Craig apparatus with the same solvent system were not successful. Similar results were encountered in earlier work[1,2] with Rh–Ir mixtures; no explanation is offered. However, almost quantitative separations of Rh–Ir mixtures were obtained with the same solvent system by 3 successive batch extractions. A Rh–Ir mixture in 4.38 *M* hydrobromic acid was extracted with 3 portions of a 90:10 TBP: benzene solvent and the combined extracts were then back-extracted once with a pure 4.38 *M* hydrobromic acid solution. Analysis of the combined extract and raffinate phases respectively, showed that 97.0% of the Ir and 93.8% of the Rh were recoverable in the extract and raffinate phases respectively.



Figs. 5–6. Separation of bromo complexes of: (5) Pt and Rh, (6) Pd and Rh, by distribution between 90% TBP–10% benzene and 4.38 *M* hydrobromic acid with a 1:1 volume ratio. (– – –) Theoretical, (—) experimental.

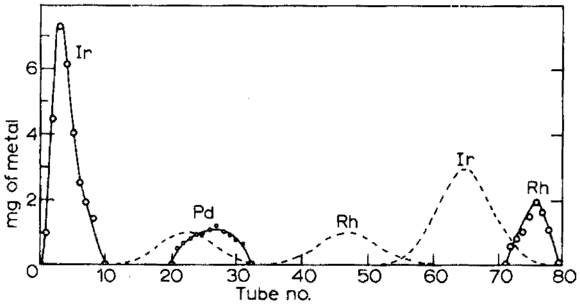


Fig. 7. Separation of bromo complexes of Rh, Ir, and Pd by distribution between methyl isobutyl ketone and 4.38 *M* hydrobromic acid with a 25:40 volume ratio. (– – –) Theoretical, (—) experimental.

Methyl isobutyl ketone offers promise (see Fig. 3) for separating 3 component mixtures of platinum group metals from 4.38 *M* hydrobromic acid solution. There are sufficient differences among the distribution coefficients of Pd, Rh, and Ir to effect a separation in 90 stages on the Craig apparatus. The theoretical distribution of solutes in the Craig apparatus after 90 equilibrations is compared with the observed distribution of solutes in Fig. 7. There is good agreement between the observed and predicted distribution of the palladium–bromo complex but it must be recognized that both the iridium– and rhodium–bromo complexes distributed themselves in an anomalous fashion. After repeated verifications of the distribution coefficients found for the iridium- and rhodium-bromo complexes we must admit to not having an explanation for their anomalous behavior. However, it should be noted that separations are possible. Palladium, rhodium and iridium are recoverable in 97.0, 87.6 and 95.5% yields, respectively. Because of the numerous raffinate and extractant fractions which had to be analyzed in this study and because no Ir, Pd or Rh was detected outside of the major solute zone, one must conclude that these recoveries are essentially quantitative.

Amyl acetate (see Fig. 2) offers promise as an appropriate solvent for the separation of various mixtures of the platinum-bromo complexes. Optimum separations of Pd-Pt-Rh or Pd-Pt-Ir would be expected from 4.38 *M* hydrobromic acid solutions. Figure 8 gives the anticipated (theoretical) distribution of a Pd-Pt-Rh mixture after 90 equilibrations in the Craig apparatus. Note that palladium should be concentrated in tube 0. After 45 equilibrations with amyl acetate solvent it was obvious that the rhodium was not being transferred through the system as expected, thus the Rh and Pd were unresolved. An arbitrary decision was made then to switch to methyl isobutyl ketone as the solvent for the last 45 equilibrations. Consequently, the observed distribution of solutes in the Craig apparatus is not comparable to the theoretical distribution given for a pure amyl acetate extractant. However, it should be noted that a good separation was effected. Pd, Rh and Pt were recovered in 96.0, 96.0, and 94.0% yields, respectively. Again, we can assume that these yields correspond to quantitative recoveries.

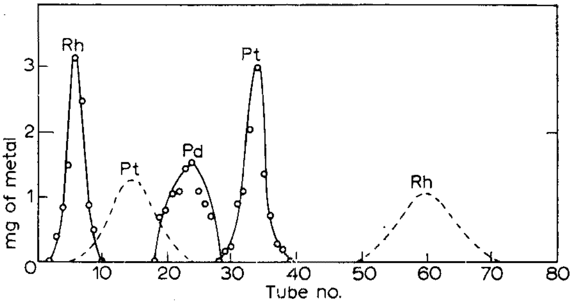


Fig. 8. Separation of bromo complexes of Rh, Pt, and Pd by distribution between amyl acetate (45 stages), methyl isobutyl ketone (45 stages) and 4.38 *M* hydrobromic acid with a 25:40 volume ratio. (– – –) Theoretical, (—) experimental.

Countercurrent distribution does offer some promise for effectively separating various mixtures of platinum group metals. A disturbing feature of this particular work is the lack of agreement between the experimental and theoretical distribution of solutes. Much work remains to be done to explain the anomalous behavior.

SUMMARY

The bromo complexes of platinum(IV), palladium(II), rhodium(III), and iridium(IV) were prepared and studies were made on their distribution between hydrobromic acid solutions and various common solvents. The solvents employed were *n*-tributyl phosphate (TBP), methyl isobutyl ketone, amyl acetate, and various

TBP–benzene mixtures. Distribution coefficients as a function of HBr concentration are given for each metal for each solvent system. A careful study of the measured distribution coefficients clearly showed that a number of binary and ternary mixtures of the metals can be resolved with a Craig countercurrent distribution apparatus. Rh–Pt and Rh–Pd mixtures in 4.38 *M* HBr solutions were quantitatively separated on a 10-stage Craig apparatus using a 90% TBP–10% benzene solvent. Rh–Ir mixtures in 4.38 *M* HBr were resolved by 3 consecutive batch extractions with 90% TBP–10% benzene. Mixtures of Pd, Rh, and Ir in 4.38 *M* HBr were resolved in 90 stages using methyl isobutyl ketone as the solvent. Pd, Rh and Ir were recovered in 97.0, 87.6 and 94.5% yields, respectively. Mixtures of Pd, Rh and Pt in 4.38 *M* HBr were resolved in 90 stages using amyl acetate and methyl isobutyl ketone as solvents. Pd, Rh and Pt were recovered in 96.0, 96.0 and 94.0% yields, respectively. Two computer programs for the IBM 1620 Computer are given; these facilitate the comparison of theoretical and actual solute distributions.

RÉSUMÉ

On a préparé des complexes bromés de platine(IV), palladium(II), rhodium(III), et iridium(IV) et effectué une étude sur leur partage entre des solutions acide bromhydrique et divers solvants (n-tributylphosphate (TBP), méthylisobutylcétone, acétate d'amyle) et des mélanges TBP–benzène. Les séparations sont effectuées par extraction à contre-courant.

ZUSAMMENFASSUNG

Es wurden die Bromkomplexe des Platin(IV), Palladium(II), Rhodium(III) und Iridium(IV) hergestellt und ihre Verteilung zwischen bromwasserstoffsauren Lösungen und den Lösungsmitteln n-Tributylphosphat (TBP), Methylisobutylketon, Amylacetat und verschiedenen TBP–Benzol-Mischungen untersucht. Die Verteilungskoeffizienten zeigten, dass eine Anzahl binärer und ternärer Mischungen der Metalle mit der Craig-Verteilung getrennt werden können. Die gemessenen Verteilungen wurden mit denen, die mit Hilfe eines Rechners theoretisch ermittelt wurden, verglichen.

REFERENCES

1 E. W. Berg and W. L. Senn, Jr., *Anal. Chim. Acta*, 19 (1958) 12.
2 E. W. Berg and W. L. Senn, Jr., *Anal. Chim. Acta*, 19 (1958) 109.
3 E. W. Berg and E. Y. Lau, *Anal. Chim. Acta*, 27 (1962) 248.
4 L. C. Craig and O. Post, *Anal. Chem.*, 21 (1949) 500.
5 R. Gilchrist, *Bur. Std. J. Res.*, 12 (1934) 292.
6 G. H. Ayres and A. S. Meyer, Jr., *Anal. Chem.*, 23 (1951) 299.
7 G. H. Ayres and B. L. Tuffley, *Anal. Chem.*, 24 (1952) 949.
8 G. H. Ayres and F. Young, *Anal. Chem.*, 24 (1952) 165.
9 G. H. Ayres and Q. Quick, *Anal. Chem.*, 22 (1950) 1403.

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DETERMINATION OF OXYGEN AND HYDROGEN IN TUNGSTEN AND OTHER METALS BY A VACUUM-FUSION GAS-CHROMATOGRAPHIC METHOD

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The fabrication of cast tungsten is difficult, because this material is extremely brittle at room temperature, and this is aggravated by the presence of interstitial impurities, particularly oxygen. In the presence of a few parts per million of oxygen, the grain boundaries become extremely weak, and this gives rise to intergranular cracking, which may result in complete fracture of the workpiece during fabrication. It is very important, therefore, that the oxygen content of cast tungsten, and tungsten alloys should be as low as possible.

To provide accurate information on the oxygen content of these materials, and enable a relationship to be established between grain size/metallurgical properties and oxygen content of the material, it was necessary to develop a reliable method for determining oxygen down to at least 5 p.p.m.

In the method currently used in I.M.I.(K) laboratories for determining oxygen in the new metals[1], the sample is submitted to vacuum fusion in a molten-platinum bath which is contained in a graphite crucible at about 1900°. The liberated gas consists mainly of carbon monoxide, hydrogen and nitrogen, and is analysed by a procedure involving differential-pressure measurements, with a sensitive McLeod gauge.

With this procedure, oxygen contents down to about 50 p.p.m. can be determined in tungsten, niobium, tantalum and other metals, on about 0.1 g of the sample. If large samples (1–2 g) are used in the examination of these materials, the fusion reaction tends to become sluggish, and recovery of oxygen is often incomplete, though quantitative recovery can often be achieved with large samples by modifying the reaction conditions. A more satisfactory solution of the problem of determining oxygen contents below about 50 p.p.m. is to limit the amount of sample, and use a more sensitive method for analysing the gas mixture.

Important techniques that have been applied for determining small amounts of oxygen and other gases include mass spectrometry[2], neutron activation[3], and gas chromatography[4,5].

Because of the relative simplicity and comparatively low cost of the additional equipment required, it was decided to investigate a procedure based on the use of gas chromatography and our existing vacuum-fusion equipment. Whilst the primary objective was the determination of oxygen, it was expedient to assess the suitability of the proposed method for determining hydrogen and nitrogen simultaneously with oxygen.

In gas chromatography, the detectors commonly used include katharometers, gas-density balances, and various types of ionization detectors. For detecting the small amounts of gases associated with the analysis of metallurgical samples, a radioactive-type ionization detector is the most suitable. Response from the detector is shown as an electrical signal, which is automatically recorded as a graph (or chromatogram) of response (concentration of gas) against time. As each component passes through the detector, a peak is recorded on the chromatogram, and the area under the peak is a measure of the quantity of the component eluted. Provided that the sample size is restricted to less than about 1 ml, and the detector response is calibrated in the range for which it is to be used, quantitative results are obtained from linear measurements of peak heights, as opposed to the less convenient procedure of measuring peak areas.

The use of an ionization detector in the application of gas chromatography to analysis of gases extracted from metals by vacuum fusion has recently been described by LILBURNE[6]. His procedure differs from that described in the present paper, principally in the method of helium purification and gas sampling technique.

EXPERIMENTAL

Apparatus

The vacuum-fusion apparatus used in this work is shown schematically in Fig. 1, and is essentially that described in *Analysis of the New Metals*[1].

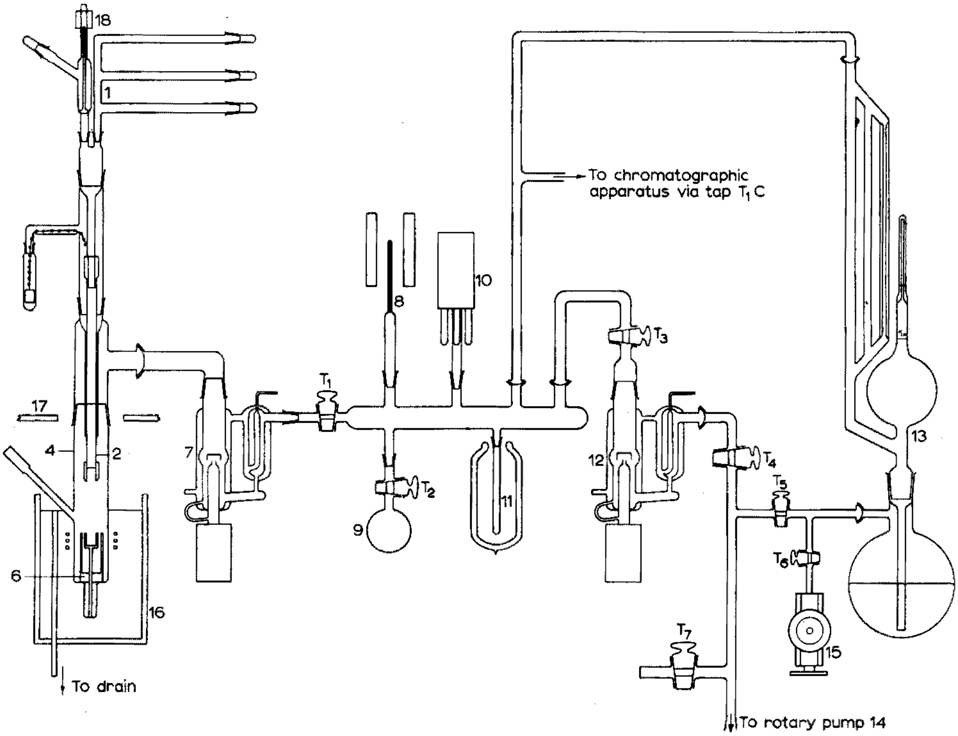

Fig. 1. Schematic outline of semi micro oxygen and hydrogen vacuum-fusion apparatus.

The chromatographic apparatus (see Fig. 2) consists essentially of a purification train for the helium carrier-gas, a gas-sampling system connected to the vacuum-fusion apparatus, a chromatographic column containing molecular-sieve 5A, and a radioactive-type ionization detector provided with amplifier and chart recorder.

Helium purification-train

To achieve high sensitivity and reproducibility, it is essential to use high-purity helium as the carrier-gas, and this was obtained as follows.

The bulk of the impurities were removed from mineral-grade helium by passing

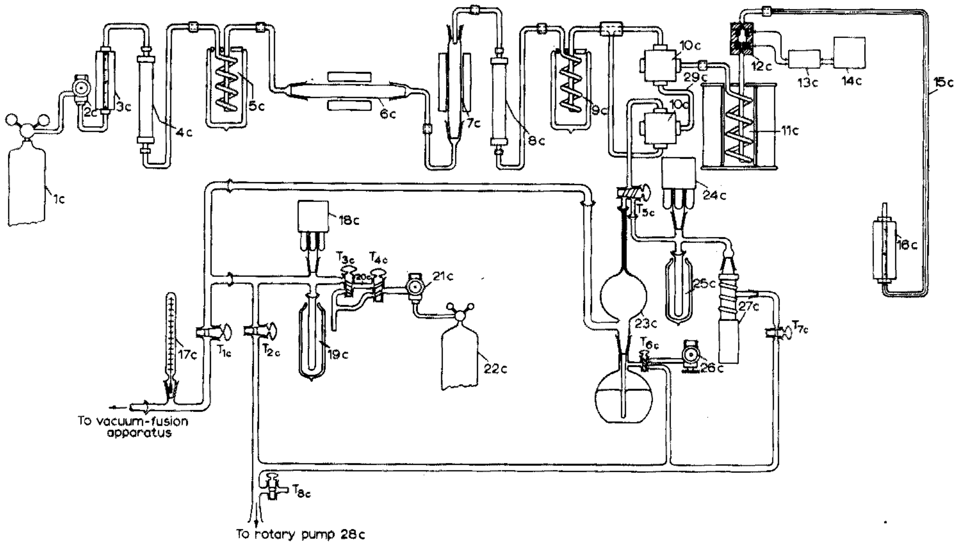

Fig. 2. Gas-chromatographic apparatus for determining oxygen and hydrogen in the gas mixture liberated in the vacuum-fusion procedure. (1C) Helium supply. Controlled at 17 lb/in^2 from a cylinder, containing high-purity gas, provided with a regulator valve (0–30 lb/in^2). (2C, 21C, 26C) Needle valves (Edwards type LB1). (3C, 16C) Rotameter gauges, 20–200 ml/min, panel type with screw connectors for 1/4-in ext. diam. tube. (4C, 8C) Stainless-steel tubes (EN58B) of 5/8-in ext. diam., 1/16-in wall thickness and 12-in long, filled with molecular-sieve 5A pellets (1/16 in), initially activated at 400° for 12 h in a stream of helium at 70 ml/min. (5C, 9C) Three-inch diameter coils made from 22 s.w.g. stainless-steel tube (EN58B), of 1/4-in ext. diam., and 4 ft long. Filled with molecular-sieve 5A (30–60 mesh) and immersed in liquid nitrogen. Initially activated in the same way as 4C and 8C. (6C) Quartz tube, of 20-mm ext. diam., 1.5-mm wall thickness and 2-ft long, packed with titanium sponge. Maintained at 900 ± 10°. (7C) Quartz tube, 20-mm ext. diam. × 1.5-mm wall thickness × 18 in long, packed with Hopcalite. Maintained at 350 ± 10°. (10C) Sampling valve–Drallim 4-way rotary switch valve (dual bank). (11C) Three-inch diameter coil made from 22 s.w.g. stainless-steel tube (EN58B), of 1/4-in ext. diam., and 5 ft long. Filled with molecular-sieve 5A (30–60 mesh) and contained in a thermostatically controlled oven at 100 ± 1°. Initially activated in the same way as 4C and 8C. (12C) Ionisation detector, type IE103B (Gas Chromatography Ltd.). (13C) Amplifier, Type IE115B (Gas Chromatography Ltd.). (14C) Chart recorder, 1-mV 1-sec response (Honeywell Controls Ltd.). (15C) Glass capillary-tube, of 6-mm ext. diam., 2-mm bore and 3-ft long. (17C) Thermometer, 0–110°, Type MF31/1 (Quickfit and Quartz Ltd.). (18C, 24C) Pirani gauge heads, Type G5-2, range 10^{-4}–1 mm Hg (Edwards High Vacuum Ltd.). (19C, 25C) Glass fingers immersed in liquid nitrogen. (20C) "Small Volume"-inlet tube for calibration gas (about 0.5 ml). (22C) Calibration gas supply (Cylinder provided with regulator valve). (23C) Mercury compression-unit (ratio 15:1 approx.). (27C) Two-stage mercury diffusion pump, Type IM2 (Edwards High Vacuum Ltd.). (28C) Two-stage rotary oil-pump, Type 2SC20A (Edwards High Vacuum Ltd.). (29C) Sample loop.

High-Vacuum Stopcocks. (T1C, T2C, T7C, T8C) 4 mm, straight bore; (T3C, T4C, T5C) 2 mm, double-oblique capillary bore; (T6C) 2 mm, double-oblique bore.

the gas through two columns of molecular-sieve 5A, one at room temperature, the other immersed in a flask of liquid nitrogen (−196°). The molecular sieve was initially activated by heating the columns for about 12 h at 400° in a thermostatically-controlled oven; during this conditioning period, helium was passed through the columns at about 70 ml/min. A duplicate set of molecular-sieve traps was provided to avoid having to shut down the system when re-activation became necessary.

Traces of oxygen, hydrogen and nitrogen remaining after this preliminary treatment of the carrier-gas were removed by passing the helium through titanium sponge at 900°, and Hopcalite at 350°, then through two molecular-sieve traps, at room temperature and −196°, respectively.

The first series of molecular-sieve traps requires re-activation at about 4-monthly intervals; the rest of the system normally requires attention after about 12 months.

The apparatus was constructed in stainless steel.

Gas-sampling system

The gas-sampling system must enable a small reproducible aliquot of the gas to be analysed, at a pressure of about $5 \cdot 10^{-2}$ torr, to be transferred from the vacuum-fusion apparatus into the carrier-gas stream, and thence on to the column; this must be accomplished with the least possible interference to the flow of carrier gas.

To obtain maximum detector response, and to avoid broadening of the chromatographic peaks, the sample must be introduced on to the column in the smallest possible volume; for this reason the sampling system must be close to the head of the column, and designed so that the sample is transferred rapidly into the carrier-gas stream. The system must be capable of operating with a carrier-gas pressure of about 25 lb/in^2 in the by-pass, whilst maintaining a high vacuum (10^{-4}–10^{-5} torr) in the adjoining sample chamber.

Various sampling devices consisting of spring-loaded high-vacuum stopcocks, or greaseless valves with PTFE seals, were constructed and tested, but they were either easily broken, incapable of allowing the sample to be introduced on to the column quickly enough, or difficult to maintain in a leak-free condition. Eventually, a completely satisfactory sampling system was devised, by using a modified Drallim Rotary-Switch Valve, fitted with a sample loop.

This valve consists essentially of two chambers, isolated from each other by an "O" ring recessed into a spindle which passes through both chambers. Each chamber has four ports fitted with spring-loaded valves. The spindle has two cam flats, and when it is rotated, the heads of the valve stems contact one of the cam flats or the periphery of the spindle; this causes the valve stems to move inwards or outwards, respectively, thus opening and closing the ports. The sequence in which the ports open and close, depends on the positions of the cam flats on the spindle. An "O" ring is recessed into the end of each valve stem, to ensure that the ports are effectively sealed.

In operation, the sample loop and one valve chamber are evacuated, and then both are allowed to fill with gas from the vacuum-fusion apparatus; meanwhile, carrier gas is passed on to the column via the other valve chamber.

Initial tests showed that if the gas from both the loop and chamber was subsequently swept through the column, broad tailing peaks were obtained on the chromatogram. Modifications were made, therefore, to enable the sample gas to be removed from the valve chamber, thereby allowing only gas from the loop to be swept through the column; after this modification had been made, sharp well-defined peaks were obtained.

Under continuous operation, the "O" ring seal between the valve chambers tended to leak, but this was overcome when a new spindle, with two "O" rings in recesses of slightly larger diameter, was fitted.

The operating sequence of the sampling valve, for collecting an aliquot of the gas from the vacuum-fusion apparatus, and transferring it to the column, is shown diagramatically in Fig. 3.

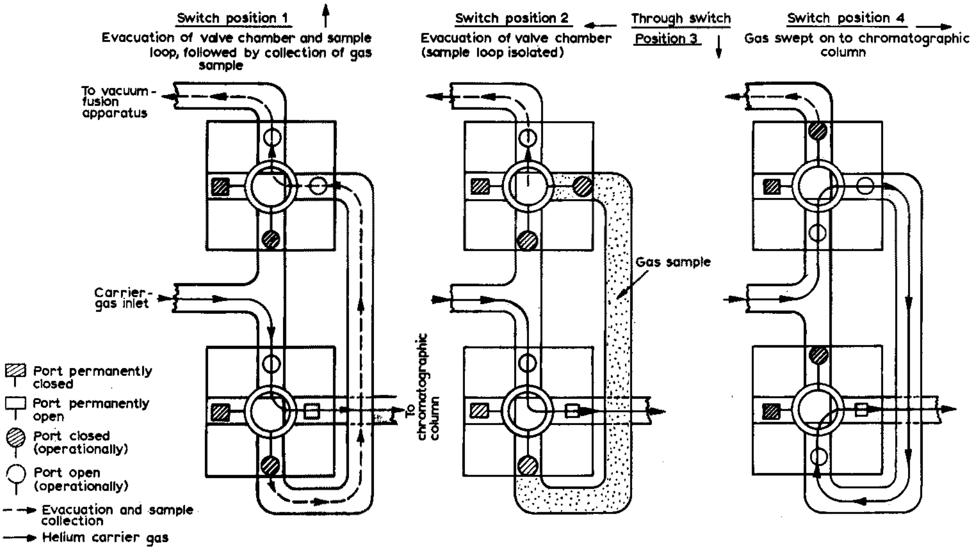

Fig. 3. Operating sequence of gas-sampling valve.

An arrangement of high-vacuum stopcocks allows any particular gas from a cylinder, to be introduced into the system for calibration purposes (see Fig. 2).

To provide for the analysis of samples that are very low in oxygen content, the sampling system is fitted with a mercury compression-unit which enables an aliquot of the gas liberated from the sample to be compressed into the sampling loop before it is swept on to the column. The compression ratio is about 15:1.

Chromatographic column

The chromatographic column consists of a 22 s.w.g. stainless-steel tube, 5 ft long × 0.25 in external diameter, packed with 30–60-mesh molecular-sieve 5A, and formed into a 5-in long spiral about 2.5 in in diameter. The molecular sieve is initially activated at 400°, in the same way as the molecular sieve used in the helium-purification system. In normal use, the column is placed in an oven controlled at 100° ±0.1°. Re-activation is carried out *in situ*, by heating the column at 220° for about 12 h, with helium flowing at about 70 ml/min; the need for re-activation is indicated by a reduction in the separating efficiency of the column, and is suspected when the positions of the peaks on the chromatogram come closer together.

Detector

Gas emerging from the column passes into the ionization chamber of a radioactive-type detector where it is bombarded with β-particles from a 200-mC tritium source. This results in the formation of both metastable and ionized helium atoms. The metastable helium atoms are capable of ionizing any gas with a lower ionization potential than 19.8 eV. Ejected electrons are accelerated in an electrical field, and excite further helium atoms.

To obtain high sensitivity and reproducibility, it is important to use helium carrier-gas of high purity; gaseous impurities in the helium become ionized, and this reduces the life and concentration of the metastable helium atoms, and hence the ionization current is reduced when the eluted sample passes through the detector.

The presence of impurities is first shown by a negative peak for oxygen; further contamination of the carrier-gas results in negative peaks for all the eluted components, and eventually the detector gives no response at all, owing to the absence of metastable helium atoms. Water has a particularly marked effect in causing negative peaks, but even with high-purity helium, peak-inversion occurs if too large a sample of gas is used. The maximum sample-load for the detector is about $5 \cdot 10^{-3}$ ml (STP), and separate components can be determined in the range 10^{-6} to about $5 \cdot 10^{-4}$ ml (STP).

Signals from the detector are amplified, and the output from the amplifier is fed to a 1-mV, 1-sec response chart-recorder.

The detector is welded as close to the column exit as possible to minimise diffusion of the separated components before they enter the ionization chamber.

Gas issuing from the detector flows to atmosphere, first through a glass capillary-tube (1 m long × 2 mm bore) to prevent back diffusion of air into the system, then through a Rotameter flow-gauge.

Influence of various factors

The analysis section of the vacuum-fusion apparatus (see Fig. 1) and the gas-sampling system of the chromatographic unit (see Fig. 2) were calibrated as described in the Method, and the combined volume was found to be 620 ml.

Tests were then made to determine the influence of various factors on the response obtained for carbon monoxide, hydrogen and nitrogen, based on peak-height measurements.

A sample of the appropriate gas (about 0.5 ml) was introduced from a cylinder, into the calibrated volume, via the high-vacuum stopcocks (T3C, T4C)*. The vacuum-fusion apparatus was isolated from the gas-sampling system by means of the high-vacuum stopcock (T1C), then evacuated. Gas remaining in the sampling system was allowed to expand throughout the calibrated volume; its pressure was measured on the McLeod gauge (13), and an aliquot was swept on to the column via the sampling valve (10C).

By repeated isolation and evacuation of the vacuum-fusion apparatus, followed by expansion of the gas from the sampling system into the calibrated volume, 1-ml aliquots of gas at pressures ranging from about 4 to $4 \cdot 10^{-3}$ torr ($5 \cdot 10^{-3}$ to $5 \cdot 10^{-6}$ ml STP) were swept on to the column and examined chromatographically, under various conditions of detector voltage, flow rate, etc.

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* Items numbered with the suffix C refer to Fig. 2, otherwise reference to Fig. 1 is intended.

Detector voltage (Helium 65 ml/min; column temperature 100°). By means of a commercially-available combined detector unit and amplifier (Gas Chromatography Ltd.), voltages of 100, and 200 to 1400 V in steps of 200 V, can be applied to the detector, but for studying the effect of detector voltage on response, a stabilised E.H.T. unit was incorporated into the circuit to enable increments of less than 200 V to be applied, between 200–1000 V.

The response for hydrogen, carbon monoxide and nitrogen, at any particular concentration, increased with voltage. Between 200–450 V, positive peaks were obtained for the three gases. From 450–600 V, peaks with negative fronts were obtained for hydrogen, particularly at low concentrations, and the response became non-linear. Above 600 V, hydrogen gave negative peaks. Peaks for carbon monoxide and nitrogen remained positive up to about 850 V, but at higher voltages, peaks with small negative fronts were obtained. Some of the peaks showing negative response are reproduced in Fig. 4.

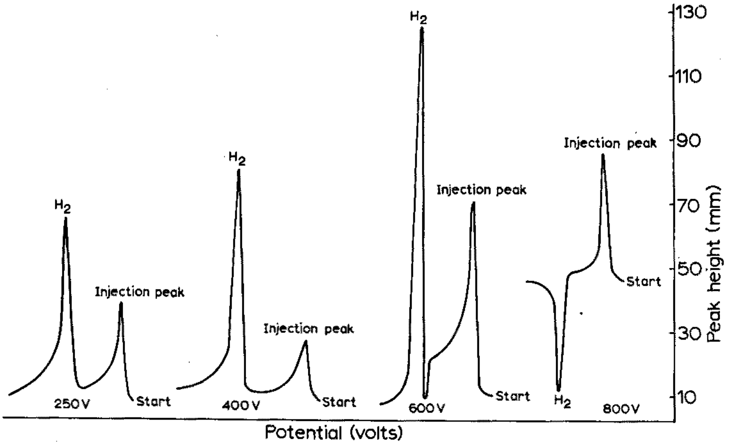

Fig. 4. Diagram of hydrogen peaks, showing negative response at high voltages.

It has been shown[5] that negative signals are caused either by (a) an impure carrier-gas, (b) too large a sample aliquot, or (c) instability of the electrical field, particularly at high voltages.

In the previous tests, negative signals for hydrogen, at comparatively low voltages, are attributed to contamination of the sample with mercury vapour from the diffusion pumps and compression-unit. To establish a procedure for the determination of oxygen and/or nitrogen, simultaneously with hydrogen, therefore, it would be necessary to apply a detector voltage below 450 V to avoid negative signals for hydrogen, and in subsequent tests a potential of 400 V was applied.

Carrier-gas flow rate (Applied potential, 400 V; column temperature, 100°). Tests with carrier-gas velocities of 50, 70, 100 and 120 ml/min, showed that an increase in flow rate resulted in a reduction in the retention times of the gases on the column, and gave rise to sharper peaks; sharpening of the peaks was most pronounced with carbon monoxide, which normally gives a very broad peak compared with the peaks obtained from other gases

The response for all gases increased by about 5%, when the flow rate was increased from 50 to 70 ml/min.

To obtain satisfactory resolution of the hydrogen and nitrogen peaks whilst maintaining a reasonably sharp carbon monoxide peak, a flow rate of 70 ml/min was selected.

Under these conditions the retention times were: hydrogen, 30 sec; nitrogen, 75 sec; carbon monoxide, 180 sec.

Pressure. The carrier-gas pressure was varied between 15 and 25 lb/in², by restricting the flow through the system with a needle valve fitted to the end of the exit Rotameter gauge.

An increase of 1 lb/in² caused a 2% loss in response. At pressures above about 20 lb/in², negative fronts were obtained on hydrogen peaks. To maintain a flow of 70 ml/min, the helium pressure was regulated to 17 lb/in².

Column temperature. Increase in the column temperature caused a reduction in retention times, but increased the sharpness of the peaks. A change from 25° to 150° caused about 50% reduction in the retention times of carbon monoxide and nitrogen, and about 20% reduction in that of hydrogen. Below 50°, the peaks were broad, and showed a marked tailing effect, particularly the carbon monoxide peak.

There is a slow deterioration in activity of the molecular-sieve column in use, and this is shown by a loss in resolving power. The rate at which this deterioration occurs, increases with temperature. To maintain sharp peaks with good separations over long periods, therefore, a temperature of 100° was selected for subsequent tests.

Limits of detection

The amplifier has two switched controls. One of these is included in the grid circuit of the first amplifying stage and is denoted "Input Sensitivity". The second is marked "Output Sensitivity" and connects the recorder to a selected fraction of the amplifier output.

With the experimental conditions established in the previous tests, responses obtained for the three gases were as shown in Table I.

Only one tenth of the maximum *input* sensitivity could be used; at maximum *input* sensitivity, the standing current was too high to be "backed off".

By using the mercury compression unit and half the maximum *output* sensitivity, satisfactory peaks were obtained for hydrogen down to the equivalent of

TABLE I

RESPONSES FOR CARBON MONOXIDE, NITROGEN AND HYDROGEN

Gas	*Maximum output sensitivity setting*	*Sample*		*Response*	
		ml at STP	*p.p.m. based on a 0.1-g sample*	*Peak height (mm)*	$A \cdot 10^{-10}$
Carbon monoxide	1/32	10^{-5}	45[a]	110	2.5
Nitrogen	1/32	10^{-5}	75	84	2.0
Hydrogen	1/8	10^{-5}	5.5	126	0.8

[a] As oxygen.

about 0.2 p.p.m., and for oxygen, or nitrogen, down to the equivalent of about 0.5 p.p.m., based on a 0.1-g sample. In practice, however, with the platinum bath at 1900° ready for the examination of samples, a gas blank, over 3 min, usually contained the equivalent of about 2 p.p.m. of oxygen, about 0.05 p.p.m. of hydrogen and the same amount of nitrogen, based on a 0.1-g sample. The determination of oxygen is, therefore, restricted to amounts above about 4 p.p.m. on this weight of sample.

At maximum output sensitivity, the baseline of the chromatogram was erratic, probably because of the influence of extraneous electrical fields from nearby arc-excitation equipment and high-frequency induction units; this made the measurement of peak heights difficult.

Twelve determinations on 10^{-5} ml (STP) of each of the three gases, carbon monoxide, hydrogen and nitrogen, gave peak height values which were reproducible to within 2%. These results provide evidence that the sampling valve is capable of introducing reproducible aliquots of gas on to the column, and also indicate the reliability of the detector signal.

Calibration graphs

Calibration graphs for carbon monoxide, hydrogen and nitrogen, each in the range $5 \cdot 10^{-6}$–$2 \cdot 10^{-4}$ ml (STP), were prepared by using a carrier-gas velocity of 70 ml/min, a column temperature of 100° and an applied potential of 400 V on the detector. All graphs were linear.

Experience indicated that the slope of the graphs varied depending on the purity of the carrier-gas, conditions of the chromatographic column, and the particular detector used.

RECOMMENDED METHODS

The final apparatus is as specified in Figs. 1 and 2.

Calibration of apparatus

Close tap T1C to isolate the gas-chromatographic system from the vacuum-fusion unit. To evacuate the gas-chromatographic system, open taps T2C, T7C and T6C to the rotary pump 28C, turn tap T4C to "Atmosphere Only" (see Note 1) and turn tap T3C to connect the inlet tube 20C to the rotary pump. Turn tap T5C to connect the sampling valve 10C with the rotary pump via the mercury compression-unit 23C. Rotate the sampling-valve switch* to position 1 (Fig. 3); this connects the sample loop 29C to the rotary pump while carrier gas is by-passing to the column. With tap T8C open to atmosphere, switch on the rotary pump, then slowly close tap T8C; when the rotary pump gives a steady knocking sound, switch on the diffusion pump 27C.

Evacuate the vacuum-fusion apparatus (see Fig. 1) and de-gas the crucible at 2100° as described in Procedure 20.1.4 in *Analysis of the New Metals*[1]. Place flasks of liquid nitrogen on the glass fingers (11, 19C and 25C) and continue to de-gas until a pressure of about 10^{-3} torr is reached. Open tap T1C to connect the vacuum-fusion unit with the sampling system of the gas-chromatographic apparatus, and close tap

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* Always rotate the switch anticlockwise

T2C. Continue to de-gas until the pressure in the whole apparatus is about 10^{-3} torr, then lower the temperature of the crucible to 1900° and check the blank rate $-1\ \mu$/min or less is acceptable (see Procedure 20.1.4, *Analysis of the New Metals*[1]).

When a satisfactory blank rate is obtained, close taps T3 and T4 to isolate the evacuation pumps on the vacuum-fusion apparatus, and connect a cylinder of high-purity hydrogen, via the needle valve 21C, to the gas-inlet tap T4C. Open the needle valve and adjust the regulator valve to about 2 lb/in^2. Open tap T3C to atmosphere and turn tap T4C to "Small Volume"; hydrogen then flows through the inlet tube 20C to atmosphere via tap T3C. After about 30 sec turn tap T4C to "Atmosphere Only". *Always ensure that tap T4C is turned to "Atmosphere Only" before turning tap T3C to "Vacuum Fusion".* Open tap T3C to allow the hydrogen from the inlet tube ("Small Volume") to expand into the vacuum-fusion apparatus. Allow 1 min for the gas to diffuse throughout the apparatus and for the pressure to reach equilibrium; raise the mercury in the McLeod gauge, then measure the pressure (P_1). With the mercury still raised, evacuate the apparatus, then isolate the evacuation pumps, and lower the mercury to allow hydrogen to diffuse throughout the whole apparatus. Allow 1 min for the pressure to reach equilibrium, then measure the pressure (P_2).

Calculation

$$V_2 = P_1 V_1 / P_2$$

where V_1 is the calibrated volume of McLeod gauge (ml); V_2 is the volume of apparatus (ml); P_1, P_2 are the measured pressures (cm).

Repeat the calibration several times and calculate the mean value.

Preparation of calibration graphs

Switch on the amplifier and recorder, and allow them to warm up for about 30 min. Set up the amplifier as directed in the manual supplied by Gas Chromatography Ltd.

To prepare a calibration graph for amounts of hydrogen ranging from about $2 \cdot 10^{-4}$–$5 \cdot 10^{-6}$ ml (STP), proceed as described under Calibration of Apparatus up to "allow 1 min for the gas to diffuse throughout the apparatus".

To obtain an aliquot of about $2 \cdot 10^{-4}$ ml (STP) of hydrogen for chromatographic examination, reduce the amount of gas in the system, as follows. Close tap T1C, open taps T3 and T4, and evacuate the vacuum-fusion side of the apparatus. Close taps T3 and T4, open tap T1C and allow gas from the sampling system to diffuse throughout the apparatus. Close tap T1C, measure the pressure of the gas (P_3) on the McLeod gauge, then remove hydrogen from the vacuum-fusion apparatus by allowing it to diffuse to atmosphere through the heated osmosis-tube 8, for 2 min. Again measure the pressure (P_4) and note the temperature (T) shown on the thermometer 17C.

Rotate the sampling valve switch to position 2 to isolate the sample loop from the valve chamber, turn tap T5C to the diffusion pump 27C, and evacuate the valve chamber until the pressure falls to about 10^{-4} torr, as shown on the Pirani gauge 24C; this usually takes about 30 sec.

Select a suitable sensitivity setting (1/32 max. is usually adequate), switch on the chart drive, then rotate the sampling-valve switch through position 3 to position 4, to allow the carrier gas to sweep the sample on to the column.

Record the chromatogram, then rotate the sampling-valve switch to position 1 to allow carrier gas to be removed from the valve chamber and sample loop by the diffusion pump 27C and rotary pump 28C. When the pressure in the valve chamber and loop has fallen to about 10^{-4} torr, as shown on the Pirani gauge 24C, turn tap T5C to connect the sampling valve with the vacuum-fusion apparatus via the mercury compression-unit. If required, a second aliquot of the gas may be analysed at a different sensitivity setting.

Measure the height of the hydrogen peak and calculate the quantity of hydrogen in the whole apparatus from the equation.

$$\text{Hydrogen } (\mu g) = \frac{V_2(P_3-P_4)}{1000} \; \frac{1}{76} \; \frac{273}{273+T} \; \frac{2 \cdot 10^6}{2.24 \cdot 10^4} \tag{1}$$

where P_3-P_4 is the difference in mercury levels (cm) on the 1000/1-scale of the McLeod gauge.

The difference in pressure (P_3-P_4) is usually about 12 cm Hg when calibrating for about $2 \cdot 10^{-4}$ ml of hydrogen (STP).

To evacuate the apparatus ready for calibrating another point on the graph, open taps T1C, T3 and T4. When the pressure has fallen to about 10^{-4} torr, as shown on the Pirani gauges 10 and 18C, close taps T3 and T4, and open tap T1C. The apparatus is then ready for admitting another sample of hydrogen.

Record at least four chromatograms at lower levels of hydrogen, down to about $5 \cdot 10^{-6}$ ml (STP). These levels are obtained by allowing one or more samples of hydrogen from the inlet tube ("Small Volume") to diffuse throughout the apparatus, then alternately evacuating the vacuum-fusion apparatus and expanding gas from the sampling system into the whole apparatus, two or more times. Measure gas pressures below about 2 cm with a 10,000/1-compression ratio, but convert to the 1000/1-scale before using the calculation (eqn. (1)).

Relate all peak heights to the same sensitivity, and plot the values against the hydrogen values obtained from eqn. (1).

By using various amounts of carbon monoxide, from about $2 \cdot 10^{-4}$ ml to about $5 \cdot 10^{-6}$ ml (STP), prepare a calibration graph for oxygen in a similar way to that for hydrogen, but before measuring the pressure (P_4), open tap T2 to allow carbon monoxide in the vacuum-fusion apparatus to be oxidised to carbon dioxide. The carbon dioxide is then condensed in the liquid nitrogen trap 11.

Caution: Because of the toxicity of carbon monoxide, the outlets from the "Small Volume" and the rotary pumps 14 and 28C must be led into a fume cupboard provided with an efficient extraction unit.

Calculate the oxygen equivalent of the carbon monoxide in the whole apparatus from the equation.

$$\text{Oxygen } (\mu g) = \frac{V_2(P_3-P_4)}{1000} \; \frac{1}{76} \; \frac{273}{273+T} \; \frac{16 \cdot 10^6}{2.24 \cdot 10^4} \tag{2}$$

Relate all peak heights to the same sensitivity and plot the values against the oxygen values obtained from eqn. (2).

These graphs cover the ranges 120–3 p.p.m. of hydrogen and 900–25 p.p.m. of oxygen, based on a 0.1-g sample. In the preparation of graphs for the examination of samples containing less than 3 p.p.m. of hydrogen and/or 25 p.p.m. of oxygen, amounts of gas suitable for chromatographic examination are obtained by using the mercury compression-unit. This provides for the analysis of samples containing down to about 0.2 p.p.m. of hydrogen and 4 p.p.m. of oxygen, based on a 0.1-g sample.

Procedure

Load the samples (Note 1), standards (Note 2) and platinum (Note 3) into the sample arms 1. Place the crucible assembly 6 in the furnace tube 4, connect the latter to the apparatus, and fix the heating coil in position.

Close tap T1C, open taps T2C, T7C and T6C to the rotary pump 28C, then continue as described under Calibration of Apparatus, up to "check the blank rate -1 μ/min or less is acceptable". Lower the temperature to about 1500°, then add the platinum. Increase the temperature to 1900° and continue to de-gas until the pressure falls to about $5 \cdot 10^{-4}$ torr.

Close taps T3 and T4, and collect the gas from the blank for 6 min. Close tap T1 and determine the blank by gas chromatography as follows. Raise the mercury in the compression unit to the graduation mark by admitting air through tap T6C via the needle valve 26C. Allow 30 sec for the gas to reach equilibrium. Rotate the sampling-valve switch to position 2 to isolate the sample loop from the valve chamber, then continue as described under Preparation of Calibration Graphs, down to "sweep the sample on to the column"; a sensitivity setting of 1/16 max. is usually suitable.

When the chromatogram has been recorded, close tap T7C and turn tap T6C to the rotary pump 28C to lower the mercury in the compression unit. Open tap T7C, rotate the sampling-valve switch to position 1, then again continue as described under Preparation of Calibration Graphs, down to "via the mercury compression-unit".

If a satisfactory blank is obtained (H_2 peak < 15 mm, CO peak < 200 mm), open taps T1, T3 and T4 and evacuate the apparatus until the pressure, as indicated by the Pirani gauge 10, has fallen to about $5 \cdot 10^{-4}$ torr. The apparatus is then ready for the examination of samples.

Introduce a sample (Note 4) into the crucible, and collect the gas until evolution is complete. Select a suitable sensitivity on the amplifier, depending on the nominal oxygen (or hydrogen) content of the sample and record a chromatogram as described for determining the blank; in the examination of samples containing more than about 25 p.p.m. of oxygen (or 5 p.p.m. of hydrogen), it is unnecessary to use the mercury compression-unit. When oxygen and hydrogen are to be determined on the same sample, and one of the component gases requires compression, the other can be determined on a separate aliquot of the gas mixture, without compression.

Measure the peak height, deduct the appropriate blank (depending on temperature used and the time taken to achieve complete evolution of gas) and calculate the oxygen (and/or hydrogen) content of the sample from the calibration graph.

After completing the run of determinations, shut down the apparatus and remove the furnace tube and crucible assembly (Note 5). Clean the furnace tube, first by filling it with a detergent solution and allowing it to stand overnight, then removing the loose deposit with a bottle brush; avoid scratching the surface of the tube. When necessary, also wash the tube with hot chromic acid solution.

Shutting down the apparatus

Close tap T1C to isolate the chromatographic system from the vacuum-fusion apparatus and shut down the latter as described in Procedure 20.1.5, *Analysis of the New Metals*[1].

Close the needle valves 15 and 26C, open tap T2C, remove the flasks of liquid nitrogen from the glass fingers 11, 19C and 25C, and de-gas the apparatus to remove water vapour. Switch off the diffusion pump, allow it to cool for about 30 min, then switch off the rotary pump and slowly open tap T8C to atmosphere.

If the vacuum-fusion apparatus has been left under vacuum overnight to enable a run of determinations to be completed without delay next morning, ensure that the gas-chromatographic system is evacuated (see Calibration of Apparatus) before opening tap T1C.

Notes

1. Samples of tungsten (0.1 g) are crushed into small pieces, with a tungsten carbide pestle and mortar, degreased with trichloroethylene, washed with acetone, air-dried, weighed, and placed in tared platinum capsules, each containing 40 mg of high-purity nickel. A blank on the platinum and nickel must be determined.

The standard samples of titanium, zirconium, hafnium, niobium and tantalum were cut to size with a hacksaw, filed to remove surface contamination, degreased, *etc.*, and weighed (see Note 4).

2. Load at least four standards, preferably of similar composition to the samples, and examine a standard sample periodically during the analysis of each run of samples. This enables a check to be kept on the condition of the platinum bath, and the reproducibility of the chromatographic system.

3. Platinum is added in the form of short lengths of 0.04-in diameter wire. If 0.1-g samples are to be examined, use a 25-g platinum bath; about 30 samples can be analysed in one run.

4. In the examination of tungsten and tungsten-base alloys, add the encapsulated sample and nickel to a 25-g platinum bath at 1600°. After 2 min, raise the temperature to 1950° and maintain at this temperature for a further 3 min to complete the conversion of oxygen into carbon monoxide.

In the examination of the standard samples of titanium, each sample (30 mg) was placed together with 10 mg of tin in a tared platinum capsule; the capsule was introduced into the crucible containing a 7-g platinum bath at 1500°. After 10 min, the temperature was raised to 1900° and maintained at this temperature for a further 3 minutes to complete the reaction.

Standard samples of zirconium, hafnium and niobium were introduced directly into a platinum bath at 1900°; 3 min were allowed for the reaction to be completed.

In the examination of the tantalum standards, the temperature of the platinum bath was raised to 1980°.

5. Platinum residues are retained for subsequent recovery of platinum by the refiners.

RESULTS

The proposed vacuum-fusion gas-chromatographic method was used to determine the oxygen, hydrogen and nitrogen contents of samples of tungsten. Standard samples of zirconium, titanium, tantalum and other metals, were also examined to provide evidence of the reliability of the method. Blank values were determined periodically during each run of samples. A typical chromatogram is shown in Fig. 5.

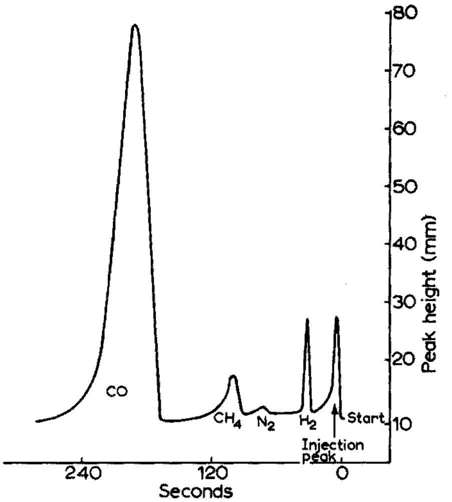

Fig. 5. Typical chromatogram obtained on gas evolved from a sample of niobium.

At the same time, oxygen and hydrogen were determined in the gas liberated from these samples by the conventional differential-pressure method[1] and nitrogen values were checked independently by a standard chemical procedure[9]. The results are shown in Table II.

For the standard samples containing oxygen in the range 100–2800 p.p.m., oxygen values obtained by the chromatographic method were reproducible, and in good agreement with those obtained by the differential-pressure method. Reproducible oxygen values were also obtained by the chromatographic method at lower levels of oxygen (in the tungsten and standard tantalum samples), but results obtained by the differential-pressure method on the same samples were slightly variable, probably due to the relatively low sensitivity of the method, and these results are reported to the nearest 5 p.p.m. in Table II.

Chromatographic values for hydrogen in the standard samples, in the range 20 to about 300 p.p.m. were also reproducible and in good agreement with values obtained by the differential-pressure method. For lower levels of hydrogen, down to about 3 p.p.m., in the tungsten and the standard niobium, tantalum and hafnium samples, a vacuum-extraction differential-pressure method[1] was used to provide results for comparison with those obtained chromatographically, because the vacuum-extraction method enables larger samples (0.5 g) to be examined. Values obtained by the two methods were in good agreement. Reproducible results were obtained by the gas-chromatographic method at levels of hydrogen down to about 0.5 p.p.m. on the tungsten and standard tantalum samples, but it was not possible to obtain satisfactory hydrogen values by the alternative methods, for comparison of these lower levels.

ABLE II

ETERMINATION OF OXYGEN, HYDROGEN AND NITROGEN IN TUNGSTEN AND STANDARD SAMPLES OF VARIOUS ETALS

ample umber	*Base material*	*p.p.m.*						
		Oxygen		*Hydrogen*			*Nitrogen*	
		Differential-pressure	*Gas chromatography*	*Differential-pressure*	*Vacuum-extraction*	*Gas chromatography*	*Chemical*	*Gas chromatography*
1	Tungsten	30, 40, 30	35, 35, 38	—	—	—	—	—
2		65, 70, 70	76, 80, 78	—	3, 3, 2.5	2.5, 3.0, 2.5	—	—
3		25, 30, 25	32, 28, 32	—	—	0.5, 0.5, 0.4	—	—
4		—	7, 7, 8	—	—	—	—	—
5		—	12, 10, 12	—	—	—	—	—
6		40, 55, 50	50, 51, 54	—	2, 2, 1.5	1.6, 1.5, 1.8	—	—
7		—	17, 20, 18	—	—	0.7, 0.7, 0.8	—	—
8		—	14, 12, 12	—	—	—	—	—
9	Niobium	260, 265	270, 265	—	6, 8	5, 6	85	60, 65
0		255, 265	255, 260	—	8, 8	7, 7, 6	80	50, 50
1		350, 325	340, 330	—	6, 5	6, 5, 5	70	40, 45
2	Tantalum	—	20, 24, 22	—	—	0.5, 0.5, 0.7	—	—
3		20, 30, 20	25, 28, 25	—	2, 3, 3	2, 2, 3	—	—
4		40, 50, 45	48, 47, 50	—	5, 5, 5	4, 5, 5	—	—
5	Titanium	—	—	280, 300	280, 290	285, 295	—	—
6		1150, 1100	1140, 1130	65, 70	65, 68	64, 68	—	—
7		2800, 2700	2650, 2700	27, 25	30, 30	30, 32	95	55, 60
8		1700, 1750	1650, 1700	70, 67	75, 72	78, 75	125	70, 75
9	Zirconium	1100, 1100	1120, 1130	25, 24	22, 22	23, 24	35	20, 20
0		1120, 1140	1120, 1130	20, 20	20, 21	19, 18	40	25, 25
1	Hafnium	200, 215	180, 185	—	5	6	20	10
2		175, 180	170, 175	—	5	4	25	10

Well-defined nitrogen peaks were obtained for the standard samples containing 20 to about 100 p.p.m. of nitrogen, and though the chromatographic values for nitrogen agreed with those obtained from differential-pressure measurements, they were invariably lower than those obtained by the chemical procedure. In most instances only about 60% of the nitrogen was recovered by the vacuum-fusion method. This low recovery supports the evidence of earlier work in this laboratory, and is in agreement with the findings of other analysts who have investigated the vacuum-fusion method[7], although some workers have claimed quantitative recovery of nitrogen by this technique[8]. Nitrogen peaks obtained in the examination of the tungsten and standard tantalum samples, were only slightly higher than those obtained for nitrogen blank values.

In the examination of the standard titanium samples, a peak was obtained with a retention time of about 100 sec, and the peak-height usually increased with the hydrogen content of the sample. This peak was attributed to the presence of methane, formed by reaction of hydrogen from the sample with carbon in the platinum bath; it is known that methane produces a chromatographic peak when a molecular-sieve column is used[5], and this peak appears between nitrogen (75 sec) and carbon monoxide (180 sec). Chromatographic examination of samples of high-purity methane, confirmed the identity of this peak, and indicated that $1.5 \cdot 10^{-5}$ ml of the gas at STP, gave a peak height of 130 mm at a sensitivity setting of 1/16 max., without compression. This quantity of methane is only about 1/600 of that in the whole apparatus, and would represent a loss of about 20 p.p.m. of hydrogen based on a 0.1-g sample.

The largest quantity of methane obtained in the examination of the titanium samples was equivalent to only about 2 p.p.m. of hydrogen (peak height 52 mm at sensitivity 1/4 max., using 0.1 g of sample). This indicates that loss of hydrogen due to methane formation is negligible, for most practical purposes, and this is confirmed by the good agreement between hydrogen values obtained by both gas-chromatographic and vacuum-extraction differential-pressure methods. A methane peak was not obtained in the examination of the tungsten samples, nor in the examination of the standard samples of niobium, tantalum and hafnium containing less than 10 p.p.m. of hydrogen.

CONCLUSIONS

The gas-chromatographic determination of permanent gases, based on the use of a molecular-sieve column, helium carrier-gas and a radioactive-type ionization detector, can be satisfactorily applied to the simultaneous determination of oxygen and hydrogen in the gas mixture liberated from samples of tungsten in the vacuum-fusion process.

The high sensitivity of this procedure enables oxygen (as carbon monoxide) and hydrogen to be determined down to about 5 p.p.m. and 0.2 p.p.m., respectively, using a 0.1-g sample; comparable limits obtained by the conventional vacuum-fusion differential-pressure method with the same weight of sample, are about 50 p.p.m. of oxygen and 20 p.p.m. of hydrogen. The gas-chromatographic method is, therefore, particularly suitable for application to samples of tungsten, which normally contain less than 50 p.p.m. of oxygen and less than 5 p.p.m. of hydrogen.

At higher levels of oxygen and hydrogen, up to 2800 and 300 p.p.m. respectively, the precision of the chromatographic method is at least as good as that obtained from differential-pressure measurements; the method can, therefore, also be applied in the examination of metals that contain relatively high concentrations of oxygen (and hydrogen).

Nitrogen recoveries obtained from the standard samples by the proposed gas-chromatographic method compare favourably with those obtained by differential-pressure measurements, but they are invariably lower than nitrogen values obtained by the chemical procedure[9]; usually only about 60% of the nitrogen is recovered. This confirms that nitrogen is not liberated quantitatively in the particular vacuum-fusion procedure used, from any of the metals examined.

Application of this relatively new method has provided evidence that a small quantity of methane is sometimes present in the gas mixture liberated when metal samples are subjected to vacuum fusion. The amount of methane present usually increases with the hydrogen content of the sample, and is probably formed by reaction of hydrogen in the sample with carbon dissolved in the molten-platinum bath. The proportion of hydrogen taking part in this reaction is usually less than 5% of the hydrogen content of the sample and, unless extreme accuracy is required, the amount formed can be ignored. If necessary, however, the quantity of hydrogen reacting in this way can be evaluated from the height of the methane peak. No such compensation can be made when the differential-pressure method is used. Hydrogen contents of the tungsten samples were all less than 4 p.p.m.

An important advantage of the gas-chromatographic method is the positive identification of the individual gases by the positions of their resulting peaks on the chromatogram; with the differential-pressure method it is not certain that the measured pressures are due solely to the gases being determined.

The chromatographic method also has the advantage that a repeat analysis can usually be made simply by examining another aliquot (or compressed aliquot) of the gas mixture, if necessary at a more suitable sensitivity setting; whereas with the differential-pressure method it is necessary to repeat the process of vacuum-fusion on a further sample.

Operation of the chromatographic-analysis system is simpler and less time-consuming than the differential-pressure method. Analysis of a gas mixture for oxygen and hydrogen takes about 4 min compared with about 8 min by the conventional method.

The method is particularly suited to the analysis of tungsten, tantalum and other materials in which oxygen and hydrogen contents are often less than about 50 and 5 p.p.m., respectively.

Whilst the prime objective of this investigation was the determination of oxygen in tungsten at about the 5 p.p.m. level, the lowest oxygen value in the samples available was about 10 p.p.m. However, oxygen values at this level were reproducible, and in view of the fairly good correlation obtained between the differential-pressure method and the gas-chromatographic method at about the 30 p.p.m. oxygen level, there are good grounds for accepting the validity of the gas-chromatographic procedure at or about the 5 p.p.m. level of oxygen. The high sensitivity of this method is such that there is every indication that oxygen values down to about 1 p.p.m. can be satisfactorily determined, by using a sample weight of about 0.2 g.

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SUMMARY

A gas-chromatographic method has been developed for the analysis of gas evolved from tungsten and tungsten-base alloys in the vacuum-fusion process. The method is suitable for determining 5–3,000 p.p.m. of oxygen and 0.2–300 p.p.m. of hydrogen, and can be applied to other metals. Above 50 p.p.m. of oxygen and 3 p.p.m. of hydrogen, the values found compare favourably with those obtained by alternative methods; below these levels, no reliable alternative procedures are readily available. In the proposed method, the sample is submitted to vacuum fusion in a molten platinum bath in a graphite crucible, and an aliquot of the evolved gas is transferred by means of a specially modified Drallim valve, to a stream of high-purity helium. The components are separated on a column of molecular-sieve 5A at 100° and detected with a radioactive-type ionization detector. Calibration and operation of the system are described in detail, and the effects of variables are discussed. Evidence was obtained that hydrogen recoveries by the conventional vacuum-fusion method are sometimes slightly low, because of methane formation. An important advantage of the method is that the evolved gases are positively identified by their retention volumes.

RÉSUMÉ

Une méthode par chromatographie gazeuse est proposée pour l'analyse de gaz formés lors du procédé de fusion sous vide du tungstène et d'alliages à base de tungstène. Elle permet de doser 5–3,000 p.p.m. d'oxygène et 0.2–300 p.p.m. d'hydrogène et peut être appliquée à d'autres métaux. L'échantillon est soumis à la fusion sous vide dans un bain de platine fondu dans un creuset de graphite. Une partie aliquote du gaz dégagé est entraîné par l'hélium de grande pureté et les composants sont séparés sur une colonne de tamis moléculaire 5 A à 100° et identifiés à l'aide d'un détecteur radioactif.

ZUSAMMENFASSUNG

Es wurde eine gaschromatographische Methode für die Analyse von Gas entwickelt, welches aus Wolfram und Wolframlegierungen beim Vakuum-Schmelz-Verfahren freigesetzt wird. Die Methode ist zur Bestimmung von 5–3000 p.p.m. Sauerstoff und von 0.2–300 p.p.m. Wasserstoff geeignet und kann auch bei anderen Metallen angewandt werden. Bei mehr als 50 p.p.m. Sauerstoff und 3 p.p.m. Wasserstoff sind die gefundenen Werte günstig im Vergleich zu denen anderer Methoden; unterhalb dieser Grenzen ist kein zuverlässiges anderes Verfahren verfügbar. Ein wesentlicher Vorteil der Methode liegt darin, dass die entwickelten Gase durch ihr Retentionsvolumen sicher identifiziert werden.

REFERENCES

1 W. T. Elwell and D. F. Wood, *Analysis of the New Metals*, Pergamon Press, Oxford, 1966, p. 80.
2 M. L. Aspinall, *Proc. International Colloquium on Vacuum Metallurgy, Brussels, 1965*, Publication T.P. 10, A.E.I. Instrument Division, Central Research Laboratories, Rugby.
3 R. F. Coleman, *Analyst*, 87 (1962) 590.
4 G. Kyryacos and C. E. Boord, *Anal. Chem.*, 29 (1957) 787.
5 R. Berry, in M. Van Swaay (ed.), *Proc. Fourth Symp. Gas Chromatog., Hamburg, 1962*, Butterworths, London, 1963, p. 321.
6 M. T. Lilburne, *Analyst*, 91 (1966) 571.
7 E. Booth, F. J. Bryant and A. Parker, *Analyst*, 82 (1957) 50.
8 N. A. Gokcen, *Trans. Metal Soc. AIME*, 212 (1958) 93.
9 Ref. 1, p. 75.

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SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF SILICON BY AN EXTRACTION METHOD

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The best known method for the determination of traces of silicon is that involving colorimetric determination as silico-12-molybdate blue which has recently been reviewed by POTTER[1] and SHELL[2]. Determinations are carried out in an aqueous medium, generally in a volume of 100 ml, making an effective working range of 20–200 μg of silicon. The determination of silicon at less than the 20-μg level is limited by the low absorbance of the blue silicomolybdate complex, the interference of large amounts of metal ions in solution, and the introduction of large amounts of salts during the dissolution and the neutralization processes (*e.g.* dissolution of aluminium or beryllium metal[3]). It is difficult to determine silicon satisfactorily below the 20 p.p.m. level in metals or salts using the well-known silicomolybdate blue method.

Silica in sea water has been extracted as the yellow silicomolybdate complex in ethyl acetate and measured directly by SCHINK[4]. This method requires a U.V. source and is not applicable when reducing agents are used before the addition of ammonium molybdate. Traces of silicon have been determined in pure chromium[5], pure nickel[6] and uranium[7]; all these methods involve the preliminary extraction of the yellow silicomolybdate either with *n*-butyl alcohol or isoamyl alcohol and subsequent reduction to silicomolybdate blue.

This paper describes a detailed investigation of the determination of silicon at trace levels in many metals and their salts, involving a preliminary extraction of the yellow silicomolybdate complex with isoamyl alcohol and subsequent reduction to silicomolybdate blue. This procedure, based on the selection of the best features of two previous papers[5,6], resulted in a simple and fast method. Although the recommended procedure is applicable to a large number of elements, some modifications were necessary to permit the determination of silicon in the presence of certain metals (*e.g.* cerium and iron). This method would be applicable to the determination of silicon in waters and in many other metals, salts or alloys.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer with 2-cm glass cuvettes was used.

pH meter. E.I.L. Model 23A direct reading pH meter.

Distilled water. Demineralized water was further purified by a single distillation in the presence of $KMnO_4$ and was used throughout the whole procedure.

Standard silicon solutions. Prepare a stock solution containing 1 mg Si/ml by fusing 0.535 g of pure SiO_2 with 5 g of anhydrous sodium carbonate. Dissolve the melt in water, dilute to 250 ml and store in a polythene bottle. Prepare a working solution (1 μg Si/ml) by diluting 2 ml of stock solution to 2 l. Store in a polythene bottle.

Ammonium molybdate solution (5%) was prepared from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and stored in a polythene bottle. The solution was found to be stable for at least 4 weeks.

Reducing solutions. Dissolve 0.25 g of iron(II) ammonium sulphate heptahydrate and 7.5 g of ascorbic acid in about 30 ml of water and dilute to 100 ml.

Isoamyl alcohol (May and Baker Ltd). Boiling range 128°–132°.

Ammonium hydroxide. Concentrated ammonium hydroxide as supplied by the manufacturer in polythene bottles was used throughout.

Recommended procedure

Transfer an aliquot of the acidic sample solution (0–15 μg Si) to a 200-ml polythene beaker. Add water to 25-ml volume. Adjust the pH to about 0.8 using 9 *N* sulphuric acid or ammonia. Add 10 ml of 5% ammonium molybdate solution and adjust the pH to 1.1 with ammonia. Let stand for 10 min. Add 5 ml of 20% tartaric acid and after 1 min add 5 ml of 9 *N* sulphuric acid. Transfer to a 100-ml separating funnel and adjust the volume to 55 ml with water. Add 10 ml of isoamyl alcohol, shake for 1 min and let stand for 2 min. Run the aqueous layer into a beaker and transfer the organic phase to a 50-ml separating funnel. Repeat the extraction with 5 ml of isoamyl alcohol. Leave the combined organic extracts to stand in the funnel for 5 min, swirl to dislodge any aqueous droplets adhering to the walls, and then run off the aqueous phase. Add 4 ml of reducing solution to the organic phase, shake for 30 sec and let stand for 5 min. Then run the contents of the funnel into a dry 25-ml volumetric flask. Wash the funnel with methanol and add the washings to the flask. Mix and dilute to volume with methanol. Measure the absorbance against a blank at 800 nm in 2-cm cells.

In the presence of large amounts of interfering ions, standard addition is recommended.

DISCUSSION

Solvent extraction

Isoamyl alcohol and *n*-butanol were considered as solvents for the extraction of the yellow silicomolybdate. Isoamyl alcohol was selected, because with *n*-butanol lower absorbances (93%) were obtained for the blue complex. When *n*-butanol is used as extractant the absorbance has to be measured at 795 nm.

Two extractions, one with 10 ml and one with 5 ml of isoamyl alcohol, are necessary because one extraction with 15 ml of solvent extracts only 93% of the yellow complex. The total amount of isoamyl alcohol should not exceed 15 ml, otherwise it is not miscible with 4 ml of reducing solution and methanol.

Sensitivity and stability of the method

The silicomolybdate blue complex formed in the isoamyl alcohol phase gives an absorbance peak at 800 nm, when measured against the blank. The molar absorptivity of the blue complex is $23.3 \cdot 10^3$, corresponding to 0.0012 μg Si/cm² on the SANDELL scale. Beer's law is obeyed to at least 1.0 μg Si/ml. Solutions containing up to 15 μg of silicon were used, but the range can be extended to 25 μg of silicon by using 1-cm cells.

The silicomolybdate blue complex in isoamyl alcohol–methanol solution is stable in the investigated temperature range 22°–28° for at least 24 h. When the method is modified by the use of hydroxylamine hydrochloride (see study of interferences) there is a gradual increase in the absorbance with standing. Addition of 1 g of hydroxylamine hydrochloride at the beginning of a silicon determination resulted in an increase in the absorbance of 3% per hour. Even in procedures where hydroxylamine hydrochloride was partially decomposed by heating at 80°–90° for 15 min, there was a change in absorbance. Therefore, when hydroxylamine hydrochloride is used in the procedure, the absorbance must be measured within 10 min of dilution with methanol.

The absorbance of the extracted blue complex did not change in the investigated temperature range 22°–28°.

Choice of pH and effect of varying reagent concentrations

A constant absorbance for the silicomolybdate blue was obtained when the yellow silicomolybdate complex was formed between pH 0.9 and 1.6 (Table I). A development time of 5 min after the pH adjustment was sufficient. However, when large amounts of salts or boric acid are present, a waiting time of 10 min is recommended. A final pH of 1.1, after ammonium molybdate addition, was found satisfactory even in the presence of large amounts of salts (Fig. 1).

TABLE I

EFFECT OF pH, AFTER AMMONIUM MOLYBDATE ADDITION, ON THE ABSORBANCE

(5 μg Si taken)

pH	*Absorbance*	*Recovery (%)*	*pH*	*Absorbance*	*Recovery (%)*
0.8	0.270	84	1.5	0.330	100
0.9	0.330	100	1.6	0.330	100
0.92	0.330	100	1.7	0.315	96
1.1	0.330	100	1.85	0.250	77
1.3	0.330	100			

Varying amounts of 9 *N* sulphuric acid were added to 50 ml of solution before extraction, and it was found that the best recoveries were obtained when the ratio of the volume of solution to the volume of 9 *N* sulphuric acid added was 10:1 (Table II). The percentage extraction was found to be independent of the solution volume between 50 and 70 ml provided that the 10:1 ratio was maintained.

It is important that the combined isoamyl alcohol phases after extraction stand for 5 min and that all of the acidic aqueous phase be removed, otherwise the results are not reproducible. The addition of only 0.2 ml of 9 *N* sulphuric acid at the reduction step decreased the percentage extraction to 85%.

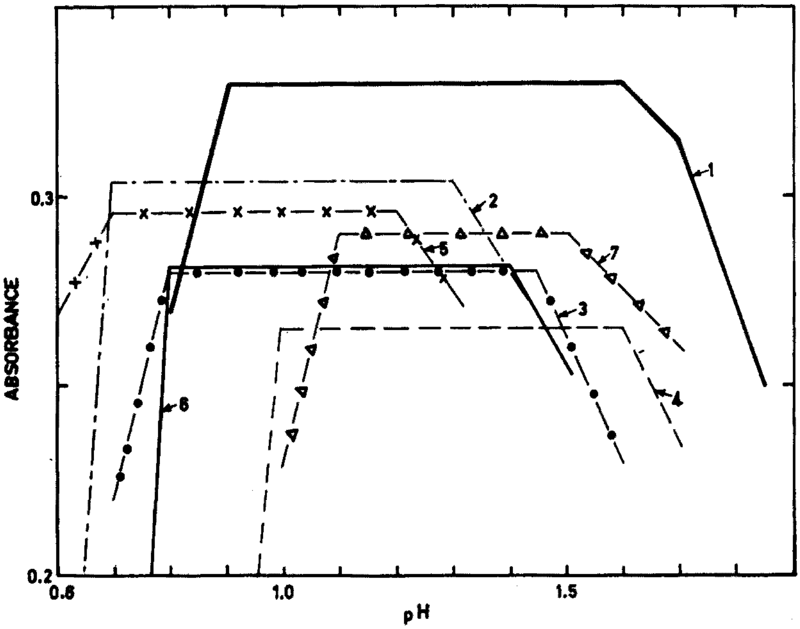

Fig. 1. Effect of salts and pH after ammonium molybdate addition on the absorbance (5 μg Si). Salts added: (1) standard curve; (2) NH_4Cl–0.8 g; (3) NH_4NO_3–0.8 g; (4) $(NH_4)_2SO_4$–1.5 g; (5) NaCl–2.0 g; (6) $NaNO_3$–2.0 g; (7) Na_2SO_4–2.0 g.

TABLE II

EFFECT OF VARYING AMOUNTS OF H_2SO_4 BEFORE EXTRACTION

(10 μg Si in 25 ml)

9 N H_2SO_4 (ml)	*Absorbance*	*Recovery (%)*
1.5	0.527	79
3.5	0.640	97
5.0	0.660	100
6.5	0.626	93

Variation of the iron(II) ammonium sulphate concentration between 0.25 and 0.5% had no effect on the absorbance.

Standard addition

All the aqueous methods for silicon determination draw attention to the changes in absorbance caused by large amounts of salt. The normal standard addition procedure was used to correct for the effect of any salt originating from neutralization or metal dissolution steps. The proportionality of standard additions of 5 and 10 μg of silicon was the criterion used to establish the feasibility of the method under various conditions. Tolerance levels were established for various ions and salts using the standard addition procedure (Table III). This procedure of standard addition is recommended for all cases, provided that the pH for formation of the yellow complex is strictly controlled.

TABLE III

EFFECT OF VARIOUS ELEMENTS

(Standard additions of 5 and 10 μg of Si)

Foreign ion	*Amount taken (g)*	*As salt*	*Recovery (%)*	*pH after $(NH_4)_2MoO_4$ addition*	*Si in salt (p.p.m.)*	*See note*
Al^{3+}	0.5[a]	$Al(NO_3)_3 \cdot 9H_2O$	83	1.1	0.3	d
Al^{3+}	0.5[a,c]	$Al(NO_3)_3 \cdot 9H_2O$	83	1.1	0.9	e
BO_3^{3-}	0.6	H_3BO_3	98	1.3	0.5	
Be^{2+}	0.2[a]	$BeSO_4 \cdot 4H_2O$	96	1.1	<0.05	
Ce^{4+}	0.25	$(NH_4)_2Ce(NO_3)_6$	90	0.8–1.0	0.5	f
Ce^{4+}	0.5	$(NH_4)_2Ce(NO_3)_6$	90	0.8–1.0		g
Ce^{4+}	0.5[c]	$(NH_4)_2Ce(NO_3)_6$	86	0.8–1.0		h
Co^{2+}	1.0[a]	$CoCl_2 \cdot 6H_2O$	94	1.1	0.4	
Cr^{3+}	0.5[a]	$CrCl_3 \cdot 6H_2O$	83	1.1	0.24	
Cu^{2+}	1.0[a]	$CuCl_2 \cdot 2H_2O$	96	1.1	0.3	
F^-	0.040	HF	99	1.3		i
F^-	0.060	HF	94	1.35		i
F^-	0.080	HF	80	1.4		i
F^-	0.080	HF	96	1.3		j
Fe^{3+}	0.050	$FeCl_3$ (60% soln.)	98	1.0	2.5	k
Fe^{3+}	0.10	$FeCl_3$ (60% soln.)	88	1.0		k
Fe^{3+}	0.20	$FeCl_3$ (60% soln.)	30	1.0		k
Fe^{3+}	0.50[a]	$Fe(NO_3)_3 \cdot 9H_2O$	90	0.9–1.1[b]	0.5	l
Mn^{2+}	0.2	$KMnO_4$	92	0.8–1.0	2.8	f
Ni^{2+}	1.0[a]	$NiSO_4 \cdot 6H_2O$	90	1.1	0.2	
PO_4^{3-}	0.0005[a]	Na_2HPO_4	100	1.1		
Th^{4+}	0.5[a]	$Th(NO_3)_4 \cdot 4H_2O$	84	1.0	0.5	m
Th^{4+}	0.25[a,c]	$Th(NO_3)_4 \cdot 4H_2O$	84	1.1	6.0	n
U(VI)	0.5[a]	$UO_2(NO_3)_2 \cdot 6H_2O$	90	1.05	7.2	o
U(VI)	0.5[a]	$UO_2(NO_3)_2 \cdot 6H_2O$	85	1.3	8.0	p
Zr^{4+}	0.2[a,c]	$Zr(SO_4)_2 \cdot 4H_2O$	90	1.35	1.0	r
NaOH	0.2	Pure	97	1.1	2.3	o
NaOH	0.2	Extra pure	97	1.1	1.2	o
$NaC_2H_3O_2$	1.5[a]	$NaC_2H_3O_2 \cdot 3H_2O$	79	1.1	0.4	s
NaCl	2.0	—	90	1.1	0.3	
$NaClO_4$	2.0	—	84	1.1	0.4	
$NaNO_3$	2.0	—	85	1.1	0.3	
Na_2SO_4	2.0	—	90	1.1	0.3	
NH_4Cl	0.8[a]	—	92	1.1	0.2	
NH_4ClO_4	0.7[a]	$HClO_4 + NH_4OH$	90	1.1	1.0	
NH_4NO_3	0.8[a]	—	85	1.1	0.3	
$(NH_4)_2SO_4$	1.0	—	88	1.1	0.2	
$(NH_4)_2SO_4$	1.5[a]	—	80	1.1		
$NH_2OH \cdot HCl$	1.0	—	92	0.8–1.0	1.7	
$NH_2OH \cdot HCl$	1.0	—	90	0.9–1.1[b]		t

[a] Maximum permissible amount of ion per determination. [b] pH adjusted before the addition of $NH_2OH \cdot HCl$. [c] Initial volume 35 ml (before ammonium molybdate addition). [d] Adjust pH to 0.7 with dil. NH_4OH. Add $(NH_4)_2MoO_4$. [e] Add 0.1 ml 40% HF and 7.5 ml 4% H_3BO_3. Adjust pH to 0.7 with dil. NH_4OH. Add $(NH_4)_2MoO_4$. [f] Add 0.5 g $NH_2OH \cdot HCl$ and 0.5 ml 9 *N* H_2SO_4. [g] Add 1.0 g $NH_2OH \cdot HCl$ and 0.5 ml 9 *N* H_2SO_4. [h] Add 2.0 g $NH_2OH \cdot HCl$. [i] 7.5 ml 4% H_3BO_3. [j] 15 ml 4% H_3BO_3. [k] Adjust pH to 0.7 with dil. NH_4OH. Add 20 ml of 5% $(NH_4)_2MoO_4$. Add tartaric acid: 50 mg Fe–5 ml; 100 mg Fe–10 ml; 200 mg Fe–20 ml. [l] Add 1 g $NH_2OH \cdot HCl$. Heat at 85° for 15 min. Add $(NH_4)_2MoO_4$. [m] Add 2 g Na_2SO_4. Adjust pH to 0.75. Add $(NH_4)_2MoO_4$. [n] Add 0.05 ml 40% HF, 2 ml HNO_3, 2 g Na_2SO_4 and 7.5 ml 4% H_3BO_3. Adjust pH to 0.85. Add $(NH_4)_2MoO_4$. [o] Add 2 ml 9 *N* H_2SO_4. [p] Add 0.1 ml 40% HF, 7.5 ml 4% H_3BO_3 and 1.5 ml 9 *N* H_2SO_4. [r] Add 0.4 ml 40% HF and 15 ml 4% H_3BO_3. [s] Add 5 ml 9 *N* H_2SO_4. [t] Heat at 85° for 15 min. Add $(NH_4)_2MoO_4$.

Blanks and corrections

The absorbance of the blanks was about 0.034, of which 0.022 units was attributable to the isoamyl alcohol and reducing solution. The remaining absorbance, corresponding to 0.2 μg of Si, was due to total silica impurities in the distilled water and reagents. Much higher absorbance blanks were obtained when mixtures of hydrofluoric and boric acids were used (0.115) or when the addition of 1 g of hydroxylamine hydrochloride was incorporated in the method (0.105).

Study of interferences

Silica can be determined using the recommended procedure when the following ions are present: BO_3^{3-}, Be^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, UO_2^{2+}, Na^+, Cl^-, ClO_4^-, NO_3^-, SO_4^{2-} and $C_2H_3O_2^-$. Some modifications are necessary when the following ions are present: Al^{3+}, Ce^{4+}, F^-, Fe^{3+}, MnO_4^-, Th^{4+}, Zr^{4+}, $NH_2OH \cdot HCl$ (Table III).

Sodium salts, in excess of 2 g, can be tolerated in the aqueous phase with some loss in recovery. However, when ammonia is used as neutralizing agent, an acid-insoluble precipitate forms and the maximum free acid to be neutralised is 13 meq of HCl, 6 meq of $HClO_4$, 16 meq of HNO_3 and 11 meq of H_2SO_4. The initial volumes must be increased when sample aliquots containing larger amounts of free acid are used.

Aluminium forms a precipitate when ammonium molybdate is added before the pH adjustment with ammonia. This can be avoided by adjusting the pH to 0.7 with dilute ammonia, while stirring with a magnetic stirrer, followed by the addition of the ammonium molybdate from a pipette. This produces a clear solution of pH 1.1. If inactive silica is present in an aluminium sample, it is necessary to heat with H_2SO_4–HF in a platinum dish at 80° for 30 min to convert the silica to the reactive form[8]. After cooling, an aliquot containing not more than 0.1 ml of 40% HF is treated with 7.5 ml of saturated boric acid. After 15 min, the above procedure for aluminium is followed.

Cerium must be present in the reduced state, otherwise on addition of ammonium molybdate, a precipitate is formed. Cerium can be reduced to cerium(III) using hydroxylamine hydrochloride. However, the pH after ammonium molybdate addition must be controlled to between 0.8 and 1.0. Even when cerium is in the reduced state, small amounts of sulphate ions (250 mg) must be present to prevent turbidity in the final solution for colorimetric determination. When larger amounts of hydroxylamine hydrochloride (2 g) are used, no sulphate ion is required.

Hydrofluoric acid may be necessary for dissolution of some metal samples, to hold cations in solution (*e.g.* zirconium), and to dissolve any insoluble silica in the sample[8]. The maximum amount of 40% hydrofluoric acid which can be satisfactorily complexed with boric acid is 0.2 ml. In this case the optimum pH before development of the yellow silicomolybdate is 1.4. A waiting time of 15 min after addition of boric acid is necessary. Varying amounts of hydrofluoric and boric acids and salts require different pH adjustments, after ammonium molybdate addition, to obtain maximum absorbance (Table IV).

Iron forms a precipitate when ammonium molybdate is added before the pH adjustment with ammonia. The correct pH is obtained by adjusting the pH of the solution to 0.7 using dilute ammonia, with stirring, followed by the addition of 20 ml of 5% ammonium molybdate from a pipette. The maximum permissible amount of iron(III) in the sample aliquot is 100 mg, but larger amounts of tartaric acid must be used when more than 50 mg of iron(III) is taken for analysis (Table III). The use of hydroxylamine hydrochloride raises this maximum iron limit to 0.5 g. It is essential that all iron be present as iron(II), which is obtained by heating solutions containing iron(III) with hydroxylamine hydrochloride for 15 min at 85°. The pH is adjusted to 0.9–1.1 using dilute ammonia, with stirring, before the addition of 10 ml of 10% hydroxylamine hydrochloride. Any slight turbidity formed during the pH adjustment dissolves on the addition of hydroxylamine hydrochloride. After heating at 85° for 15 min and cooling, ammonium molybdate solution is added, but no further pH adjustment is made, even though the pH after heating is below 0.4.

TABLE IV

pH RANGE REQUIRED TO OBTAIN MAXIMUM ABSORBANCE, AFTER AMMONIUM MOLYBDATE ADDITION, IN THE PRESENCE OF VARYING CONCENTRATIONS OF HF, H_3BO_3 AND SALTS

40% HF (ml)	*4% H_3BO_3 (ml)*	*Salt added*	*pH range*
—	7.5	—	0.9–1.6
0.1	7.5	—	1.2–1.8
0.1	7.5	0.8 g NH_4NO_3	1.1–1.5
0.1	7.5	2.0 g Na_2SO_4	1.4–1.8
0.2	7.5	—	1.4–1.9
0.1	15.0	—	1.1–1.7
0.2	15.0	—	1.2–1.8

Phosphate interferes seriously and only 500 µg of phosphate ion can be tolerated in the recommended procedure.

Thorium solutions form precipitates during the adjustment of pH. This can be overcome by adding 2 g of sodium sulphate to the sample aliquot. Then the pH of the solution is adjusted to 0.75 using dilute ammonia, with stirring, followed by the ammonium molybdate addition from a pipette. The general procedure for dissolution of thorium metal or oxide is as follows. Dissolve 1 g of sample in 25 ml of 5 *N* nitric acid containing 0.1 ml of 40% hydrofluoric acid at 80° for 30 min. Cool and transfer solution to a 100-ml polythene cylinder containing 30 ml of saturated boric acid solution. Dilute to volume, mix and take 25 ml for the determination of silicon. A synthetic solution of all the reagents was prepared and standard additions of 5 and 10 µg of silicon were made. Recoveries of 84% indicate that, so long as standard additions are made, silicon at trace levels can be determined satisfactorily in thorium metal or thoria.

Uranium forms a precipitate when the pH is raised above 0.9. Sample aliquots must not contain more than 0.5 g of uranium whereas 1.25 g of sodium sulphate must be added to prevent the formation of a precipitate. Smaller amounts of uranium require proportionately less sodium sulphate. The pH after ammonium molybdate addition should be controlled between 1.0 and 1.1. When hydrofluoric acid has been used to dissolve any insoluble silica, the following procedure is recommended. Take an aliquot containing not more than 0.5 g of uranium and 0.1 ml of 40% hydrofluoric acid, add 1 g of sodium sulphate and 7.5 ml of saturated boric acid. After 15 min add

10 ml of ammonium molybdate solution and adjust the pH between 1.2 and 1.4. Continue as in the recommended procedure.

Zirconium can be held in solution with fluoride ion (0.2 g of zirconium requires 0.4 ml of 40% HF). The following procedure is recommended for the dissolution of zirconium metal. Place 1 g of metal in a platinum dish, add 2 ml of 40% hydrofluoric acid, 4 ml of nitric acid, 1 ml of sulphuric acid and 20 ml of water. Use gentle heating to control the rate of dissolution. A special blank for zirconium must be used because the normal reagent blank, containing large amounts of fluoride ions, cannot be prepared. The blank is prepared by taking a similar sample aliquot, adding 0.2 ml of hydrofluoric acid and 1 ml of sulphuric acid and fuming off silicon tetrafluoride until the salts start to crystallize; the precipitate is dissolved in water and the required amount of hydrofluoric acid is then added.

The modified procedure for zirconium is as follows. Transfer an aliquot of acidic sample solution containing not more than 0.2 g of zirconium to a 200-ml polythene beaker. For every 0.1 g of zirconium add 0.2 ml of 40% hydrofluoric acid, if not already added at the dissolution step. Add 15 ml of saturated boric acid and let stand for 15 min. Add ammonium molybdate solution and adjust the pH to 1.35. Continue as in the recommended procedure.

Hydroxylamine hydrochloride was used in the modified procedure to allow the determination of silicon in cerium, large amounts of iron, and oxidizing agents, *e.g.* potassium permanganate and potassium dichromate. When large amounts of hydroxylamine hydrochloride are used as a reducing agent in the cold, the pH of the solution after ammonium molybdate addition should be between 0.8 and 1.0. Of the many reducing agents investigated, only hydroxylamine hydrochloride did not reduce molybdenum(VI) to a lower valency state. It tends partially to reduce the yellow silicomolybdate complex, and the organic extracts are light blue in colour. When hydroxylamine hydrochloride has been used, the absorbance of silicomolybdate blue is unstable (3% increase per hour), which appears to be due to the extraction of residual amounts of hydroxylamine hydrochloride into the organic phase. On reduction and decomposition, hydroxylamine hydrochloride forms poisonous gases and all operations should be carried out in fume hoods or well-ventilated rooms.

Reproducibility of the method

Readings on a series of 10 standards showed the relative standard deviation at the 0.2 μg Si/ml level to be ±1%. Slightly lower absorbances were obtained in the lower temperature range. This would be due to the extraction step rather than the colour intensity, which is independent of temperature. The effect appears to be due to an increase in the acid–water concentration in the organic layer at lower temperatures.

APPLICATIONS

The results obtained for a variety of standard materials are shown in Table V.

Samples must not be dissolved in glass beakers, but platinum dishes or teflon beakers may be used for dissolution. It was found that 5 μg of silicon is leached from a 250-ml pyrex beaker when 20 ml of (1:9) sulphuric acid is used to dissolve pure iron granules (BCS 149).

The amount of acid used for dissolution of the samples must be kept to a minimum, otherwise large amounts of salts, which are formed in the neutralization step, will interfere with the procedure. Recoveries from standard addition (5 μg is recommended) should be more than 80%, otherwise the results are not reliable. The amount of acid can be reduced by evaporating solutions to a smaller volume before the addition of hydrofluoric acid.

TABLE V

SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN VARIOUS MATERIALS

Sample	*Certificated Si (%)*	*Si found (%)*	*Recovery on standard addition (%)*
Pure iron BCS 149	0.003 (Range 0.002–0.003)	0.0020[a]	—
		0.0012[b]	—
		0.0011[c]	90
		0.0020	90
Pure iron BCS 149/2	0.002	0.0010[b]	—
		0.0010[c]	90
		0.0018	90
Free cutting steel BCS 152/1	0.034 and 0.04	0.0403	98
Ni–Cr–Mo steel BCS 225/1	0.165 (Range 0.155–0.175)	0.175	99
"18–8" stainless steel + Ti BCS 235/1	0.60 (Range 0.59–0.615)	0.596	99
Cupro-nickel "A" BCS	0.12 (Range 0.10–0.14)	0.109	99
BeO NBL 72-5	0.0083	0.0077	80
BeO NBL 96-2	0.0225	0.0217	92
$UO_2(NO_3)_2 \cdot 6H_2O$	—	0.0008[d]	85
U_3O_8	—	0.0008[d,e,f]	87
U_3O_8	10 μg of Si added per 1 g of U	0.0018[d,e,f]	87

[a] Dissolved in "pyrex" beaker, analysed to BS 1121: Part 19: 1951. [b] Dissolved in teflon beaker, analysed to BS 1121: Part 19: 1951. [c] 0.4 ml of 40% HF added after dissolution in acids. [d] Expressed on uranium basis. [e] Prepared from $UO_2(NO_3)_2 \cdot 6H_2O$. [f] Checked spectrographically, agrees with NBL 95 series.

Hydrofluoric acid must be used for the dissolution of metals when total silicon is required. Silica in oxide samples is in an unreactive form and hydrofluoric acid must be added to convert it to the reactive form, either after sample dissolution (U_3O_8) or during the dissolution step (BeO). In general, oxide samples must be left to stand overnight after dissolution. However, in the case of U_3O_8 (ignited at 850°) a reaction time of 60 h was necessary. Results indicate that silica in highly ignited oxides is less reactive towards hydrofluoric acid and therefore hydrofluoric–sulphuric acid dissolution is not applicable to the determination of silicon in sintered or high-temperature fired oxides. It is recommended that when oxide standards are prepared for spectrographic analysis, the coprecipitate should be ignited at lower temperatures, a fraction analysed for silicon content, and then the remainder ignited at the required temperature. The amount of silicon then can be calculated from the difference in the weights.

When oxidizing acids have been used, it is necessary to add small amounts of hydroxylamine hydrochloride (0.2 ml of 10% solution) to remove any traces of oxidants from the solution.

When hydroxylamine hydrochloride has been added to solutions containing copper, the preliminary pH adjustment must be such that after ammonium molybdate addition, the correct pH is obtained. The ammonium molybdate should be added from a pipette with stirring.

Iron

Weigh 1 g of low silicon iron into a 250-ml teflon beaker, add 20 ml of double strength No. 3 dissolving acid[1] (72 ml of sulphuric acid and 91 ml of nitric acid diluted to 1 l) and 4 ml of 4% hydrofluoric acid. Dissolve the sample at 85°. Add 20 ml of water and let stand at 85° for 30 min. Transfer the sample to a 100-ml polythene cylinder containing 30 ml of saturated boric acid, dilute to 100 ml with water and mix. After 15 min pipette 25 ml into a polythene beaker, adjust the pH to 0.9–1.1, add 10 ml of 10% hydroxylamine hydrochloride solution, dilute to 40 ml, and continue as for iron (modified procedure). Prepare a blank, and make a standard addition of 5 μg of silicon.

Steel

Weigh 0.25 g of sample into a 250-ml teflon beaker, add 50 ml of No. 2 dissolving acid[1] (125 ml of hydrochloric acid and 45.5 ml of nitric acid diluted to 1 l) and 0.4 ml of 40% hydrofluoric acid. Dissolve the sample at 85°. Transfer the sample to a 100-ml polythene cylinder containing 30 ml of saturated boric acid, dilute to 100 ml with water and mix. Pipette an aliquot containing 5–10 μg of silicon into a polythene beaker and add saturated boric acid to increase the total volume of boric acid to 7.5 ml. Add 0.2 ml of 10% hydroxylamine hydrochloride solution, dilute to 25 ml and let stand for 15 min. Adjust the pH to 0.7, with stirring, add 20 ml of 5% ammonium molybdate from a pipette and continue as in the recommended procedure. Prepare a blank, and make a standard addition of 5 μg of silicon.

Cupro-nickel

Weigh 0.20 g of sample into a 250-ml teflon beaker, add 30 ml of water, 6 ml of nitric acid, 2 ml of hydrochloric acid and 0.4 ml of 40% hydrofluoric acid. Dissolve the sample at 85°. Transfer the sample to a 100-ml polythene cylinder containing 30 ml of saturated boric acid, dilute to 100 ml with water and mix. After 15 min, pipette an aliquot containing 5–10 μg of silicon into a polythene beaker; add boric acid and hydroxylamine as in the case of steel, dilute to 25 ml and let stand for 15 min. Adjust the pH to 1.1, add ammonium molybdate from a pipette, with stirring, and continue as in the recommended procedure. Prepare a blank, and make a standard addition of 5 μg of silicon.

Beryllium oxide

Weigh 0.5 g of BeO into a 250-ml teflon beaker, add 20 ml of 9 *N* sulphuric acid, 2.5 ml of 40% hydrofluoric acid and 30 ml of water. Dissolve the sample at 85° and leave the solution to stand overnight. Transfer the sample to a 100-ml polythene cylinder, containing 30 ml of saturated boric acid, dilute to 100 ml and mix. Pipette an aliquot of 10 ml or less, containing 5–10 μg of silicon into a polythene beaker, and add saturated boric acid to increase the total volume of boric acid to 15 ml. Adjust the volume to 40 ml with water and let stand for 15 min. Adjust the pH to 1.05, add 10 ml of ammonium molybdate, readjust to pH 1.4 and continue as in the recommended procedure. Prepare a blank, and make a standard addition of 5 μg of silicon.

Uranium oxide

Weigh 1.18 g of U_3O_8 into a 250-ml teflon beaker, add 5 ml of water, 4 ml of nitric acid and 1 ml of hydrochloric acid. Heat the sample at 85° until almost all of the oxide has been dissolved. Add 30 ml of water and 0.4 ml of 40% hydrofluoric acid, and let the sample stand at 85° for 30 min. Depending on the ignition temperature, leave the sample to stand up to 60 h. Transfer the sample to a 100-ml polythene cylinder containing 30 ml of saturated boric acid, dilute to 100 ml with water and mix. Pipette an aliquot, 25 ml or less, containing 5–10 μg of silicon into a polythene beaker and add saturated boric acid to increase the total volume of boric acid to 7.5 ml. Add 0.75 ml of 9 *N* sulphuric acid, 0.2 ml of 10% hydroxylamine hydrochloride and dilute to 40 ml. Add 10 ml of ammonium molybdate, adjust pH to 1.3 and continue as in the recommended procedure. Prepare a blank, and make a standard addition of 5 μg of silicon.

It is a pleasure to acknowledge the assistance given by Mrs. B. MCALLISTER with some of the experimental work.

SUMMARY

A general method is presented for the spectrophotometric determination of silicon at trace levels. It involves the extraction of the yellow silicomolybdate with isoamyl alcohol and subsequent reduction to silicomolybdate blue. The method covers the range 0.2–15 μg of silicon. A comprehensive study of interferences using standard additions of 5 and 10 μg of silicon was carried out and many modifications are incorporated to permit the determination of silicon in a wide variety of metals and salts.

RÉSUMÉ

Une méthode générale est proposée pour le dosage spectrophotométrique du silicium (0.2 à 15 μg Si). Elle consiste à effectuer une extraction du silicomolybdate jaune dans l'alcool isoamylique, puis une réduction sous forme de bleu de molybdène. On propose plusieurs modifications de la méthode pour permettre le dosage du silicium dans de nombreux métaux et sels.

ZUSAMMENFASSUNG

Für die spektralphotometrische Bestimmung von Spuren Silicium wird eine allgemeine Methode angegeben. Bei ihr wird das gelbe Silicomolybdat mit Isoamylalkohol extrahiert und anschliessend zum Silicomolybdat-Blau reduziert. Die Methode eignet sich für den Bereich von 0.2–15 μg Si. Eine umfassende Untersuchung der Störungen wurde durchgeführt und zahlreiche Modifikationen eingefügt, welche die Bestimmung des Siliciums neben einer Anzahl von Metallen und Salzen erlauben.

REFERENCES

1 G. V. POTTER in D. F. BOLTZ, *Colorimetric Determination of Non-metals*, Interscience, New York, 1958, p. 47.
2 H. R. SHELL, in I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Part II, Vol. 2, Interscience, New York, 1962, p. 107.
3 P. PAKALNS, *Australian At. Energy Commission Report AAEC/TM144*, 1962.
4 D. R. SCHINK, *Anal. Chem.*, 37 (1965) 764.
5 J. MINCZEWSKI AND J. CHWASTOWSKA, *Chem. Anal. (Warsaw)*, 6 (1961) 715.
6 F. H. HARRISON, *Metallurgia*, 66 (1962) 300.
7 K. J. JENSEN AND C. J. RODDEN, in C. J. RODDEN, *Analytical Chemistry of the Manhattan Project*, National Nuclear Energy Series, Div. VIII, Vol. 1, McGraw-Hill, New York, 1950, p. 218.
8 A. G. CARLSON AND C. V. BANKS, *Anal. Chem.*, 24 (1952) 472.

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PRELIMINARY STUDIES OF PRECIPITATION TITRATIONS OF ORGANIC COMPOUNDS USING POLAROVOLTRIC END-POINT INDICATION

PART III. TITRATION OF NITROGEN BASES WITH IODINE

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Iodine in organic solvents or in iodide-containing aqueous solution is a well known direct titrant in organic analysis. Most determinations have been based on oxidation, *e.g.* those of ascorbic acid, mercaptans and hydrazines. Iodine has the advantage of being a much milder oxidising agent than bromine and others commonly used. Some direct titrations have been based on precipitation of a periodide salt, usually a triiodide. The compounds thus determined have been chiefly quaternary ammonium salts[1-3]; some other "onium" salts (arsonium, phosphonium, sulphonium)[1,4] and certain dyes have also been determined[5]. With one exception[3], end-point determination has been either potentiometric or with an external starch indicator.

In the present work, the use of the polarovoltric end-point indication and the titration of nitrogen bases, as opposed to "onium" salts have been investigated.

EXPERIMENTAL

Reagents and solutions

Sulphuric, hydrochloric and acetic acid solutions, ranging from 0.01 *N* to *N*.

Acetate buffers, pH 3.6, 4.6 and 5.6, *ca.* 0.1 *M*.

Iodine solutions 0.1 *M* in water, *ca.* 0.15 *M* in iodide; and 0.1 *M* in 3:2 ethanol/water, *ca.* 0.1 *M* in iodide.

Aqueous 1% solution of the colloid stabiliser, polyvinyl pyrrolidone.

The nitrogen bases were commercial reagent-grade materials, or technical materials purified by crystallisation. Stock solutions, mostly 0.1 *M*, were made in *n*-propanol (miscible with water, inert to iodine under the conditions used and less volatile than ethanol and methanol); acetic acid had to be mixed with the propanol to allow a sufficiently concentrated stock solution of the weaker bases to be attained.

Apparatus and procedure

These were essentially the same as in Parts I[6] and II[7], using the "Titravit" and platinum indicator electrodes. *Ca.* 20 ml solution were titrated, made up of buffer or acid solution and an aliquot of sample containing 0.1 μmol. Varying amounts of potassium iodide and/or stabiliser solution were also added. The point of maximum gradient of the curve of permanent instrument deflection against added reagent was taken as the end-point. Further aliquots were added and titrated where possible. In some cases the sample was added to buffer or acid, plus about 90% of the expected iodine amount and titration then completed in the usual way. Some blank titrations were also carried out.

RESULTS

Primary and secondary amines could not be titrated (unless containing a basic tertiary nitrogen atom also), even when the molecular weight neared 300. Thus stearylamine, N-methylstearylamine, di(2-ethylhexyl)amine, dibenzylamine and 2,4,6-trimethylaniline did not yield a periodide precipitate under the conditions used. Tertiary bases with less than 3 aromatic or heterocyclic nuclei also gave no periodide precipitate (*e.g.*, tri-*n*-amylamine, α-phenylpyridine, quinoline, 2-methyl- and 2,4-dimethylquinolines).

TABLE I

TITRATIONS AT DIFFERENT pH VALUES

(Results as mol ratio iodine/base)

Base	*mmols*	*Medium*												
		Sulphuric acid normality		*Hydrochloric acid normality*					*Acetic acid normality*			*Acetic acid/acetate pH*		
		1	*0.1*	*1*	*0.5*	*0.25*	*0.1*	*0.01*	*1*	*0.5*	*0.1*	*3.6*	*4.6*	*5.6*
Acridine	1	0.48	0.54	0.42 0.49	— —	— —	0.56	—	0.49			0.26	0.26	
	2		0.53		—	—	0.52	—						
9-Amino-acridine (hydro-chloride)	1		0.47			—	0.47	—	←		0.47			→
	2		0.47			—	0.47	—	←		0.47			→
Proflavine (hemi-sulphate)	0.5					—	0.99	—	←		0.99			→
	1					—	0.99	—	←		0.99			→
Phen-anthridine	1		0.40	0.33	—	—	0.39	—	0.26 0.41[a]	—	0.33 0.46[a]	0.35 0.46[a]		
	2		0.40		—	—	0.41	—	0.30 0.42[a]					
o-Phen-anthroline	1							—			0.20	0.26	0.31	0.36
	2							—						0.36
α-Phenyl-quinoline	1		0.41	0.52	0.52	0.49	0.46	—	0.26	0.29				
	2		0.41	0.51	0.51	0.47	0.46	—	0.30	0.31				
	3		0.39	0.45	—	—	0.43	—						
Tribenzyl-amine	1	0.98	0.97		0.93	0.94	0.96	0.97	0.96	0.96				
	2	0.97	0.97		0.92	0.94	0.95	0.97	0.95	0.95				
	3	0.95	0.96				0.94	0.94						
Dibenzyl-aniline	1			0.68										
	2			0.68										

[a] Second end-point.

(—) Intermediate acid concentration not tried.

The positive results are given in Table I. They are averages of at least 4 values, reproducible to within 1–5%. The absence of a quoted value indicates that no titration was possible under the conditions, for one of 4 reasons: the base precipitated (as with the weaker bases at higher pH values); the sulphate or hydrochloride precipitated and changed too slowly into a periodide; no periodide or a too soluble periodide was formed; no end-point could be observed. Except in the cases mentioned below, titration duration ranged from 10 to 25 min.

Influence of pH and anion

The pH had a variable influence. Thus the iodine consumption of *o*-phenanthroline and phenanthridine rose with increase in pH in acetic acid and acetate buffers. Acridine, phenanthridine and tribenzylamine also gave increased titration values in hydrochloric acid of lower concentrations and higher pH; this effect was however small with the last-named base. In contrast, α-phenylquinoline required less iodine with increase in pH in hydrochloric acid and the titrations of 9-aminoacridine and of proflavine were essentially independent of the medium and its pH between *ca.* 1.1 (0.1 *N* hydrochloric and sulphuric acids) and 5.6. Broadly speaking, hydrochloric and sulphuric acids gave the same results.

Influence of stabiliser

Stabiliser was advantageous and subsequently used (4 drops) only with acridine in acetate buffers, where otherwise a coarse precipitate was formed which contaminated the electrodes and impeded end-point indication. An early end-point was obtained with proflavine which corresponded with the minimum in titration speed without stabiliser, mentioned below. Tribenzylamine could be titrated more rapidly (30–40 min) than in absence of stabiliser. No such acceleration was found in the other titrations and α-phenylquinoline could not be titrated at all.

Influence of iodide concentration

Although some former data on methylene blue had indicated that the stoichiometry of iodine titration depended on the iodide concentration, no influence could be established in the present work.

Stoichiometry

The mole ratio varied greatly. Simple definite products correspond to mole ratios of 2, 1, 0.66 etc. For monoacid bases, the products would then be, respectively, $(\text{Base.}\,H^+)I_5^-$; $(\text{Base.}H^+)I_3^-$ and $(\text{Base.}H^+)_3I_7^{3-}$, etc. Such ratios were rarely observed, so that mixed precipitates must often have been formed. It is of interest that no ratio above 1.0 was found, suggesting that penta-, hepta- and higher periodides are not formed under direct titration conditions; they have of course been reported in indirect titration, *e.g.*, a pentaiodide of caffeine[8] and an enneaiodide of choline[9].

Sometimes an intermediate slowing up of titration speed was observed. This was semiquantitatively followed by measuring the time of return to its starting position of the Titravit instrument needle from the deflection produced by each successive addition of reagent. In a normal titration, this time is at first short, remains fairly constant and finally increases rapidly, announcing the imminence of the end-point; this point is associated with essentially permanent deflections, *i.e.*, maintained for at least several minutes. With proflavine, tribenzylamine and dibenzylaniline, the time of return of the needle first increased to a maximum, then decreased and finally increased again, heralding the normal end-point. The point of maximum time of return cannot strictly be considered as an end-point since the deflections were not permanent and the needle moved back continuously, if slowly; it could however be estimated fairly accurately and the corresponding iodine/base ratios are given in Table II. These titration "delays" were accompanied by a colour change of the precipitate, also given in Table II. Evidently they were due to the slow conversion of an iodine-poorer into an iodine-richer product. It was found that a partially indirect titration procedure bypassed the formation of the former. In this, an iodine amount about 80–90% of the expected total consumption was added to the acid or buffer, the sample then introduced and titration completed as usual. Practically the same end titrations were obtained and the duration was reduced from well over an hour to 10–30 min. It is noteworthy that this indirect titration stage did not lead to the permanent formation of higher periodides like those mentioned above with caffeine and choline.

TABLE II

FORMATION OF DIFFERENT REACTION PRODUCTS DURING TITRATION

(Results as mol ratio iodine/base)

Base	*mmols*	*Medium*	*End-points*		*Colour change at 1st end-point*
			1st	*2nd*	
Tribenzylamine	1	Sulphuric acid, 0.1 *N*	0.50	0.97	Yellow-brown to dark red-brown
Dibenzylaniline	1	Hydrochloric acid, *N*	0.45	0.68	Yellow-brown to black
Proflavine (hemisulphate)	0.5	Acetate buffer, pH 4.6	0.30	0.99	Black to light brown
Phenanthridine	1	Acetic acid, *N*	0.26	0.41	Black to light brown
	2	Acetic acid, *N*	0.30	0.42	
	1	Acetic acid, 0.1 *N*	0.33	0.46	
	1	Acetate buffer, pH 3.6	0.35	0.46	
Acridine	1	Hydrochloric acid, *N*	0.42	0.49	Black to light brown

Similar phenomena but with a distinct intermediate end-point were observed with phenanthridine and acridine. The former yielded black precipitates with lower iodine titrations in acetate buffers and acetic acid; and light brown precipitates with higher titrations in the inorganic acids. Accordingly, after the end-point in acetate or acetic acid had been attained, the mixture was energetically stirred and after about 5 min the instrument needle did in fact move back to its starting position and the precipitate become pale brown. A second end-point was then found with titration values close to those in the inorganic acids. Acridine behaved similarly in *N* hydrochloric acid, giving a second end-point after a colour change from black to the light brown associated with higher titrations in sulphuric acid, 0.1 *N* hydrochloric acid and *N* acetic acid. Acridine showed also low titrations and black precipitates in acetate buffers but no change to brown and return of the instrument pointer could be brought about by stirring. This may be related to the use of stabiliser in the acetate buffers. The data for phenanthridine and acridine are also in Table II.

The widely fluctuating data are difficult to interpret. The titratable bases can, however, be divided into two groups: a first group of proflavine, 9-aminoacridine, tribenzylamine and possibly dibenzylaniline; all showed a steep and large jump in potential difference at the end-point and good reproducibility of about 1%. The remaining 4 bases form the second group with less favourable features of a flatter and smaller potential jump and reproducibility of only about 5 %. The periodides of the first group are evidently more sparingly soluble and more quantitatively precipitated. Filtration of the solution at the end-point and addition of further iodine to the filtrate gave no turbidity or additional precipitate; the same treatment of the titrated solutions from the second group yielded distinct precipitates. Data are given in Table III which contains also pK_B values where known. It is noticeable that these values are much lower for the first group. Summing up, it appears that direct titration is possible for tertiary bases containing 3 aromatic and/or heterocyclic rings and is more satisfactory with stronger bases. Bases containing more than 3 rings are likely too often to yield precipitates of salt (*e.g.*, sulphate or hydrochloride) or to precipitate before the titration. An interesting point to be investigated is how far the benzene or

TABLE III

SENSITIVITY OF END-POINT DETERMINATION

Base	*Medium*	*mV jump by addition of 1 µmol iodine (0.1 ml 0.1 M solution)*	*Precipitation at end-point*	*Approx. reproducibility*	*Approx. pK_B in water or in 1:1 water/ethanol*
9-Aminoacridine		500–750	Complete	±1%	4–4.5
Proflavine		600–850	Complete	±1%	4.5
Tribenzylamine		420–625	Complete	±1%	
Dibenzylaniline		250	Complete	±2%	
Acridine	Acids acetate buffers	125–300 375–660	Incomplete	±4%	8.4
Phenanthridine	Acids acetate buffer	200–300 375–420	Incomplete	±3%	9.5–11
o-Phenanthroline		250–550	Incomplete	±2%	10
α-Phenylquinoline		200–375	Incomplete	±5%	

pyridine rings can be replaced by other similarly-sized heterocyclic rings or by aliphatic chains to yield a titratable base. Cetyltrimethylammonium salts with two carbon atoms less than tribenzylamine have been directly titrated with iodine[2,3] although it differs from the compounds studied in this work in being a quaternary salt, derived from a strong base.

SUMMARY

Precipitation titrations of a number of organic bases have been carried out in acid solution with iodine. The influence of several factors, principally the pH value, on the stoichiometry of the reaction has been examined.

RÉSUMÉ

Les auteurs ont effectué des titrages par précipitation, d'un certain nombre de bases organiques, en solution acide, au moyen d'iode. Ils ont examiné l'influence de divers facteurs (principalement le pH) sur la stoéchiométrie des réactions.

ZUSAMMENFASSUNG

Fällungstitrationen mehrerer organischer Basen wurden in saurer Lösung mit Jod durchgeführt. Der Einfluss einiger Faktoren, hauptsächlich der des pH-Wertes, auf die Stöchiometrie wurde untersucht.

REFERENCES

1 A. S. Dubois, *Am. Dyestuff Reptr.*, 34 (1945) 245.
2 O. B. Hager, E. M. Young, T. L. Flanagan and H. B. Walker, *Anal. Chem.*, 19 (1947) 885.
3 M. R. F. Ashworth and W. Walisch, *Z. Anal. Chem.*, 181 (1961) 193.
4 H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 186.
5 L. Pelet and V. Garuti, *Bull. Soc. Vaudoise Sci. Nat.*, 43 No. 158 (1907) 30.
6 M. R. F. Ashworth, H. Göttel and J. Schneider, *Anal. Chim. Acta*, 31 (1964) 17.
7 M. R. F. Ashworth and R. Fehringer, *Anal. Chim. Acta*, 35 (1966) 111.
8 M. Gomberg, *J. Am. Chem. Soc.*, 18 (1896) 331.
9 W. Roman, *Biochem. Z.*, 219 (1930) 218.

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REACTION OF TELLURIUM(IV) WITH DITHIZONE*

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Tellurium was not listed by HELLMUT FISCHER among the many elements found by him to be extracted into carbon tetrachloride or chloroform solutions of dithizone (diphenylthiocarbazone, H_2Dz). In 1956, MABUCHI[1] reported that tellurium-(IV) is extracted from mineral acid solutions by carbon tetrachloride solutions of dithizone. Tellurium may be called a dithizone fringe element. Except at very low concentrations it cannot easily be extracted quantitatively. The dithizone extraction of tellurium is unusual in having an extraction coefficient dependent on the aqueous tellurium concentration at equilibrium. Hitherto, tellurium has been considered to be extracted as Te(IV). Evidence will be presented here that points to its extraction as Te(II). The increasing difficulty in extracting tellurium as its aqueous concentration increases as a consequence of this reduction.

EXPERIMENTAL

Reagents

Carbon tetrachloride and dithizone were purified essentially as described earlier[2]. The purity of the dithizone was 99.6% as found by spectrophotometric titration with silver ion.

Tellurium was obtained free from selenium by 2 precipitations of the latter with sulfur dioxide from concentrated hydrochloric acid solutions of tellurium(IV). Tellurium was precipitated with sulfur dioxide from 6 *M* hydrochloric acid and the washed precipitate was dissolved in concentrated nitric acid. $2TeO_2 \cdot HNO_3$ was crystallized from this solution and converted to TeO_2 by ignition at 450°. Standard tellurium(IV) solutions were prepared by dissolving TeO_2 in perchloric acid (or hydrochloric acid when required).

Solutions of perchloric acid, hydrochloric acid and lithium perchlorate were purified by shaking with saturated solutions of dithizone in carbon tetrachloride. Ammonia was distilled isothermally. Sodium iodide was recrystallized to remove iodate.

General procedure

Equal volumes of aqueous tellurium and carbon tetrachloride–dithizone

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solutions were shaken together mechanically (300 cycles per minute) for 15 min at 25°. The period of shaking was approximately double that required for attainment of extraction equilibrium. Separation of the phases was aided by centrifuging. The ionic strength of all tellurium solutions was maintained constant at 1.0 *M* by addition of lithium perchlorate.

Tellurium in the aqueous phase was determined by the iodide method, essentially as described by JOHNSON AND KWAN[3]. Oxygen was removed from the sample solution by bubbling with nitrogen before addition of iodide. The absorbance was measured at 335 nm; a blank correction was applied. The standard curve (Fig. 1) is of a type seldom encountered, consisting of 2 straight line segments. Sodium iodide, not potassium iodide, was used to supply iodide because of the presence of perchloric acid in most of the runs.

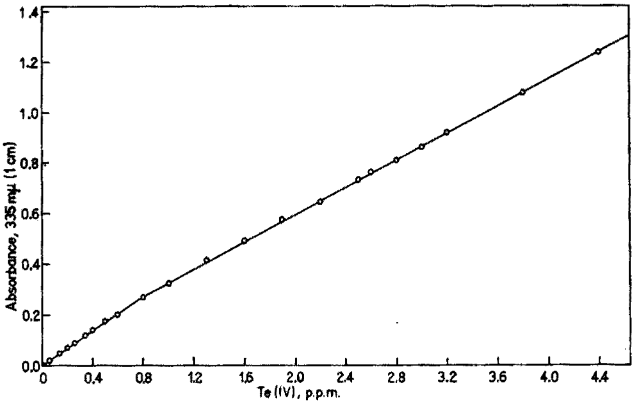


Fig. 1. Standard curve for determination of Te(IV) by the iodide method.

Tellurium in the carbon tetrachloride phase was determined after destroying organic matter with sulfuric–perchloric acid in the presence of 20 mg of sodium sulfate. The acids were finally fumed off and the residue was neutralized with sodium hydroxide. After acidification with perchloric acid, tellurium was determined by the iodide method. The extraction coefficients were calculated from determinations of tellurium in both phases. The reproducibility of the tellurium determination in the aqueous phase was usually *ca.* 1%, in the carbon tetrachloride phase *ca.* 2%.

A Beckman Model DU spectrophotometer was used to measure absorbances in determinations, and a Cary Model 15 was used to obtain spectral curves.

TELLURIUM EXTRACTION VALUES

Especially because the extractability of tellurium as dithizonate depends upon its aqueous concentration, other factors remaining the same, it is convenient to have a series of curves showing the extractability of tellurium(IV) from mineral acid solution as a function of the initial concentrations of tellurium and dithizone. Such curves enable the analyst to predict approximately the extractability for his experimental conditions. A set of these curves for 1 *M* perchloric acid is given in Fig. 2.

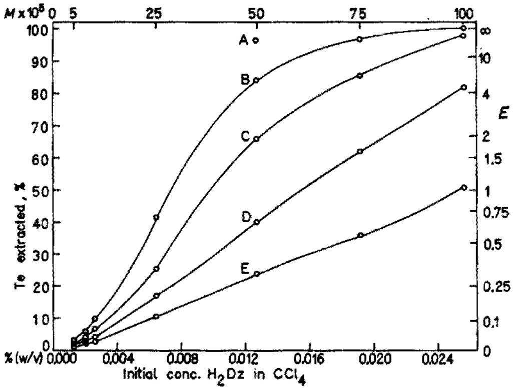


Fig. 2. Extractability of Te(IV) from 1.00 *M* perchloric acid as a function of the initial concentration of dithizone in CCl_4; equal volumes of phases. Initial Te concentrations of aqueous solutions as follows: (*A*) 2.50 p.p.m., $1.96 \cdot 10^{-5}$ *M*; (*B*) 5.00 p.p.m., $3.92 \cdot 10^{-5}$ *M*; (*C*) 10.0 p.p.m., $7.84 \cdot 10^{-5}$ *M*; (*D*) 20.0 p.p.m., $1.57 \cdot 10^{-4}$ *M*; (*E*) 40.0 p.p.m., $3.13 \cdot 10^{-4}$ *M*.

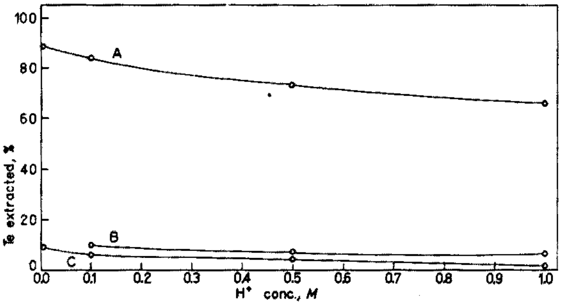


Fig. 3. Extractability of Te(IV) from perchloric acid solutions as a function of $[H^+]$ at constant ionic strength of 1.0 *M*. Initial aqueous Te concentration = 10.0 p.p.m., $7.84 \cdot 10^{-5}$ *M* and initial H_2Dz concentrations in CCl_4 as follows: (*A*) 0.0128% w/v, $5.0 \cdot 10^{-4}$ *M*; (*B*) 0.00256% w/v, $1.00 \cdot 10^{-4}$ *M*; (*C*) 0.00128% w/v, $5.00 \cdot 10^{-5}$ *M*.

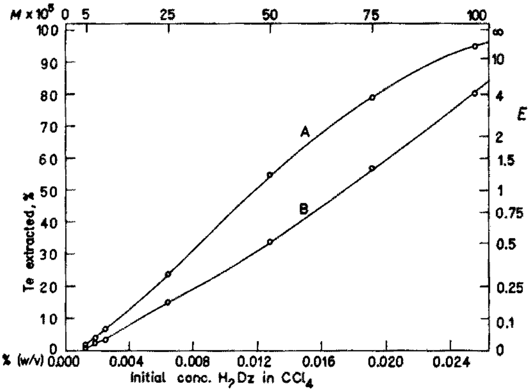


Fig. 4. Extractability of Te(IV) from 1.00 *M* HCl as a function of initial dithizone concentration in CCl_4. Initial Te concentration: (*A*) 10.0 p.p.m., $7.84 \cdot 10^{-5}$ *M*; (*B*) 20.0 p.p.m. Phases equal in volume.

The effect of perchloric acid concentration is shown in Fig. 3. More limited data for tellurium extraction from 1 M hydrochloric acid are represented in Fig. 4.

These curves represent the raw data obtained in this study, which have been replotted to arrive at the conclusions regarding the nature of the extraction reaction which are drawn in the next section. Later an expression will be given for the extraction coefficient of tellurium in terms of the equilibrium concentrations of dithizone and tellurium in the aqueous phase.

NATURE OF THE EXTRACTION REACTION

Tellurium(IV) species in acid solution

The predominant tellurium(IV) species in mineral acid solutions is the cation $TeO(OH)^+$ or an analogous species. This conclusion follows from the linear increase in the solubility of TeO_2 with the hydrogen-ion concentration in perchloric acid solutions (of constant ionic strength) up to at least 1 M (Fig. 5). (SCHUHMANN[4], in solubility determinations in which the ionic strength was not maintained constant, found an approximate linear relationship.) The intrinsic solubility of the tellurium oxide used, as found by extrapolation in Fig. 5, is $8 \cdot 10^{-6}$ M ($\pm 25\%$). The equilibrium constant for the reaction

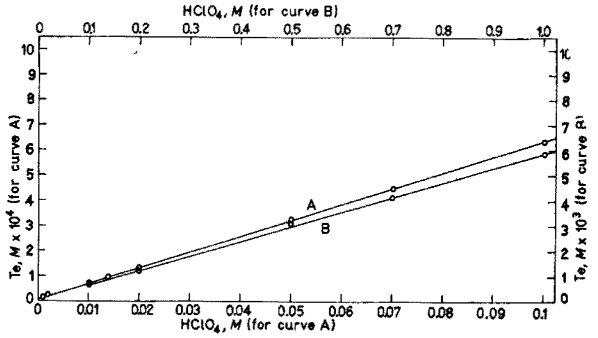


Fig. 5. Solubility of TeO_2 in perchloric acid below 1 M H^+; ionic strength maintained constant with $LiClO_4$ at 1.00 M.

$$TeO_2\text{ (solid)} + H^+ \rightleftarrows TeO(OH)^+$$

is

$$K_s = [TeO(OH)^+]/[H^+] = 6.3 \cdot 10^{-3}$$

based on the slope of the solubility line (A) from 0 to 0.10 M H^+. The values $6.2 \cdot 10^{-3}$ and $5.9 \cdot 10^{-3}$ are obtained from the slopes of the lines from 0 to 0.5 M and to 1.0 M H^+ respectively. Probably the changing ionic composition of the solutions largely accounts for the somewhat lower values at higher acidities.

Also

$$[TeO(OH)^+]/\{[TeO_2]_{soln.}[H^+]\} = 6.3 \cdot 10^{-3}/8 \cdot 10^{-6} = 8 \cdot 10^2 .$$

Since line A in Fig. 5 shows no deviation from linearity near 0.1 M H^+, it seems likely that

$$[TeO^{2+}]/\{[TeO(OH)^+][H^+]\} < 0.03 .$$

Because the highest acidity of any solution in the present extraction work was 1 *M* H^+, TeO^{2+} can be neglected in comparison to $TeO(OH)^+$.

As a matter of interest, the solubility curve of TeO_2 above 1 *M* perchloric acid is given in Fig. 6. The varying ionic strength at the higher acidities makes interpretation of the course of the curve uncertain. Possibly a binuclear tellurium ion is formed in strong perchloric acid. The salt $2TeO_2 \cdot HClO_4$, crystallized from concentrated perchloric acid solution, can be formulated as a binuclear compound, $O(OH)Te{-}O{-}Te(ClO_4)O$.

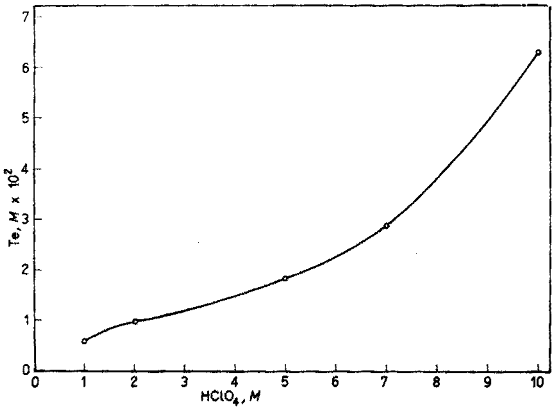


Fig. 6. Solubility of TeO_2 in perchloric acid above 1 *M* (ionic strength not constant).

The reacting ratio $H_2Dz/Te(IV)$

This ratio is difficult to determine exactly. It is impossible, by extracting an aqueous tellurium solution, to obtain a carbon tetrachloride extract of tellurium dithizonate which also does not contain much unreacted dithizone. The mixture of dithizone and the reaction products has a brownish green color. Figures 7a–7d illustrate the absorbance curves obtained by shaking carbon tetrachloride solutions of dithizone with increasing amounts of tellurium(IV). The major absorption peak of dithizone at 620 nm decreases in height on reaction, but the secondary peak at 450 nm changes relatively little. An approach to an isosbestic point appears at *ca.* 490 nm and also at 525 nm. The curves cross at about 425 nm, but definitely do not pass through an isosbestic point. Evidently more than one colored reaction product is formed, but the absorption curves of the products are similar.

A minimum value for the reaction ratio $H_2Dz/Te(IV)$ can be obtained by assuming that the reaction products do not absorb at 620 nm, and relating the decrease in absorbance due to dithizone at that wavelength to the amount of tellurium extracted. This method gives ratios that lie mostly in the range 3.5–4.0, usually closer to 3.5. More nearly correct values require an estimation of the absorbance of the reaction products at 620 nm. By careful washing of a tellurium dithizonate–dithizone mixture with ammonia (see later), a solution containing mostly tellurium dithizonate is obtained. An approximate value of 6200 for ε_{620} of tellurium dithizonate (based upon moles of tellurium) was thus found. However, the oxidation product of dithizone, which is also formed in the tellurium(IV)–dithizone reaction, is apparently removed also with the excess dithizone. Hence, the estimated absorbance

TABLE I

CALCULATED REACTION RATIOS BETWEEN DITHIZONE AND TELLURIUM

Initial		Dilution factor	Initial A_{620}	Final A_{620}	$[Te]_o$ (M) (undiluted)	Final A_{620} due to products	% of H_2Dz reacted	Concentration of reacted H_2Dz (M) (undiluted)	Reaction ratio
$[Te]_w$ (M)	$[H_2Dz]_o$ (M) (undiluted)								
$3.92\cdot10^{-5}$	$5.00\cdot10^{-5}$	1.00	1.618	1.492	$1.04\cdot10^{-6}$	0.006	8.8	$4.40\cdot10^{-6}$	4.23
$3.92\cdot10^{-5}$	$1.00\cdot10^{-4}$	3.33	0.971	0.816	$4.07\cdot10^{-6}$	0.007	16.7	$1.67\cdot10^{-5}$	4.11
$3.92\cdot10^{-5}$	$5.00\cdot10^{-4}$	16.7	0.973	0.716	$3.29\cdot10^{-5}$	0.012	27.7	$1.38\cdot10^{-4}$	4.20
$3.92\cdot10^{-5}$	$1.00\cdot10^{-3}$	33.3	0.981	0.845	$3.90\cdot10^{-5}$	0.007	14.6	$1.46\cdot10^{-4}$	3.74
$7.84\cdot10^{-5}$	$5.00\cdot10^{-5}$	1.00	1.618	1.440	$1.57\cdot10^{-6}$	0.009	11.6	$5.80\cdot10^{-6}$	3.69
$7.84\cdot10^{-5}$	$1.00\cdot10^{-4}$	3.33	0.971	0.781	$5.15\cdot10^{-6}$	0.010	20.6	$2.06\cdot10^{-5}$	3.99
$7.84\cdot10^{-5}$	$5.00\cdot10^{-4}$	16.7	0.973	0.613	$5.15\cdot10^{-5}$	0.019	39.0	$1.94\cdot10^{-4}$	3.78
$7.84\cdot10^{-5}$	$1.00\cdot10^{-3}$	33.3	0.981	0.706	$7.65\cdot10^{-4}$	0.014	29.5	$2.95\cdot10^{-4}$	3.85
$1.57\cdot10^{-4}$	$5.00\cdot10^{-5}$	1.00	1.618	1.395	$3.01\cdot10^{-6}$	0.019	14.9	$7.40\cdot10^{-6}$	2.48
$1.57\cdot10^{-4}$	$1.00\cdot10^{-4}$	3.33	0.971	0.721	$8.71\cdot10^{-6}$	0.013	27.1	$2.71\cdot10^{-5}$	3.75
$1.57\cdot10^{-4}$	$5.00\cdot10^{-4}$	16.7	0.973	0.520	$6.29\cdot10^{-5}$	0.023	49.0	$2.44\cdot10^{-4}$	3.89
$1.57\cdot10^{-4}$	$1.00\cdot10^{-3}$	33.3	0.981	0.507	$1.28\cdot10^{-4}$	0.024	50.7	$5.07\cdot10^{-4}$	3.96
$3.13\cdot10^{-4}$	$5.00\cdot10^{-5}$	1.00	1.618	1.297	$3.49\cdot10^{-6}$	0.022	21.2	$1.06\cdot10^{-5}$	3.03
$3.13\cdot10^{-4}$	$1.00\cdot10^{-4}$	3.33	0.971	0.649	$8.71\cdot10^{-6}$	0.016	34.8	$3.48\cdot10^{-5}$	4.00
$3.13\cdot10^{-4}$	$5.00\cdot10^{-4}$	16.7	0.973	0.438	$7.38\cdot10^{-5}$	0.027	57.8	$2.89\cdot10^{-4}$	3.92
$3.13\cdot10^{-4}$	$1.00\cdot10^{-3}$	33.3	0.981	0.385	$1.59\cdot10^{-4}$	0.029	63.8	$6.38\cdot10^{-4}$	4.01

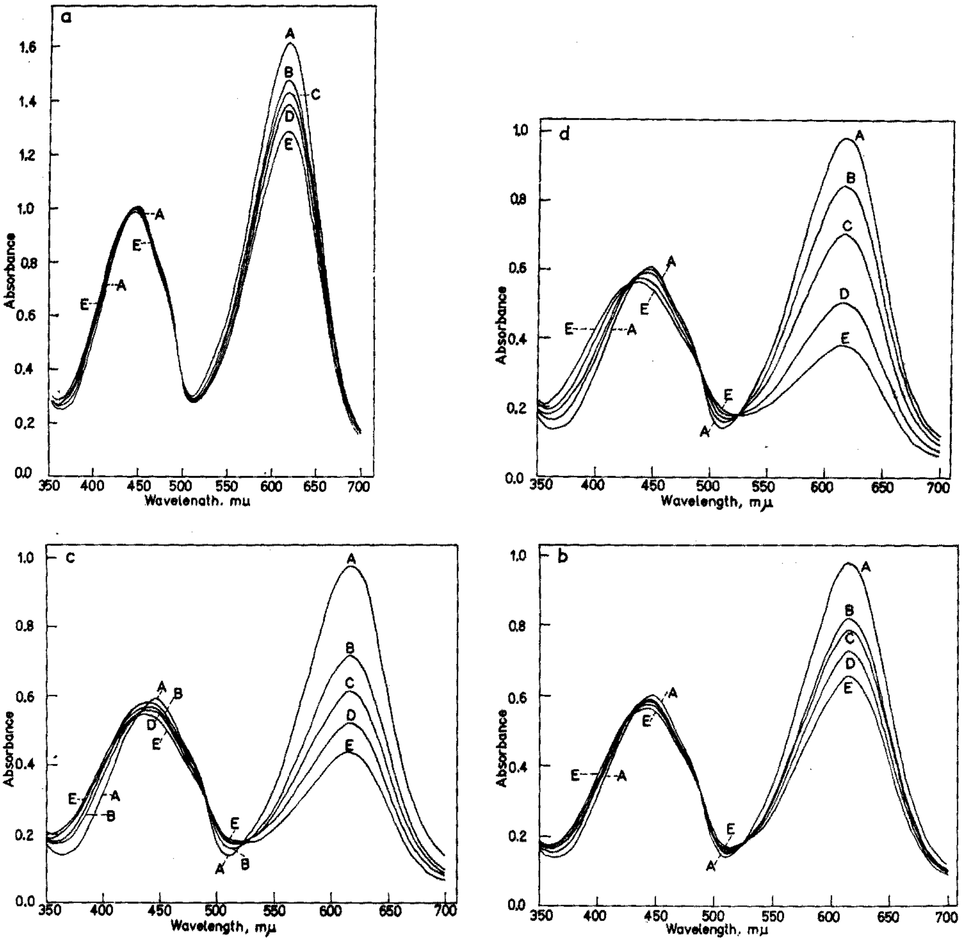


Fig. 7. Absorbance curves (1-cm cells) of carbon tetrachloride solutions of dithizone (initial concns.: (*a*) $5.00 \cdot 10^{-5}$ *M*; (*b*) and (*c*) $5.00 \cdot 10^{-4}$ *M*; (*d*) $1.00 \cdot 10^{-3}$ *M*) shaken with equal volumes of 1.00 *M* $HClO_4$ solutions of Te(IV). Initial Te concentrations as follows: (*A*) 0; (*B*) $3.92 \cdot 10^{-5}$ *M*; (*C*) $7.84 \cdot 10^{-5}$ *M*; (*D*) $1.57 \cdot 10^{-4}$ *M*; (*E*) $3.13 \cdot 10^{-4}$ *M*. (*a*) Solutions not diluted before measurement. (*b*) Solutions diluted 3.33 times before measurement. (*c*) Solutions diluted 16.7 times before measurement. (*d*) Solutions diluted 33.3 times before measurement.

of the reaction products may be too small. The estimate will be approximately correct if the oxidation product does not absorb appreciably at 620 nm. Whether it does or not is unknown; it seems unlikely that ε_{620} of the oxidation product will exceed *ca.* 6000.

More accurate values for the reaction ratio were then calculated by applying a correction corresponding to $\varepsilon_{620} = 6200$ for the reaction products. This correction increases the reaction ratios calculated on the basis of no product absorbance at 620 nm by about 5% ($6200/4 \cdot 32{,}700 = 0.05$, 32,700 being ε_{620} for dithizone found in this work). The reaction ratios found for various concentrations of reactants are summarized in Table I. With two exceptions, the ratios lie in the approximate range 3.7–4.2, the average being 3.95. The exceptions, 2.5 and 3.0, are believed to be real.

These low ratios are obtained at high aqueous tellurium concentrations and the lowest dithizone concentrations. Except with this combination, 4 may be accepted as the reaction ratio. Of course, if more than one reaction is occurring, the actual ratio may not be 4.0, but close to it, and not necessarily constant.

It will be noted that the curves in Fig. 7a, unlike those in Figs. 7b, 7c, 7d, do not cross at 525 nm. This set of curves includes those representing systems in which $[Te]_w$ exceeds $[H_2Dz]_o$, and, especially, two runs giving reaction ratios of 2.5 and 3.0, and another a somewhat low value of 3.69. Apparently, with low concentrations of dithizone and high concentrations of tellurium, another dithizonate, with a smaller ratio H_2Dz/Te may be formed. This possibility was not investigated further, because the chief interest lies in systems in which dithizone outweighs tellurium.

Relation between tellurium extraction coefficient and dithizone concentration

The extraction coefficient, E, of tellurium is defined as the ratio of the analytical concentrations of tellurium in the immiscible organic solvent (o, here carbon tetrachloride) and aqueous phases at equilibrium:

$$E = \frac{\Sigma p[Te_p]_o}{\Sigma q[Te_q]_w} = \frac{\Sigma p[Te_p]_o}{[TeO(OH)^+]} \text{ (the subscript w may be omitted)}$$

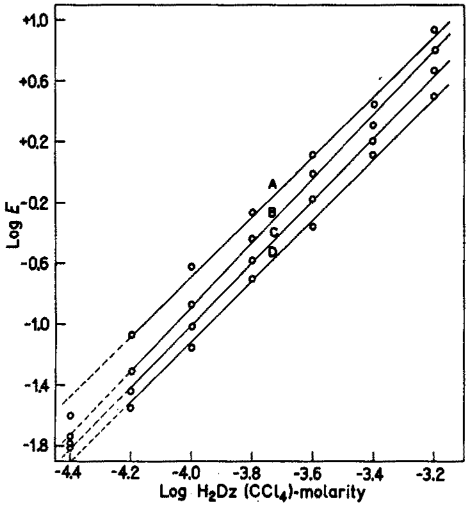
Tellurium will be present in the carbon tetrachloride phase as a dithizonate (less likely as a chelate of an oxidation product of dithizone). No tellurium is extracted by carbon tetrachloride in the absence of dithizone under the experimental conditions.

Since E is a function of the equilibrium concentration of tellurium in the aqueous phase, this variable must be kept constant when $[H_2Dz]_o$ is varied to find its effect on E. The equilibrium concentration of dithizone in a carbon tetrachloride extract was calculated from its initial concentration and the concentration of the extracted tellurium by using the reaction ratios calculated from the absorbance curves as described in the previous section. A preliminary plot was made of log E as a function of equilibrium values of log $[H_2Dz]_o$ for the 4 initial values of $[Te]_w$ that were used. Values of log E were taken from these 4 curves and used to calculate values of $[Te]_w$ at equilibrium for specific values of log $[H_2Dz]_o$. From each value of log $[H_2Dz]_o$ a curve was drawn, plotting log E as a function of log $[Te]_w$, in which $[Te]_w$ is the equilibrium value. (See Figs. 10 and 11 for examples of this type of plot.) Another preliminary plot was made, consisting of a set of log E *versus* log $[Te]_w$ curves for various values of log $[H_2Dz]_o$. Points can be taken from these curves to give the set of curves shown in Fig. 8.

In Fig. 8, straight lines are obtained over the greater part of the range, and the slope of each is close to 2.0:

$$\left(\frac{\partial \log E}{\partial \log [H_2Dz]_o}\right)_{[Te]_w, [H^+]} = 2 \quad (\text{avg.} = 2.03)$$

Apparently the linear relation fails below log $[H_2Dz]_o = -4.2$. As already pointed out, the reacting ratio becomes less than 4 at high aqueous tellurium concentrations and low dithizone concentrations, so that deviations may be expected in this region. Moreover, the analytical error in the determination of tellurium, and therewith the calculated dithizone concentration, becomes large here, and some uncertainty arises from this factor.



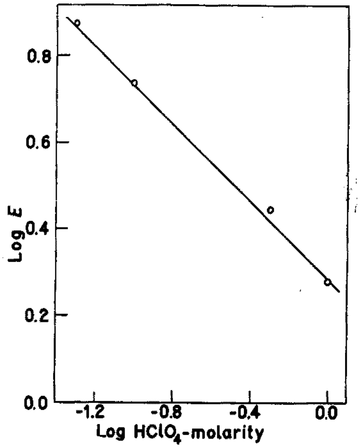


Fig. 8. Logarithm of extraction coefficient E as a function of logarithm of dithizone concentration (CCl_4). Aqueous phase 1.00 M in perchloric acid. Equilibrium Te concentrations of aqueous solution: (A) $2.50 \cdot 10^{-5}$ M; (B) $5.00 \cdot 10^{-5}$ M; (C) $1.00 \cdot 10^{-4}$ M; (D) $2.50 \cdot 10^{-4}$ M. Slopes of lines (least squares): (A) 1.97; (B) 2.10; (C) 2.05; (D) 1.99; average, 2.03.

Fig. 9. Log E as a function of log [$HClO_4$] at a constant ionic strength of 1.0 M for equilibrium concentrations of $[H_2Dz]_0 = 2.94 \cdot 10^{-4}$ M and $[TeO(OH)^+] = 2.69 \cdot 10^{-5}$ M.

From the linear relations holding over the range log $[H_2Dz]_0 = -4.2$ to -3.2, in which range $[Te]_0$ increases 100-fold, it may be concluded that association of tellurium dithizonate (or adduct formation) does not occur.

Effect of hydrogen-ion concentration on extraction of tellurium

In Fig. 3, E is plotted as a function of the perchloric acid concentration at a constant ionic strength of 1.0 M, with the same initial concentration of dithizone in the carbon tetrachloride phase and tellurium in the aqueous phase. But we require E as a function of the hydrogen-ion concentration alone, the other variables being kept constant, so that the E's for Curve A in Fig. 3 have been reduced to the same $[H_2Dz]_0$ and $[Te]_w$, namely that existing at equilibrium in the extraction from 1.0 M perchloric acid ($2.94 \cdot 10^{-4}$ M H_2Dz and $2.69 \cdot 10^{-5}$ M Te in the aqueous phase). The reductions were made on the basis of the relationships

$$E = \text{constant} \cdot [H_2Dz]_0{}^2$$

$$E = \text{constant} \cdot [Te]_w{}^{-\frac{1}{2}} \text{ (see later)}$$

The corrected plot is given in Fig. 9. From the slope of the line in the Fig., we find

$$\left(\frac{\partial \log E}{\partial \log[H^+]}\right)_{[H_2Dz]_0, [Te]_w} = -0.45$$

Curves B and C in Fig. 3 have not been reduced because it is not certain that they represent systems with sufficiently high equilibrium dithizone concentrations to fall in the range treated in this paper.

Relation between tellurium extraction coefficient and aqueous tellurium concentration

In Fig. 10, log E is plotted against log $[Te]_w$ in 1.0 M perchloric acid at constant $[H_2Dz]_o$. This plot is derived from Fig. 8 and thus represents averaged values in the range log $[H_2Dz]_o = -4.2$ to -3.2. The best straight line through the points has a slope of -0.45. In addition, a series of E values were available for a constant equilibrium dithizone concentration of $6.3 \cdot 10^{-4}$ M (log $[H_2Dz]_o = -3.2$), covering the range log $[Te]_w = -6$ to -4.4; these values are plotted in Fig. 11. A straight line of slope -0.47 satisfactorily represents the points.

If only a single extraction reaction is occurring, it seems justifiable to conclude that

$$\left\{\frac{\partial \log E}{\partial \log[Te]_w}\right\}_{[H_2Dz]_o, [H^+]} = -0.5$$

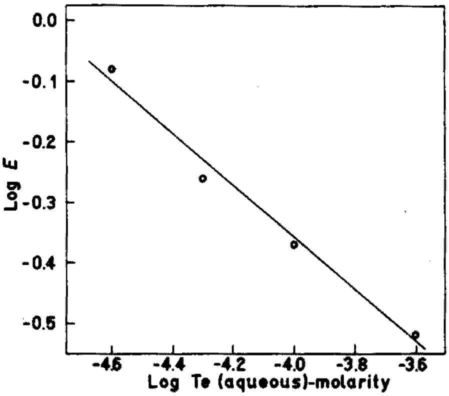


Fig. 10. Log E as a function of log $[TeO(OH)^+]$ in 1 M $HClO_4$ at constant equilibrium concentration of log $[H_2Dz]_o = -3.7$.

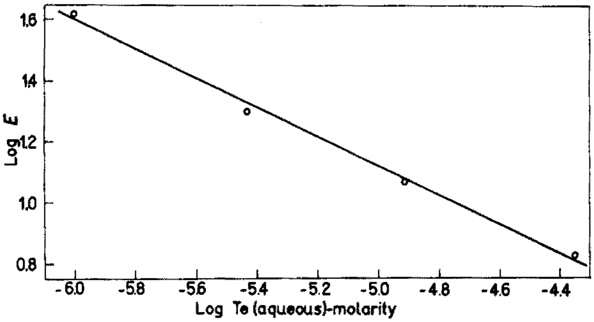


Fig. 11. Log E as a function of log $[TeO(OH)^+]$ in 1 M $HClO_4$ at $[H_2Dz]_o = 6.3 \cdot 10^{-4}$.

Miscellaneous experiments

Ammonia washing of extracts. When a brownish green carbon tetrachloride extract of tellurium dithizonate and dithizone is carefully mixed with dilute ammonia (e.g., 2 M), as by slowly inverting a separatory funnel holding the two phases, the carbon tetrachloride becomes orange after a few inversions. Further mixing results in the decomposition of tellurium dithizonate, and the carbon tetrachloride phase becomes almost colorless. Dithizone is transferred more rapidly to the aqueous phase than tellurium dithizonate is decomposed into HDz^- and tellurite ion by ammonia washing. A sharp separation cannot be obtained, however. Moreover, the orange solution is not stable. It becomes brownish green on standing (Fig. 12); dithizone is formed.

The ratio dithizone/tellurium was determined in 18 carbon tetrachloride extracts that had been washed with ammonia; dithizone was determined by shaking an aliquot of the extract further with ammonia until the dithizonate was completely dissociated, and measuring the absorbance due to HDz^- in the aqueous phase at 470 nm. As might have been expected, variable ratios, ranging from 1.95 to 4.7, were obtained.

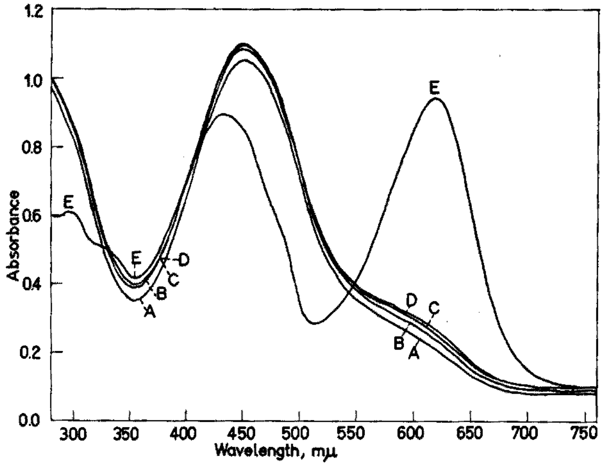


Fig. 12. Absorbance curves of ammonia-washed carbon tetrachloride solution of reaction products in which $\Sigma[H_2Dz]_0/[Te]_0 = 1.95$ ($\Sigma[H_2Dz]_0$, as dithizonate $= 5.12 \cdot 10^{-5}$; $[Te]_0 = 2.63 \cdot 10^{-5}$). Curves recorded at various times after the end of washing: (*A*) 0.5 min; (*B*) 1.8 min; (*C*) 3.5 min; (*D*) 4.8 min; (*E*) 24 h.

From Fig. 12, ε of tellurium dithizonate (thought to be $Te(HDz)_2$ as shown later) may be estimated as roughly 40,000 at the peak near 450 nm and 6000 at 620 nm. Absorbances were extrapolated to zero time after ammonia washing to minimize the effect of the decomposition of the solution.

Solid reaction products. Attempts were made to prepare a solid tellurium dithizonate by adding a mixture of potassium tellurite and dithizone in sodium hydroxide to an excess of hydrochloric acid. For example, 125 ml of 0.5 *M* sodium hydroxide solution containing 5 g of potassium tellurite and 125 mg of unpurified dithizone ($Te/H_2Dz = 40$) was added with vigorous stirring to 700 ml of 3 *M* hydrochloric acid. A black precipitate was obtained, which was washed with 3 *M* hydrochloric acid and dried at room temperature. This solid dissolved readily in chloroform (less easily in carbon tetrachloride) to give a yellow-brown solution, changing quickly in color to greenish brown. It dissolved in absolute ethanol, giving a stable brownish yellow solution. This solution showed a single absorbance peak at 440 nm; little or no free dithizone was present. ε at 440 nm, based on tellurium, was approximately 25,000. The solid contained 10.9% Te and 12.4% Cl. The product is a mixture, and the presence of chloride makes interpretation of the composition difficult. Presumably the dithizone oxidation product postulated to be formed in the dithizone–tellurium(IV) reaction (see later) is present in the mixture, but ammonia decomposition seemed to show an H_2Dz/Te ratio of 2. However, other preparations (including one formed in perchloric acid solution) gave higher ratios.

It may be mentioned in this connection that when finely powdered elemental tellurium is shaken with a chloroform or carbon tetrachloride solution of dithizone (in the presence of air), the solution becomes greenish brown after some days. Complete conversion of dithizone to tellurium dithizonate is apparently not possible. Solid TeO_2 also reacts with dithizone in carbon tetrachloride to give tellurium dithizonate, but more slowly than tellurium.

Attempts to separate chromatographically the components of an alcoholic solution of the solid above on a mixture of Al_2O_3 and $KHSO_4$, were unsuccessful. Likewise, attempts to separate the components of carbon tetrachloride extracts were not fruitful.

INTERPRETATION

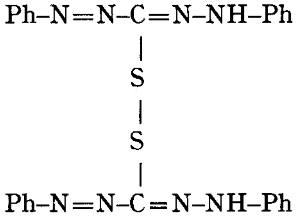
The extracted tellurium species is not $Te(HDz)_4$ or $TeO(HDz)_2$. Certainly the extraction of one or the other of these as the main species is not in accord with the tellurium–dithizone reaction ratio and the effect of the variables $[H_2Dz]_o$, $[H^+]$ and $[Te]_w$ on the extraction coefficient.

Because the combining ratio H_2Dz/Te is 4 and $\left\{\frac{\partial \log E}{\partial \log[H_2Dz]_o}\right\}_{[Te]_w,[H^+]_w} = 2$,

it is natural to consider whether the extracted species is not $Te(HDz)_2$. The extraction reaction may then be written:

$$\underset{w}{TeO(OH)^+} + 4\,\underset{o}{H_2Dz} \rightleftarrows \underset{o}{Te(HDz)_2} + \underset{o}{(HDz)_2} + \underset{w}{H^+} + 2\,H_2O$$

The effect of the variables mentioned requires that the oxidation product of dithizone be $(HDz)_2$, not Dz (the carbadiazone). The postulated compound $(HDz)_2$ apparently has not been prepared. Presumably it is the disulfide



$$\begin{array}{l} Ph{-}N{=}N{-}\overset{}{C}{=}N{-}NH{-}Ph \\ \qquad\qquad\;\; | \\ \qquad\qquad\;\; S \\ \qquad\qquad\;\; | \\ \qquad\qquad\;\; S \\ \qquad\qquad\;\; | \\ Ph{-}N{=}N{-}C{=}N{-}NH{-}Ph \end{array}$$

The evidence for the presence of more than one absorbing species in the carbon tetrachloride extract is reasonably good. We take the oxidation product (or products if need be) to represent all or most of the additional absorbing species. All the (principal) reaction products have similar absorbance curves, as we have seen. The presumed mixtures of $Te(HDz)_2$ and $(HDz)_2$ show an absorption peak in the vicinity of 435 nm (Figs. 7a–d), whereas $Te(HDz)_2$ shows a peak at 450 nm (Fig. 12), at the same or very nearly the same wavelength as the secondary peak of dithizone. ε at *ca.* 435 nm for $(HDz)_2$ is roughly 40,000 (a little less), or about twice that of dithizone at the same wavelength. It is of interest that ammonia-washed carbon tetrachloride mixtures of H_2Dz, $Te(HDz)_2$ and $(HDz)_2$ showed H_2Dz/Te ratios ranging from 1.95 to 4.7, which is taken to indicate that $(HDz)_2$ partitions into basic aqueous solutions, but less easily than H_2Dz, so that most of washed extracts contained $(HDz)_2$ in addition to $Te(HDz)_2$ but little H_2Dz. A ratio of 4 would represent the equimolar mixture of the reaction products, free from dithizone. As already mentioned, a good separation of the components cannot be obtained by ammonia washing. Presumably $(HDz)_2$ forms HDz_2^- in basic solutions with an absorption peak near that of HDz^- (470 nm) but with a larger ε, so that it will be counted as an approximately equivalent amount of dithizonate ion.

The extraction constant of tellurium from the foregoing reaction equation is

$$K_{\mathrm{ext}} = \frac{[\mathrm{Te(HDz)_2}]_o[\mathrm{(HDz)_2}]_o[\mathrm{H^+}]}{[\mathrm{TeO(OH)^+}][\mathrm{H_2Dz}]_o^4}$$

$$= \frac{[\mathrm{Te(HDz)_2}]_o^2[\mathrm{H^+}]}{[\mathrm{TeO(OH)^+}][\mathrm{H_2Dz}]_o^4}$$

The extraction coefficient of tellurium then is

$$E = \frac{[\mathrm{Te(HDz)_2}]_o}{[\mathrm{TeO(OH)^+}]} = \frac{K_{\mathrm{ext}}^{\frac{1}{2}}[\mathrm{H_2Dz}]_o^2}{[\mathrm{TeO(OH)^+}]^{\frac{1}{2}}[\mathrm{H^+}]^{\frac{1}{2}}}$$

According to this expression E should vary as $[H_2Dz]_o^2$, $[H^+]^{-\frac{1}{2}}$ and $[TeO(OH)^+]^{-\frac{1}{2}}$ if the predominant species in the aqueous phase is $TeO(OH)^+$, *i.e.*, if $TeO(OH)_2$ is negligible. Over the greater part of the range investigated (dithizone in excess over tellurium), this expression for E holds reasonably well. From the 4 curves in Fig. 8, the following values of log K_{ext} are calculated: 9.80, 10.74, 10.42 and 10.10, average of 10.3. From Fig. 11, log $K_{\mathrm{ext}} = 10.4$. $K_{\mathrm{ext}}^{\frac{1}{2}}$ may be taken as $10^{5.15}$, or about $1.5 \cdot 10^5$, and this value can then be used in the expression for $[Te(HDz)_2]_o/[TeO(OH)^+]$ to obtain the distribution of tellurium between the 2 phases. For example, it may be calculated that when equal volumes of $1 \cdot 10^{-5}$ *M* Te(IV) (*ca.* 1.3 p.p.m. Te) in 1 *M* perchloric acid and $5 \cdot 10^{-4}$ *M* dithizone in carbon tetrachloride (*ca.* 0.013% w/v) are shaken together to equilibrium, approximately 98% of the tellurium will be extracted. A second dithizone extraction will remove approximately 99.98% of the tellurium remaining in the aqueous phase (assuming that $Te(HDz)_2$ in the aqueous phase can be neglected). Thus it may be expected that microgram quantities of tellurium can be extracted from acid solutions and separated from metals that are extracted easily only from neutral or basic solutions.

Because dilute (*e.g.*, 0.001% w/v) dithizone solutions in carbon tetrachloride extract tellurium poorly, dithizone is not a suitable reagent for the spectrophotometric determination of tellurium.

SUMMARY

With an excess of dithizone over tellurium, the extraction of Te(IV) from 1 *M*

perchloric acid solutions into a carbon tetrachloride solution (o) of dithizone follows the relation

$$\frac{[\mathrm{Te(HDz)_2}]_o}{[\mathrm{TeO(OH)^+}]} = 1.5 \cdot 10^5 \, [\mathrm{H_2Dz}]_o^2[\mathrm{TeO(OH)^+}]^{-\frac{1}{2}} .$$

When the acidity is varied, again with a sufficiently large excess of dithizone, the following relation seems to be approached:

$$\frac{[\mathrm{Te(HDz)_2}]_o}{[\mathrm{TeO(OH)^+}]} = 1.5 \cdot 10^5 \, [\mathrm{H_2Dz}]_o^2[\mathrm{TeO(OH)^+}]^{-\frac{1}{2}}[\mathrm{H^+}]^{-\frac{1}{2}} \quad (\mu = 1.0).$$

RÉSUMÉ

Lors de l'extraction du tellure(IV) en solution dans l'acide perchlorique 1 *M*, au moyen d'une solution de dithizone dans le tétrachlorure de carbone, en présence d'un excès de dithizone, on a la relation:

$$\frac{[\mathrm{Te(HDz)_2}]_o}{[\mathrm{TeO(OH)^+}]} = 1.5 \cdot 10^5[\mathrm{H_2Dz}]_o^2[\mathrm{TeO(OH)^+}]^{-\frac{1}{2}}$$

Lorsqu'on change l'acidité, avec un excès suffisamment grand de dithizone, on tend vers la relation:

$$\frac{[\mathrm{Te(HDz)_2}]_o}{[\mathrm{TeO(OH)^+}]} = 1.5 \cdot 10^5[\mathrm{H_2Dz}]_o^2[\mathrm{TeO(OH)^+}]^{-\frac{1}{2}}[\mathrm{H^+}]^{-\frac{1}{2}} \, (\mu=1.0).$$

ZUSAMMENFASSUNG

Es wird die Extraktion von Tellur(IV) mit Tetrachlorkohlenstoff und einem Überschuss an Dithizon aus 1 *M* perchlorsaurer Lösung beschrieben. Für die Verteilung des Tellurs werden Werte in Abhängigkeit von den Konzentrationen des Tellurs, des Dithizons und der H-Ionen angegeben und entsprechende Gleichungen aufgestellt.

REFERENCES

1 H. MABUCHI, *Bull. Chem. Soc. Japan*, 29 (1956) 842; H. MABUCHI AND I. OKADA, *ibid.*, 38 (1965) 1478.
2 O. B. MATHRE AND E. B. SANDELL, *Talanta*, 11 (1964) 295.
3 R. A. JOHNSON AND F. P. KWAN, *Anal. Chem.*, 23 (1951) 651.
4 R. SCHUHMANN, *J. Am. Chem. Soc.*, 47 (1925) 356.

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SUBMICRO METHODS FOR THE ANALYSIS OF ORGANIC COMPOUNDS
THE DETERMINATION OF HYDROXYL GROUPS

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Very many methods have been described for the determination of hydroxyl groups in organic compounds[1-4]. The reactivity of this group is highly dependent on its particular combination in a molecule, so that no single method can be applied to all classes of compound. Esterification methods are the most widely applicable and were therefore examined for adaptation to the submicro scale. However, the difficulties found made it necessary to develop alternative procedures and submicro adaptations of bromination methods and acidimetric titrations were also studied.

Several variations of bromination methods were tested, but even where a submicro procedure proved feasible, the conditions with regard to excess of brominating agent and time of bromination were found to be extremely critical[5]. Reasonably satisfactory results could be achieved for a particular compound by careful control of these variables, but the procedure[5] has obviously no practical value and is not discussed further in this paper.

The esterification and acidimetric procedures which are discussed in detail in this paper suffice to cover most types of organic hydroxyl compounds. Submicro procedures for the determination of vicinal hydroxyl groups based on oxidation with periodate have been dealt with in previous papers[6].

ESTERIFICATION METHODS

Acetylation methods are the most widely used of the various esterification procedures[1]. The most attractive procedures for microgram-scale application seemed to be those of FRITZ AND SCHENK[7] and SCHENK AND SANTIAGO[8] in which acetic anhydride is employed as the acylating agent in pyridine or ethyl acetate media in the presence of perchloric acid catalyst. Scaling down to the microgram level involves a considerable dilution of reaction media compared to the milligram scale so that the solutions can be readily handled. For the micro-scale acetylation method[8], it was found that very little deviation from the recommended proportions of sample, reagent and diluent could be tolerated; indeed a two-fold dilution of the acetylating agent led to virtually no acetylation taking place even on prolonged standing[5]. These experiments indicated that even if a submicro method were feasible, such a large excess of reagent would be needed that the slight difference between the blank and sample titration values must lead to gross error. Attention was therefore turned to other esterification methods.

A relatively simple method for the determination of up to 100 μg of hydroxyl groups in primary and secondary alcohols has been described by JOHNSON AND CRITCHFIELD[9]. The method is based on the reaction of the alcoholic hydroxyl group with 3,5-dinitrobenzoyl chloride (DNBC) in a pyridine medium; after complete reaction and neutralization of the pyridine, the dinitrobenzoate ester is extracted into hexane and subsequent treatment of a portion of the extract with alkaline acetone causes the formation of a blue colour which can be measured spectrophotometrically. The colour depends on an aromatic quinoidal ion formation and not on the particular alcohol, hence the absorbance measured is proportional to the concentration and thus to the molecular weight for most alcohols.

The original method required very little modification to make it suitable for application to microgram samples containing up to 30 µg of hydroxyl. A straight calibration graph was obtained under the conditions specified below for samples of ethanol; these samples were obtained by weighing a milligram sample, dissolving in purified pyridine and taking suitable aliquots of this solution. Certain difficulties were encountered in the application of the method; either no, or a much too intense, blue colour sometimes appeared in the extract on addition of alkaline acetone. These anomalous results were traced to the presence of either water or hydroxylic impurities in the pyridine. In other cases, heavy white precipitates (probably 3,5-dinitrobenzoic

TABLE I

DETERMINATION OF ALCOHOLIC HYDROXYL GROUPS WITH 3,5-DINITROBENZOYL CHLORIDE

Sample	*Weight taken (µg OH-group)*	*Theor. OH-group present (%)*	*OH-group found*[a] *(%)*	*Recovery (%)*
Isopropanol	7.75	28.29	27.01	95.5
	15.50		28.47	100.6
	23.25		30.42	107.5
Isobutanol	7.29	22.94	22.81	99.5
	11.58		24.30	106.2
	21.87		23.28	101.5
Isoamyl alcohol	8.89	11.93	11.94	100.0
	17.78		12.07	101.2
	26.67		11.54	96.7
2-Methoxy-ethanol	11.76	22.34	21.67	97.0
	23.52		22.56	101.0
	35.28		22.47	100.6
n-Decanol	5.38	10.74	10.48	97.6
	10.76		10.68	99.4
	16.14		10.91	101.6
n-Octadecanol	7.61	6.28	6.19	98.6
	13.50		7.07	112.6
	22.83		6.88	108.9
n-Dodecanol	7.83	9.12	9.32	102.2
	15.70		9.53	104.5
	23.50		9.66	105.9

[a] These values were calculated from a calibration graph established with ethanol.

acid) appeared on neutralization of the pyridine, and intensely blue colours were ultimately developed. However, provided that the pyridine was rigorously purified and the other operational conditions were closely controlled, reasonably satisfactory results were obtained.

The results obtained for a series of alcohols are shown in Table I; in general the relative error did not exceed ±5%. Methanol gave results which were consistently 20% low based on the calibration graph found with ethanol; a calibration graph prepared with methanol samples provided a good straight line up to at least 35 µg of hydroxyl but the slope was less than that of the ethanol graph. The compounds of aromatic character examined did not react quantitatively; for benzyl alcohol and benzhydrol, the percentage recoveries were about 85% and 70% respectively but the results were not reproducible or consistent.

The method of JOHNSON AND CRITCHFIELD was originally proposed for the determination of trace amounts of alcohols in the presence of acid-hydrolysable substances. The results described above show that it has also sufficient accuracy for utilization with very small samples of aliphatic alcohols.

TITRATION IN NON-AQUEOUS MEDIA

Acidic hydroxyl groups, *e.g.* in substituted phenols, have often been determined on the macro scale by titration with alkali or quaternary ammonium base in non-aqueous media; a neutral or basic solvent can be used. Information on such methods is given in many reviews and books[1,3,10,11]. Of the many possible procedures, the most widely applicable[1] for weakly acidic compounds seems to be that of CUNDIFF AND MARKUNAS[12] who titrated with 0.1 N tetra-n-butylammonium hydroxide in 10:1 benzene–methanol solution; the samples were titrated in a pyridine medium to a visual thymol blue or azo violet end-point or potentiometrically using a glass–methanol-modified calomel electrode system.

Preliminary studies with samples of 50–80 µg in *ca.* 0.3 ml of pyridine showed that this titration was quite satisfactory on the submicro scale, provided that a nitrogen atmosphere was used to prevent interference from carbon dioxide. It was important to pass the nitrogen over rather than through the solution to avoid volatilization of the small sample with some compounds. For substituted phenols of moderate acidity, both thymol blue and azo violet gave correct end-points when checked against a potentiometric end-point, but the thymol blue end-point was the more easily observed. A glass–silver electrode pair[13] gave more satisfactory performance than a submicro glass–modified calomel electrode pair.

The thymol blue and glass–silver pair end-points were checked for a variety of compounds. Satisfactory results (Table II) were obtained for highly acidic compounds such as picric acid, and for moderately acidic compounds such as mononitrophenols. When strongly acidic phenols (di- and trinitrophenols) were titrated potentiometrically, two potential breaks were observed in the titration curves. This effect has been noticed in macro work by VAN DER HEIJDE[14] who attributed it to insufficient solvation of the polar molecules and their ions by the weakly basic solvent. The second potential break was taken as the end-point. The dissociation constants of compounds in aqueous solution[15] can provide a rough guide to their likely behaviour in pyridine media. On the submicro scale, m-nitrophenol (pK_a 8.4)

TABLE II

TITRATION OF VARIOUS PHENOLIC COMPOUNDS WITH 0.01 *N* TETRA-*n*-BUTYLAMMONIUM HYDROXIDE IN 10:1 BENZENE–METHANOL SOLVENT IN PYRIDINE MEDIA

Compound	*Percentage recoveries*			
	Potentiometric end-point[a]		*Visual end-point*[b]	
	Average[c]	*Range*	*Average*[c]	*Range*
p-Nitrophenol	100.7	99.4–102.0	101.4	100.5–102.4
o-Nitrophenol	101.3	100.6–101.8	100.7	99.4–101.7
m-Nitrophenol	101.5	100.2–102.7	No end-point	
1-Nitro-2-naphthol	100.5	99.8–101.5	101.8	99.6–103.2
2,4-Dinitrophenol	100.3	98.2–101.9	98.3	97.3–100.2
2,4,6-Trinitrophenol	101.6	99.5–104.6	100.3	99.8–101.0
4-Nitro-2,6-dichlorophenol	100.7	98.8–103.3	97.2	94.3–100.2
p-Hydroxybenzaldehyde	101.3	98.1–104.4	102.2	101.2–103.1
p-Hydroxyacetophenone	102.1	100.2–103.7	99.2	97.8–101.2

[a] Glass–silver electrode system.
[b] Thymol blue indicator.
[c] Average of at least 3 determinations.

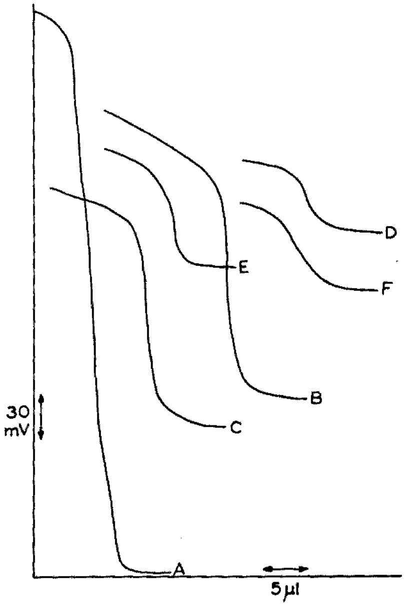
could not be accurately titrated using thymol blue indicator, and other compounds of lower acidity gave very poor potential breaks even with the glass–silver electrode pair. With *p*-hydroxybenzaldehyde (pK_a *ca.* 8) the potential break amounted to *ca.* 30 mV and the course of the potential change could be followed quite reproducibly using amplification, but this was not so for compounds of lower acidity.

Several indicators were examined for the titration of compounds with pK_a values greater than 8.5. With 1-naphthol (pK_a 9.3) and phenol (pK_a 10), alkali blue 6B and 1-naphtholbenzein gave no end-points; azo violet and *o*-nitroaniline[16] changed colour at approximately the correct volume of titrant but gave indistinct end-points that would have introduced an error of 10–20% into the titration. Azo violet is reported[12] to be a satisfactory indicator for the titration of these compounds on the macro scale but its performance deteriorated much more rapidly on the submicro scale.

In attempts to improve the sensitivity of end-point detection with the glass–silver electrode pair, various solvents including acetone, dimethylformamide, methyl ethyl ketone and acetonitrile were tested with *p*-hydroxyacetophenone as the sample. As on the macro scale with a glass–calomel pair[12], none of these solvents provided more definitive titration curves than those obtained in pyridine media.

Other electrode systems were then tested in the pyridine medium. The best potential breaks were obtained with a glass–platinum pair; placing the bare platinum electrode in the titrant stream instead of in the titration medium resulted in a 2–3-fold increase in sensitivity. Several solvents were re-examined with this glass–platinum pair with 2-naphthol as sample; the potential breaks decreased in the following order of solvents: pyridine $>$ acetonitrile $\simeq$ dimethylformamide $>$ acetone $>$ methyl ethyl ketone. Difficulties were caused by the volatility of some solvents on this scale of working and no solvent seemed to combine the end-point definition obtainable in pyridine with its low volatility, solvating power and general ease of use. *Tert.*-butanol, which has been highly recommended by FRITZ AND MARPLE[17] showed no advantage over pyridine; the potential was slow in reaching equilibrium and the solvent tended to solidify at room temperature (m.p. 26°). The addition of tetra-*n*-butylammonium iodide to the *tert.*-butanol–acid mixture[18] did not seem to have an appreciable effect on the definition of the end-point.

Simple titrations with tetra-*n*-butylammonium hydroxide solution in benzene–methanol using a pyridine medium and a glass–in-stream platinum electrode pair were therefore used for all further work. Typical titration curves are shown in Fig. 1, and results for a large series of phenolic compounds are shown in Table III. These results showed that reasonable accuracy and precision (*ca.* ±2% relative error) were obtainable for compounds with pK_a values up to *ca.* 8.4, but that, while compounds of weaker acidity could be titrated, the results were generally 2–5% high. These calculations were based on standardization of the quaternary base solution against benzoic acid using the same potentiometric end-point.



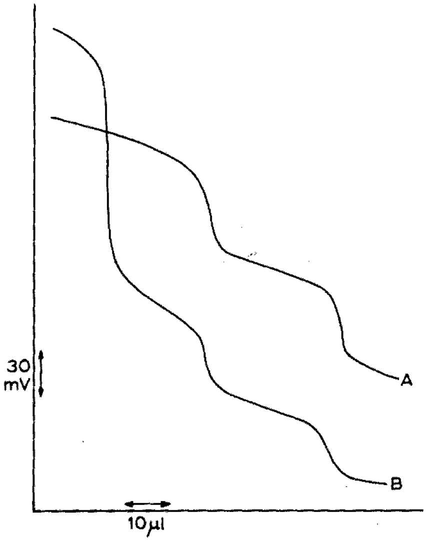


Fig. 1. Potentiometric titration curves for phenolic compounds. Glass–in-stream platinum couple (A) 2,4-Dinitrophenol. (B) *p*-Hydroxyacetophenone. (C) *m*-Nitrophenol. (D) Phenol. (E) 2-Naphthol. (F) Thymol.

Fig. 2. Differentiating titrations. (A) *p*-Nitrophenol and 2-naphthol. (B) 2,4-Dinitrophenol, *p*-hydroxyacetophenone and *p*-cresol.

Various tests were made to establish the source of this error. Up to 5% of water in the pyridine solvent had little effect on the results for *p*-hydroxyacetophenone and rigorous drying of the pyridine led to no improvement. The presence of methanol in the titrant solvent is said to affect the inflections obtained with very weak acids[19] but addition of up to 5% methanol in the titration medium again had little effect on the results; about 1% of methanol would have been introduced in the titrant during a normal titration.

Eventually, it was found that the most probable cause of the errors was the

TABLE III

TITRATION OF VARIOUS HYDROXYL COMPOUNDS WITH A GLASS–PLATINUM ELECTRODE PAIR

(Sample weight 50–80 μg; pyridine volume 0.3 ml)

Compound	*Aqueous* pK_a[15]	*Percentage recoveries*			
		Conventional end-point		*Empirical end-point*	
		Average	*Range*[a]	*Average*	*Range*[a]
2,4,6-Trinitrophenol	0.4	99.3	97.8–100.7	—	—
2,4-Dinitrophenol	4.4	99.3	98.0–101.5	—	—
p-Nitrophenol	7.1	100.0	99.7–100.2	—	—
o-Nitrophenol	7.2	99.2	98.8–99.5	—	—
m-Nitrophenol	8.4	102.0	101.7–102.7	—	—
2,6-Dichloro-4-nitrophenol	—	98.7	98.4–99.1	—	—
Vanillin	8.0	99.6	99.3–100.3	—	—
p-Hydroxybenzaldehyde	8.7	100.8	100.7–100.9	—	—
2-Hydroxynaphthaldehyde	—	101.2	100.5–101.7	—	—
m-Hydroxybenzaldehyde	9.4	104.9	104.7–105.2	100.8	99.2–102.6
p-Hydroxyazobenzene	—	100.3	99.3–101.4	—	—
p-Hydroxyacetophenone	9.05	101.6	100.9–102.6	—	—
p-Hydroxyethylbenzoate	—	102.8	101.4–104.0	—	—
1-Nitro-2-naphthol	—	98.9	97.8–100.3	—	—
p-Chlorophenol	9.4	104.9	104.3–105.9	101.1	99.5–102.1
p-Bromophenol	9.4	107.8	104.3–114.2	97.8	95.7–99.7
1-Naphthol	9.5	107.9	106.4–109.9	100.6	99.5–102.0
2-Naphthol	9.5	102.3	100.6–103.4	99.5	98.5–101.1
p-Hydroxydiphenyl	9.6	105.2	104.9–105.4	99.3	98.9–99.6
o-Hydroxydiphenyl	10.0	105.3	104.3–106.2	98.5	97.5–99.4
p-Benzylphenol	—	105.8	102.5–108.5	99.4	99.0–99.6
Phenol	10.0	109.6	105.6–111.3	102.9	99.9–104.5
p-Methoxyphenol	10.2	103.8	100.4–105.8	99.9	98.3–101.2
Resorcinol	—	104.0	101.3–108.6	97.9	95.7–100.5
Catechol	—	104.2	103.9–104.6	98.9	97.3–100.9
Thymol	10.0	105.5	104.3–107.5	99.3	97.4–100.8
p-Cresol	10.3	106.5	105.6–107.9	99.7	98.7–100.5
2,6-Xylenol	10.0	104.6	103.9–105.4	100.8	98.1–102.9

[a] At least 3 determinations were carried out on each sample.

presence of carbon dioxide in the titrant. When an aged 0.01 *M* solution of TBAH was standardized against benzoic acid, 2-naphthol and *p*-methoxyphenol, the titre found on standardization against the strong acid differed by about 12% from the figure found with the weak acids; similar tests for a fresh TBAH solution showed a difference of only 5%. Tests with neutral solvent media which would contain no, or at least less, carbon dioxide, gave essentially the same results for weak acids as the pyridine medium. When the pyridine was saturated with carbon dioxide, the effect on the titration of benzoic acid was only slight, but the titration of 2-naphthol gave results 15% higher than expected.

FRITZ AND MARPLE[17] have suggested that the high (2–4%) results obtained in the titration of acids weaker than phenol are caused by decomposition of the TBAH titrant in the presence of such acids; with stronger acids decomposition does not occur until an excess of base is added so that the titration is not affected. Phenols weaker than phenol itself were not tested in the present work because such weakly acidic compounds did not give sufficiently well-defined curves; but when 2-naphthol was titrated over times ranging from 5 to 20 minutes, the results showed no time-dependence. Moreover, when TBAH was added to pyridine and back-titrated after 3–4 minutes, there was no evidence for decomposition. Addition of tri-*n*-butylamine—the expected decomposition product of TBAH—to the pyridine solvent had no effect on the titration of either benzoic acid or 2-naphthol.

The elimination of these various factors as possible sources of error seems to provide confirmation that carbon dioxide in the titrant causes the high results for weak phenols. Better accuracy should be obtainable by taking stringent precautions during the preparation and storage of the TBAH solution. For many purposes a relative error of 5% would be tolerable on this very small scale of working, and this can be readily achieved provided that the TBAH solutions are reasonably fresh. Better results (*ca.* ±3%) can be obtained if the TBAH solution is standardized against 2-naphthol instead of benzoic acid, in the case of compounds with aqueous pK_a values greater than *ca.* 8.5. The approximate pK_a value can be estimated from the size of the potential break at the equivalence point. However, it was found in the present work that results which were as accurate as, and generally more precise than, those obtained with the 2-naphthol standardization factor, could be achieved by determining the end-point from the titration curve in a completely empirical manner; this was done by regarding the first point of inflection in the titration curve as the end-point. The results obtained in this way for a series of 15 weakly acidic compounds showed an average recovery of 99.7% compared with an average of 105.3% when calculated conventionally. This empirical method has the advantages of simplicity and of allowing the use of benzoic acid as standard throughout the work. The results obtained are shown in Table III. Neither catechol nor resorcinol behaved as a dibasic acid, presumably because of the extremely weak acidity of the second hydrogen in these compounds.

Titration of compounds containing other acidic groups

In order to check that the range of titratable compounds on the submicro scale was similar to that on the macro-scale, a variety of thiol, imide and sulphonamide

TABLE IV

TITRATION OF VARIOUS THIOLS, IMIDES AND SULPHONAMIDES

(Sample weight 50–80 μg; pyridine volume 0.3 ml; glass–platinum electrode pair)

Compound	*Percentage recoveries*			
	Conventional end-point		*Empirical end-point*	
	Average	*Range*	*Average*	*Range*
			—	—
2-Mercaptobenzothiazole	98.4	97.5–99.3	—	—
2-Mercaptobenzimidazole	102.5	101.8–102.9	—	—
4-Methyl-2-thiouracil	100.7	100.1–101.7	—	—
Succinimide	103.9	103.3–105.1	99.9	98.9–100.5
cis-Δ^4-Tetrahydrophthalimide	105.9	105.6–106.3	100.9	100.0–101.9
Sulphathiazole	100.1	98.8–101.4	—	—
Sulphamerazine	101.4	100.6–101.9	—	—
Sulphadiazine	101.2	99.6–103.9	—	—
Sulphapyridine	100.9	100.5–101.5	—	—
Sulphanilamide	108.0	108.0–108.1	101.6	100.3–102.9

samples were analysed. Typical results are shown in Table IV. No difficulties were found with simple thiol and imide compounds. The titration curve for glutathione showed three potential breaks none of which was sufficiently large to be of analytical value. Sulphonamides have quite often been titrated in protophilic media[11]. The submicro titration with 0.01 M TBAH was straightforward despite the greatly varying acidic nature of the various samples tested.

Differentiating titrations

An advantage of pyridine as the titration medium is that it is sufficiently protophilic to enhance the acidity of weak acids and yet allows some differentiating titrations to be done. It was considered of interest to find out how far such titrations could be used on the submicro scale.

In the initial tests, several dicarboxylic acids were examined. Maleic acid and salicylic acid both behaved as monobasic acids, giving only one potential break corresponding to the neutralization of the first acidic group; possibly these *cis*-acids when half neutralized have extensive hydrogen bonding which prevents the introduction of a further bulky organic base group. The curve for fumaric acid showed two potential breaks; the first was small and appeared too early (*ca.* 94% recovery) but results calculated from the second well-defined break were excellent (99.8% recovery). 3,5-Dinitrosalicylic acid showed two well-defined end-points, presumably because the electron-attracting nitro groups enhance dissociation of the acidic groups and weaken any hydrogen bonding effects.

Both *m*- and *p*-hydroxybenzoic acid gave titration curves with two inflections, the first being well-defined; quantitative recoveries were obtained based on either inflection, though results from the second break tended to be high unless the above-mentioned empirical method of end-point detection was used.

A few tests were made with mixtures of phenolic compounds. Some titration curves are shown in Fig. 2. Since only *ca.* 30 μg of each component was taken, the percentage errors were greater than those found for single compounds. The titration of *p*-nitrophenol and 2-naphthol was reasonably satisfactory; the average percentage recovery for *p*-nitrophenol was 99% while that for 2-naphthol was 110.2% (or 98% based on the empirical end-point detection). However, only approximate results were obtained in the simultaneous titration of 2,4-dinitrophenol, *p*-hydroxyacetophenone and *p*-cresol; the average recoveries were *ca.* 95, 103 and 105% respectively. CUNDIFF AND MARKUNAS[20] have noted in the titration of strong mineral acid mixtures with TBAH in pyridine media, that the results calculated from the first equivalence point are 5–6% low whereas those from the second inflection are high; they ascribed the effect to an impurity in the titrant which could be removed by ion exchange. Probably, the same factors intervene in the submicro titration of strong organic acids.

EXPERIMENTAL

Spectrophotometric 3,5-dinitrobenzoyl chloride method

Apparatus

A Unicam SP600 spectrophotometer was used with 1-cm cells.

Reagents

3,5-Dinitrobenzoyl chloride solution. Prepare a 10% (w/v) solution of the reagent in pure pyridine immediately before use. If necessary, heat to dissolve the reagent.

Pyridine, dry, redistilled. Pyridine (for Karl Fischer reagent, Hopkin and Williams, Ltd.) was dried with 20–30 g of ignited barium oxide per 500 ml and then distilled in a carefully protected apparatus; the fraction of b.p. 114–115° was collected and stored over P_2O_5*.

Procedure

Weigh or measure a sample containing 5–25 μg of hydroxyl group into a 50-ml glass-stoppered flask and dissolve it in 1 ml of pure pyridine. Add 0.5 ml of hot (70–90°) reagent from a calibrated teat pipette, stopper the flask and mix gently. Allow the reaction to proceed for 15 min at room temperature and then add 12.5 ml of 2 *N* hydrochloric acid from a burette. Mix, pipette in 10.0 ml of hexane and shake vigorously for 1 min. After phase separation, transfer 1.00 ml of the hexane layer to a 25-ml flask followed by 5.0 ml of acetone and 0.30 ml of 2 *N* sodium hydroxide. Stopper, shake for 10 sec and measure the absorbance at 575 nm against a blank prepared in the same way.

Derive the hydroxyl content by reference to a calibration graph prepared with ethanol. A separate graph is needed for methanol.

Titrimetric method with tetra-n-butylammonium hydroxide

Apparatus

A Vibron electrometer model 33B was used in conjunction with a C-33B pH measuring unit (Electronic Industries, Ltd., Richmond, Surrey). Submicro glass electrodes, specially made by Electronic Industries, Ltd., had a bulb diameter of 3.5 mm; these electrodes were stored in distilled water and, before use, were rinsed with water and methanol and dried carefully with a soft paper tissue.

Electrode burette. Agla micrometer all-glass syringe burettes were used throughout the work. For titrations involving a platinum electrode, a length of 0.5-mm diameter platinum wire was sealed into the burette outlet tube near the right-angle bend. Normally, the burette was flushed with titrant several times and left for *ca.* 30 min after which time volatilization of the titrant at the syringe end was negligible.

Titration vessels. Titrations were done in borosilicate glass tubes of diameter *ca.* 1 cm and length *ca.* 4 cm. A gentle stream of nitrogen, purified by passage through Anhydrone and soda-asbestos, was directed on to the surface of the solution through a small glass capillary.

Reagents

Tetra-n-butylammonium hydroxide solution. Prepare a 0.01 *N* solution by dilution of standard 0.1 *N* solution (British Drug Houses, Ltd.) with a 10:1 benzene–methanol mixture; the methanol used was the commercial grade for non-aqueous titrations.

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* After the completion of this work, Dr. CRITCHFIELD (private communication) stated that none of the difficulties mentioned on p. 436 were found when the pyridine was dried with molecular sieve which removes not only water but also small polar organic molecules.

Store the solution in tightly stoppered polythene bottles. Standardize regularly against M.A.S. grade benzoic acid under the conditions described below.

Pyridine. The grade used was that specified for Karl Fischer titrations.

Procedure for visual titrations

Weigh a 30–80 μg sample into the titration vessel and dissolve in 0.3 ml of pyridine. Add 0.02–0.03 ml of thymol blue indicator solution (0.08 g in 50 ml of A.R. isopropanol) and titrate to the first appearance of a blue colour. Direct a slow stream of nitrogen over the solution during titration and stir magnetically. Carry out a blank titration in the same way.

Procedure for potentiometric titration

Weigh a 30–80 μg sample into the titration vessel and dissolve in 0.3 ml of pyridine. Add a glass-encased rotor for magnetic stirring, adjust the glass electrode so that its tip is 1–2 mm below the liquid surface and place the burette and the capillary for nitrogen introduction in position. (When the silver reference electrode is used, a little thymol blue solution serves to give warning of the approach of the end-point.) Titrate with 0.01 *N* TBAH by adding 5-μl portions and allowing the potentiometer to reach equilibrium between additions. Near the end-point, add 1.0-μl portions of titrant.

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SUMMARY

Various procedures were examined for the determination of organic hydroxyl groups. Conventional acetylation methods could not be used on the submicro scale, but the spectrophotometric method based on esterification with 3,5-dinitrobenzoyl chloride followed by extraction of the ester and colour development with alkaline acetone proved reasonably satisfactory for aliphatic alcohols. Acidic hydroxyl groups *e.g.* in phenolic compounds, were titrated accurately with 0.01 *M* tetrabutylammonium hydroxide in benzene–methanol solution in a pyridine medium; visual end-points or potentiometric end-points with glass–silver or glass–in-stream platinum electrode pairs were used depending on the strength of the acidic group. Some differentiating titrations were possible. A general submicro bromination method for phenols was not feasible.

RÉSUMÉ

Divers procédés ont été examinés pour le dosage de groupes organiques hydroxylés. Les méthodes conventionnelles par acétylation ne peuvent pas être utilisées à l'échelle submicro. Par contre la méthode spectrophotométrique basée sur l'estérification à l'aide du chlorure de dinitro-3,5-benzoyle a donné des résultats satisfaisants pour les alcools aliphatiques. Les groupes hydroxyles acides (par exemple: composés phénoliques) ont pu être titrés avec précision au moyen d'hydroxyde de tétrabutylammonium 0.01 *M* dans le benzène–méthanol, en milieu pyridine. Les points finals sont déterminés visuellement ou potentiométriquement.

ZUSAMMENFASSUNG

Verschiedene Verfahren zur Bestimmung organischer Hydroxylgruppen wurden geprüft. Die konventionelle Acetylierungsmethode konnte im Submikrobereich nicht verwendet werden. Die spektralphotometrische Methode, die auf der Veresterung mit 3,5-Dinitrobenzoylchlorid, der Extraktion dieses Esters und der Farbentwicklung mit alkalischem Aceton beruht, ergab zufriedenstellende Ergebnisse für aliphatische Alkohole. Saure Hydroxylgruppen, z.B. in phenolischen Verbindungen, wurden in Pyridin mit 0.01 *M* Tetrabutylammoniumhydroxid in benzol–methanolischer Lösung genau titriert unter Verwendung der visuellen oder potentiometrischen Endpunktsanzeige. Eine allgemeine Bromierungsmethode für Phenole im Submikromasstab war ungeeignet.

REFERENCES

1 See, *e.g.* S. SIGGIA, *Quantitative Organic Analysis via Functional Groups*, 3rd Edn., J. Wiley and Sons, New York, 1963.
2 E. D. OLLEMAN, *Anal. Chem.*, 24 (1952) 1425.
3 V. C. MEHLENBACHER, in *Organic Analysis*, Vol. I, Interscience, New York, 1953, pp. 1–65.
4 G. DRYHURST, *Ind. Chem. Manuf. (London)*, 40 (1964) 41, 97.
5 G. DRYHURST, *Ph. D. Thesis*, Birmingham University, 1965.
6 R. BELCHER, G. DRYHURST AND A. M. G. MACDONALD, *J. Chem. Soc.*, (1965) 3964, 4543.
7 J. S. FRITZ AND G. H. SCHENK, *Anal. Chem.*, 31 (1959) 1808.
8 G. H. SCHENK AND H. SANTIAGO, *Microchem. J.*, 6 (1962) 77.
9 See, F. E. CRITCHFIELD, *Organic Functional Group Analysis*, Pergamon Press, Oxford, 1963, p. 99.
10 J. MITCHELL, B. A. MONTAGUE AND R. H. KINSEY, in *Organic Analysis*, Vol. III, Interscience, New York, 1956.
11 J. KUCHARSKÝ AND L. ŠAFAŘÍK, *Titrations in Non-aqueous Solvents*, Elsevier, Amsterdam, 1965.
12 R. H. CUNDIFF AND P. C. MARKUNAS, *Anal. Chem.*, 28 (1956) 792; *cf.* G. A. HARLOW, C. M. NOBLE AND G. E. A. WYLDE, *Anal. Chem.*, 28 (1956) 787.
13 M. G. YAKUBIK, L. W. SAFRANSKI AND J. MITCHELL, *Anal. Chem.*, 30 (1958) 1741.
14 H. B. VAN DER HEIJDE, *Anal. Chim. Acta*, 16 (1957) 392.
15 G. KÖRTUM, W. VOGEL AND K. ANDRUSSOW, *Dissoziationskonstanten organischer Säuren in wässeriger Lösung*, Butterworths, London, 1961.
16 *cf.* J. S. FRITZ AND F. E. GAINER, *Talanta*, 13 (1966) 939.
17 J. S. FRITZ AND L. W. MARPLE, *Anal. Chem.*, 34 (1962) 921.
18 J. S. FRITZ AND L. W. MARPLE, *Anal. Chem.*, 35 (1963) 1431.
19 G. A. HARLOW AND G. E. A. WYLDE, *Anal. Chem.*, 30 (1958) 73.
20 R. H. CUNDIFF AND P. C. MARKUNAS, *Anal. Chem.*, 30 (1958) 1450.

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TRACE ELEMENTS IN MARINE WATERS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY*

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Interest in atomic absorption spectrophotometry has accelerated dramatically since the general introduction of this method by WALSH[1]. The techniques have found wide application in the agricultural, medical, and metallurgical sciences and many papers have reviewed the instrumentation and methods employed in these and many other areas. Their use in water analysis, however, has been strangely restricted since it is in these fields that the method should be particularly advantageous. Pre-analysis preparation is minimized and very frequently unnecessary, with a resultant saving in time, sample loss, and contamination. Also, many elements may be determined in the same small water sample.

This work is concerned with the analytical chemistry of those trace elements in marine waters that have received the most attention in atomic absorption spectrophotometry. These elements may be conveniently considered in two groups. The alkali and alkaline earth metals occur as non-associated ions or weak complexes and with concentrations in the mg/l range. With the absence of complications from different species, analytical efforts may be totally concentrated on methods for processing large batches of samples with the greatest speed and efficiency. The second subdivision—the transition group—presents far more complexity in terms of both determination and characterization.

Table I[2,3] indicates the mean abundance of these elements in sea water. It must be emphasized that world-wide data for each individual element vary between wide limits; iron, for example, ranges from 0.01 to 860 μg/l[4]. However, on the average, concentrations fall one or more orders of magnitude below the detection limits of commonly-used equipment. Concentration as a prerequisite to trace analysis is common practice in marine chemistry, but there are obvious limitations in terms of tediousness and the possibility of introduced contamination. Analysts have thus tended to balance pre-concentration techniques which render routine control feasible, with various modifications to the basic instrumentation which extend detectabilities to lower concentration levels.

In contrast to the alkaline elements, the transition metals may be present in sea water in the form of a variety of strong complexes. Since atomic absorption spectrophotometry yields a total analysis, any attempt at species differentiation must be accomplished during the pre-analysis preparation phase. In addition, colloidal

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and particulate forms of these elements are common and appreciable quantities may be adsorbed onto the suspended inorganic and organic matter of sea water[5]. Traditionally, 0.45-μ membrane filters have been designated as the boundary between particulate and soluble fractions; this demarcation is one of convenience rather than of scientific exactitude.

TABLE I

ABUNDANCE, DETECTION LIMITS, AND SENSITIVITIES OF SELECTED TRACE METALS IN SEA WATER[2,3,18]

Element	*Sea water concentration (mg/l)*	*Detection limits (mg/l)*	*Sensitivities (mg/l for 1% absorption)*
Sr	8.0	0.01	0.12
Li	0.17	0.005	0.05
Rb	0.12	0.015	0.15
Mn	0.002	0.01	0.10
Fe	0.01	0.06	0.14
Cu	0.003	0.01	0.12
Zn	0.01	0.005	0.04
Co	0.0001	0.07	0.16
Ni	0.002	0.10	0.27

INSTRUMENTATION

A Perkin-Elmer Model 303 double-beam spectrophotometer was mainly used for this work. Certain alkali determinations were duplicated using an atomic absorption accessory with a Beckman DU photometer, which operates with a single beam and thus requires a highly-regulated lamp-current supply. Both instruments utilize either hollow-cathode or vapor-discharge lamps as spectral sources; the former may be either single or multi-element, the choice being dictated by the relevant spectral complexity and monochromator resolution. The emission of both instruments is modulated to eliminate D.C. signals emitted by the flame at the same resonance wavelength.

At present, the atomizing system of commercial atomic absorption equipment limits sensitivity. The basic problem is to obtain as large a quantity as possible of the test element in the atomic state within the emission beam path. Since water chemistry deals essentially with solution analysis, it was found expedient to aspirate samples into a flame although, in a typical burner, the quantity of samples thus placed in the reaction zone has been diluted by many orders of magnitude. The essential step in the system is the production of metal atoms from liquid droplets via a solid residue phase. Regardless of the efficiency of this sequence, common burners pass the atoms rapidly through the reaction zone and sample oxidation cannot be easily avoided. Both common types of burners were used for this work; both leave much room for improvement. Laminar flow—Lundegardh burners—used in conjunction with the Perkin-Elmer 303 proved the most effective; this type nebulizes the sample within a pre-mix gas chamber. Baffle plates, designed to pass only the finest droplets, effectively filter out up to 90% of the original sample, especially if organic solvents are used. Work with the Beckman equipment was accomplished using turbulent flow burners. In this case, the sample is aspirated directly into the base of the flame but the quantity of sample placed in the optical path is far smaller and the use of the multi-pass mode fails to pass the beam through the optimum flame zone.

Results were both read and recorded individually or continuously by means of auxiliary chart recorders. Signal integration and scale expansion devices were also employed where applicable. Various data processing sequences are discussed below.

TRACE ALKALI AND ALKALINE EARTHS

Analytical procedures

Routine analyses were conducted for strontium, lithium, and rubidium in a wide range of marine water samples. As examples, data are presented for a series of open sea samples at 1-m depths procured on Cruise 48 of the R/V CHAIN in the South Atlantic during the months of May and June, 1965. Samples for lithium and rubidium determinations were aspirated directly with no pre-analysis preparation. Strontium data were obtained from aliquots diluted by a factor of 10 in a modified Seligson automatic pipette. No differences were detected between filtered and unfiltered, or between acidified and unmodified samples; this confirms the work of BILLINGS AND HARRISS[6].

Many elemental analyses by atomic absorption are subject to a variety of interference effects, both chemical and physical. In the work under discussion, no chemical interference effects were noted for the alkali elements. For materials where the matrices contain large quantities of aluminum, silica, or calcium and phosphate together, serious depression of strontium absorption has been recorded[7], but this phenomenon was absent for the sea water matrix. Tests to determine possible "light-scattering" effects were applied but, again, their absence agrees with the findings of BILLINGS AND HARRISS. It was thought that variations in the major cationic constituents of the samples might result in errors attributable to viscosity differences. The negative results of tests applied to test this hypothesis over the salinity spread of the relevant samples agree with the recent data of ANGINO AND BILLINGS[8]. The determination of barium in sea water was hindered as a result of an atypical depressive interference phenomenon. This has been recently shown[9] to be due to the superimposition of the molecular calcium oxide absorption band. A nitrous oxide–acetylene flame may be used to decompose the refractory calcium oxide produced in cooler flames.

Standards for the lithium, rubidium, and strontium determinations were prepared in artificial sea water after the recipe given by LYMAN AND FLEMING[10], the formula for strontium being suitably modified. The excess sodium present in both standards and samples thus uniformly inhibited the ionization of the trace alkali elements. Both propane–air and acetylene–air combustion mixtures were used; under the given conditions, the latter mixture was superior in terms of suppression of electronic noise and reproducibility.

Discussion

Table II lists data for strontium, lithium, and rubidium. This is presented in the form of metal–chlorinity ratios to facilitate comparison with similar work recently given by FABRICAND *et al.*[11], but a discussion of the oceanographic significance of these data would be superfluous here. Errors are reported as standard deviations recorded for repeated analysis of one sample. These deviations may be assumed as solely attributable to instrument instability since contributions from other sources are negligible.

TABLE II

METAL–CHLORINITY RATIOS IN SEA WATER BY ATOMIC ABSORPTION SPECTROSCOPY (μg/kg/‰)

Element	FABRICAND[11]	*This paper*
Li	8.71 ± 0.14	9.0 ± 0.2
Rb	5.25 ± 0.42	5.2 ± 0.5
Sr	409 ± 8	359 ± 7

Previous data[12–14] for these elements in sea water have been obtained primarily from flame emission analysis. Under carefully controlled conditions, flame emission photometry will yield superior detection limits for the alkali elements but atomic absorption techniques are more amenable to controlled routine analysis. Thus working curves for lithium were obtained by means of emission photometry (flame photometer accessory with a Beckman DU spectrophotometer) and atomic absorption (Perkin-Elmer 303). The detection limits are comparable (Table I), but atomic absorption offers superior sensitivity: 0.05 and 0.25 mg/l/1% absorption respectively. Also, it should be noted that the lithium emission line from sea water samples occurs on the edge of a broad emission band.

TRANSITION ELEMENTS

Pre-analysis treatment

Sea water samples for trace transition analysis need to be pre-concentrated to bring abundances to the working range of atomic absorption equipment. Data from unmodified samples have been published[15], and the author has similarly obtained copper values from certain Alaskan coastal waters, but these examples are probably exceptional. The most common concentration techniques that have been employed are co-precipitation, solvent extraction, and the use of ion-exchange columns. A 20-fold concentration of heavy metals in industrial waste waters has been achieved[16] using Dowex A-1 resin, but the higher concentration factor required for marine water analysis generally lengthens the procedure considerably. A 98% recovery of chelated cobalt from 20 liters of sea water onto a strongly basic, anion-exchange column has also been recorded[17].

Chelation and solvent extraction of the trace metals for atomic absorption analysis offer several advantages. Primarily, the technique affords a simple separation into ionic and complex-bound fractions. Also, the reagents may be easily purified and the simplicity of the steps involved minimizes potential sample contamination. A third advantage is the gain in instrument sensitivity afforded by the use of organic solvents. Table III[18], for example, indicates the increased sensitivity recorded for cobalt and nickel in aqueous, 2-propanol and methyl isobutyl ketone (MIBK) solvents. The combination of ammonium pyrrolidine dithiocarbamate (APDC) and MIBK as the extractant has proved very useful[18] and a wide range of elements may be extracted from acidic solution. Sodium diethyldithiocarbamate (DEDTC) has also been routinely employed in this laboratory to extract iron, cobalt, nickel, and manganese at pH 6.5. Isoamyl acetate is 10 times less soluble in water than MIBK and preliminary results for the extraction of chelated radio-tracers are encouraging. For total analyses, any organic complexed metals present must be degraded to a form amenable to chelation. This may most easily be accomplished using peroxydisulphuric acid[19] followed by reduction where necessary.

TABLE III

DETECTION LIMITS (mg/l) AND SENSITIVITIES (mg/l/1% ABSORPTION) FOR COBALT AND NICKEL IN VARIOUS SOLVENTS[18]

Solvent	*Cobalt*		*Nickel*	
	Detection limit	*Sensitivity*	*Detection limit*	*Sensitivity*
Aqueous	0.07	0.16	0.10	0.27
2-Propanol	0.06	0.13	0.10	0.25
MIBK	0.04	0.08	0.09	0.18

TABLE IV

SELECTED TRACE ELEMENT DATA FROM 2 FIORD-TYPE ESTUARIES IN SOUTHEAST ALASKA

Sample number	*Na*[a]	*Co*[b]	*Cu*[b]	*Mn*[b]	*Zn*[b]
TI-F	0.011 ± 0.001	5.0 ± 0.5	1.5 ± 0.2	5.0 ± 0.2	5.1 ± 0.3
TI-G	1.2 ± 0.1	2.5 ± 0.3	4.7 ± 0.1	20.7 ± 0.1	4.3 ± 0.2
TI-E	6.5 ± 0.1	4.2 ± 0.2	8.6 ± 0.1	19.6 ± 0.1	4.1 ± 0.1
TI-I	9.4 ± 0.1	6.5 ± 0.3	5.7 ± 0.2	2.5 ± 0.1	2.8 ± 0.2
TA-A	8.5 ± 0.1	6.8 ± 0.2	19.8 ± 0.1	3.4 ± 0.1	5.3 ± 0.1
TA-B	9.9 ± 0.1	7.7 ± 0.3	5.2 ± 0.1	3.0 ± 0.2	2.6 ± 0.2
TA-C	9.4 ± 0.1	4.0 ± 0.2	7.0 ± 0.1	1.4 ± 0.1	2.0 ± 0.1
TA-D	9.4 ± 0.1	7.5 ± 0.3	8.0 ± 0.1	2.2 ± 0.1	3.7 ± 0.2

[a] Expressed as ‰.
[b] Expressed as μg/l.

At present, a single-stage solvent extraction step is generally insufficient for routine sea water analysis and may most effectively be combined with an initial coprecipitation. The trace transition data presented in Table IV were obtained by means of such a two-stage concentration process. Iron(III) hydroxide was used as the absorbant; full experimental details have been given elsewhere[18]. Blank correction data must be rigorously applied to compensate for heavy metal impurities—especially manganese—in the original iron(III) compounds. A second objection to the use of an iron(III) hydroxide scavenger is the lengthy process required to remove the iron from the re-dissolved co-precipitate. These difficulties have been avoided[20] by co-precipitating with magnesium hydroxide.

Analytical procedures

Single-stage co-precipitation and organic extraction steps, and two-stage combination concentration procedures, were applied in this laboratory. Each method presented its own analytical problems in terms of varying sample viscosity, potential chemical interference effects and "light scattering" phenomena. The latter problems were enhanced since non-specific concentration techniques were favored. Enhancements resulting from the use of organic solvents were noted above (Table III)[18]; such effects are more pronounced if cooler flames are employed[21]. Chemical interferences, also, are a function of the various combustion mixtures[3] and with low-temperature propane flames, small quantities of foreign elements have been noted[22] seriously to depress absorbances. Varying matrices were found to produce "light scattering" enhancements of the transition metals in broad agreement with the data recently published[23] on this subject. In view of the foregoing, it was found expedient to standardize the routine transition element analysis by using the method of standard additions. Data for samples from 2 estuarine systems in southeast Alaska are presented as examples in Table IV.

Discussion

Many analytical techniques have been previously employed to determine the transition metals in sea water. A comprehensive bibliography on the subject has been compiled by HØGDAHL[4], and this has been updated and exhaustively discussed by RILEY[5].

Only a very few data determined by atomic absorption spectrophotometry have appeared in the literature, but this technique would seem to offer much in terms of rapidity, precision, and versatility. Of particular interest to the practical oceanographer is the fact that the methods and equipment discussed above are potentially capable of being utilized at sea.

AUTO-ANALYSIS AND DATA PROCESSING

Individual samples

At present, rapid routine atomic absorption spectrophotometer analysis is generally limited by 2 time-consuming operations: manual aspiration of individual samples and conversion of data from per cent absorption to metal concentrations. For sample batches which require no pre-analysis treatment, as with the trace alkali metals in sea water, conventional methods of sample introduction and data handling were found to impede seriously the full operating potentialities of the method. The improved procedures, briefly reported here, have been utilized for many months in the laboratory with excellent results. It was appreciated initially that a system allowing maximum flexibility was required inasmuch as in this type of research, batch samples would be interspersed with certain samples which would require individual attention necessitating, for example, unique standards and instrumentation. Different analytical sequences were employed for these 2 types of sample.

Many samples required individual corrections for "light scattering" effects and for baseline corrections where the instrument was zeroed on a solvent differing from the sample, and others necessitated a sequence of standard additions. Such solutions, including the necessary standards, were individually aspirated and per cent absorptions were recorded from the instrument counter so that continuous monitoring of the data was possible. Satisfactory results were key punched onto cards and fed into either an IBM 1620 or a 360 computer. The simple accompanying program was designed to provide the necessary variety of computations. This infinitely flexible system is to be preferred over on-line computers[24] for this type of work.

Batch samples were fed into the machine via a Technicon Autoanalyzer sample changer. Samples were interspersed with standards and duplicate results were obtained by allowing the table to rotate several times. Speed of analysis was much reduced but the operator was released for other work. Absorption peaks were recorded on a coupled Texas Instruments strip-chart recorder. At intervals, these data were reduced directly to punched card form using a Benson-Lehner Model F Oscar and, thereafter, final computation was as noted above. Use of a rotatable short-pathlength burner would further simplify this sequence by eliminating the initial dilution step required, for example, for strontium. A second approach might be the use of an on-line auto-dilutor[25].

Stream analysis

Atomic absorption analysis seems ideally suited to continuous stream analysis. For shipboard work, this would offer the tremendous capability of continuously monitoring selected ions, or following water masses. To test the potentialities of this procedure, laboratory experiments were conducted on tapwater for a range of metals present in both major and minor quantities.

Water was circulated through ¼″ tubing and continuously sampled into the instrument mixing chamber via a needle set into the line. Pressure fluctuations were eliminated by use of a constant head device and the flow rate was regulated in arbitrary units on a gauge to prevent turbulent flow around the sampling needle. A second constant head reservoir and regulator were added to provide double distilled water for flushing when necessary and also to dilute the sample stream by reproducible quantities.

TABLE V

DETECTION LIMIT AND OPTIMUM WORKING RANGE DATA FOR STREAM ANALYSIS

Metal	*Detection limit (mg/l)*	*Optimum working range (mg/l)*
Cu	0.1	0.2– 6.0
Fe	0.2	0.4–10.0
Mn	0.07	0.2– 4.0
Zn	0.1	0.2– 3.0

The principle disadvantage of the system as described was a constant erroneous decrease in per cent absorption due to systematic clogging of the burner-atomizer components. This problem was alleviated to some extent by using wide-slot propane–air and BOLING[26] burner heads. Accurate data, however, could only be obtained by passing matched-matrix standards through the system at regular intervals. Table V lists the detection limits and optimum working ranges for the minor cations. The poorer limits obtained as compared with the data of Table I reflect the relative inefficiency of the sampling device used. The system offers promise for continuous trace analysis data, and it should be noted that scale expansion and noise suppression accessories may be used to full advantage since use of the latter necessitates extended aspiration times.

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SUMMARY

Trace elements of interest in sea water fall into two well-defined categories. Strontium, lithium, and rubidium are ideally suited to determination by atomic absorption spectrophotometry since minimal sample preparation is required and standard equipment may be utilized; standardization of techniques by which large batches of samples may be rapidly and accurately processed, is important. The transition elements are present in significantly lower concentrations and in complex, and largely unknown, chemical forms; pre-concentration is vital. Solvent extraction can also provide a crude differentiation between total and extractable fractions.

RÉSUMÉ

Les éléments intéressants, à l'état de traces, dans l'eau de mer peuvent être divisés en deux catégories. Strontium, lithium et rubidium conviennent très bien pour un dosage spectrophotométrique par absorption atomique. Pour les éléments de transition une préconcentration est indispensable. On peut procéder à une extraction par un solvant.

ZUSAMMENFASSUNG

Spurenelemente, die im Seewasser von Interesse sind, lassen sich in 2 Gruppen unterteilen. Für Strontium, Lithium und Rubidium ist die Flammenabsorptionsspektroskopie ideal geeignet, da eine geringe Probenvorbereitung erforderlich ist und Standardeinrichtungen verwendet werden können. Die Übergangselemente sind in bedeutend geringeren Konzentrationen vorhanden, was eine Anreicherung erforderlich macht.

REFERENCES

1 A. WALSH, *Spectrochim. Acta*, 7 (1955) 108.
2 E. D. GOLDBERG, in J. P. RILEY AND G. SKIRROW, *Chemical Oceanography*, Vol. 1, Academic Press, London, 1965, p. 164.

3 D. W. Hood, L. I. Knowles and D. C. Burrell, *Progress Report 1965–66* for A.E.C. Contract No. AT-(04-3)-310.

4 O. T. Høgdahl, *The Trace Elements in the Ocean: A Bibliographic Compilation*, Central Inst. Indust. Research, Oslo, 1963.

5 J. P. Riley, in J. P. Riley and G. Skirrow, *Chemical Oceanography*, Vol. 2, Academic Press, London, 1965, p. 324.

6 G. K. Billings and R. C. Harriss, *Texas J. Sci.*, 17 (1965) 129.

7 D. J. David, *Analyst*, 87 (1962) 576.

8 E. E. Angino and G. K. Billings, *Geochim. Cosmochim. Acta*, 30 (1966) 153.

9 S. R. Koirtyohann and E. E. Pickett, *Anal. Chem.*, 38 (1966) 585.

10 J. Lyman and R. H. Fleming, *J. Marine Res.*, 3 (1940) 134.

11 B. P. Fabricand, E. S. Imbimbo, M. E. Brey and J. A. Weston, *J. Geophys. Res.*, 71 (1966) 3917.

12 J. P. Riley and M. Tongudai, *Deep-Sea Res.*, 11 (1964) 563.

13 R. C. Smith, K. C. Pillar, T. J. Chow and T. R. Rolsom, *Limnol. Oceanog.*, 10 (1965) 226.

14 T. J. Chow and T. G. Thompson, *Anal. Chem.*, 27 (1955) 18.

15 B. P. Fabricand, R. R. Sawyer, S. G. Ungar and S. Adler, *Geochim. Cosmochim. Acta*, 26 (1962) 1023.

16 D. G. Biechler, *Anal. Chem.*, 37 (1965) 1054.

17 T. Joyner and J. S. Finley, *Atomic Absorption Newsletter*, 5 (1966) 4.

18 D. C. Burrell, *Atomic Absorption Newsletter*, 4 (1965) 309.

19 J. E. Noakes and D. W. Hood, *Deep-Sea Res.*, 8 (1961) 121.

20 T. Joyner, Presented at *11th Pacific Science Congress in Tokyo, August, 1966.*

21 D. C. Burrell, *Norsk Geol. Tidsskr.*, 45 (1965) 21.

22 R. J. Firman, *Spectrochim. Acta*, 21 (1965) 341.

23 G. K. Billings, *Atomic Absorption Newsletter*, 4 (1965) 357.

24 E. A. Boling, *Anal. Chem.*, 37 (1965) 482.

25 M. W. Gaumer, S. Sprague and W. Slavin, *Atomic Absorption Newsletter*, 5 (1966) 58.

26 S. Sprague and W. Slavin, *Atomic Absorption Newsletter*, 4 (1965) 293.

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SHORT COMMUNICATIONS

A rapid colorimetric method for the determination of thorium in human urine

The determination of thorium in urine is needed because of the health hazard for workers exposed to internal contamination by this element; control of thorium elimination is essential. The colorimetric procedures used for this purpose are often very sensitive but complicated and time-consuming. In a recent method[1], both sensitivity and speed of analysis were improved (5 samples could be analysed per day) but it was felt that further simplification could be achieved with a more sensitive and selective reagent. Since the maximum permissible excretion of thorium for professionally exposed people is generally considered to be 10 µg/l of urine, a suitable analytical procedure must be capable of determining thorium at the 2 µg/l level.

Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis(azo-2-phenylarsonic acid)) is the most sensitive colour reagent for thorium and is highly selective for quadrivalent ions[2-4]. This reagent has been used for the determination of thorium in biological samples[5]; the method is rapid but not sensitive enough for toxicological purposes. The method described below, utilizing arsenazo III, was developed for the toxicological control of thorium in human urine; *ca.* 24 samples can be analysed per working day.

Development of the method

The usual colorimetric determinations of thorium[1,6-8] in urine involve several preliminary steps. Mineralization can be done on the urine itself or on the precipitate obtained by making the sample alkaline. Thorium is then separated by various steps usually ending with solvent extraction or ion-exchange chromatography and stripping of the thorium back into a suitable aqueous solution.

The use of arsenazo III restricts the seriously interfering inorganic substances to the quadrivalent cations, which are not likely to be found in urine; however, the large amounts of calcium present in urine interfere and must be eliminated. The bulk of organic substances must also be removed, because of their low solubility in concentrated hydrochloric acid, which is the optimum medium for the colour development. The procedure described below comprises partial destruction of the organic precipitate obtained by alkalinization of 100-ml urine samples, by means of hot concentrated sulphuric acid and hydrogen peroxide, followed by precipitation of thorium with aluminium hydroxide as carrier, in concentrated ammonium sulphate medium to precipitate most of the calcium.

The choice of the hydrochloric acid concentration for the colour development is governed by a peculiar feature of the method; since the final solution is obtained by dissolution of the aluminium hydroxide precipitate, which may incorporate variable amounts of the mother liquid, the final concentration of hydrochloric acid depends appreciably on the extent of this entrainment. Accordingly, the final acidity must be chosen to give both a good molar extinction coefficient for the thorium–arsenazo complex and a low variation of absorbance with acidity changes; this acidity effect decreases as the acidity decreases. Figure 1 shows the variation of the absorbances of the arsenazo III and the thorium–arsenazo III complex with increasing concentrations of hydrochloric acid; measurements were made at 665 nm, the best wavelength for the determination of thorium[4]. On this basis, the range 7–8 *M* hydrochloric acid was chosen as the best compromise for the development medium; checks of the preliminary steps showed that this acidity could be reproduced within ±4%.

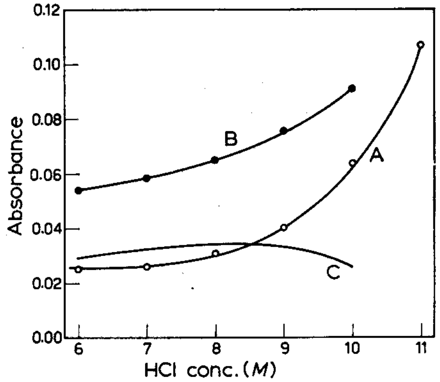

Fig. 1. The effect of HCl concentration on the absorbance of arsenazo III (curve A) and of arsenazo III+Th (curve B). Colour read against water; 1-cm optical path. Curve C is the difference between the former 2 curves. Arsenazo concentration: 40 μg/ml; Th concentration: 0.06 μg/ml.

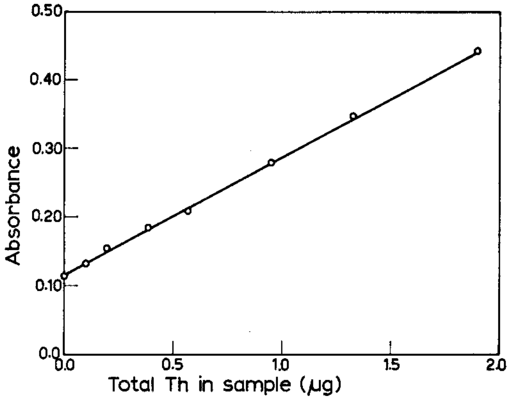

Fig. 2. Calibration curve.

Tests on 7 μg Th/l samples at a final acidity of 7.5 *M* hydrochloric acid showed that the optimum amount of arsenazo III to be added was 400 μg; lower amounts caused lower absorbances while higher amounts had no effect. A calibration curve (Fig. 2) was prepared by adding known amounts of thorium to urine just before it was made alkaline; the absorbance was measured against water to avoid the repeated preparation of reagent blank solutions.

A value of $1 \cdot 10^5$ was obtained for the molar extinction coefficient; this is quite similar to the figure obtained for direct development of the complex at this acid concentration[4].

Equipment and reagents

The spectrophotometric determinations were carried out with a Uvispek spectrophotometer (Hilger & Watts, London), glass optics, and 4-cm glass cuvettes.

A normal centrifuge with a 45° conical head was used with 100-ml neutral glass centrifuge tubes, at a speed of about 4000 rev./min.

Arsenazo III was produced by Fluka (Switzerland). Other chemicals were RP products of C. Erba (Milan).

Several stock solutions of thorium, *ca.* 0.01 *M*, were prepared by dissolving reagent-grade thorium nitrate (Merck, Germany) in 0.1 *M* hydrochloric acid; they were standardized by compleximetric titration[9]. The solutions used throughout this work were obtained by dilution of these stock solutions.

Fresh urine samples showed no difference in behaviour from samples several days old; old samples were stored at 4°, and some were acidified with a few drops of concentrated hydrochloric acid before storage.

All experiments were carried out at room temperature, *i.e.* $23 \pm 2°$.

Procedure

Pour 100 ml of urine into a centrifuge tube, add 4 ml of concentrated (17 *M*) ammonia solution, mix and centrifuge for 10 min. Discard the supernate and heat the residue with 5 ml of concentrated sulphuric acid for 5 min on a sand bath. Cautiously add 1 ml of 100-vol hydrogen peroxide and heat for another 10 min. Cool, dilute to 50 ml with distilled water and clear any turbidity by warming. Add 2 ml of 10% potassium aluminium sulphate solution and adjust the pH to *ca.* 8 with concentrated ammonia solution (10–12 ml suffices). Mix thoroughly during these additions, allow to stand for a few minutes and then centrifuge for 10 min, discarding the supernate. Dissolve the precipitate in about 3 ml of 11 *M* hydrochloric acid and transfer to a 10-ml calibrated flask, rinsing the tube with *ca.* 1.5 ml of 11 *M* hydrochloric acid.

Add 1 ml of arsenazo III solution (0.4 mg/ml in water), adjust the volume to the mark with 11 *M* hydrochloric acid, mix and transfer to a centrifuge tube. Centrifuge for 10 min and then measure the colour at 665 nm in 4-cm cells using water as reference. The colour is stable for at least 1 h.

Discussion

The number of analyses that can be done obviously depends on the number of tubes which can be centrifuged simultaneously. With a 4-place centrifuge, 24 analyses per working day are feasible.

The precision of the method was determined at the 0.0 and 1.9 μg/l thorium levels in urine samples. Average absorbances were 0.117 and 0.153 respectively; the standard deviation was 0.002 for both thorium levels, as calculated from 19 and 13 independent results. The standard deviation calculated from 6 independent runs with samples of the same urine was 0.001 at both thorium levels. The uncertainty of the method, calculated as 3σ, is 0.006 absorbance units, *i.e.* 0.3 μg Th/l.

On the conservative assumption that the procedure allows for a $6\sigma = 0.012$ A.U. detection threshold, the lowest thorium amount detected would be 0.06 μg, or 0.6 μg/l, which is more than 3 times below the minimum investigation level (2 μg/l).

The effect of the presence of uranium was investigated. Up to 40 μg of uranium per litre can be neglected, because the presence of this element was found to increase the thorium results by only $1.4 \cdot 10^{-4}$ A.U. per µg of uranium per litre. This contribution increases linearly up to 500 µg U/l, so that if necessary the thorium absorbance can be corrected after uranium has been determined. However, the maximum permissible excretion level of uranium for professionally exposed people is 50 µg/l and this amount would increase the absorbance value by an amount corresponding to only 0.4 µg Th/l.

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1 C. TESTA, *Radiological Health and Safety in Mining and Milling of Nuclear Materials*, Vol. II IAEA, Vienna, 1964, p. 489.
2 S. B. SAVVIN, *Talanta*, 8 (1961) 673.
3 S. B. SAVVIN, *Talanta*, 11 (1964) 1.
4 S. B. SAVVIN, *Arsenazo III—Photometric Methods for the Determination of Rare Elements and Actinides*, Atomisdat, Moscow, 1966.
5 P. A. PAVLOVSKAYA AND T. N. CHERKASHINA, *Materialy po Toksikol. Radioaktivn. Veshchestv. Akad. Med. Nauk SSSR*, 4 (1964) 73; *C.A.*, 62, 5566 d.
6 R. W. PERKINS AND D. R. KALKWARF, *Anal. Chem.*, 28 (1956) 1989.
7 L. JEANMAIRE AND H. JAMMET, *CEA Report No. 1227*, 1959.
8 G. A. WELFORD, D. C. SUTTON, R. S. MORSE AND S. TARRAS, *J. Am. Industr. Hyg. Ass.*, 19 (1958) 464.
9 G. SCHWARZENBACH, *Complexometric Titrations*, Methuen, London–Interscience, New York, 1957, p. 75.

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Indirect determination of caesium by compleximetric titration of calcium after extraction with calcium dipicrylaminate in nitrobenzene

The indirect compleximetric determination of the heavy alkali metals involves either previous isolation of the alkali metal by precipitation [$Rb_2NaCo(NO_2)_6$[1], $Cs_2AgCo(NO_2)_6$[2], $CsClO_4$[2], $CsBiI_4$[2], $CsB(C_6H_5)_4$[2]] or exchange of the alkali metal for calcium or magnesium[2,3] on a cation-exchanger under dynamic conditions. The method described below is based on the exchange of caesium(I) for calcium(II) when a nitrobenzene solution of calcium dipicrylaminate ($CaDPA_2$) is shaken with a slightly alkaline aqueous caesium(I) solution. The use of this extraction system for the determination of caesium labelled with ^{137}Cs has been reported[4].

This method was expected to have advantages because of the omission of the troublesome precipitation step[2] and because of the high value of the equilibrium constant of the reaction[5]

$$2\,Cs^{+}_{aq} + Ca^{2+}_{org} \rightleftharpoons 2\,Cs^{+}_{org} + Ca^{2+}_{aq} \qquad \log K_{Cs/Ca} = 6.7 \tag{1}$$

which shifts the above equilibrium entirely to the right even with rather high aqueous calcium concentrations.

Two alternative indirect determinations of caesium were examined: (*1*) the solution containing caesium was adjusted to pH 8–11 with lithium hydroxide and the calcium content in the aqueous phase was determined with EDTA; and (*2*) the calcium was determined in the extract after back-extraction with dilute mineral acid.

Reagents

Reagent-grade chemicals were used throughout. The preparation of calcium dipicrylaminate, the purification of nitrobenzene, the equilibration and radiometrical techniques were reported previously[4].

Procedure A

To a neutral solution containing only a mineral salt of caesium ($G_{Cs}=0.1$–2 mg Cs) add 0.30 ml of $5\cdot10^{-3}$ *M* lithium hydroxide and dilute to 3.00 ml with water. Equilibrate with 3 ml of $3\cdot10^{-3}$ *M* $Ca(DPA)_2$ in nitrobenzene and titrate calcium in the aqueous phase with 0.005 *M* EDTA (*t* ml) using erio T indicator[2]. Prepare a calibration curve (*t vs.* G_{Cs}). Treat unknown samples in the same way.

Procedure B

To a neutral solution containing caesium salt ($G_{Cs}=5$–20 mg Cs) add 1.0 ml of 0.005 *M* $Ca(OH)_2$ and dilute to 10 ml with water. Equilibrate with 10 ml of 0.010 *M* $Ca(DPA)_2$. To 9 ml of the organic phase add 9 ml of 0.1 *M* hydrochloric acid and back-extract. Determine calcium in an aliquot of this extract by titration with 0.005 *M* EDTA after pH adjustment. Calculate the amount of caesium from $G_{Cs}=A-kG_{Ca}$, where G_{Ca} is the amount of calcium present in the first extract, and *A* and *k* are established by 2 analogous runs with known amounts of caesium.

With smaller G_{Cs} values, appropriately lower initial concentrations of the calcium dipicrylaminate must be used.

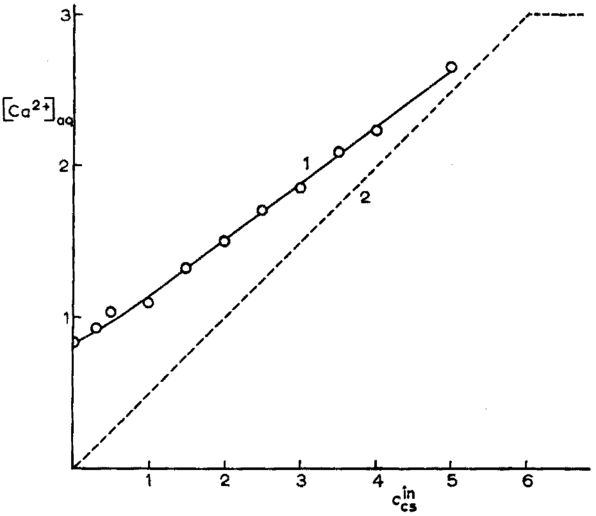

Fig. 1. The dependence of the calcium concentration found in the aqueous phase upon the initial concentration of caesium. $[Ca^{2+}]_{aq}=$ the equilibrium analytical concentration of calcium in the aqueous phase (m*M*), C_{Cs}^{in} = the initial concentration of caesium (m*M*); $3\cdot10^{-3}$ *M* $Ca(DPA)_2$. (1) Experimental points; (2) theoretical dependence provided that side reactions do not interfere.

Results and discussion

Typical results for calcium determinations in the equilibrium aqueous phase are given in Fig. 1; the consumption of EDTA was not stoichiometrically related to the initial caesium concentration, but experiments with ^{137}Cs showed that more than 99.8% of caesium was extracted in all cases. The higher calcium values are due partly to the exchange of some of the lithium ions present for calcium (log $K_{\mathrm{Li\text{-}Ca}} \doteq -2$, see ref. 5), and partly to the fact that some calcium passes from the nitrobenzene layer to the aqueous layer even in the absence of other salts:

$$\mathrm{Ca^{2+}_{org}} + 2\ \mathrm{DPA^{-}_{org}} \rightleftharpoons \mathrm{Ca^{2+}_{aq}} + 2\ \mathrm{DPA^{-}_{aq}} \qquad \log K_{\mathrm{Ca/DPA}} = -2.4$$

The use of an empirical calibration curve is therefore necessary in all cases. The average error of the caesium determination (0.4–2 mg) with 3 ml of $3 \cdot 10^{-3}$ *M* Ca(DPA)$_2$ was found to be ±2%.

When the calcium is determined in the organic phase (after back-extraction), the pH value can be adjusted with calcium hydroxide and the complicating influence of the exchange reaction of lithium for calcium obviated. This results in a linear dependence of the amount of calcium in the first extract (G_{Ca}) upon G_{Cs} values.

The theoretical *k* value is 6.632, but it was found (Table I) that the actual values are up to 15% higher, *i.e.* the amount of EDTA consumed in the titration is *ca.* 15% lower than expected for an equivalent exchange of caesium for calcium. Since extraction of caesium is quantitative (see above), and as the "calcium loss" increases with increasing pH values in the initial aqueous phase, the low results are ascribed to precipitation of calcium by carbon dioxide from the air; the invisible precipitate is probably captured on the interfacial surface and is not withdrawn in the transfer of

TABLE I

THE DETERMINATION OF CAESIUM BY THE CALCIUM CONTENT IN THE EXTRACT

A initial concentration $1 \cdot 10^{-2}$ *M* Ca(DPA)$_2$ in nitrobenzene; $k = 7.6070$; $\varphi = 0$.
B $3 \cdot 10^{-3}$ *M* Ca(DPA)$_2$; $k = 7.3682$; $\varphi = 0$.
C $1 \cdot 10^{-2}$ *M* Ca(DPA)$_2$; $k = 7.5020$; variable molar ratio of calcium and caesium ($\varphi = G_{\mathrm{Ca}}/G_{\mathrm{Cs}}$) in the initial aqueous phase.

Cs taken (mg)	*Ca found (mg)*	*Cs found*[a] *(mg)*	*Relative deviation (%)*	*Remark*
A. 0	2.862[a]			[b]
19.93	0.242			[b]
7.974	1.813	7.979	+0.06	
13.29	1.127	13.20	−0.7	
B. 0	0.9965			[b]
5.980	0.1849			[b]
2.658	0.6419	2.613	−1.7%	
3.987	0.4515	4.015	+0.7%	
C. 5.021	2.210			[b] $\varphi = 0$
14.076	1.003			[b] $\varphi = 0$
7.949	1.823	7.925	+0.3%	$\varphi = 0.28$
12.445	1.230	12.373	−0.6%	$\varphi = 0.18$
10.273	1.521	10.191	−0.8%	$\varphi = 0$

[a] All data are average values of 2 parallel determinations.
[b] These results were used to calculate the values of *k* and *A*.

the organic phase for the back-extraction. When carbon dioxide was largely excluded, the *k* values were closer to theoretical, but the reproducibility of the determination was not enhanced.

For practical analyses, it is satisfactory to find empirically the *k* and *A* values using 2 known solutions of caesium (preferably from both ends of the concentration range involved) under exactly the conditions used for samples. Typical results are listed in Table I.

Procedure B includes back-extraction as an additional step, but affords certain advantages. Apart from the constancy of the *k* and *A* parameters mentioned, it allows the determination of caesium in the presence of some other cations.

It was found that the values *k* and *A* depend very little on the initial concentration of calcium in the aqueous phase up to 0.1 *M* Ca^{2+}. Consequently, caesium can be determined with satisfactory precision in the presence of a large excess of calcium (molar ratio ~100) if the calcium concentration is constant, or at least known, so that the construction of the calibration curve $G_{Cs}=f(G_{Ca})$ is feasible. So long as the calcium concentration does not exceed $4\cdot10^{-3}$ *M*, it does not influence the determination of caesium at all (see experiments C, Table I). If the calibration curve is calculated from solutions with 0.1 *M* $CaCl_2$ in the initial aqueous phase, sodium, barium and strontium do not interfere at concentrations below $4\cdot10^{-3}$ *M*.

The method proposed is less time-consuming than the cation-exchange method (the extraction equilibria are attained in less than 1 min with effective stirring) and is more precise in the presence of alkaline earth metals. It can also be used for the determination of caesium after the precipitation of caesium perchlorate as an alternative to the rather complicated procedure proposed by DE SOUSA[6]. Analogous determinations of rubidium and potassium could probably be developed, though because of the smaller values of the equilibrium constants of the reactions involved, the usefulness of the method would decrease from caesium to potassium.

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1 A. CYGANSKI, *Chem. Anal. (Warsaw)*, 9 (1964) 749.
2 See G. SCHWARZENBACH AND H. FLASCHKA, *Die komplexometrische Titration*, F. Enke, Stuttgart, 1965.
3 G. N. BABATSCHEW, *Z. Anal. Chem.*, 173 (1960) 121.
4 M. KYRŠ AND L. KADLECOVÁ, *Anal. Chim. Acta*, 36 (1966) 215.
5 M. PIVOŇKOVÁ AND M. KYRŠ, to be published.
6 A. DE SOUSA, *Talanta*, 8 (1961) 686.

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On the use of the sodium electrode

Several papers[1-4] have recently appeared dealing with the use of specific cation electrodes. A comprehensive review of their use has been given by EISENMAN[5]. It is clear from the literature that their use is attractive for certain studies *e.g.* ion exchange. The present work describes some experiments with a sodium electrode and the measures needed to approach the accuracy claimed (see, *e.g.*, HYMAN[6]), particularly in the presence of other cations.

Experimental

Equipment. Potentials were measured on a Radiometer Titrator TTT 1, fitted with a Scale Expander calibrated to read to 0.5 mV. The electrodes used were the Beckman 39278 Laboratory Sodium Ion Electrode and a Titron calomel reference electrode.

Reagents. The sodium content of analytical-grade ammonium chloride, potassium chloride, barium chloride and magnesium sulphate was determined by atomic absorption spectroscopy. Allowance was made for the sodium content of these salts in the calculations of the pNa values.

The sodium content of the magnesium chloride was 0.37 % being much higher than the 0.005% specified. This precluded the attainment of pNa values greater than 2.4 in the presence of magnesium chloride.

To minimize interference by the hydrogen ion and to reduce streaming potentials at low sodium concentrations all solutions were made up in 0.2 *M* reagent grade tris(hydroxymethyl)aminomethane, made 0.1 *N* with respect to chloride by the addition of hydrochloric acid giving a final pH value of 8.28.

Procedure. Measurements were made on solutions placed into an earthed and electrostatically screened crucible.

To obtain maximum reproducibility the procedure was rigorously standardised. The crucible and electrodes were gently wiped with tissue to remove residues of the previous solution, and rinsed with a sample of the next solution. With the electrodes in place, the contents of the crucible were swirled for 3 min and allowed to stand for 2 min before the reading was taken. The reading was subtracted from that obtained in a standard sodium chloride solution which was usually chosen to be the highest concentration in the series. This difference is subsequently referred to as Δ. To allow for any drift with time and for variation associated with large changes in concentration, readings were obtained in the standard solution before and after each observation and the mean of these 2 values was used in deriving Δ values. When the electrodes stood in a given solution for 24 h a change of about 4 mV was commonly observed, the magnitude of the change depending on the recent history of the electrode. Similarly, when gross changes were made in concentration, say, from a standard of *N* sodium chloride to 0.0005 *N* sodium chloride in magnesium sulphate and back again, the potential of the standard changed by about 1 mV.

Results and discussion

Fig. 1D shows the difference (Δ) between the potential measured in *N* sodium chloride and any other concentration plotted against pNa.

For convenience Fig. 1 has been divided into 3 parts, pNa <1 [Fig. 1 (i)], a central linear part which has been omitted, and pNa >2.0 [Fig. 1 (ii)]. The central section of Fig. 1D, from pNa 1 to 2.5 is linear with a slope of 56.3 (Table I). At high pNa the curve [Fig. 1 (ii)D] becomes concave to the pNa axis, probably because the hydrogen ion concentration and the sodium from the buffer reagents are becoming important.

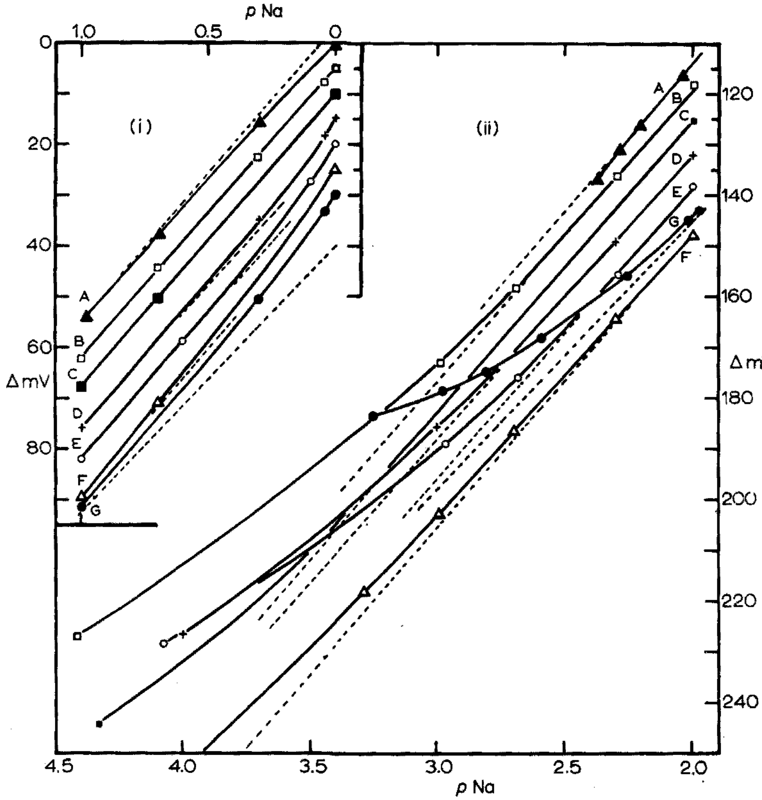

Fig. 1. Δ *versus* pNa curves for NaCl and mixtures of NaCl with other salts. Ionic strengths of mixed systems = 1.0. (A, ▲) MgCl$_2$; (B, □) CaCl$_2$; (C, ■) BaCl$_2$; (D, +) NaCl; (E, ○) NH$_4$Cl; (F, △) MgSO$_4$; (G, ●) KCl. For convenience the curves have been divided into 3 portions, pNa <1.0 [Fig. 1(i)], a central linear portion which has been omitted and pNa>2.0 [Fig. 1(ii)]. Dashed lines are extrapolations of central linear portions of curves with slopes as shown in Table I. The ordinate origin of each curve has been increased by 5.0 mV from the preceding one in the order A, B, C, D, E, F, G.

At pNa <1, the line [Fig. 1 (i)D] again deviates from linearity, the slope acquiring a greater value than that expected from the simple Nernst equation ignoring activity coefficients[7]. This seems to be associated with the junction potential since PORTNOY *et al.*[3] have shown that the discrepancy can be eliminated by the use of a reference electrode without a liquid junction. The anomaly is not due to the neglect of activity coefficients[3] but may be caused by the existence of a bi-ionic potential at the junction of the potassium chloride bridge and the solution resulting from the greater mobility of the potassium and chloride ions compared to that of the sodium ion.

When there is more than one cation present, the performance of the electrode will be determined by the selectivity for the sodium ion compared to the other cation.

When the electrode has decreased selectivity for sodium because of the presence of a second cation, as in the case of potassium, then the calibration curve will not be identical with the sodium curve until the concentration of the second cation is sufficiently small compared to sodium. If the concentration of the second cation is constant then a non-linear calibration curve is obtained which may nevertheless be useful. A different calibration curve will be obtained for each level of the second cation, thus in the absence of knowledge about the second cation a given sodium concentration could give rise to several values of Δ. It is therefore necessary to know either the concentration of the second cation or the total electrolyte concentration, *e.g.* chloride ion in an unknown mixture of potassium chloride and sodium chloride when a calibration curve at constant ionic strength could be used. For example, Fig. 1 shows curves of Δ *versus* pNa measured at constant ionic strength in the presence of a series of salts with monovalent and divalent cations. The values for the slopes of the central linear portions are shown in Table I.

TABLE I

THE SLOPE OF THE Δ *versus* pNa CURVE FOR DIFFERENT SALTS FOR pNa 1.0–2.0
(Total ionic strength (NaCl + salt) = 1.0)

Salt	*Slope (mV per unit pNa)*	*Salt*	*Slope (mV per unit pNa)*
NH_4Cl	56.7	$BaCl_2$	57.8
NaCl	56.3	$MgCl_2$	58.8
KCl	~53[a]	$MgSO_4$	58.0
$CaCl_2$	57.3		

[a] This represents an average value since there is a significant curvature present.

The slopes for all systems except those measured in potassium chloride itself, fall very close to the range 57.5 to 58.3 determined from the Nernst equation for the temperature range (17 to 21°) within which the experiments were carried out. The results for sodium chloride could not be carried out at constant ionic strength which may contribute to the low values of the slope. There is less selectivity in the presence of potassium, leading to a greater curvature at a lower pNa, than for any other system.

At pNa < 1 the results are similar for sodium chloride alone and in the presence of potassium or ammonium chlorides, the curves having slopes of about 62 mV which is significantly greater than that predicted from the Nernst equation. At pNa > 1 the results in the presence of ammonium chloride are similar to those for sodium chloride itself.

Linear relationships were obtained over a wide range of pNa values (0–2.5) in the presence of the divalent ions, calcium and barium and no initial deviation from the Nernst slope was found. The deviations at the larger pNa values are of the same order as those of the curves in the presence of sodium alone. At pNa < 1.0 in the presence of magnesium chloride the Δ *versus* pNa curves have a slope that is less (*viz.* 54 mV) than that expected from the Nernst equation. If magnesium sulphate is used in place of magnesium chloride the results are similar to those obtained in the presence of the monovalent ions but without the marked decrease in selectivity at pNa > 3.0. Selectivities for sodium appear to be greatest in the presence of barium and calcium and least in the presence of potassium.

A solution of 0.1 *N* sodium chloride (pNa 1) gives a Δ value of 61.0 mV when only sodium chloride is used, but because of the differing slopes of the calibration curves, values of Δ from 54.0 to 64.5 mV could be obtained for the same amount of sodium chloride added to solutions of magnesium chloride and sulphate respectively [Fig. 1 (i)]. If the reading of 54.0 mV is interpolated onto the sodium chloride curve a pNa value of 0.88 will be obtained corresponding to 0.132 *N* sodium chloride, an error of 32%.

To obtain the likely limits of accuracy a detailed calibration curve was determined for a narrow range of pNa (1 to 1.3) in which the potassium to sodium ratio varied from 9 to 19. The value of $[Na^+ + K^+]$ was maintained at 1.0 *N*.

The pNa *versus* voltage curve had a linear correlation coefficient, r, of 0.999 and would enable sodium to be determined with a standard error of 1% and 95% confidence limits of ±2.3%. This standard error corresponds approximately to the reading error of the expanded scale pH meter.

It is concluded that the sodium electrode can be used with considerable accuracy for determining the concentration of sodium ions in a simple solution. In mixed solutions the concentration of other ions affects the response of the sodium electrode to changes in sodium ion concentration. However, sodium may be determined with a similar accuracy in mixtures provided that a calibration curve is obtained with standard solutions which contain all but sodium and one other ion at the same concentration as in the unknown sodium solution. For example, if the unknown were a mixture of sodium, magnesium, chloride and sulphate, and the magnesium and sulphate were present in equivalent concentrations the calibration solutions should contain this amount of magnesium sulphate and differing amounts of sodium chloride; if sulphate were at a greater concentration than the magnesium then the standard solutions to be used in calibration should, in addition to magnesium sulphate, contain a fixed amount of sodium sulphate equivalent to the difference between sulphate and magnesium.

In the work reported here for heterovalent ionic mixtures a constant ionic strength was used in arriving at a calibration curve. In such circumstances the concentration of all but sodium and two other ions needs to be known. For instance, once the ionic strength of a solution containing sodium, calcium and chloride ions is defined no further information is required to arrive at a series of calibrating solutions.

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1 G. Mattock, *Analyst*, 87 (1962) 930.
2 S. M. Friedman, *Methods Biochem. Anal.*, 10 (1962) 71.
3 H. D. Portnoy, L. M. Thomas and E. S. Gurdjian, *Talanta*, 9 (1962) 119.
4 C. A. Bower, *Soil Sci. Soc. Am. Proc.*, 23 (1959) 29.
5 G. Eisenman, *Advan. Anal. Chem. Instr.*, 4 (1965) 213.
6 E. S. Hyman, *Anal. Chem.*, 34 (1962) 365.
7 J. A. M. Hinke, *J. Physiol.*, 156 (1961) 314.

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Internal electrolysis for the separation of ions
Part III. Separation and determination of selenium and tellurium

Separation of ions by internal electrolysis has been discussed in earlier communications[1,2]. In this communication the separation of selenium and tellurium from each other and from other ions is reported. At pH 7.5–9.0 both selenium and tellurium can be deposited on a nickel-coated platinum cathode in presence of tartrate and can thus be determined after separation from Fe, Al, Cr, Ti, Th, Zr, Be, Zn, Mn, W, V, UO_2^{2+}, Mo, La, Ta and alkali and alkaline earth metals. Since only selenium is completely deposited from a tartrate solution at pH 1.0–2.0 on a platinum cathode when nickel is used instead of zinc as anode, it is easily separated from tellurium, which afterwards is deposited from the residual solution, maintained at a pH 3.0–4.0 on the nickel-coated platinum cathode with zinc as anode.

Apparatus and solutions

The Cambridge pH indicator and the apparatus assembly consisting of a platinum gauze cathode and a zinc plate anode were the same as used earlier[1]. A nickel plate in place of zinc as anode was used when required. The nickel-plated platinum cathode was prepared as follows. To a cobalt-free nickel chloride solution were added sodium potassium tartrate in an amount 10 times the nickel weight, and 4–5 g of ammonium chloride; after dilution to 250 ml, the pH was adjusted to 7.5 with dilute ammonia. A Pt/Zn electrode assembly was then immersed and electrolysis was allowed to proceed for *ca.* 6 h. The electrodes were then removed and the cathode was washed with water and ethanol and dried. The nickel coating amounted to 3–4 mg.

The chemicals used were of the highest available purity. Standard solutions of selenium or tellurium were prepared by dissolving selenium dioxide or telluric acid in water. The selenium solution contained a few drops of hydrochloric acid. The selenium solution was standardized gravimetrically by reduction with hydroxylamine hydrochloride[3]. The tellurium solution was also standardized gravimetrically by reducing with a mixture of sulphur dioxide and hydrazine hydrochloride[3].

Standard solutions of other cations and anions as well as the 10% solution of sodium potassium tartrate were the same as reported previously[1].

General procedure

The solutions of the ion to be deposited and of other ions, each 5–10 times the quantity of the former, were placed in a tall beaker. To study the influence of a particular ion, a 50–100-fold weight, compared to the ion to be deposited, was taken. Tartrate (at least 10 times the total quantity of the ions) was then added and the solution was diluted with water to 250–300 ml or to any required volume to keep the ions in solution. The pH was then adjusted to 7.5–9.0.

The nickel-coated platinum cathode and the zinc plate anode were then placed in the solution. Selenium took *ca.* 6 h and tellurium *ca.* 12 h for complete deposition. The electrode assembly was then removed and rinsed with water, and the cathode was disconnected and washed with alcohol, dried and weighed[1].

For all subsequent separations, the platinum cathode was cleaned[2] before use.

Results obtained for the separation of selenium or tellurium from the ions mentioned above are shown in Table I.

TABLE I

SEPARATION OF SELENIUM (deposition time 6.0 h) AND OF TELLURIUM (deposition time 12.0 h) FROM OTHER IONS

pH	*Selenium*		*Tellurium*	
	taken (mg)	*found (mg)*	*taken (mg)*	*found (mg)*
7.5	2.3	2.3	2.9	2.88
8.0	2.3	2.3	2.9	2.90
8.5	1.15	1.14	1.45	1.45
9.0	3.45	3.43	4.35	4.34
9.0			2.9	2.88

TABLE II

SEPARATION OF SELENIUM AND TELLURIUM FROM EACH OTHER

Selenium		*Tellurium (taken 58.0 mg)*	
taken (mg)	*found (mg)*	*present in aliquot (mg)*	*found (mg)*
2.3	2.3	2.9	2.88
3.45	3.42	2.9	2.89
1.15	1.15	1.16	1.16

Separation of selenium and tellurium from each other

The procedure was essentially the same as that given above. Selenium was deposited quantitatively at pH 1.0–2.0 in the presence of tartrate on a platinum cathode with nickel as anode; this deposition required 3 h and the cathode was then cleaned and weighed in the usual way.

The residual solution containing tellurium was diluted to 500 ml in a volumetric flask, and an aliquot, mixed with some tartrate, was diluted to 250 ml. After adjustment of the pH to 3.0–4.0, tellurium was deposited in 12.0 h on a nickel-coated platinum cathode with a zinc anode. Results obtained by this method are shown in Table II.

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1 A. K. MAJUMDAR AND SM. GOURI BHOWAL, *Anal. Chim. Acta,* 35 (1966) 206.
2 A. K. MAJUMDAR AND SM. GOURI BHOWAL, in press.
3 A. I. VOGEL, *A Text Book of Quantitative Analysis,* 3rd Edn., Longmans Green, London, 1962.

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Über Galliumdithizonat und Germaniumdithizonat

PILIPENKO[1] hatte beim trockenen Erhitzen von Ga_2O_3 und Dithizon (HDz) eine Rotviolettfärbung beobachtet. ALI und Mitarbeiter[2] isolierten eine rote Koordinationsverbindung von der Zusammensetzung $Ga(HDz)_2GaCl_4$. PIERCE UND PECK[3] haben eine verdünnte Ga^{3+}-Lösung (+ markierten ^{72}Ga) mit einem 10^3-fachen Überschuss an HDz in Tetrachlorkohlenstoff bei pH 5 behandelt und auf die Existenz von $GaDz_3$ geschlossen.

Bei der Bestimmung von Cu^{2+}-Spuren mittels einer Dithizon (HDz)/Tetrachlorkohlenstofflösung in konzentrierten $GaCl_3$-Lösungen (18 mg Ga^{3+}/ml) bei pH 2.5–3 wurde eine Störung beobachtet derart, dass nur der erste organische Extrakt von $CuDz_2$ violett war, während die weiteren Extrakte stets eine braunviolette Färbung annahmen. Die braunviolette Farbe erwies sich als Mischfarbe aus freiem Dithizon (grün) und Galliumdithizonat (rotviolett).

BILDUNG UND EIGENSCHAFTEN DES GALLIUM(III)-DITHIZONATES

Die Bildung des Galliumdithizonates muss gegen die Wassersolvatation, Hydrolyse und Hydratation erzwungen werden und wird begünstigt durch die Darbietung einer hohen Konzentration an Ga^{3+} oder an HDz/o unter Vorgabe des optimalen pH-Bereiches von 2.5–3 (gemessen mit Lyphanpapier 652). So erhält man mit gelförmigem $GaCl_3$ und HDz/CCl_4 bzw. $HDz/CHCl_3$ eine praktisch auf das HDz bezogene quantitative Umsetzung zum rein rotvioletten Galliumdithizonat (Fig. 1); bei verdünnteren Lösungen ist die Umsetzung nicht vollständig, wie aus Tabelle I ersichtlich, wo jeweils 10 ml der Reaktanten geschüttelt wurden und die freie Dithizonkonzentration über die Absorption bei 620 nm ermittelt wurde.

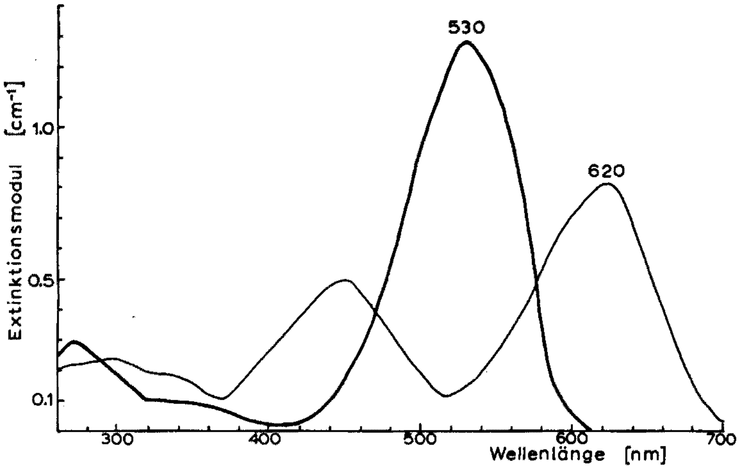


Fig. 1. —— Spektrale Absorption der eingesetzten 25 μM HDz/CCl_4-Lösung; **——** Spektrale Absorption der korrespondierenden Gallium-di-dithizonat/CCl_4-Lösung.

Die spektrale Absorption (Fig. 1) zeigt innerhalb der Fehlergrenzen für HDz/

CCl_4 als auch für $HDz/CHCl_3$ den gleichen Verlauf. Im flachen Absorptionsmaximum 530 nm beträgt der normale Extinktionskoeffizient (auf 1 HDz bezogen) $51 \cdot 10^3$ [l/Äquivalent.cm], während oberhalb von 600 nm die Lichtabsorption gering ist.

Aufgrund der beobachteten Farbkonstanz sind Ga-Dithizonatlösungen isoliert oder in Kontakt mit dem Extraktionsmilieu sehr zeit- und lichtbeständig. Mit anders zusammengesetzten wässrigen Lösungen wird das Ga-Dithizonat rasch zerlegt unter Freisetzung des HDz.

TABELLE I

UMSETZUNG VON $GaCl_3$-LÖSUNGEN MIT HDz–CCl_4

Nr.	*$GaCl_3$-Lösung pH 2.8 (mg Ga^{3+}/ml)*	*Ausgangslösung HDz/CCl_4 (μM)*	*Anteil nicht umgesetztes HDz (%)*
1	107	990	8
2	17	990	29
3	107	500	12
4	17	500	52

Dampft man bei einer Galliumdithizonatlösung das Solvens ein, so hinterbleibt das Ga-Dithizonat als dunkelroter Rückstand, der leicht mit CCl_4 und spielend mit $CHCl_3$ wieder in Lösung geht.

Die Galliumdithizonatreaktion ist etwa 10^3-mal empfindlicher wenn anstelle von HDz/CCl_4—oder $HDz/CHCl_3$—eine HDz/Aceton-Lösung genommen wird. So lassen sich noch 10 μg Ga mit einer 250 μM acetonischen HDz-Lösung an der auftretenden Rosafärbung erkennen. Enthält die $GaCl_3$-Lösung Tartrat oder Citrat, so wird die Reaktion inhibiert.

Die Reaktion des Ga^{3+} mit HDz/o ist, trotzdem die entstandene Verbindung unter den Dithizonaten den höchsten Extinktionsmodul von 1.44 [cm^{-1}] pro μg Ga in 1 ml $CHCl_3$ besitzt, noch zu unempfindlich und störanfällig, um selbst analytisch angewandt zu werden. Sie kann aber im pH-Bereich 2.5–3 und Vorliegen einer recht hohen Ga^{3+}-Konzentration die Bestimmung anderer Dithizonmetalle (z.B. Cu^{2+}, Hg^{2+}) stören, falls das Verhältnis $1:10^5$ überschritten wird. Die Störung kann behoben werden, wenn man dem optimalen pH-Bereich ausweicht.

Bestimmung des Umsetzungsverhältnisses Gallium : Dithizon

10 ml $GaCl_3$ (107 mg Ga^{3+}/l = 1.53 M), auf pH 2.8 (Lyphanpapier 652) eingestellt werden mit 10 ml HDz/CCl_4 (950 μM) geschüttelt, die organische Phase nach 1/4-stündigem Stehen separiert und durch ein trockenes Filter filtriert (Bem. a). Durch Schütteln mit 5 ml 0.5 M HCl wird das Dithizonat zerlegt (Bem. b). Nach Ablassen der organischen Phase und Nachspülen mit 3 ml Tetra wird die saure Lösung in einem Bechergläschen gesammelt, die Schüttelbirne kurz mit 2 ml Wasser nachgespült und diese auch in das Becherglas gegeben. Die Bestimmung des Galliums erfolgte nach Eindampfen der Lösungen bis nahe zur Trockne mit Oxin (Bem. c).

Bemerkungen: (*a*) Durch Messung bei 620 nm wurde das nicht umgesetzte HDz bestimmt und in Abzug gebracht.

(*b*) Kontrollmessungen bei 620 nm ergaben, dass praktisch wieder die Ausgangskonzentration der HDz-Lösung erhalten worden war.

(*c*) Blindwertversuche—sonst gleich—mit reinem CCl_4 verliefen negativ (< 20 μg Ga).

Betrachtungen zum Aufbau von Gallium(III)-dithizonat

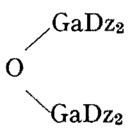
Unter den aufgeführten pH-(2.5–3) und Konzentrationsbedingungen ($Ga^{3+} \sim 1\ M$ und $HDz \sim 1 \cdot 10^{-3} M$) beträgt das Umsetzungsverhältnis Ga^{3+}: HDz $= 1 : 2$, was nicht ausschliesst, dass bei grossem Überschuss an HDz dessen Anteil bis zum Verhältnis 1 : 3 ansteigen kann unter Bildung des Gallium(III)-tri-dithizonates[3]. Abgesehen von Koordinationspartnern muss bei dem von uns erhaltenen Gallium(III)-di-dithizonat die III. chemische Valenz von einem Partner "X" abgesättigt werden. Als Partner "X" könnten im Falle $GaCl_3$ einzeln oder gemischt auftreten: Cl—, HO—, —O—, was zu folgenden Formeln führt, die ihrer Klärung harren:

TABELLE II

ERGEBNISSE ZUR BESTIMMUNG DES UMSETZUNGSVERHÄLTNISSES Ga : HDz

Versuch Nr.	*Gefunden Gallium (µg)*	*Umgesetzt HDz (µg)*	*Gefunden Umsetzungsverhältnis (Ga : HDz)*
1	315	2340	$1 : 2.0_3$
2	318	2340	$1 : 2.0_0$
Blindwert	< 20		
3	286	2190	$1 : 2.0_6$
4	289	2190	$1 : 2.0_5$
5	279	2180	$1 : 2.1_3$
6	267	2180	$1 : 2.2_0$
Blindwert	< 20		

$Cl—GaDz_2$ $HO—GaDz_2$



$O{<}^{GaDz_2}_{GaDz_2}$

I II III

Formel I dürfte sich bei niederen pH-Werten einstellen, während Formel II im höheren pH-Bereich bevorzugt wäre (aus Acetonlösung gefälltes Gallium-di-dithizonat erwies sich als Cl-frei). Für Formel III existiert bisher kein Anhalt.

BILDUNG UND EIGENSCHAFTEN DES GERMANIUM(III)-DITHIZONATES

Beim Zusammenbringen von $GeCl_2$ mit Dithizon (HDz) gelöst in trockenen organischen Solventien (Benzol, Aceton, CCl_4, $CHCl_3$ ...) erhält man eine rote Färbung, deren Intensität proportional der Stärke der eingesetzten grünen Dithizonlösung ist. Vor Luft und Feuchtigkeit geschützt ist die rote Verbindung mindestens mehrere Tage lang stabil, mit Sauerstoff oder wässrigen Lösungen tritt Zerlegung ein unter Freisetzung des grünen HDz infolge Oxidation bzw. Hydrolyse des Ge^{2+}.

In Tetrachlorkohlenstoff liegt das Absorptionsmaximum bei 530 nm, während bei 620 nm (dem Absorptionsmaximum des freien Dithizons) praktisch keine Absorption vorliegt. Der molare Extinktionskoeffizient liegt (auf $GeDz_2$ bezogen) über $52 \cdot 10^3$ [l/Mol. cm]. Versetzt man eine benzolische $GeCl_4$-Lösung mit Dithizon, so resultiert eine rotbraune Färbung, die sehr wasserempfindlich ist. Auch hier dürfte ein Dithizonat entstanden sein.

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1 A. T. PILIPENKO, *Zh. Analit. Khim.*, 5 (1950) 14.
2 S. M. ALI, F. M. BREWER, J. CHADWICK AND G. GARTON, *J. Inorg. & Nucl. Chem.*, 9 (1959) 124.
3 T. B. PIERCE AND P. F. PECK, *Anal. Chim. Acta*, 27 (1962) 392.

(Eingegangen den 7. November, 1966)

Anal. Chim. Acta, 38 (1967) 470–473

BOOK REVIEWS

Trace Analysis: Physical Methods, Edited by G. H. MORRISON, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1966, xx + 582 pp., price 120 s.

This volume presents a well-integrated account by several specialist authors of the various physical methods available for the analysis of trace amounts of material. There are 12 main chapters, the first of which covers the general aspects of trace analysis, particularly with respect to detection limits. This is followed by two fairly general accounts of the part played by trace elements in physics (*e.g.*, the various atomic and electronic phenomena in solids) and biology (trace elements in soil, plants and animals) which give a useful indication of the problems of trace analysis. A chapter on the important topics of separations and preconcentrations introduces the detailed accounts of the various physical techniques available for the detection and determination of traces; these include spectrophotometry and fluorimetry, emission spectroscopy, flame emission and absorption methods, X-ray emission spectrography, nuclear activation methods, electrochemical methods, mass spectrometry and miscellaneous non-specific methods, involving for example, the measurement of resistivity, Hall effect, thermal conductivity, etc.

Most analytical chemists will be familiar with at least 2 or 3 of the techniques described in this book, but there will be few whose knowledge of the lesser known methods will not be improved by reading this book. Although each chapter could be considered as a separate short monograph, Dr. MORRISON, as editor, has maintained an admirable continuity of approach to the problems of trace analysis throughout the entire book. This is a valuable addition to the literature on trace analysis and should be of great use, particularly to those concerned with the analytical aspects of materials science.

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Anal. Chim. Acta, 38 (1967) 473

D. D. Perrin, W. L. F. Armarego and Dawn R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966, viii + 362 pp., price 70 s.

The research worker in chemistry and biochemistry is often faced with the problem of how to purify the reagents he may need to use. In some cases, the problem may be fairly simple, but in others it may prove to be quite difficult because of lack of suitable information. The present volume is designed to overcome many of these difficulties by providing details of the purification of a large number of laboratory chemicals. Two short introductory chapters describe, with suitable references to standard textbooks, the common laboratory techniques used in purification, and the newer specialised methods which are beginning to find a wider use in the laboratory. In the third chapter the purification of individual organic compounds is discussed in alphabetical order; this chapter amounts to about two-thirds of the entire text. The fourth chapter deals with the purification of individual inorganic and organometallic compounds; the fifth and final one describes general methods for the purification of certain classes of organic compound.

Purity-conscious chemists will welcome this book for the definitive information that it contains; others, with less pressing problems of chemical purification, will find this a valuable reference book to have available in the laboratory next to the ubiquitous "Rubber Handbook".

W. I. Stephen (Birmingham)

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Lectures will be given by members of the scientific staff of Charles University or of the J. Heyrovský Polarographic Institute. The enrolment fee is Kčs 600.—. This includes the costs of practical training, a sight-seeing tour and a farewell dinner on the last day. Accommodation at moderate cost is available in a student hostel.

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