68.

ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 25, No. 1, p. 1—100, July 1961

ANALYTICA CHIMICA ACTA

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to: Prof. PHILIP W. WEST, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. (U.S.A.)
or to
Dr. A. M. G. MACDONALD, Department of Chemistry, The University, Edgbaston, Birmingham 15 (Great Britain)

Authors should preferably submit two copies in double-spaced typing on pages of uniform size. Tables and legends for figures should be typed on a **separate** page. The figures should be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in **thin pencil**. The sheets of drawing or tracing paper should preferably be of the same dimensions as those on which the article is typed. Photographs should be submitted as clear black and white prints on glossy paper.

Standard symbols should be used in line drawings. The following are available to the printers:

▼ ▽ ■ □ ● ◎ ■ ◘ ⦵ ▣ ▪ □ + ×

All references should be given at the end of the paper. They should be numbered and the numbers should appear in the text at the appropriate places. The abbreviations of journals should conform to those adopted by *Chemical Abstracts* (see Vol. 50 (1956) 1 J – 314 J).
A summary of 50 to 200 words should be included. Authors of papers in French or German are encouraged to supply also a translation of the summary in English.

Reprints

Twenty-five reprints will be supplied free of charge. Additional reprints can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

Analytica Chimica Acta will have six issues to the volume, approx. 600 pages per volume, two volumes per year.
Subscription prices (post free): $ 15.— or £ 5.7.6. or Dfl. 57.— per volume; $ 30.— or £ 10.15.- or Dfl. 114.— per year. Additional cost for copies by airmail available on request.
For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, P. O. Box 211, Amsterdam-C., The Netherlands

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 25, No. 1, July 1961

RELATIVE DATA OF CHEMICAL EQUILIBRIA GOVERNING THE SEPARATION OF ZIRCONIUM FROM HAFNIUM

I. DETERMINATION OF EQUILIBRIUM CURVES

(in French)

Factors influencing the extraction of macro amounts of zirconium by tributylphosphate and his separation of zirconium from hafnium are discussed.

J. Huré, M. Rastoix and R. Saint-James *Anal. Chim. Acta*, 25 (1961) 1–9

A PROCEDURE FOR THE DETERMINATION OF THE RARE EARTH ELEMENTS, LANTHANUM THROUGH LUTETIUM, IN CHONDRITIC, ACHONDRITIC AND IRON METEORITES BY NEUTRON-ACTIVATION ANALYSIS

The abundances of the rare earths, lanthanum through lutetium, have been determined in chondritic, achondritic, and iron meteorites by neutron-activation analysis. The procedure used should also be applicable to the analysis of terrestrial stones and sediments. After exposure to a thermal-neutron flux of $2 \cdot 10^{12}$ neutrons/cm^2/sec for 2 h, the chondritic or achondritic sample, with added rare earth carriers, is dissolved after sodium peroxide fusion. Iron specimens are dissolved in a hydrochloric acid medium. The rare earths are then separated as a group from the matrix and are individually separated by means of a Dowex 50 W-X12 cation resin column and elution with 1 *M* ammonium lactate. This method is sensitive to fractional parts per million of the individual rare earths. The abundance of scandium may also be determined in the same procedure.

A. W. Mosen, R. A. Schmitt and J. Vasilevskis, *Anal. Chim. Acta*, 25 (1961) 10–24

EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

I. DETERMINATION OF COBALT

A method for the determination of cobalt by the addition of excess EDTA and back-titration with standard cobalt solution is recommended. The titration involves an extractive method of end-point detection, depending upon the appearance of the blue colour of the ion-association pair $[Ph_3MeAs]_2[Co(SCN)_4]$ in chloroform. The method is therefore suitable for the estimation of cobalt in highly coloured aqueous solutions. Average errors can be expected to be less than 0.5%.

A. J. Cameron and N. A. Gibson, *Anal. Chim. Acta*, 25 (1961) 24–27

A SOLVENT EXTRACTION METHOD FOR THE SEPARATION OF IODIDE

Solvent extraction is proposed for the isolation of anions. Data obtained in the extraction of iodide using cadmium as complexing agent under the influence of such factors as pH, addition of excess cadmium ions, initial concentration of the cadmium iodide solution and temperature are presented.

P. W. West and A. S. Lorica, *Anal. Chim. Acta*, 25 (1961) 28–33

TITRIMETRIC METHODS FOR THE MICRO DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

II. THE SIMULTANEOUS DETERMINATION OF THE HALOGENS IN THE PRESENCE OF EACH OTHER

The absorption of the gaseous combustion products from the rapid, empty tube combustion procedure has been studied. Organic compounds containing any combination of chlorine, bromine, and iodine as well as oxygen, nitrogen and sulphur have been examined. Several methods based on established titration procedures have been developed for the simultaneous microdetermination of any two or all three halogens in organic materials.

R. Belcher and J. E. Fildes, *Anal. Chim. Acta*, 25 (1961) 34–41

ON THE CONCENTRATION AND SEPARATION OF THE TRACE ELEMENTS: Fe, Cu, Zn, Mn, Pb, Mo and Co

I. ION EXCHANGE METHODS

Cation-exchange materials and selective elution with acetone–hydrochloric acid mixtures are used to concentrate the constituents of biological ashes and to separate them into the groups: MoO_4^{-2}, SO_4^{-2}, PO_4^{-3}; Fe^{+3}, Zn^{+2}, Pb^{+2}, Cu^{+2}; Co^{+2}, Mn^{+2}; Na^{+}, K^{+}, Ca^{+2} and Mg^{+2}.

P. C. van Erkelens, *Anal. Chim. Acta*, 25 (1961) 42–50

ANALYSIS OF ARSENIC–IRON ALLOYS

Contrary to expectation and to published recommendation it is not possible to separate Fe(III) quantitatively from As(V) on a cation-exchange resin. Ion-exchange can however be utilised for the analytical separation of iron and arsenic if the iron is reduced to Fe(II) before the mixture is passed through the cation-exchange column.

G. R. Duval, R. Ironside and D. S. Russell, *Anal. Chim. Acta*, 25 (1961) 51–56

CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, USING AQUEOUS ETHANOL AS SOLVENT. II

The separation of Al, Cr(III), Fe(III), Zn, Mn(II), Ni, Co, Ba, Sr, Ca, Mg, Na, K and NH_4 in ternary mixtures with or without the addition of complexing agents (oxalate, tartrate and citrate) by filter paper strip chromatography has been studied with aqueous ethanol as solvent.

E. J. SINGH AND A. K. DEY, *Anal. Chim. Acta*, 25 (1961) 57–58

COLORIMETRIC MICRODETERMINATION OF BORON IN STEELS WITH AZOMETHINE-H AS REAGENT

(in French)

A method is described for the determination of soluble and insoluble boron in steels based on preliminary separation with ion-exchange resin and colorimetric determination by means of azomethine-H.

R. CAPELLE, *Anal. Chim. Acta*, 25 (1961) 59–68

CRITICAL FACTORS IN THE COLORIMETRIC DETERMINATION OF SILICA

The development of rapid colorimetric analytical techniques for silicates has catalysed many fundamental research programs in the geological sciences. Despite a multitude of papers on the silicomolybdate colorimetric technique for the analysis of silica which appear in the journals of nearly all sciences, it was found extremely difficult to adapt any published method for a particular purpose, and obtain reliable results. This is due to a lack of appreciation of the factors which control the silicomolybdate reaction. Data are given which indicate that the major factors are the polymer species of molybdate, which is controlled largely by the pH of molybdate stock solution; the concentration of molybdate; the ratio of acid to molybdate in reaction; and the type of acid used in the reaction. The effect of these variables is outlined, and an analytical procedure for both "soluble" and total silica outlined.

G. J. S. GOVETT, *Anal. Chim. Acta*, 25 (1961) 69–80

THE SPECTROPHOTOMETRIC DETERMINATION OF STRONTIUM WITH MUREXIDE (AMMONIUM PURPURATE)

A procedure for the spectrophotometric estimation of μg-quantities of strontium with murexide is described. Conditions for the optimum stability of the coloured strontium complex have been determined, the main feature being the addition of large quantities of ethylene glycol to the system. Most elements interfere so that it is necessary to isolate the metal before the determination.

D. S. RUSSELL, J. B. CAMPBELL AND S. S. BERMAN, *Anal. Chim. Acta*, 25 (1961) 81–84

SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF ALCOHOLS

A spectrophotometric method for the determination of small amounts of methyl, ethyl, butyl and amyl alcohols is described. The sensitivity of the method is of the order of 10 μg/ml of test solution in the case of butyl and amyl alcohols and 20–30 μg/ml in the case of ethyl and methyl alcohols. The molar extinction coefficient rises with the molecular weight of the alcohol. The nature of the alcoholic complex is not yet known.

M. Stiller, *Anal. Chim. Acta*, 25 (1961) 85–89

SPECTROGRAPHIC DETERMINATION OF BORON IN NUCLEAR GRAPHITE

A spectrographic method is described for the determination of boron (0.2–1.0 p.p.m.) in nuclear graphite and for the estimation of 0.1–0.2 p.p.m. of boron. Neither boron-free graphite electrodes nor additional foreign substances as internal standard are required. Both the electrodes consist of sample powder, properly bakelite-processed. The standard deviation is 10%.

F. Gianni and F. Potenza, *Anal. Chim. Acta*, 25 (1960) 90–92

PILOT-ION COULOMETRY WITH DROPPING MERCURY ELECTRODES

The theory and the experimental and chemical requirements of pilot-ion coulometry with the dropping mercury electrode are outlined, and several examples are given of its application to the determination of n-values for half-reactions occurring in polarographic experiments.

R. E. Cover and L. Meites, *Anal. Chim. Acta*, 25 (1961) 93–96

ANALYTICA CHIMICA ACTA

Vol. 25 (1961)

ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 25 (1961)

Printed in the Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

DONNÉES RELATIVES AUX ÉQUILIBRES CHIMIQUES RÉGISSANT LA SÉPARATION ZIRCONIUM–HAFNIUM

I. ÉTABLISSEMENT DES COURBES D'ÉQUILIBRE

J. HURÉ, M. RASTOIX ET R. SAINT-JAMES

Département de Métallurgie, Service A.R.C.A., Gif-sur-Yvette (France)

(Reçu le 21 novembre 1960)

INTRODUCTION

Lorsque fut publié pour la première fois à Genève le procédé de séparation du zirconium et de l'hafnium par le phosphate tributylique[1], les teneurs préconisées pour la solution de zirconium alimentant l'extracteur étaient les suivantes: Zr: 10 g/l; HNO_3: 3 N; $NaNO_3$: 3.5 M.

Nos conditions de travail actuelles sont les suivantes, pour cette même solution: Zr: 60 g/l; HNO_3: 6 N; $NaNO_3$: néant.

Ce sont tout d'abord les études nous ayant conduits à ces modifications que nous présenterons ici. Nous examinerons ensuite le problème de la "3ème phase", phase bien connue de tous ceux qui ont utilisé le phosphate tributylique (TBP) en mélange avec un solvant paraffinique, pour l'extraction du zirconium et du thorium et qui consiste en une démixtion du solvant en 2 phases, l'une riche en TBP, l'autre en diluant paraffinique.

Enfin, nous aborderons le problème du "vieillissement" du solvant et de sa régénération.

(*1*) *Suppression du nitrate de sodium.* Bien que plus favorable que l'acide nitrique à une bonne séparation du zirconium de l'hafnium, l'usage de $NaNO_3$ en exploitation industrielle comporte certains inconvénients: plus cher et moins pur que l'acide nitrique, il augmente la viscosité de la solution et, par conséquent, le temps de décantation. De plus, sa présence interdit la récupération de l'acide nitrique, facteur important du prix de revient. Il a donc été décidé d'établir les courbes d'équilibre complètes pour le zirconium et pour l'hafnium, pris isolément, à différentes concentrations et différentes acidités en présence d'acide nitrique seul.

(*2*) *Interaction Zr–Hf.* La séparation est meilleure que les coefficients de partage respectifs du zirconium et du hafnium ne le laissent prévoir, indiquant une interaction sur laquelle, à notre connaissance, aucun chiffre n'a été publié. Nous traiterons principalement de l'influence du rapport Zr/Hf sur l'extraction de Hf.

(*3*) Au delà d'une certaine teneur en zirconium et en acide nitrique, on constate, lors de l'extraction en ampoule à décanter, l'apparition d'une deuxième phase solvant. Les anglais HUDSWELL *et al.*[2] ont publié les résultats d'essais systématiques sur ce sujet. Malheureusement, ils ne relient pas cette apparition à la concentration en zirconium des phases solvant, mais uniquement à la concentration de la phase aqueuse de départ. Or, en production industrielle, où les rapports de débits, les acidités et les températures des solutions risquent de varier, il importe de connaître la concentration limite du zirconium dans le solvant, avant l'apparition de la 3ème phase. Les résultats intéressants du rapport anglais demandent à être complétés.

(*4*) Enfin, la dernière partie de notre exposé traitera de l'évolution du solvant, en milieu acide, en présence ou en l'absence de zirconium et en fonction du temps; cette étude devant être complétée par des essais synthétiques permettant d'apprécier l'influence des produits connus de l'hydrolyse du solvant, sera faite à la température ambiante.

MODE OPÉRATOIRE

Méthodes analytiques utilisées

Dosages volumétriques

La concentration en zirconium ou hafnium de la phase aqueuse est déterminée par voie complexométrique en utilisant le fer ferrique comme titrant et l'acide salicylique comme indicateur[3].

Le zirconium dans le solvant est dosé de la même manière, après précipitation à la potasse alcoolique et redissolution en milieu aqueux; ce mode de dosage étant utilisé pour des teneurs supérieures à 5 mg Zr dans la prise d'essai.

Dosages colorimétriques

Pour les faibles teneurs en zirconium, on utilise la colorimétrie du composé zirconium-acide chloranilique en milieu perchlorique, telle qu'elle est pratiquée depuis longtemps au laboratoire[4].

Dosages acidimétriques

Il est important de connaître "l'acidité libre" de la phase aqueuse. Ce dosage sera fait par potentiométrie de la neutralisation par la soude; on déduira du résultat trouvé, l'acidité due au zirconium qu'on suppose être, pour simplifier, sous la forme ZrO^{+2}, c'est-à-dire consommant 2 molécules d'hydroxyde de sodium par molécule, pour sa neutralisation. Cette hypothèse donne à tout le moins un point de repère, valable dans des conditions opératoires toujours identiques.

Utilisation des traceurs radioactifs

Pour étudier l'interaction Zr-Hf dans le processus d'extraction, nous avons choisi d'utiliser ^{181}Hf comme traceur, ce qui permettait d'éviter les méthodes longues comme la spectrographie. On dosera donc Hf par comptage et Hf + Zr par volumétrie.

Préparation des solutions

Solution nitrique de zirconium

Nous disposons d'une tourie (30 l) d'une solution contenant 107 g/l de zirconium, 2.6 g/l d'hafnium et 6.66 moles d'acide nitrique libre. Cette solution mère sera ajustée aux conditions de concentration et d'acidité voulues.

N.B. On constate que la solution mère n'est pas stable, se trouble et dépose très lentement. Sa concentration a varié en six mois de 107 à 100 g/l. Toutefois, après filtration, cette solution donne des coefficients de partage indépendants de son âge.

Solutions de traceurs

La solution contenant le traceur Hf est préparée par attaque, à l'acide nitrique fumant, de son oxyde irradié (l'attaque est d'ailleurs longue et souvent incomplète). Les solutions filtrées sont ensuite ajustées selon les besoins. On vérifie par comptage et volumétrie que le comportement de ces solutions est bien identique à celui de la solution inactive.

Préparation du solvant

Le tributylphosphate est dilué, comme il est courant, avec du white spirit dans la proportion: TBP 60%, white spirit 40%, en volume. Le white spirit est un solvant paraffinique désaromatisé de densité 0.75 et de point d'ébullition compris entre 130° et 190°. Préalablement à l'extraction, le solvant est acidifié de manière à réduire au maximum l'échange d'acide nitrique pour que le zirconium puisse être raisonnablement considéré comme intervenant seul dans le transfert.

Ceci n'est qu'une première approximation, dont le degré de précision dépend et de l'acidité et de la concentration en zirconium, mais l'approximation est inchiffrable puisqu'on ignore quels ions de Zr existent en solution et qu'on ne sait pas définir rigoureusement l'acidité libre d'une solution de zirconium.

Quoiqu'il en soit, pour les extractions 4, 5, 6 ou 8 *N*, on acidifiera donc le solvant en l'agitant pendant quelques minutes avec un volume égal d'une solution d'acide nitrique 4, 5, 6 ou 8 *N*. Le solvant ainsi acidifié peut être conservé pendant quatre ou cinq jours. Nous avons vérifié par ailleurs que, en ce qui concerne l'extraction, des lots de TBP de différentes origines se comportaient de manière comparable.

Extraction

Des volumes égaux de phase aqueuse et de phase solvant, en général 10 ml, sont mis en présence dans une ampoule à décanter et agités à la main pendant deux minutes environ. Les volumes respectifs des phases ne varient pratiquement pas ($<3\%$). On prélève ensuite une aliquote de phase aqueuse et de phase solvant, dans lesquelles on fait le dosage. Dans le cas où l'on a apparition d'une troisième phase, on note le volume respectif de chaque phase et sa concentration en zirconium.

RÉSULTATS

Extraction du zirconium par le TBP

Nous avons cherché à tracer les courbes de partage du zirconium à diverses concentrations et dans différents milieux nitriques. Les dosages ont été faits par volumétrie, systématiquement dans les phases aqueuses, pour vérification seulement dans les phases solvants.

Un milieu nitrique 4 *N* doit s'entendre: milieu contenant 4 moles d'acide nitrique libre. Les résultats sont reproduits sur le Tableau I (*cf.* Fig. 1).

Le Tableau I nous donne déjà quelques éléments sur l'importance de la teneur en zirconium de la phase solvant au moment où elle se sépare en deux. Plus la solution est acide, mieux le zirconium s'extrait, ce qui explique la constatation faite par

TABLEAU I

PARTAGE DE Zr ENTRE UNE PHASE AQUEUSE NITRIQUE ET LE SOLVANT ACIDE

Acidité N	*g/l φ_a départ*	*Vol. φ_a à l'éq.*	*Vol. φ_s à l'éq.*	*g/t φ_a à l'éq.*	*g/l φ_s à l'éq.*	*Vol. 3ème φ*	*g/l φ 3*	*E%*	*α_{Zr}*
4	1.03	10	10	0.47	0.56			54.8	1.19
4	5.16	10	10	3.04	2.12			41.2	0.69
4	10.3	10	10	7.2	3.1			34	0.49
4	20.6	10	10	16	4.6			22.4	0.28
4	23.2	10	10	18.2	5			21.6	0.27
4	25.8	10	10	20.5	5.3			20.5	0.25
4	41.2	10	10	34	7.2			17.5	0.21
4	61.8	10	10	52	9.8			15.9	0.18
5	0.9	10	10	0.2	0.7			77.8	3.5
5	5.82	10	10	1.82	4			68.8	2.2
5	9.25	10	10	3.93	5.32			57.5	1.36
5	17.2	10	10	8.8	8.4			48.8	0.95
5	28.8	10	10	16.8	12			41.6	0.71
5	52.8	10	10	33.2	19.6			37.2	0.59
5	68.8	10	9.6	46.6	22.2	0.4	indosable	32.3	
6	1.03	10	9.6	0.13	0.90			87.5	6.65
6	5.60	10	9.6	0.88	4.72			84.2	5.36
6	10.2	10	9.6	1.84	8.40			82.4	4.56
6	13.8	10	9.6	3.24	10.6			76.7	3.27
6	13.9	10	9.6	3.41	10.5			75.5	3.08
6	17.1	10	9.6	4.30	12.8			75.0	2.98
6	19.7	10	9.6	5.38	14.3			72.5	2.66
6	27.3	10	9.6	9.50	17.8			65.2	1.87
6	30.9	10	9.6	11.2	19.7			63.7	1.76
6	35.0	10	9.6	13.7	21.3			60.8	1.55
6	36.7	10	9.6	14.7	22.0			60.0	1.50
6	37.1	10	9.6	15.1	22.0			59.4	1.45
6	48.0	10	8.5	21.5	26.5	1.5	non dosé	55.2	1.23
6	59.8	9.5	8.5	28.3	31.5	2	non dosé		
6	69	9.5	8.5	35.3	33.7	2	non dosé		
6	77	9.5	8.4	40	39.7	2.1	non dosé		
6	96.4	9.5	8	53.3	43.1	2.5	non dosé		
8	20.6	10	10	0.92	19.7			95.6	21.9
8	41.2	10	7.8	7.5	42.5	2.4	0.32	79.1	
8	61.8	10	7.8	13.9	61.2	2.5	0.79	75.7	

HUDSWELL suivant laquelle la troisième phase apparaît pour une concentration en zirconium, d'autant plus faible dans la phase aqueuse, que l'acidité de cette même phase est plus élevée. La concentration limite en zirconium dans le solvant au moment de l'apparition de la 3ème phase, se situerait à 22–25 g/l. Nous reviendrons plus loin sur ce problème.

La Fig. 2 donne une autre représentation du phénomène d'extraction. α_{Zr} n'est autre que la pente de la courbe précédente.

Par suite de l'intérêt présenté par le milieu d'acidité "libre" 6 *N* (intérêt dont nous trouverons la justification dans la suite de ce texte), nous avons été amenés à étudier ce milieu avec particulièrement de soin. Par la méthode des moindres carrés, nous avons ensuite déterminé la courbe théorique représentant le mieux les résultats expérimentaux. On trouvera sur la Fig. 3 le tracé de la courbe théorique (qui est une hyperbole) par rapport aux points expérimentaux, lesquels donnent une bonne idée de la reproductibilité des résultats.

Extraction du hafnium par le TBP

Les dosages ont été faits par complexométrie pour les concentrations supérieures à 5 mg Hf/ml, et par colorimétrie au-dessous. Les modes opératoires sont bien entendu les mêmes que pour le zirconium, seul l'étalonnage change. Les résultats sont reproduits sur le Tableau II et les Figs. 3 et 4.

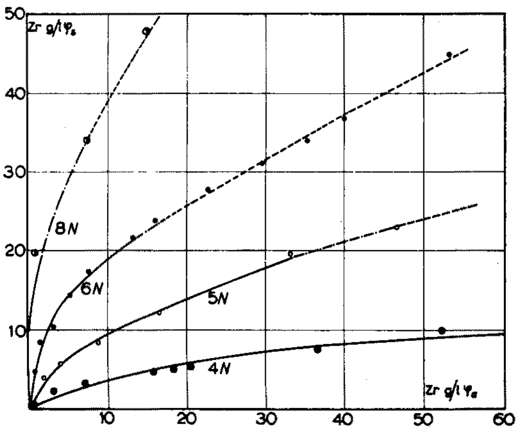


Fig. 1. Distribution de Zr à diverses concentrations en HNO$_3$. ——— 2 phases, – – – – 3 phases, – · – · – zone d'apparition de la 3ème phase.

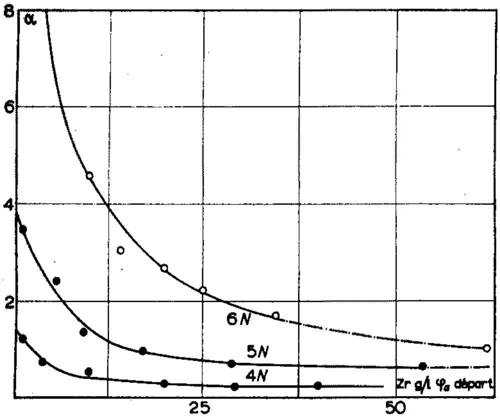


Fig. 2. Coefficient de partage α_{Zr}.

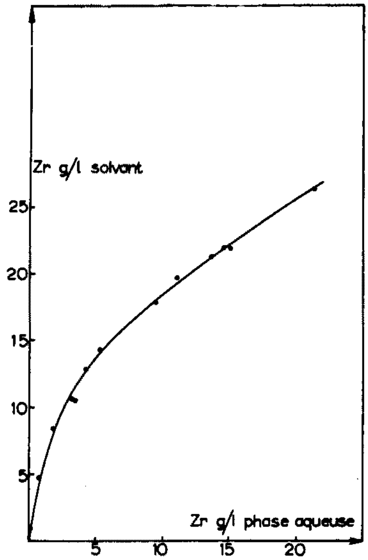


Fig. 3. Extraction Zr en milieu nitrique 6 *N*. ——— courbe théorique; . . . . points expérimentaux.

Si nous examinons maintenant les trois Tableaux et les courbes représentant nos résultats, quelques remarques s'imposent:

(*1*) La précision sur la détermination de α_{Hf} est très mauvaise pour les faibles teneurs (<1 g/l). Ceci est dû au fait que nous nous trouvons dans une partie de courbe très verticale où de très faibles variations ont une influence notable, et également à l'imprécision des dosages à ces teneurs.

(*2*) α_{Hf} reste très inférieur à 1 pour des acidités libres <4 *N*, même pour les faibles concentrations.

TABLEAU II

PARTAGE DE Hf ENTRE UNE PHASE AQUEUSE NITRIQUE ET LE SOLVANT ACIDE[a]

Acidité *N*	*g/l* φ_a *départ*	*Vol.* φ_a *à l'éq.*	*Vol.* φ_s *à l'éq.*	*g/l* φ_a *à l'éq.*	*g/l* φ_s *à l'éq.*	*E* %	α_{Hf}
4	5.5	10	10	4.82	0.74	13	0.15
4	16.5	10	10	15.1	0.77	4.7	0.05
4	27.5	10	10	26.4	0.74	2.7	0.028
5	0.275	10	10	0.100	0.175	63	1.75
5	0.550	10	10	0.265	0.285	51	1.08
5	1.10	10	10	0.570	0.530	48	0.93
5	1.27	10	10	0.930	0.34	26.8	0.36
5	2.2	10	10	1.72	0.48	21.8	0.27
5	2.6	10	10	2.02	0.58	22.1	0.29
5	5.5	10	10	4.92	0.58	10.5	0.18
5	6.4	10	10	5.5	1.0	15.6	0.18
5	11	10	10	9.58	1.48	13.5	0.15
5	13	10	10	11.2	1.8	13.7	0.16
5	22	10	10	19.3	2.8	13	0.14
5	38.5	10	10	34.8	3.85	10	0.11
6	0.275	10	10	0.050	0.225	81.5	4.4
6	0.550	10	10	0.150	0.400	72.7	2.67
6	1.10	10	10	0.400	0.700	63.5	1.75
6	1.09	10	10	0.535	0.555	51	1.04
6	2.2	10	10	1.28	0.92	41.7	0.72
6	2.24	10	10	1.2	1.0	44.6	0.83
6	5.5	10	10	3.68	1.82	33	0.51
6	5.6	10	10	3.6	2.0	35.7	0.55
6	11	10	10	7.12	3.9	35.2	0.55
6	22	10	10	15.6	6.4	29.4	0.41
6	44	10	10	33.8	10.2	23.2	0.3
7	5.5	10	10	1.58	3.92	71.2	2.48
7	11	10	10	3.84	7.2	65.5	1.85
7	22	10	10	9.6	12.4	56.3	1.29
7	55	10	10	32	23	41.8	0.72
8.5	5.5	10	10	0.2	5.3	96.5	26.5
8.5	11	10	10	0.64	10.3	94.5	16.2
8.5	22	10	10	1.9	20.1	91.5	10.6
8.5	38.5	10	10	7.3	31.2	81.3	4.3

[a] *cf.* Figs. 4 et 5

(*3*) Mais α_{Zr} restant également petit à ces acidités, le travail dans ces conditions ne serait pas économiquement rentable.

(*4*) Inversement, au dessus de 6 *N*, Zr et Hf s'extraient tous deux ($\alpha > 1$), la séparation serait donc mauvaise. C'est donc entre 5 et 6 *N* que doivent se trouver les meilleures conditions de travail.

Bien que par suite de l'interaction, il soit sans signification de calculer un coefficient de séparation $\beta = \alpha_{Zr}/\alpha_{Hf}$, nous ferons néanmoins le calcul pour évaluer, au moins

TABLEAU III

CALCUL DE β AVEC LES DONNÉES DES TABLEAUX I ET II

Acidité N	*Zr g/l départ*	*Hf g/l départ*	α_{Zr}	α_{Hf}	β
5	2.5	2.5	3	0.28	10.7
5	5	5	2.2	0.18	12.2
5	10	10	1.3	0.16	8.1
5	20	20	0.85	0.14	6.0
5	40	40	0.62	0.11	5.6
5	2.5	0.25	3	1.75	1.7
5	5	0.5	2.2	1.08	2.0
5	10	1	1.3	0.7	1.8
5	20	2	0.85	0.25	3.4
5	50	5	0.6	0.18	3.3
6	2.5	2.5	7.6	0.7	10
6	5	5	6.6	0.6	11
6	10	10	4.5	0.52	8.6
6	20	20	2.7	0.41	6.6
6	35	35	1.6	0.35	4.7
6	2.5	0.25	7.6	4.4	1.7
6	5	0.5	6.6	2.67	2.5
6	10	1.0	4.5	1.5	3.0
6	20	2.0	2.7	0.8	3.5
6	55	3.5	1.6	0.7	2.3

grossièrement, l'influence de l'acidité et pour mieux mettre en évidence l'importance de cette interaction que nous voulons étudier. Nous ferons ce calcul de deux manières également arbitraires: 1. Nous prendrons comme référence le α pour $|Zr| = |Hf|$. 2. Nous ferons le rapport β pour $|Hf| = |Zr|/10$ (*cf.* Tableau III).

On voit que le calcul de β est entaché d'une grosse imprécision dans la zône Hf $<$ 1 g/l, ce qui est logique. Malgré cela, on constate que le facteur de séparation reste comparable, que le milieu soit 5 *N* ou 6 *N*. Pour des questions de rendement, il semble donc préférable de choisir le milieu 6 *N*. C'est dans ce milieu que nous étudierons l'interaction.

Étude de l'interaction Zr-Hf dans le processus d'extraction

Influence de Zr sur l'extraction de Hf

Pour cette étude, nous avons utilisé du hafnium marqué. Le dosage a été fait par comptage dans les deux phases. La somme zirconium plus hafnium a été ensuite dosée dans la phase aqueuse par voie chimique. Les résultats obtenus donnent une bonne évaluation de l'influence du zirconium sur Hf.

Les essais ont été faits dans trois domaines: 1. Sur un mélange initial contenant en poids 90% Zr et 10% Hf à des concentrations totales variant de 10 à 50 g/l, 2. Sur un mélange contenant 50% Zr et 50% Hf à des concentrations variant de 1 à 20 g/l, 3. Sur un mélange contenant 90% Hf et 10% Zr à des concentrations variant de 1 à 20 g/l. Ces concentrations correspondent, en gros, aux conditions expérimentales dans lesquelles nous pouvons nous trouver. Les résultats sont reportés sur le Tableau IV. La somme des comptages en phase solvant et en phase aqueuse donne une idée de la précision des mesures. Les différentes courbes de partage de Hf pour différents rapports Hf/Zr sont figurés sur les courbes Fig. 5.

On voit que pour des teneurs en Hf égales, la présence de Zr divise le facteur α par un coefficient 4 à 10 (dans le domaine où les rapports sont 10% Hf, 90% Zr).

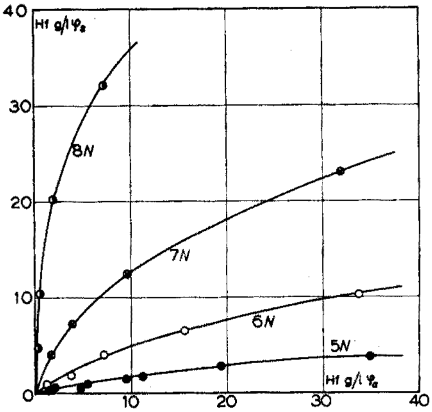


Fig. 4. Distribution de Hf à diverses concentrations en HNO_3.

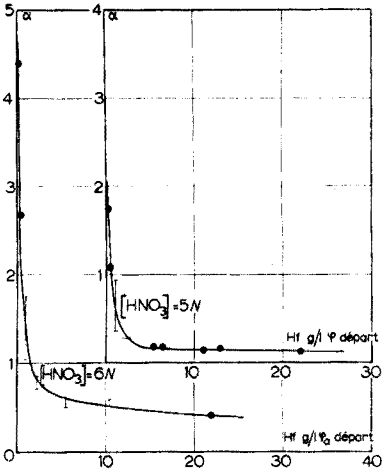


Fig. 5. Coefficient de partage α_{Hf}.

TABLEAU IV

INFLUENCE DE Zr SUR L'EXTRACTION DE Hf

Solvant 60% TBP–40% WS, acide; milieu HNO_3 6 *N*

Composition	*Hf + Zr g/l départ*	*% Hf* φ_a	*% Hf* φ_s	$\frac{\varphi_a + \varphi_s}{\varphi_{ai}}$ %	α_{Hf}
10% Hf 90% Zr	10	71.5	28.3	99.8	0.39
	20	84.7	17.5	102.2	0.20
	35	87.5	11.4	98.9	0.13
	50	93.0	7.5	100.5	0.08
50% Hf 50% Zr	1	45	55.1	100.1	1.22
	5	66	29.6	95.6	0.45
	15	80.5	25.0	105.5	0.31
	35	88.8	12.2	101.0	0.14
90% Hf 10% Zr	1	40.6	57.0	97.6	1.4
	5	65.2	31.5	96.7	0.48
	10	78.5	25.8	104.3	0.33
	20	80.7	19.3	100	0.24
100% Hf	1	36.5	63.5		1.74
	5	56.0	44.0		0.78
	11	64.8	35.2		0.54
	22	76.6	29.4		0.38

Comme on peut affirmer que, pour des teneurs de 50 à 90%, l'extraction du zirconium ne se trouve pas diminuée, au contraire*, on peut raisonnablement dresser

---

* En effet on retrouve, dans le cas Hf et Zr, le cas du thorium et de l'uranium: le premier, qui s'extrait moins bien que le second, lui sert de relargant alors que son propre passage en phase solvant est inhibé.

un tableau des valeurs approximatives de β dans les conditions de travail actuelles soit: % Hf variant de 0.1 à 15% d'une extrêmité à l'autre de l'extracteur (*cf.* Tableau V).

Ce coefficient est en effet supérieur à celui que nous avons calculé en prenant les hypothèses les plus favorables.

On voit aussi qu'il se compare favorablement avec les coefficients de séparation des autres procédés de séparation: cristallisation du fluozirconate ($\beta \# 4$) et extraction du thiocyanate de zirconium par l'hexone ($4 < \beta < 5$).

TABLEAU V

COEFFICIENT DE SÉPARATION TENANT COMPTE DE L'INTERACTION Zr–Hf

Zr + Hf *g/l*	β
1	6.6
2	10
5	10
10	11.4
20	12.9
35	12.6

REMERCIEMENTS

Nous tenons à exprimer nos remerciements à Mme PILLARD du Service de Physique Mathématique qui a calculé l'équation de la courbe d'extraction du zirconium.

RÉSUMÉ

On a examiné l'importance de divers facteurs influençant l'extraction par le tributylphosphate du zirconium en quantités pondérales et sa séparation du hafnium.

SUMMARY

Factors influencing the extraction of macro amounts of zirconium by tributylphosphate and this separation of zirconium from hafnium are discussed.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten des Zirkoniums und seine Trennung von Hafnium bei der Extraktion mit Tributylphosphat.

BIBLIOGRAPHIE

[1] J. HURÉ ET R. SAINT-JAMES, *Procédé de séparation du zirconium et de l'hafnium*, Rapport No. P/347, Conférence de Genève, 1955.
[2] F. HUDSWELL, J. C. H. WALDRON ET B. R. HARDER, AERE C/R 1520.
[3] G. W. C. MILNER ET P. J. PHENNAT, AERE C/R 1354.
[4] B. J. THAMER ET A. F. VOIGT, *J. Am. Chem. Soc.*, 73 (1951) 3198.

A PROCEDURE FOR THE DETERMINATION OF THE RARE EARTH ELEMENTS, LANTHANUM THROUGH LUTETIUM, IN CHONDRITIC, ACHONDRITIC AND IRON METEORITES BY NEUTRON-ACTIVATION ANALYSIS

A. W. MOSEN, R. A. SCHMITT AND J. VASILEVSKIS*

John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of General Dynamics Corporation, San Diego, Calif. (U.S.A.)

(Received November 21th, 1960)

INTRODUCTION

A knowledge of the relative abundances of the elements is important in the formulation of a theory of nucleosynthesis[1-3]. SUESS AND UREY[3] have critically examined compilations of atomic abundances, and CAMERON[2] has published a revised table of the relative abundances of nuclides.

The abundances of the rare earths have been measured by NODDACK[4] by X-ray spectroscopy on two silicate meteoritic samples (one a composite of eight silicate meteorites and the other a composite of fourteen) and on a composite of seven iron meteorites. MINAMI[5] made similar X-ray spectroscopic analyses on four different sediments.

The most serious disagreement between the two investigations is that the abundances of the light rare earths are shown to be about eight times greater in the sediments than in the meteorites.

Neutron-activation analysis combined with an ion-exchange separation of the rare earths provides a powerful new tool for accurately determining the abundances of the rare earths. The principal advantages of the neutron-activation technique are (*1*) that it allows determinations of abundances in the parts per million to fractional parts per billion range and (*2*) that there is freedom from contamination because the chemical processes follow the neutron irradiation. The chief disadvantage, namely, the necessity of handling extremely radioactive materials, is obviated by shielding and remote manipulation.

Neutron-activation analysis has been discussed by several authors[6-9]. The determination of the abundances of uranium in stone meteorites by HAMAGUCHI, REED AND TURKEVICH[10], of thorium in iron meteorites by BATE, POTRATZ AND HUIZENGA[11], and of bismuth, thallium, and mercury in stone meteorites by EHMANN AND HUIZENGA[12] has adequately demonstrated the feasibility and reliability of the neutron-activation technique.

A procedure for the determination of individual rare earths in graphite employing neutron activation and ion exchange separation of the rare earths has been described by CORNISH[13].

---

* Permanent address: Department of Chemistry, Graduate Division, California Institute of Technology, Pasadena, Calif.

An unpublished procedure developed by R. SCHMITT AND A. MOSEN for the determination of high-cross-section rare earths in reactor-grade zirconium was modified for application to samples of chondritic, achondritic, and iron meteorites. This paper describes in detail the radiochemical procedure used in the successful analysis of the meteorites Allegan, Richardton, Nuevo Laredo, Pasamonte, and Odessa. The results of some of these analyses have been reported elsewhere[14]. The procedure should also be applicable to the analysis of terrestrial stones and sediments.

REAGENTS AND APPARATUS

Solutions of rare earth standards

Solutions containing about 0.5 mg/ml of the rare earth element are prepared by dissolving suitable compounds in HCl and diluting with deionized distilled water. In the meteorite analyses reported here, Johnson-Matthey spectrographic-standard quality oxides of Sc, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu were used. Oxides of lanthanum and terbium were obtained from Spex Industries and from Research Chemicals, respectively. The cerium standard was prepared from G. F. Smith Chemical Company $(NH_4)_2 Ce(NO_3)_6$ (99.99% pure). Other cerium compounds were found to be unacceptable because of lanthanum contamination. The G. F. Smith cerium standard was found to contain 0.021 lanthanum atoms per 100 cerium atoms. Small amounts of lanthanum will cause difficulty in the activation analysis, because the induced ^{140}La activity in the cerium standards will swamp the induced ^{143}Ce activity. The standard rare-earth solutions are also used as rare-earth carrier solutions. Promethium carrier is added in the form of a 2.6-yr ^{147}Pm tracer, which is a pure β-emitter.

β,β-Dichlorodiethyl ether

Bis(2-chloroethyl)ether, Eastman No. 866, is prepared for use by passing it through a column of neutral alumina, 100 to 200 mesh (Bio-Rad AG-7, Bio-Rad Laboratories, Richmond, California).

Ion-exchange column

The apparatus and ion-exchange procedures used to separate the individual rare earths are essentially those of NERVIK[15]. The column is 60 cm long by 0.6 cm in diameter, and is packed with Dowex 50W-X12, minus-400 mesh, ion-exchange resin. This resin (specially prepared by Bio-Rad Laboratories) has a settling rate of 0.5 to 2.0 cm/min. The resin is washed three times with deionized distilled water, and then is washed twice with 1 *M* ammonium lactate, pH 3.2. Before the resin is put into the column, it is boiled and stirred in 1 *M* ammonium lactate, pH 3.2, to remove gases (the resin-to-solution ratio is about 3). The rare earths are eluted with 1 *M* ammonium lactate, whose initial pH of 3.2 is changed at the rate of approximately 0.1 pH unit per hour. This is accomplished by having a 1 *M* ammonium lactate solution, pH 7, dilute the initial pH 3.2 solution at about 1 drop every 10 sec. The solutions are mixed by a magnetic stirrer. The column is heated by a water jacket, which is maintained at about 80° by heating tape. A pressure of about 5 lb/in.^{2} of N_2 gas is kept over the solutions and is maintained by an ordinary pressure regulator. The column effluent is caught in 10-mm by 100-mm test tubes, using a Packard ion-exchange turntable set to collect 10 drops per tube.

PROCEDURE

Separation of rare earths from meteoritic matrices

Irradiation

Samples (about 5 g) of the meteorite to be analyzed are prepared for irradiation in one of two ways. Stony (chondritic or achondritic) samples are crushed in a hardened-steel diamond mortar that is reserved for such analyses to avoid contamination. Iron samples are etched with rare-earth-free 6 *N* hydrochloric acid. If the stony specimen is etched with hydrochloric acid, as much as 20% of the rare earths may be leached away, presumably through the dissolution of the sulfide phase (in some chondrites this phase is concentrated in veins). The sample is then weighed on an analytical balance and transferred to a clean polyethylene vial.

The sample and the fourteen rare earth standards are irradiated simultaneously in the General Atomic TRIGA reactor in a flux of about $2 \cdot 10^{12}$ thermal neutrons/cm^2/sec for 2 h. The meteorite sample and the standards are placed in separate containers in the rotary specimen rack of the TRIGA reactor. This rack is continuously rotated at 1 rev./min during irradiation, so that all specimens are exposed to the same neutron flux. The amounts in μg of the irradiated rare-earth standards and scandium are: La, 60; Ce, 380; Pr, 70; Nd, 60; Sm, 6; Eu, 3; Gd, 9; Tb, 80; Dy, 80; Ho, 8; Er, 50; Tm, 50; Yb, 5; Lu, 5 and Sc, 50.

The radioactivities induced in the rare earths of a chondritic meteorite and the sensitivities for each of the rare earths are summarized in Table I.

Initial separation steps for stony meteorites

After the sample has been irradiated, the polyethylene sample tube and vial are opened with a special tool. The tube is handled with 4-ft. tongs, and the chemistry is carried out in a filtered hood behind a 4-in.-thick lead shield. Rare earth carriers are added to the sample in the form of oxides prior to the fusion step, described below. The carriers are prepared in the following manner. Exactly 1.00 ml (0.5 mg) of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc, and 2.00 ml of the ^{147}Pm tracer carrier are pipetted into a 100-ml beaker. The hydroxides are precipitated with ammonium hydroxide that has been prepared by bubbling ammonia into a polyethylene bottle of deionized, distilled water. After the addition of paper pulp, the solution is filtered on a Whatman No. 42 filter paper and all the precipitate is transferred from the beaker. Dilute ammonia solution is used for the wash solution. The filter paper is placed in an 80-ml zirconium crucible (obtained from Oregon Metallurgical Corporation, Albany, Oregon) that is used to fuse the sample. The crucible is covered and heated gently to dry the paper. The heat is gradually increased to char the paper and, finally, the full heat of a Meker burner is applied. This ignition must be carried out carefully to avoid loss of carrier.

To fuse a 5-g sample, 25 g of sodium peroxide is used. About half of the peroxide is poured into the crucible on top of the carriers. The sample is then added, followed by the remainder of the peroxide. The mixture is then carefully stirred with a glass rod using care not to disturb the carriers on the bottom of the crucible.

The crucible is held with a pair of 4-ft. tongs in the flame of a Meker burner until the mixture is completely molten. The heating is continued for at least five more minutes to ensure complete fusion of the sample and complete exchange of the carriers with the rare earths. This step is very critical.

TABLE I

RARE EARTH RADIOACTIVITIES IN METEORITES AFTER NEUTRON ACTIVATION[a]

Element	*Neutron-capture reaction*[b]	*Isotopic abundance*[c] *(%)*	*Half life*	*Activity 24 h after irradiation*[d] *(counts/min)*	*Elemental abundance*[e] *(p.p.m.)*	*Sensitivity for 1-g sample*[f] *(p.p.m.)*
$_{57}$La	^{139}La (n,γ) $^{140}\underline{\text{La}}$	99.9	40 h	$2 \cdot 10^4$	0.33	0.002
$_{58}$Ce	^{140}Ce (n,γ) $^{141}\underline{\text{Ce}}$	88.5	32 day	$2 \cdot 10^2$	—	—
	^{142}Ce (n,γ) $^{143}\underline{\text{Ce}}$	11.1	33 h	$1 \cdot 10^3$	0.51	0.05
$_{59}$Pr	^{141}Pr (n,γ) $^{142}\underline{\text{Pr}}$	100	19 h	$1 \cdot 10^3$	0.12	0.01
$_{60}$Nd	^{146}Nd (n,γ) $^{147}\underline{\text{Nd}}$	17.2	11.6 day	$3 \cdot 10^2$	0.63	0.2
	^{148}Nd (n,γ) ^{149}Nd	5.7	—	—	—	—
	1.8-h ^{149}Nd → $^{149}\underline{\text{Pm}}$		50 h	$\sim 1 \cdot 10^2$	—	—
	^{150}Nd (n,γ) ^{151}Nd	5.6	—	—	—	—
	12-min ^{151}Nd → $^{151}\underline{\text{Pm}}$		27.5 h	$\sim 2 \cdot 10^2$	—	—
$_{62}$Sm	^{152}Sm (n,γ) $^{153}\underline{\text{Sm}}$	26.8	47 h[g]	$1 \cdot 10^5$	0.22	0.00002[h]
$_{63}$Eu	^{151}Eu (n,γ) $^{152}\underline{\text{Eu}}^{m}$	47.8	9.2 h	$4 \cdot 10^5$	0.083	0.000001[h]
	^{151}Eu (n,γ) $^{152}\underline{\text{Eu}}$	47.8	12.5 yr	$1 \cdot 10^3$	—	—
$_{64}$Gd	^{158}Gd (n,γ) $^{159}\underline{\text{Gd}}$	24.9	18 h	$2 \cdot 10^3$	0.34	0.02
	^{160}Gd (n,γ) ^{161}Gd	21.9	—	—	—	—
	3.7-min ^{161}Gd → $^{161}\underline{\text{Tb}}$		7.0 day	$3 \cdot 10^2$	—	—
$_{65}$Tb	^{159}Tb (n,γ) $^{160}\underline{\text{Tb}}$	100	72 day	$4 \cdot 10^2$	0.051	0.01
$_{66}$Dy	^{164}Dy (n,γ) $^{165}\underline{\text{Dy}}$	28.2	2.3 h	$6 \cdot 10^3$	0.37	0.006
$_{67}$Ho	^{165}Ho (n,γ) $^{166}\underline{\text{Ho}}$	100	27.2 h	$2 \cdot 10^4$	0.075	0.00002[h]
$_{68}$Er	^{168}Er (n,γ) $^{169}\underline{\text{Er}}$	27.1	9.4 day	70	—	—
	^{170}Er (n,γ) $^{171}\underline{\text{Er}}$	14.9	7.5 h	$3 \cdot 10^3$	0.21	0.007
$_{69}$Tm	^{169}Tm (n,γ) $^{170}\underline{\text{Tm}}$	100	129 day	300	0.038	0.01
$_{70}$Yb	^{168}Yb (n,γ) $^{169}\underline{\text{Yb}}$	0.14	32 day	$8 \cdot 10^2$	—	—
	^{174}Yb (n,γ) $^{175}\underline{\text{Yb}}$	31.8	4.2 day	$4 \cdot 10^3$	0.19	0.005
$_{71}$Lu	^{175}Lu (n,γ) $^{176}\underline{\text{Lu}}$	97.4	3.7 h	$4 \cdot 10^2$	—	—
	^{176}Lu (n,γ) $^{177}\underline{\text{Lu}}$	2.62	6.8 day	$2 \cdot 10^3$	0.036	0.002

[a] Neutron-induced rare-earth activities in 5-g chondritic meteorite irradiated at 300 kw for 2 h, *i.e.*, at a thermal flux of $2 \cdot 10^{12}$ neutrons/cm^2/sec in the TRIGA reactor.

[b] Abundances of stable isotopes are determined from the activity of radioisotopes, underscored once.

[c] Isotopic percentage of the stable isotopes that undergo neutron capture.

[d] The activity observed 24 h after irradiation is expressed in integral counts per min and is uncorrected for chemistry yield. All γ-rays greater than 20 keV, emitted by the rare earths in the combined two or three test tubes of the peaks, were measured by a 1–3/4 in. by 2 in. NaI(Tl) well-type scintillation spectrometer. Exceptions were 18-h ^{159}Gd, which was window-counted between 20 and 120 keV; 9.4-day ^{169}Er and 129-day ^{170}Tm, which were β-counted; and 32-day ^{141}Ce, which should be window-counted between 100 and 180 keV.

[e] Elemental abundances of natural elements were calculated by assuming terrestrial and meteoritic isotopic abundances to be identical. The four rare earth isotopic ratios observed in Allegan and Richardton have checked the validity of the above assumption[14]. Units are expressed in parts per million by weight. Abundances are averaged for the meteorites Allegan and Richardton.

[f] Sensitivities in parts per million for determination of elemental abundances are given for a thermal-neutron flux of $2 \cdot 10^{12}$ neutrons/cm^2/sec and an irradiation of 2 h. The sensitivity is based on a minimum of 20 integral or window γ-ray counts per minute 24 h after irradiation. A chemical yield of 50% is assumed.

[g] A half life of 46 h was observed for ^{153}Sm.

[h] Sensitivities in parts per million are based on a minimum of 20 β-counts per min 24 h after irradiation.

When the melt has cooled, the uncovered crucible is placed on its side in an 800- or 1000-ml beaker. To dissolve the melt, 150 ml of 6 *N* hydrochloric acid are poured into the beaker in small increments. The reaction is vigorous. After the melt has dissolved, the crucible is removed from the beaker and rinsed with deionized, distilled water. The rinsings are added to the sample solution. The beaker is placed on a hot plate and heated to decompose the peroxides. A boiling tube is placed in the beaker to prevent bumping. Some silica is precipitated at this point, and the solution is centrifuged in 90-ml centrifuge tubes to remove the silica. The centrifuge is shielded with 4 in. of lead.

The solution is decanted into an 800-ml beaker, and an equal volume of ethyl alcohol is added. The beaker is placed in an ice bath, and a stream of hydrogen chloride gas (from a cylinder) is bubbled through the solution for 1 to 2 h to precipitate sodium chloride. Ice is added to the bath as needed. The solution is centrifuged in 90-ml glass tubes to remove the sodium chloride, the tubes being handled with tongs. The solution is then decanted into an 800-ml beaker.

The solution is now boiled to reduce its volume by half. This removes most of the alcohol and precipitates a large amount of silica, which is removed by centrifuging. The solution is decanted into a 500-ml open-top separatory funnel, and iron is extracted from the solution using β,β-dichlorodiethyl ether. The ether and solution are mixed with a three-bladed polyethylene stirrer driven by a small, variable-speed electric motor. It is advisable to avoid turbulent stirring, since suspensions may result. The ether is added in two or three portions. Usually, the ether from the second extraction shows only a faint coloration from the iron (further steps are described below in *Further procedure for both stony and iron meteorites*).

Initial separation steps for iron meteoritic matrices

After the iron meteorite has been dissolved in 150 ml of hot 6 *N* hydrochloric acid by moderate heating on a hot plate, about 10 ml of 30% hydrogen peroxide is added to oxidize the iron to the tervalent state. Rare-earth carriers, in amounts given in the procedure for separation of rare earths from a stony meteoritic matrix, are added to the beaker containing the iron and 6 *N* hydrochloric acid immediately before dissolution begins. The solution is heated to decompose excess hydrogen peroxide and centrifuged to separate small amounts of insoluble matter. To the solution, an equal volume of concentrated hydrochloric acid is added to bring the HCl normality to about eight.

The solution is transferred to a large separatory funnel. About nine iron extractions are performed, using 50-ml portions of β,β-dichlorodiethyl ether. Again, the ether and solution are stirred with a three-bladed polyethylene stirrer driven by a small, variable-speed electric motor, and turbulent stirring is avoided. The final green aqueous solution is attributed to the nickel chloride ion.

After the iron extractions, the aqueous solution is transferred to a large beaker and the solution is heated to drive off any dissolved ether.

Further procedure for both stony and iron meteorites

The aqueous solution is transferred to a 600-ml beaker, and ammonia is bubbled into the solution to precipitate the hydroxides of the rare earths and zirconium. Three lecture bottles of ammonia are used simultaneously to speed the precipitation.

Since the solution is very acidic, it takes a considerable amount of ammonia to neutralize it and precipitate the hydroxides. Before centrifuging, hot water should be added to dissolve any ammonium chloride that may form. The solution is centrifuged in a 90-ml glass tube, so that all of the hydroxide precipitate is collected directly in one tube. The solution is discarded in a "hot waste" bottle.

The precipitate is dissolved by adding about 5 ml of concentrated hydrochloric acid to the centrifuge tube and stirring. This solution is diluted with 10–20 ml of water, and any insoluble material is centrifuged. It may be necessary to repeat the HCl dissolution step. The hydroxides are precipitated with ammonia. An excess of ammonia is used to complex any nickel that may be present. The solution is centrifuged, and after the supernatant liquid is discarded the precipitate is dissolved with about 1 ml of concentrated hydrochloric acid. This solution is transferred drop by drop to a small polyethylene centrifuge tube containing 3 ml of 48% hydrofluoric acid in order to precipitate the rare-earth fluorides. The solution is centrifuged, and the supernate, which contains about 80–90% of the scandium, is decanted into a centrifuge tube labeled "Sc" to be saved for the scandium procedure. Since scandium forms a complex ion, ScF_4^-, only a small fraction (20%) of the scandium is coprecipitated with the rare earth fluorides. The rare earth fluorides are dissolved with 2 ml of saturated boric acid and 1 ml of concentrated nitric acid. The solution is diluted to 10 ml and the rare earth hydroxides are precipitated with ammonia. The solution is centrifuged and the supernate is discarded. The precipitate is dissolved in 1 ml of 6 *N* hydrochloric acid and then diluted to 10 ml. The solution is transferred a drop at a time into a tube containing 3 ml of 48% hydrofluoric acid (scandium holdback carrier should not be added, since this leads to interference with the ion-exchange separation). The solution is centrifuged and the supernate is discarded. The rare earth fluorides are dissolved with 2 ml of boric acid and 1 ml of concentrated nitric acid and diluted to 10 ml. Concentrated ammonia solution is used to precipitate the hydroxides, and the supernate is discarded after the solution is centrifuged. The precipitate is dissolved in 1 ml of hydrochloric acid and is then diluted to 10 ml. The rare earths are decontaminated of scandium twice more by repeating the rare earth fluoride precipitation and boric acid dissolution steps described above. After the final boric acid dissolution, the hydroxides are reprecipitated with ammonia.

After being centrifuged, the precipitate is dissolved with hydrochloric acid and again precipitated with ammonia. This solution is centrifuged, and the remaining solution is decanted. 5 ml of 6 *N* hydrochloric acid is added to dissolve the precipitate. The solution is transferred to a 500-ml separatory funnel and diluted to 25 ml. Ice chips (of demineralized, distilled water) are added to cool the solution to approximately 0°. About 2 g of ammonium thiocyanate is added, followed by 100 ml of diethyl ether. The flask is shaken and the aqueous layer drawn off. The ether layer is discarded. This extraction is repeated until the ether layer shows only a slight pink coloration from the iron thiocyanate complex. Cobalt is also removed by this extraction.

The solution is boiled to remove ether and carbon dioxide, and it is then transferred to a glass centrifuge tube, where a series of three ammonia precipitations is carried out. The hydroxides are dissolved in 1 ml of concentrated hydrochloric acid and diluted to 10 ml with water before precipitation with ammonia. After the final ammonia precipitation, the hydroxides are dissolved in 2 ml of concentrated hydrochloric acid.

This is poured into a prepared ion-exchange column. The concentrated-HCl form of Bio-Rad Dowex-2, 100- to 200-mesh resin, is used in a column about 0.6 cm in diameter by 10 cm long. The anion exchange resin is prepared by passing 10 ml of concentrated hydrochloric acid through the column before the rare earth solution. The rare earths pass through the column, and elements such as iron, which form complex anions in concentrated hydrochloric acid, are held in the column. When the liquid meniscus reaches the resin, 2.5 ml of concentrated hydrochloric acid is added. This is eluted until the liquid meniscus again reaches the resin.

The rare earth hydroxides are once again precipitated from the column eluant with ammonia gas. Water is added to dissolve the ammonium chloride which precipitates with the hydroxides. After being centrifuged, the hydroxides are dissolved in the minimum amount of 6 N hydrochloric acid, diluted with 10 ml of water, and reprecipitated with ammonia. The solution is centrifuged, and the supernate is decanted. The rare earths are now ready to be dissolved and passed through a Dowex 50W-X12, minus-400 mesh ion-exchange column to separate them from one another.

Ion-exchange separation of rare earths

The precipitate of rare earth hydroxides is dissolved with a minimum amount of dilute hydrochloric acid and is diluted with 10 ml of water. About 0.5 ml of Dowex 50W-X12, minus-400 mesh ,cation resin (about 2 ml of neutral resin mixture of which about 0.5 ml is resin) is added. The solution is heated to boiling, stirred, centrifuged, and decanted. While being stirred, the resin is washed with about 10 ml of hot water, centrifuged, and decanted. While being stirred, about 2 ml of water is added to the resin, and the gases are boiled off. Before transferring the 0.5 ml of resin, which contains the adsorbed and activated rare earths, to the top of the ion-exchange column, 1 M ammonium lactate (pH 3.2) is run through the column until the effluent has a constant pH of 3.2 (this equilibration may take as long as 12 h). The rare earths are eluted at about 3 drops/min, or 0.5 ml/cm^2/min, and 10 drops are collected in each test tube.

Preparation of scandium for counting

To the contents of the tube labeled "Sc", about 3 mg of praseodymium carrier and 6 ml of concentrated perchloric acid are added. After being heated for some time (5 min to a day) on a steam bath and cooled, the solution is centrifuged and decanted. The PrF_3 and ScF_3 are dissolved in 2 ml of saturated boric acid and 1 ml of concentrated nitric acid. After dilution to 10 ml, concentrated ammonia solution is added to the solution to precipitate the hydroxides. The solution is centrifuged and decanted.

The hydroxides are dissolved in 2 ml of concentrated hydrochloric acid and are poured into a prepared ion-exchange column. The concentrated-HCl form of Bio-Rad Dowex-2, 100- to 200-mesh resin, is used in a column about 0.6 cm in diameter and 10 cm long. The anion resin is prepared by passing 10 ml of concentrated hydrochloric acid through the column before the addition of the scandium–praseodymium solution. The scandium–praseodymium ions pass through the column. When the liquid reaches the top of the column, 2 ml of concentrated hydrochloric acid is added. This is eluted until the liquid level reaches the top of the column.

The scandium and praseodymium hydroxides from the column eluant are precipitated with ammonia gas and centrifuged. After the supernate has been decanted, the precipitate is dissolved in the minimum amount of 3 *N* nitric acid, transferred to a culture tube, and diluted to the same volume as the scandium standard that was irradiated simultaneously with the specimen. The 85-day ^{46}Sc is counted integrally above 750 keV for low counting rates or is window-counted for the ^{46}Sc 0.89-MeV γ-ray in a standard scintillation spectrometer with a NaI(Tl) crystal.

Radioactivity measurements of the rare earths

Each of the test tubes containing 10 drops of effluent is placed in a well-type scintillation spectrometer with a 1-3/4 in. by 2 in. NaI(Tl) crystal, and all γ-rays corresponding to pulses greater than 20 keV are integrally counted. Almost all of the neutron-activated rare earth elements decay by negatron emission, accompanied by hard γ-ray emission; thus, they lend themselves to γ-ray spectroscopy. A plot of the integral counting rate *versus* the number of the test tube containing the effluent is given in Fig. 1, where it may be observed that the rare earths elute in the order of their decreasing atomic numbers. In order to ascertain the order of elution and to identify unequivocally the elution peaks, the effluents in the two or three test tubes making up each peak (or shoulder near a peak, as in the case of gadolinium) are combined into a single, standard-size culture tube. A γ-ray spectrum of the activated rare earth is taken with a 256-channel analyzer coupled to a well-type 1-3/4 in. by 2 in. NaI(Tl) crystal. For comparison, γ spectra of each of the fourteen rare earth standards are also obtained with the multichannel analyzer.

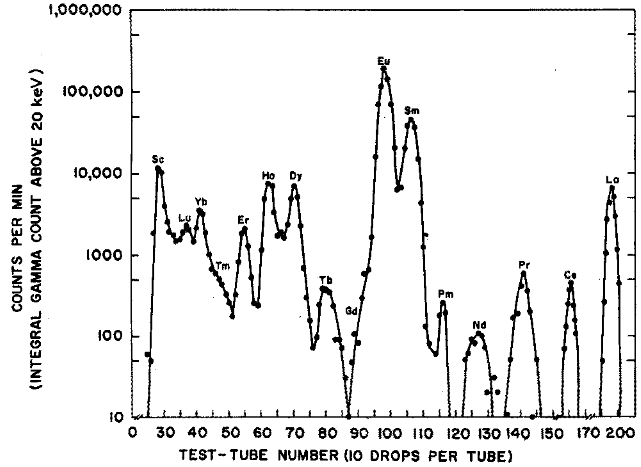


Fig. 1. Ion-exchange separation of rare earths from the Allegan meteorite Ion-exchange resin: Dowex AG50W-X12, minus 400 mesh, 0.5–2.0 cm/min; settling rate, according to Livermore specifications (processed by Bio-Rad Company). Column: 0.5 cm in diameter by 60 cm long; column temperature: 80°; flow rate of eluant: 0.5 $ml/cm^2/min$; gradient elution: 0.08 pH unit change per h. Rare-earth activities induced in 5.1 g of Allegan meteorite exposed to $\sim 10^{16}$NVT.

After identification of the rare earths by γ-ray spectra and elution position, the culture tubes are placed in alternate positions in the circular indexing rack of an automatically operated, well-type scintillation spectrometer (Packard Autogamma) with a 1-3/4 in. by 2 in. NaI(Tl) crystal. The irradiated rare earth standards (in solution) are also transferred to culture tubes and placed in alternate positions in the automatic spectrometer. Specifically, each rare earth standard is placed adjacent to its column-separated rare earth counterpart. To ensure identical counting geometries, the volume of rare earth standard in each culture tube is identical to the volume of rare earth from the meteoritic source. Furthermore, a ^{137}Cs standard γ-ray source and culture tubes containing pure water (the same volume as in the activated-rare-earth tubes) are placed at uniform points in the rack in order to check any drift in the scintillation spectrometer and to count the background at regular intervals. All tubes are counted for a preset time or for a preset total count of 10^6, whichever occurs first.

It is necessary to count only two of the separated rare earths and their respective standards — 9.4-day ^{169}Er and 129-day ^{170}Tm — by β-counting methods. After the γ radioactivity of 7.5-h ^{171}Er has been measured, a definite amount of praseodymium carrier (10 mg) is added to the erbium effluent (part of the erbium effluent before the addition of praseodymium carrier should be kept for activation analysis) and to the erbium standard, which are transferred to separate test tubes. An identical procedure is followed for the determination of ^{170}Tm. The precipitates of praseodymium oxalate, prepared by standard radiochemical techniques, are filtered onto paper disks, mounted on 1/16-in.-thick aluminum plates, and covered with 0.00025 in. of Mylar. Since the praseodymium oxalate precipitates are uniformly thick and of nearly the same weight, and are counted in the same geometry in the Geiger region of a Sugarman-type, methane-flow, proportional β-counter, it is unnecessary to apply β-counting corrections. Aluminum absorption measurements of the ^{169}Er and ^{170}Tm β's are taken for both the separated rare earths and the standards.

The radioactivity of each of the rare earths is counted and plotted for a decay of usually three or more half lives, with the exceptions of the long-lived 129-day ^{170}Tm and 85-day ^{46}Sc. All half lives found in the decay graphs are in agreement with those previously observed for the neutron-activated rare earths. The only exception is ^{153}Sm, which shows a half life of 46 h rather than 47 h. Where sufficient radioactivity is present, it is estimated that decontamination factors of greater than 10^4 are achieved.

Radiochemical yields of the rare earth carriers and scandium are ascertained by comparing the activities resulting from neutron-activation analysis of the decayed carriers with the neutron-induced activities of a known amount of the individual rare earth standards. In some cases, it is desirable to follow the decay of the rare earth for long periods of time; consequently, their chemical yields are determined by neutron-activation analysis on known aliquots of the partially decayed carriers. After the decay of promethium activity resulting from the decay of neodymium precursors, 2.6-yr ^{147}Pm atoms are coprecipitated with praseodymium oxalate, and ^{147}Pm is β-counted to determine the promethium chemical yield. For all rare earths, during chemical-yield determinations the induced activities in the carriers are at least 100 times greater than the residual activity from the meteorite activation. Yields of about 25% to 50% are obtained.

In addition to the neutron-induced rare earth activities in the rare earth carriers during chemical-yield determinations, an appreciable amount of 15-h ^{24}Na activity is produced. This ^{24}Na activity is particularly troublesome for Pr, Gd, Ho and Er, since the half lives for these elements are comparable to that of ^{24}Na. To subtract the

^{24}Na activity from the total activities of ^{24}Na and rare earths, the γ-rays of the respective rare earths and of a separate ^{24}Na source are both measured at two γ-ray energy settings of the scintillation spectrometer; one corresponds to the rare earth γ-ray energy (usually a low-energy γ ray), and the other setting detects only the highly energetic 2.75-MeV γ ray of ^{24}Na.

When the 2.75-MeV γ ray counting rate of the ^{24}Na source is normalized to the counting rate of the 2.75-MeV γ ray in the rare-earth carrier, the contribution of the ^{24}Na counting rate to the total is easily calculated and subtracted. For the worst cases, as much as 30% of the total radioactivity may be from 15-h ^{24}Na.

If the activity level of the ^{24}Na is too high, it is helpful to separate sodium from the rare earth lactate solution before the neutron-activation analyses are made. Separation of sodium is easily performed by repeated ammonium hydroxide precipitations (NH_3 gas is used) of the rare earths. In order to coprecipitate the individual rare earths, which are present in about 0.2- to 0.3-mg quantities, a few milligrams of ferric carrier (Johnson and Matthey, spectrographic grade) is added to the rare earth lactate solution. After the rare earth lactate solution has been made ammoniacal by ammonia gas, the hydroxide precipitates when the lactate complex has been oxidized by the addition of 1 ml of 30% hydrogen peroxide.

After the values for the rare earth activities have been corrected for chemical yield, the elemental abundances of the rare earths are determined by comparing the radioactivity of each eluted rare earth with the specific activity of the corresponding rare earth radioisotope. All comparisons of activities must be made an equal time after the neutron irradiation has ended. In the analyses performed by the authors to calculate the elemental abundances of the rare earths, it was assumed that the isotopic abundances of meteoritic and terrestrial rare earths would be identical. During this work, the abundance ratios for the isotope pairs ^{140}Ce/^{142}Ce, ^{146}Nd/^{150}Nd, ^{158}Gd/^{160}Gd, ^{168}Er/^{170}Er, ^{168}Yb/^{174}Yb and ^{175}Lu/^{176}Lu were measured, and the ratios were, indeed, found to be the same for both meteoritic and terrestrial rare earths.

DISCUSSION

The neutron intensities and spectra must be nearly identical throughout the specimen and the standards. Particularly in a large specimen, *e.g.*, one of *ca.* 5–10 g of low- and medium-mass constituency, it is possible that the specimen might behave as a moderator, thereby increasing the thermal-neutron flux in the specimen relative to that in the standards. On the other hand, the specimen could act as a thermal and/or epithermal neutron sink and decrease the neutron flux available for activation of the rare earths throughout the specimen. The absorption and scattering cross sections for the constituents of a typical 5-g chondritic and 10-g iron meteorite indicate that, compared with standards that are very thin to neutron absorption, differences of about 1% and 7% in the neutron intensities and spectra are expected from the combined effects of absorption and scattering in stony and iron meteorites, respectively.

In order to test the absorption and scattering effects of meteoritic specimens experimentally, an extreme method was chosen. Thin sources of each rare earth (thin to *ca.* 1% of thermal-neutron absorption in most cases) were prepared. The thin sources were individually placed in the center of separate chondritic mockup specimens and in the center of iron bars 1.27 cm in diameter and 1.27 cm long. Both the mockups and the rare earth standard sources were simultaneously irradiated in separate containers in the circular rotating rack of the TRIGA reactor. The radioactivities of the thin sources were then measured. The results are compiled in Table II. The effect of the average specimen on the neutron flux in the stony mockup was only about 3%, and that in the iron mockup was 17%. The stony mockup was made to approximate the composition of the meteorite Allegan reported by MERRILL AND STOKES[16].

In the actual neutron activation of meteorites, the rare earth standards that were irradiated simultaneously with the meteoritic specimens were in 1.00 ml of an aqueous medium. Since the experiment described above showed that there was no significant difference in the activity induced in the thin rare earth sources inside the 5-g chondritic mockups and outside the mockups (see Table II), it was necessary to determine whether any difference in absorption and scattering effects occurred between the thin rare earth sources and the rare earths in 1.00 ml of aqueous medium. An average ratio of 1.00 ± 0.05 for the fourteen rare earths was determined as the activity ratio between thin-rare earth sources and a rare earth in 1.00 ml of solution, both of which were irradiated simultaneously. Therefore, it was concluded that the neutron intensities and spectra throughout the 5-g chondritic or achondritic specimens are identical within ±8% to those of the rare earth standards in 1.00 ml of aqueous medium.

TABLE II

RATIO OF NEUTRON FLUXES INSIDE AND OUTSIDE OF CHONDRITIC AND IRON MOCKUPS AS MEASURED BY RARE EARTH STANDARDS[a]

Rare earth[b]	*Ratio of activity outside to activity inside of mockups*		*Rare earth*[b]	*Ratio of activity outside to activity inside of mockups*	
	Chondritic mockup	*Iron mockup*		*Chondritic mockup*	*Iron mockup*
${}^{140}_{57}\text{La}$	1.02	1.19	${}^{160}_{65}\text{Tb}$	1.03	1.13
${}^{141}_{58}\text{Ce}$	1.04	1.23	${}^{165}_{66}\text{Dy}$	1.05	≅1.21
${}^{143}\text{Ce}$	1.03	≅1.20	${}^{166}_{67}\text{Ho}$	1.02	1.21
${}^{142}_{59}\text{Pr}$	0.97	1.16	${}^{171}_{68}\text{Er}$	1.01	1.21
${}^{147}_{60}\text{Nd}$	1.04	—	${}^{170}_{69}\text{Tm}$	1.05	<1.11
${}^{141}_{61}\text{Pm}$	1.04	—			
${}^{151}_{61}\text{Pm}$	1.01	≅1.15	${}^{175}_{70}\text{Yb}$	1.04	≅1.11
${}^{153}_{62}\text{Sm}$	1.00	1.15	${}^{177}_{70}\text{Yb}$	1.00	—
${}^{152m}_{63}\text{Eu}$	1.02	≅1.23	${}^{176}_{71}\text{Lu}$	1.01	≅1.10
${}^{152}_{63}\text{Eu}$	—	1.23	${}^{177}_{71}\text{Lu}$	0.98	1.17
${}^{159}_{64}\text{Gd}$	1.03	≅1.12			

[a] The chondritic mockup was a 10-g sample with a thin rare earth oxide source in the center. The iron mockup was a 12-g pure iron bar (1.27 cm in diameter and 1.27 cm long) with a thin rare earth oxide source in the center.

[b] See Table I for the neutron-capture reactions.

Since the average ratio of the radioactivity of the source irradiated inside the iron bar to that of the source irradiated outside of the bar is 1.17 ± 0.05, the average effect throughout an iron specimen is about 9%. Therefore, it is concluded that the neutron intensities and spectra of 10-g meteoritic iron specimens are 1.09 ± 0.08 times less than the corresponding neutron intensities and spectra of the rare-earth standards in 1.00 ml aqueous medium.

Usually the meteoritic iron specimens are not machined to the dimensions of the iron bars that were used to obtain approximate measurement of the reduction in neutron intensities. Applying an average correction factor of 1.09 to all of the rare earth abundances in iron meteorites will not significantly alter the ratio of absolute abundances of the rare earths in chondrites to those in irons of $\sim 10^4$, found recently by VASILEVSKIS *et al.*[17]. At most, an error of *ca.* 5% would be introduced in the relative rare earth abundances if the factor of 1.09 were applied to all rare earth abundances in 10-g specimens of iron meteorites.

It is evident from the discussion above that both relative and absolute abundances of all rare earths may be precisely determined by neutron-activation analysis only if all the rare earths are distributed homogeneously throughout the entire meteoritic specimen. Since many of the rare earth elements have high thermal and epithermal neutron-absorption cross sections, they may be responsible for self-shadowing effects. In such a case, only the relative rare earth abundances may be ascertained, since the rare earth elements may be concentrated (homogeneously with respect to themselves) in minuscule crystals or grains throughout the meteorite. Furthermore, if the rare earth elements are individually concentrated in separate minuscule crystals and grains throughout the matrix, the absolute abundances may be determined only for elements that have relatively low neutron-absorption cross sections (200 barns or less).

A consideration of ion-radii shows that occurrence of individual rare earth separation is highly unlikely. However, it is possible that the light and heavy rare earth groups may be fractionally separated and may thereby introduce errors in both the absolute and relative abundance values.

A few simple calculations illustrate the seriousness of self-shadowing. Let us assume that all the lanthanum in a meteorite is concentrated in a sphere in the form of the oxide, and that the quantity of lanthanum is equal to that found in the chondrites Allegan or Richardton[14], namely, $1.6 \cdot 10^{-6}$ g of lanthanum per 5 g of meteorite. Since lanthanum has a thermal-neutron absorption cross section of 8.9 barns, the neutron flux at the center of the La_2O_3 sphere would be slightly depressed by about 0.1%. On the other hand, let us assume that a quantity of europium equal to $0.4 \cdot 10^{-6}$ g of europium per 5 g[14] of meteorite is concentrated in a sphere in the form of Eu_2O_3. The europium neutron-absorption cross section of 4300 barns would cause a severe neutron-flux depression of approximately 22%. If lanthanum and europium were homogeneously mixed and concentrated in a single sphere, the neutron flux would again be depressed by about 20%, which would make the determination of the absolute abundance of either lanthanum or europium impossible. However, the relative abundance ratio of lanthanum to europium could be precisely determined, since the neutron flux in each infinitesimal volume element in the sphere would be the same for both lanthanum and europium.

In order to determine the extent of the rare earth self-shadowing effect, it is necessary to determine and to compare the abundances of the rare earths in meteorites by using different analytical methods. The most obvious method is the standard spectrographic technique. One of its principal disadvantages is the possible introduction of rare earths during chemical manipulation. By far the best method is to determine the rare earth elemental abundances by photoneutron-activation analysis. This method differs from the standard neutron-activation analysis in that the activated rare earth radioisotopes are induced by (γ,n) reactions. The necessary γ-ray fluxes are generated by a high-intensity, 20- to 50-MeV electron linear accelerator. The rare earths Ce, Nd, Sm, Eu, Gd, Er, Tm, Yb and Lu are amenable to the photoneutron analysis with no accompanying self-shadowing effect.

Approximately 250 mg of zirconium is dissolved from the crucible during the fusion. Since the rare-earth mineral xenotime is accompanied by the mineral zircon, from which the zirconium crucible was probably derived, an activation analysis was carried out on a part of a zirconium crucible lid. No rare earth γ-lines were observed. Upper limits were calculated for the individual rare earth abundances that diluted the added carriers. The maximum carrier dilution was calculated to be less than 2%, and the average less than 1%.

A typical elution spectrum for rare earths and scandium removed from a cation ion-exchange column is given in Fig. 1. This spectrum applies to the rare earths activated in the chondritic meteorite Allegan. γ-ray intensities vary from a few hundred to several hundred thousand counts per min. It is apparent that a single elution through an ion-exchange column is satisfactory. However, in this case the long-lived ^{46}Sc (85 days) contributed appreciably to the lutetium, ytterbium, and thulium peaks; this can be avoided by removing most of the scandium from the rare earths before separating them in the ion-exchange column. This modification of the technique has been included in the procedure outlined above in *Further procedure for both stony and iron meteorites.*

Thulium, represented by 129-day ^{170}Tm, is on the trailing edge of the peak for the eluted element ytterbium. Consequently, some 32-day ^{169}Yb may interfere with the assaying of the thulium abundance if time is not allowed for the ^{169}Yb to decay. To separate thulium from ytterbium, a second elution of the collected thulium peak activity may be performed by passing thulium through a freshly prepared and uncontaminated ion-exchange column at a pH of 3.2.

From Fig. 1, it also appears that gadolinium, separated on the leading edge of the high europium peak, should be subjected to a second elution for better resolution. However, one ion-exchange pass is adequate for gadolinium, because (*1*) any 9.2-h ^{152m}Eu atoms present in the separated 18-h ^{159}Gd decay at approximately twice the rate of the ^{159}Gd; (*2*) the leading edge of the europium peak is sufficiently steep that only a small percentage of the europium fraction will be found in the gadolinium fraction; and (*3*) the high-energy γ-rays of 9.3-h ^{152m}Eu are discriminated against by selectively counting (window counting) the low-energy γ-rays of 18-h ^{159}Gd. In other meteorite analyses for rare earths, the gadolinium and europium peaks were clearly resolved.

In some cases, it is desirable to measure only the relative abundance ratio of the light and heavy rare earth groups and to eliminate employment of the ion-exchange technique to analyze the abundances of the entire rare earth group. For example, in meteorites, sediments, and rocks, the fractionation of rare earths into different phases may be measured. Two rare earths, lanthanum, via ^{139}La (n,γ) 40-h ^{140}La, and dysprosium, via ^{164}Dy (n,γ) 2.32-h ^{165}Dy, are particularly representative of the light and heavy groups, respectively. Furthermore, when the γ-rays and half lives of all the neutron-activated rare earths are considered, the characteristic high-energy γ-ray (1.60 MeV) of 40-h ^{140}La and the short half life of 2.32-h ^{165}Dy make the determination of the abundances of these two elements in a mixture of all the neutron-activated rare earths particularly suitable. The only assumed condition is that the relative abundances of all the rare earths do not markedly differ (perhaps by a factor of ten) from the abundances given for the two chondritic meteorites in Table I.

In addition to the rare earth elements and scandium, the abundance of the element yttrium may be determined by neutron-activation analysis. The general chemical and ion-exchange operations used for the separation of the rare earths are applicable to the separation of yttrium. Elution of yttrium from the ion-exchange column is at, or near, the elution of dysprosium. The β-radioactivity of 64-h ^{90}Y and an yttrium standard are counted and compared to determine the abundance of the yttrium.

ACKNOWLEDGEMENTS

We wish to thank Professor HANS E. SUESS of the University of California, La Jolla, for proposing to us the problem of determining the abundances of rare earths in meteorites through neutron-activation analysis. We are indebted to Professor JOHN W. IRVINE, JR., of the Massachusetts Institute of Technology for valuable suggestions. We also thank J. E. LASCH for help in the radioactivity measurements and D. A. OLEHY for his assistance in running the ion-exchange column.

SUMMARY

The abundances of the rare earths, lanthanum through lutetium, have been determined in chondritic, achondritic, and iron meteorites by neutron-activation analysis. The procedure used should also be applicable to the analysis of terrestrial stones and sediments. After exposure to a thermal-neutron flux of $2 \cdot 10^{12}$ neutrons/cm^2/sec for 2 h, the chondritic or achondritic sample, with added rare earth carriers, is dissolved after sodium peroxide fusion. Iron specimens are dissolved in a hydrochloric acid medium. The rare earths are then separated as a group from the matrix and are individually separated by means of a Dowex 50 W-X12 cation resin column and elution with 1 *M* ammonium lactate. This method is sensitive to fractional parts per million of the individual rare earths. The abundance of scandium may also be determined in the same procedure.

RÉSUMÉ

Un procédé a été mis au point pour le dosage des éléments des terres rares dans divers météorites et roches, en utilisant la méthode par activation au moyen de neutrons. Les terres rares sont isolées en un groupe, puis séparées individuellement au moyen d'une résine Dowex et élution par le lactate d'ammonium. Le scandium peut être déterminé par le même procédé.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung der seltenen Erden in Meteoriten und Gesteinen durch Aktivierung mit Neutronen. Die seltenen Erden werden als Gruppe abgeschieden und anschliessend mit einem Austauscherharz getrennt. Scandium kann nach der gleichen Methode bestimmt werden.

REFERENCES

[1] E. M. BURBIDGE, G. R. BURBIDGE, W. A. FOWLER AND F. HOYLE, *Revs. Modern Phys.*, 29 (1957) 547.
[2] A. G. W. CAMERON, *Astrophys. J.*, 129 (1959) 676.
[3] H. E. SUESS AND H. C. UREY, *Revs. Modern Phys.*, 28 (1956) 53.
[4] I. NODDACK, *Z. anorg. u. allgem. Chem.*, 225 (1937) 337.

[5] E. MINAMI, *Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. IV, N.F.L.*, 1 (1935) 155.
[6] G. E. BOYD, *Anal. Chem.*, 21 (1949) 335.
[7] E. N. JENKINS AND A. A. SMALES, *Quart. Revs. (London)*, 10 (1956) 83.
[8] G. W. LEDDICOTTE AND S. A. REYNOLDS, *Nucleonics*, 8 (3) (1951) 62.
[9] T. I. TAYLOR AND W. W. HAVENS, *Nucleonics*, 6 (4) (1950) 54.
[10] H. HAMAGUCHI, G. W. REED AND A. TURKEVICH, *Geochim. et Cosmochim. Acta*, 12 (1957) 339.
[11] G. L. BATE, H. A. POTRATZ AND J. R. HUIZENGA, *Geochim. et Cosmochim. Acta*, 14 (1958) 118.
[12] W. D. EHMANN AND J. R. HUIZENGA, *Geochim. et Cosmochim. Acta*, 17 (1959) 125.
[13] F. W. CORNISH, *Atomic Energy Research Establishment of Great Britain*, C/R 1224 (1953).
[14] R. A. SCHMITT, A. W. MOSEN, C. S. SUFFREDINI, J. E. LASCH, R. A. SHARP AND D. A. OLEHY, *Nature*, 186 (1960) 863.
[15] W. E. NERVIK, *J. Phys. Chem.*, 59 (1955) 690.
[16] G. P. MERRILL AND H. N. STOKES, *Proc. Wash. Acad. Sci.*, 2 (1900) 41.
[17] R. A. SCHMITT, J. VASILEVSKIS, A. W. MOSEN, J. LASCH AND D. A. OLEHY, to be published.

EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

I. DETERMINATION OF COBALT

A. J. CAMERON AND N. A. GIBSON

Chemistry School, Sydney University, Sydney, N.S.W. (Australia)

(Received December 9th, 1960)

INTRODUCTION

The triphenylmethylarsonium cation has been applied to permanganate[1], dichromate[2] and iodine[3] titrations, using extractive end-points. This paper describes its application to the determination of cobalt by the addition of an excess but known amount of EDTA, and back-titration with a standard cobalt solution. At the end-point, the blue ion-association pair triphenylmethylarsonium tetrathiocyanato cobaltate(II) is extracted into chloroform.

A number of methods have been proposed for the estimation of cobalt with EDTA, including back-titration with other metals using Eriochrome Black T indicator[4–6] and direct titration using murexide indicator[7]. Thiocyanate has been used as an indicator in various aqueous solvent mixtures[7,8]. For example, cobalt has been determined in a 1 : 1 acetone–water mixture by addition of an excess of EDTA, and back-titration with standard cobalt(II) solution; the method has been applied to the determination of a number of other metals[9–11].

Although the extractive method of end-point detection introduces an additional step in an analysis, this disadvantage is outweighed by several advantages, the two most important being: (*1*) the end-point is in no way affected by the presence of unreactive coloured ions or highly coloured metal–EDTA complexes; (*2*) the sensitivity of the end-point is increased by the use of a relatively small volume of extracting solvent.

APPARATUS AND REAGENTS

Titrations were performed in a glass-stoppered 500-ml conical flask fitted near the base with a horizontal closed side-arm approximately 3 cm long and 2 cm in diameter. The appearance of the blue colour at the end-point is more easily seen when the chloroform is run into this closed side-arm.

Solutions used

A.R. quality reagents were used wherever possible. Standard EDTA solution, 0.01 *M* solution of the disodium salt. This solution was standardised against zinc solution using Eriochrome Black T as indicator. Standard cobalt(II) solution, 0.01 *M* solution of iron-free cobalt ammonium sulphate. Buffer solution of pH 9.3 was prepared from 150 ml of concentrated aqueous ammonia (sp.gr. = 0.880) and 160 g of ammonium chloride, diluted to 1 l with water.

Solutions were prepared using distilled water which had been passed through a column containing cation exchange resin in the sodium form. Polythene containers were used for storage.

TABLE I

mg of Co added	*mg of Co found*	*% Deviation from Co added*	*Mean mg of Co found*	*% Deviation of mean from Co added*	*Maximum % deviation of Co found from mean*
1.214	1.244	+2.5	1.228	+1.2	1.6
1.214	1.208	−0.5			
1.214	1.220	+0.5			
1.214	1.238	+2.0			
1.214	1.232	+1.5			
3.035	3.047	+0.4	3.034	−(<0.1)	0.4
3.035	3.029	−0.2			
3.035	3.029	−0.2			
3.035	3.023	−0.4			
3.035	3.041	+0.2			
6.070	6.137	+1.1	6.098	+0.5	0.6
6.070	6.082	+0.2			
6.070	6.088	+0.3			
6.070	6.100	+0.5			
6.070	6.082	+0.2			

PROCEDURE

The sample cobalt solution (containing from 2 to 12 mg of cobalt* and 25 ml of standard EDTA solution are pipetted into the titration flask. If necessary, approximately 1 *M* ammonia is added until litmus paper just turns blue. Approximately 10 ml of chloroform are then added, followed by 2 ml of buffer solution, 5 ml of 50% potassium thiocyanate solution and 3 ml of 1% triphenylmethylarsonium chloride solution. The excess EDTA is then back-titrated with the standard cobalt solution.

---

* For the estimation of more than 12 mg of cobalt, more EDTA solution should be added, or the concentrations of both EDTA and the cobalt solution used as back-titrant should be increased. The sample volume should not be more than 150 ml for the quantities of buffer, potassium thiocyanate and triphenylmethylarsonium chloride specified. For larger sample volumes, more of these reagents should be used.

The cobalt solution should be added dropwise as the end-point is approached, the flask being stoppered and shaken after the addition of each drop. The end-point is indicated by the appearance of a blue colour in the chloroform layer.

RESULTS

The cobalt content of three different volumes of a solution of known concentration was determined by the suggested procedure. Results are shown in Table I.

With the exception of the first group of results, which were obtained by determining a smaller quantity of cobalt than that recommended in the procedure, it can be seen that the mean cobalt determined may be expected to be within 0.5% of the true value, while the maximum variation about this mean is also of the same order, thus leading to a maximum expected error of about 1% for any single determination. In the case of the samples with 1.214 mg of cobalt, the corresponding figures are approximately doubled; this is due not only to the comparatively large error in pipetting a small volume of solution (2 ml), but also to the large percentage errors inherent in calculations based on a small titration difference (*i.e.* the difference between the back-titration of excess EDTA and the titration of 25 ml of EDTA solution alone).

DISCUSSION

Preliminary work indicated that sharp end-points could be obtained over the pH range 5–10. In order to stabilise the cobalt–EDTA complex as much as possible, the titration should be done at a high pH. An ammoniacal buffer of pH 9.3 was chosen, since it has maximum buffering capacity, and titrations performed in alkaline solutions up to pH 10 were highly reproducible.

The effect on the titration of varying the volumes of potassium thiocyanate, triphenylmethylarsonium chloride and buffer solutions was investigated. The titration results did not vary by more than 0.1 ml from that obtained using the specified reagent amounts, when the volumes of the reagents were varied within the limits: potassium thiocyanate, 1 to 30 ml; triphenylmethylarsonium chloride, 1 to 30 ml; and buffer, 0.5 to 8 ml (the volume of the aqueous solution at the end-point was in each case between 70 and 100 ml). However, the end-points observed when using the limiting amounts were in general less sharp than those obtained with the recommended quantities. When large volumes of the triphenylmethylarsonium chloride solution were used, lengthy shaking was required to avoid premature end-points.

The greater part of the work described in this paper was performed with $M/100$ solutions of EDTA and cobalt, and sharp end-points were obtained. However, titrations carried out using $M/1000$ solutions gave somewhat diffuse end-points. In contrast, titrations using $M/10$ solutions gave very sharp end-points, provided that more buffer was used. Consequently, solutions of this concentration could be used in the determination of comparatively large amounts of cobalt without interference from the colour of the red cobalt–EDTA complex.

The blank was found to be approximately 0.02 ml when using $M/100$ solutions, and was therefore neglected.

The solution of cobalt and excess EDTA should, if necessary, be first neutralised with ammonia. The order of addition of the chloroform and the other reagents was found to have no effect on the result.

The effect of using other quaternary arsonium cations in the extractive end-point titration was investigated. For this purpose, 3 ml of a 1% aqueous solution of the arsonium salt under test was used. The Me_4As^+ and $PhMe_3As^+$ cations failed to form chloroform-soluble ion association pairs with the $[Co(SCN)_4]^{-2}$ anion. In contrast, the $Ph_2Me_2As^+$ and Ph_4As^+ ions gave titration results identical with those obtained when using the Ph_3MeAs^+ ion.

SUMMARY

A method for the determination of cobalt by the addition of excess EDTA and back-titration with standard cobalt solution is recommended. The titration involves an extractive method of end-point detection, depending upon the appearance of the blue colour of the ion-association pair $[Ph_3MeAs]_2[Co(SCN)_4]$ in chloroform. The method is therefore suitable for the estimation of cobalt in highly coloured aqueous solutions. Average errors can be expected to be less than 0.5%.

RÉSUMÉ

Une méthode est proposée pour le dosage du cobalt, par addition d'EDTA en excès et titrage en retour au moyen d'une solution étalon de cobalt. Le point final est décelé par extraction du composé bleu $[Ph_3MeAs]_2[Co(SCN)_4]$ dans le chloroforme (Ph_3MeAs = triphénylméthylarsonium).

ZUSAMMENFASSUNG

Beschreibung einer indirekten komplexometrischen Methode zur Bestimmung von Kobalt mit EDTA in Gegenwart von Triphenylmethylarsoniumchlorid, Rhodankalium und Chloroform. Der Endpunkt wird durch das Auftreten einer blauen Färbung in der Chloroformschicht angezeigt.

REFERENCES

[1] N. A. Gibson and R. A. White, *Anal. Chim. Acta*, 12 (1955) 115.
[2] N. A. Gibson and R. A. White, *Anal. Chim. Acta*, 12 (1955) 413.
[3] N. A. Gibson and R. A. White, *Anal. Chim. Acta*, 13 (1955) 546.
[4] W. F. Harris and T. R. Sweet, *Anal. Chem.*, 26 (1954) 1648.
[5] W. F. Harris and T. R. Sweet, *Anal. Chem.*, 26 (1954) 1649.
[6] J. Kinnunen and B. Wennerstrand, *Chemist Analyst*, 44 (1955) 33.
[7] H. Flaschka, *Mikrochemie*, 39 (1952) 38.
[8] R. N. Sen Sarma, *Sci. and Culture (Calcutta)*, 20 (1955) 448.
[9] S. Takamoto, *Nippon Kagaku Zasshi*, 76 (1955) 1339.
[10] S. Takamoto, *Nippon Kagaku Zasshi*, 76 (1955) 1342.
[11] S. Takamoto, *Nippon Kagaku Zasshi*, 76 (1955) 1344.

A SOLVENT EXTRACTION METHOD FOR THE SEPARATION OF IODIDE

PHILIP W. WEST AND A. S. LORICA

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

(Received December 21st, 1960)

The present study was undertaken as a means of establishing the possible usefulness of solvent extraction methods in the separation of anions. Although the separation of anions[1-3] has always remained a difficult problem, and although solvent extraction methods have become increasingly popular in the separation of cations, the possibility of combining the two fields has remained essentially unexplored. The separation of iodide, as reported here, is only one of a number of promising anion separations now under investigation.

Following the classification proposed by MORRISON AND FREISER[4], it can be seen that anion extraction systems might be envisaged, based on the extraction of either an ordinary coordination compound,

$$M^{+n} + nX^{-} = MX_n$$

or an ion-association complex,

$$M^{+n} + (n + a)X^{-} = MX^{-a}_{(n+a)}$$

$$MX^{-a}_{(n+a)} + aY^{+} = [aY^{+}, MX^{-a}_{(n+a)}] \qquad \text{[ion-association complex]}$$

Because the halides form stable complexes with a number of metal ions, it was decided to investigate them first. High concentrations of iodide have been used for the solvent extraction of metal ions such as mercury(II), cadmium, antimony(III), gold(III), indium(III), lead(II), thallium(III), and tin(II). Iodides of bismuth(III), iron(II), copper(II) and palladium(II) are also extractable, albeit to a lesser degree[5]. Preliminary qualitative work showed the iodide ion to extract very well with either cadmium or mercury(II) as the coordinating cation using a 1 : 1 solvent mixture of tributyl phosphate (TBP) and methyl isobutyl ketone (MiBK). WEST AND TRON[6] studied the extraction of the halides of mercury(II) and found that optimum extraction (about 97%) was obtained only at a Hg : halide ratio of 1 : 2; at a ratio of 2 : 1, the amount of halide extracted decreased to about 82%. On the other hand, excess cadmium had very little effect on the efficiency of extraction of iodide. Because in actual analysis the amount of a constituent is seldom known beforehand, it is generally impossible to anticipate the optimum amount of a critical reagent to be added; therefore, a procedure that can tolerate a reasonable excess of reagent is to be preferred. The cadmium iodide system using 1 : 1 TBP–MiBK as extractant seemed to possess many favorable characteristics and thus to warrant detailed study.

EXPERIMENTAL

Reagents

Reagents required for the isolation of iodide include: (*1*) Cadmium nitrate (1 *N*); (*2*) Carbon tetrachloride; (*3*) Sulfuric acid (6 *N*); (*4*) Sodium hydroxide (1 *N*); (*5*) Methyl isobutyl ketone; (*6*) Tri-*n*-butyl phosphate.

All chemicals used in these studies were A.R. grade.

Choice of solvents

WEST AND TRON[6] found that a mixture of tributyl phosphate and ethyl acetate gave essentially complete extraction of the halides of mercury in a single pass. On the other hand, MORRISON AND FREISER[4] recommend methyl isobutyl ketone for the extraction of various cations using iodide as the complexing additive. After considering these and other solvents, a 1 : 1 TBP-MiBK mixture was selected because of its extractive efficiency and because it was found to be relatively insensitive to changes in acidity.

Recovery of iodide

For the recovery of extracted iodide, the usual technics used in extraction methods were tried and found ineffective. Finally, a new approach[7] was introduced, that of adding a third solvent, miscible with the non-aqueous solvents but very poor at extracting iodide. The addition of carbon tetrachloride, about twice as much as the volume of the TBP-MiBK layer, produced dramatic results. A yellow color developed after a minute or two of standing. At this point, addition of 1 *N* sodium hydroxide (20 ml) gave a two-phase system composed of an upper aqueous layer and a lower non-aqueous layer. The large proportion of carbon tetrachloride made the non-aqueous layer the heavier one. After a minute of vigorous shaking, a white precipitate of cadmium hydroxide formed in the aqueous phase, and the yellow color disappeared from the TBP-MiBK-CCl_4 layer. The recovery of the iodide from the non-aqueous phase using the solvent displacement technic just outlined proved to be remarkably efficient. It is of interest to note that this is a reverse of the established practice of using solvent mixtures to effect increases in solvent extraction efficiencies.

Experimental procedures

10 ml of cadmium iodide solution were pipetted into a 60-ml separatory funnel. Dilute sulfuric acid was then added to bring the solution to the desired pH. To this acidified solution, an equal volume of a 1 : 1 mixture of TBP and MiBK was added, and the mixture shaken for about 30 sec to insure contact between the two immiscible liquids. The separatory funnel containing the mixture was immersed in a thermostat kept at 30°, where the system was allowed to come to equilibrium.

After equilibration, the non-aqueous layer was treated with 20 ml of carbon tetrachloride and the mixture then shaken with 20 ml of 1 *N* sodium hydroxide to recover the cadmium and iodide. Copious precipitation of white cadmium hydroxide resulted, and the iodine was released in the form of I^-, possibly including small amounts of OI^-.

The CCl_4-TBP-MiBK layer was washed twice with 20-ml portions of 1 *N* sodium hydroxide, and the washings were combined with the first one containing the cadmium hydroxide precipitate. This mixture was made 6 *N* in regard to hydrochloric acid, and the iodine determined using a conventional iodine monochloride procedure.

Cadmium was determined in the aqueous layer using a dithizone extraction procedure on suitable aliquots of the solution. The cadmium in the non-aqueous layer and the unextracted iodide were obtained by difference.

Cadmium iodide solutions used for the initial concentration studies were standardized using hot alkaline permanganate oxidation of the iodide followed by thiosulfate titration. A small amount of silver nitrate solution was added halfway in the titration to sharpen the end-point[8].

To acquire a better understanding of the extraction of cadmium iodide, and in particular, the iodide, the effects of various factors were studied. These factors were the hydrogen ion concentration, the cadmium to iodide molar ratio, the initial concentration of the cadmium iodide solution, and the effect of temperature.

The hydrogen ion concentration

As shown in Table I, the system is not very sensitive to changes in hydrogen ion concentration. A twenty-fold change in pH occasioned only a 2% decrease in the iodide extracted.

TABLE I

	pH					
	0.3	*0.6*	*1.0*	*2.0*	*3.0*	*6.0*
Percentage I extracted	96	95	95	94	94	94
Percentage Cd extracted	68	70	82	93	95	96
Cd: I mole ratio in extract	1/2.8	1/2.7	1/2.4	1/2	1/2	1/2
Δ pH in aqueous phase	+0.2	+0.1	+0.1	+0.5	+0.3	−3.2

For pH values less than 0.3, there is extensive atmospheric oxidation of the iodide. On the other hand, starting at pH 2, a whitish emulsion forms in the non-aqueous layer which takes longer to clear up as the pH increases further.

Unless otherwise stated, the cadmium iodide solutions used were approximately 0.05 *M* in concentration.

The cadmium to iodine molar ratio

If any metal ion is to be of practical use in the separation of anions by solvent extraction, its presence in excess should not appreciably decrease the extraction efficiency. Fortunately, the cadmium ion proved to be very satisfactory for iodide extractions when considered on this basis.

TABLE II

CADMIUM TO IODIDE RATIO IN AQUEOUS LAYER

	1:2	*1:1*	*2:1*	*4:1*
Percentage I extracted	95	95	92	89
Percentage Cd extracted	70	50	24	20
Cd : I mole ratio in extract	1/2.7	1/1.8	1/1.9	1/1.3

The above data were obtained at 30° and at pH 0.6 of the aqueous layer.

The initial concentration of the cadmium iodide solution

Data show that starting with solution strengths approximating those usually encountered in analysis (0.05–0.1 *M*), almost complete separation of the iodide ion using Cd^{+2} as the coordinating cation can be attained in two or three extractions.

TABLE III

INITIAL CONCENTRATION OF THE CdI_2 SOLUTION

	0.001 M	*0.003 M*	*0.006 M*	*0.01 M*	*0.03 M*	*0.05 M*	*0.1 M*
Percentage I extracted	61	77	87	91	95	95	96
Percentage Cd extracted	60	53	66	69	70	70	75
Cd : I mole ratio in extract	1/2	1/3.7	1/2.6	1/2.7	1/2.7	1/2.7	1/2.6

Temperature = 30°, pH = 0.6

Effect of temperature

Because the solvent mixture is inflammable, the study of temperature effects was not extended beyond 40°. Moreover, the system seems to behave in accordance with BJERRUM's theory. For solvents of low dielectric constant, theory predicts a decrease in ion association with increase in temperature. Since the extracting species are presumably ion association complexes, the decrease in extraction as the temperature was raised to 40° is in agreement with theory.

TABLE IV

	Temperature		
	25°	*30°*	*40°*
Percentage I extracted	97	95	94
Percentage Cd extracted	68	70	68
Cd : I mole ratio in extract	1/2.9	1/2.7	1/2.8

Selectivity

A qualitative survey of the common anions was conducted to find out which of them would be extracted under the same conditions. Varying degrees of extractability were encountered and may be classified according to the following groups:

(*1*) Anions that were extracted with approximately the same efficiency as the iodide: CN^- and CNS^-.

(*2*) Anions extracted to a moderate degree: Cl^-, Br^-, $C_2O_4^{-2}$, and NO_3^-.

(*3*) Anions that were extracted very poorly or not at all: F^-, $S_2O_3^{-2}$, SO_4^{-2}, PO_4^{-3}, Ac^-, S^{-2}, $Fe(CN)_6^{-4}$, and BO_3^{-3}.

No evidence of coextraction was found.

DISCUSSION

Cadmium iodide solutions are known to contain the following ionic and molecular species: Cd^{+2}, CdI^+, CdI_2, CdI_3^-, CdI_4^{-2} and I^-. The simple cadmium and iodide ions are probably found only in negligible amounts, since cadmium iodide is a weak electrolyte, except in very dilute solutions[9]. Working with neutral solutions of ionic strength 3, LEDEN[10] found the iodide complexes of cadmium present in the following decreasing order of abundance: CdI_4^{-2}, CdI_3^-, CdI_2 and CdI^+. ALBERTY AND KING[11], on the other hand, obtained from mobility data, using solutions of ionic strength of 0.5 and a total iodide concentration of 0.1 *M*, the following values for the cadmium iodide complexes:

Cd^{+2} ------ negligible
CdI^{+} ------ 6%
CdI_2 ------ 12%
CdI_3^{-} ------ 16%
CdI_4^{-2} ------ 62%

Their graphs of fraction of complex *vs.* total iodide concentration where the above values were read off showed that the relative amounts of the different complexes varied with the total iodide concentration. HARRIS[12] reported from ion exchange experiments, using 0.0666 *M* CdI_2, the presence of CdI_4^{-2}, CdI_2 CdI_3^{-} and CdI^{+}, in that order of increasing abundance.

In the present studies, the solutions were acidic. Undoubtedly, all the different complexes of cadmium with iodide would still be present. The question is which forms predominate over the others? For simplicity, the formulas of the cadmium iodide complex ions were written unhydrated, although it is known that molecules of water are coordinated to the central ion. CdI_2, for example, is really $Cd(H_2O)_4I_2$. With this in mind, it is possible that the addition of hydrogen ions, which have a great affinity for water molecules, makes it relatively easier for the coordinated water to leave the sphere of influence of the central metal ion and for the simple iodide ions to take over the vacated positions. In solutions of low pH, say 0.3 and 0.6, the principal cadmium iodide complexes are probably, in decreasing order of abundance, CdI_3^{-}, CdI_2 and CdI_4^{-2}. At higher pH values, the following are probably present to a greater extent: CdI_2 and CdI^{+}. The data in Table I point to the following as the uncharged species extracted from solutions of low pH: $[H^{+}, CdI_3^{-}]$, CdI_2 and $[2\ H^{+}, CdI_4^{-2}]$. The increased participation of the last named ion association complex should be expected with further increase in acidity. From pH 2 on up to higher pH values, the extracted species are probably CdI_2 and $[CdI^{+}, OH^{-}]$ with the latter making its greatest participation at pH 6, as evidenced by the increase in the acidity of the aqueous phase, an increase which is too great to attribute to a possible increase in the solubility of water in the TBP-MiBK phase.

The relative insensitivity to pH change may be due to the existing equilibria among the different complexes of cadmium and iodide which allow interconversion from one major ionic species to another that can form an uncharged extractable complex at the new pH.

As long as the higher ion association complexes are the major species being extracted, the extraction efficiency of iodide is high. Addition of cadmium ions to vary the Cd : I mole ratio increases the ionic strength of the solution, making extensive ion association possible. However, the concurrent chemical effect limits the ion association to the lower complexes as shown by the following equations:

$$Cd^{+2} + CdI_4^{-2} \rightarrow 2\ CdI_2$$
$$Cd^{+2} + CdI_3^{-} \rightarrow CdI_2 + CdI^{+}$$
$$Cd^{+2} + CdI_2 \rightarrow 2\ CdI^{+}$$

The uncharged species being extracted are probably CdI_2, and $[CdI^{+}, NO_3^{-}]$ with the latter increasing in importance with increase in Cd : I ratio. The solution added to increase the cadmium to iodide ratio was cadmium nitrate which explains the appearance of the nitrate ion here. No attempt was made to estimate the amount of nitrate extracted, but its presence was detected.

The increase in extraction with increase in initial concentration of the cadmium iodide solution may be due to the ionic-strength and mass-action effects. The former favors ion-association complex formation which, because of the mass-action effect and the presence of hydrogen ions, would in turn favor the higher complexes, CdI_3^- and CdI_4^{-2}:

$$2\ CdI_2 \rightarrow CdI_3^- + CdI^+$$
$$3\ CdI_2 \rightarrow CdI_4^{-2} + 2\ CdI^+$$

At lower concentrations, the amount of simple cadmium and iodide ions increases, but enough complexes are still present to sustain the formation of extractable species. The data in Table III point to $[2\ H^+, CdI_4^{-2}]$, $[H^+, CdI_3^-]$ and CdI_2 as the predominant forms being extracted with the participation of $[2\ H^+, CdI_4^{-2}]$ reaching its peak at 0.003 *M*. Apparently, the CdI^+ ion, which is the predominant species at very low CdI_2 concentrations, is unable to form an extractable uncharged ion association complex, the pH of the solutions (~pH 0.6) being so low as to make the formation of $[CdI^+, OH^-]$ highly improbable.

Bjerrum's theory predicts that an increase in temperature will cause a decrease in ion association in the TBP–MiBK phase. In the aqueous layer, the number of ion association complexes should increase. Of these two opposing effects, the data seem to indicate the predominance of the former.

ACKNOWLEDGEMENT

The financial support of the Esso Standard Oil Company is gratefully acknowledged.

SUMMARY

Solvent extraction is proposed for the isolation of anions. Data obtained in the extraction of iodide using cadmium as complexing agent under the influence of such factors as pH, addition of excess cadmium ions, initial concentration of the cadmium iodide solution and temperature are presented.

RÉSUMÉ

L'extraction par solvant est proposée pour la séparation des anions. Les auteurs ont examiné l'influence de divers facteurs sur l'extraction de l'iodure au moyen de cadmium comme réactif complexant.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung von Anionen durch Lösungsmittelextraktion. Jodide werden als Cadmiumkomplexe mit einem Gemisch von Tributylphosphat–Methylisobutylketon abgetrennt. Der Einfluss verschiedener Faktoren auf die Extrahierbarkeit wurde untersucht.

REFERENCES

[1] G. B. S. Salaria, *Anal. Chim. Acta*, 21 (1959) 312.
[2] I. K. Taimni and M. Lal, *Anal. Chim. Acta*, 17 (1957) 367.
[3] I. K. Taimni and M. Lal, *Anal. Chim. Acta*, 21 (1959) 105.
[4] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957.
[5] Ph. W. West and J. K. Carlton, *Anal. Chim. Acta*, 6 (1952) 406.
[6] Ph. W. West and F. Tron, unpublished studies.
[7] K. Alcock, S. S. Grimley, R. B. Healy, J. Kennedy and H. A. C. McKay, *Trans. Faraday Soc.*, 52 (1956) 39.
[8] H. V. A. Briscoe and P. F. Holt, *Inorganic Microanalysis*, Edward Arnold and Co., London, 1950, p. 74.
[9] M. C. Sneed and R. C. Brasted, *Comprehensive Inorganic Chemistry*, Vol. 4, Van Nostrand, Princeton, N. J., 1955, p. 83.
[10] I. Leden, *Z. physik. Chem. (Leipzig)*, A 188 (1941) 160.
[11] R. A. Alberty and E. L. King, *J. Am. Chem. Soc.*, 73 (1951) 517.
[12] L. E. Harris, *Ph.D. Dissertation*, Louisiana State University, 1961.

TITRIMETRIC METHODS FOR THE MICRODETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE*

II. THE SIMULTANEOUS DETERMINATION OF THE HALOGENS IN THE PRESENCE OF EACH OTHER

R. BELCHER AND J. E. FILDES**

Chemistry Department, University of Birmingham (Great Britain)

(Received January 19th, 1961)

INTRODUCTION

Most of the methods proposed for the simultaneous microdetermination of two or more halogens in organic compounds have been based either on lengthy gravimetric determinations[1,2], or have involved separations of the individual halogens. It would seem from the work of MAHR AND OTTERBEIN[3] that the completeness of such halogen separations is rather questionable on the micro scale.

Few titrimetric methods have been reported for the simultaneous determination of halide mixtures. The method of BERG[4] has been reported as unreliable[3]. VOROB'EV[5] has modified this method, but his optimum concentrations for each halogen are not suitable for application on the micro scale. A method has been proposed[6] for the micro determination of the three halogens in the presence of fluorine, and this was considered the most promising for adaptation to the rapid combustion procedure.

The titrimetric procedures recommended previously for the individual halogens were based on this work, but it was still necessary to establish satisfactory absorption conditions for the simultaneous determination of any combination by the rapid combustion method. Moreover, because the method required the use of aliquots for the determination of the individual halogens, the accuracy of the titrations involved had to be studied to ensure that it did not fall below the generally accepted limits.

DISCUSSION

The absorption of halogen combustion products

Earlier work[7] has shown that the principal products of the rapid combustion are carbon dioxide, water vapour, the free halogens and, depending on the original elemental composition of the compound, variable amounts of nitrogen, nitrogen oxides and sulphur oxides together with some nitric and sulphuric acids. Some hydrogen

---

* Part I, *Anal. Chim. Acta*, 24 (1961) 121.

** Present address: Department of Medical Chemistry, Australian National University, Canberra, A.C.T. (Australia).

chloride is formed during the combustion of certain types of chloro compounds, notably those which also contain sulphur. In the selection of suitable absorbents for these gaseous mixtures, any possible side-reactions between the halogens or their absorption products must be considered because of possible interference in the later titrations. For example, halate formation would vitiate a direct halide determination; to prevent this, an efficient reductant must be present in the absorbent.

Hydrogen peroxide as a reductant

Hydrogen peroxide has some advantages as a reductant for the absorption of the combustion products of organic chloro and bromo compounds because the determination can be completed acidimetrically when nitrogen and sulphur are absent[7]; the possibility of a total acidity determination on chloro-bromo materials of this type was considered, but the absorption behaviour of such compounds proved to be variable.

When neutral hydrogen peroxide solution was used as absorbent, chlorine was quantitatively absorbed but bromine gave results which were about 1% low. Hydrogen peroxide was generally satisfactory under alkaline conditions, but in one case there was evidence that some bromate formation had occurred. In this exceptional case mixtures of *p*-bromobenzoic acid and hexachlorobenzene were used and the amounts of elemental chlorine formed were substantially greater than those from most single chloro-bromo compounds. Presumably, either the chlorine reacted preferentially with bromide instead of peroxide, or, under the alkaline conditions some transiently formed hypochlorite reacted with elemental bromine. Either reaction would lead to bromate formation.

Not unexpectedly, similar evidence was obtained of iodate formation (to the extent of 30–50%) when the combustion products from chloro-iodo compounds were absorbed in alkaline peroxide. When, however, these halogenated compounds also contained sulphur, it was found that absorption was quite satisfactory in alkaline peroxide. It would seem that the sulphur dioxide formed during such combustions preferentially reduces all traces of hypohalite ions, before the hydrogen peroxide can assume its dual role as an oxidising and reducing agent in this absorption. Except for this particular application, the use of hydrogen peroxide cannot be recommended for the absorption of the mixed halogen products from the rapid combustion procedure.

Sulphur dioxide as a reductant

Sulphur dioxide under alkaline conditions was found to be the best general reductant for the absorption of any of the halogen combinations. All excess had to be destroyed before the recommended titrimetric finishes were applied. High concentrations of electrolytes, such as sodium sulphate, formed during the neutralisation of the solutions interfered with the end-point in the chlorine determination; this difficulty was eliminated by keeping the alkali strength of the bisulphite absorption medium below 0.1 *N*.

Accuracy of the simultaneous evaluation procedures

In general the percentages of the individual halogens in di- and trihalogenated organic compounds are lower than those in mono-halogenated substances. The percentage of chlorine in organic compounds containing one or both of the other halogens is usually small.

The use of aliquots also reduces the effective concentrations of the various halogens. This difficulty is largely compensated for the iodine and bromine micro determinations by use of the amplification methods of LEIPERT[8] and KOLTHOFF AND YUTZY[9] but there is no analogous amplification procedure available for chlorine.

For the evaluation of the total halogens, the mercuric oxycyanide method of VIEBÖCK[10] appeared to be the most convenient. The chloride can be determined subsequently by means of a comparison titration procedure[6,7] after deduction of the independently determined acid equivalents for the other halogens, but because the titration values for such chloride determinations are usually small, more care is needed during the titration; however, if sufficient sample (10–12 mg) is taken and if the titration is done from a 5-ml microburette (preferably graduated in 0.01-ml intervals) with a 0.005 *N* titrant solution, reasonably satisfactory results (within ±0.30%) can be obtained for the chlorine.

The accuracy of the amplification procedures for bromine and iodine, was found to be well within the usual limits for microanalysis (±0.15%), despite the reduced concentrations in the aliquots. Accordingly, in view of the lower stability of 0.01 *N* solutions of sodium thiosulphate, it was considered advisable to retain the usual 0.02 *N* solution.

Simultaneous determination of chlorine and bromine

With neutral hydrogen peroxide as absorbent, these two halogens were incompletely recovered from organic compounds containing oxygen or nitrogen. An alkaline bisulphite absorbent must, therefore, always be used for such compounds. On the other hand, alkaline peroxide absorbents cause no trouble when sulphur is also present in the compound, whether or not oxygen and nitrogen are present.

With either of these absorbents, chlorine and bromine are recovered as their halides in association with small concentrations of other electrolytes, notably sodium sulphate and nitrate. Two aliquots of the absorption solution are taken: the bromine is determined in one aliquot by the hypochlorite oxidation procedure[9], and the second aliquot neutralised and treated with mercuric oxycyanide to obtain the total halide content. The acid equivalent of the bromide is deducted and the chloride is then determined on the same aliquot by means of the comparison titration method mentioned earlier[6,7].

TABLE I

Compound	*Sample weight in mg*	*% Bromine*		*% Chlorine*	
		found	*calculated*	*found*	*calculated*
p-bromobenzoyl chloride	8.166	36.39	36.40	16.06	16.15
	7.017	36.29		16.11	
p-chlorobromobenzene	6.987	41.72	41.74	18.63	18.53
	6.856	41.58		18.57	
2-bromo-2′-chloroazobenzene	7.867	26.92	27.04	11.90	12.00
2:6-dibromoquinone-4-chlorimide	6.473	53.51	53.39	11.83	11.84
6-chloro-2:4-dibromoaniline	6.870	56.09	56.01	12.39	12.42
p-bromobenzene sulphonyl chloride	6.979	31.20	31.27	13.97	13.87
S-benzyl thiouronium chloride +	3.786				
p-bromobenzoic acid	5.838	39.70	39.75	17.41	17.49

Satisfactory values were obtained on a variety of organic materials; the results given in Table I show that both chlorine and bromine can be determined simultaneously with an accuracy of 0.10%.

Simultaneous determination cf chlorine and iodine

Preliminary experiments showed that peroxide media are unsuitable for the simultaneous absorption of these two halogens. However, alkaline bisulphite solutions were quite satisfactory absorbents, whether or not nitrogen and/or sulphur were present. The titrimetric methods for these two halogens are analogous to those outlined above. Thus, the iodide in one aliquot is determined by the LEIPERT method[8] and chloride plus iodide is determined in a second aliquot by the mercuric oxycyanide method.

TABLE II

Compound	*Sample weight in mg*	*% Chlorine*		*% Iodine*	
		found	*calculated*	*found*	*calculated*
p-chloroiodobenzene	6.449	14.84	14.87	53.09	53.22
	7.185	14.82		53.13	
p-chlorobenzoic acid + *o*-iodobenzoic acid	3.755				
	3.989	22.42	22.65	51.22	51.17
5-chloro-7-iodo-8-hydroxyquinoline	5.144	11.43	11.60	41.70	41.54
p-chloroacetanilide + *o*-iodobenzoic acid	3.079				
	4.457	20.72	20.90	50.98	51.17
p-chloroiodobenzene + benzyl disulphide	6.886				
	3.359	14.63	14.87	53.32	53.22
5-chloro-7-iodo-8-hydroxyquinoline + benzyl disulphide	5.172				
	3.164	11.52	11.60	41.43	41.54

The results on typical test compounds (Table II) show that chlorine and iodine can be determined by this method with an average absolute accuracy of ±0.14%. In view of the relatively small amounts of chlorine present in these compounds and the unfavourable conversion factor for the iodide acid equivalent, this accuracy must be considered satisfactory.

Simultaneous determination of bromine and iodine

Of the micro determinations available for bromine and iodine, those based on iodometric titration of the halates are undoubtedly the best. Attempts were made to exploit a controlled, two-stage iodometric titration of bromate and iodate based on studies by VAN DER MEULEN[11]; the method was satisfactory on pure halate solutions under the recommended acid-buffering conditions, but poor results were obtained when halides were oxidised to halates. The iodate recoveries were quite satisfactory but those for bromate were low. Detailed studies of this reaction have been postponed.

In the recommended method two aliquots are again required, iodine being determined in one by the LEIPERT procedure and the total iodine and bromine in the other by the hypochlorite oxidation procedure; the bromine is then calculated by difference[6].

Alkaline bisulphite solution was again found to be the most suitable absorbent for these two halogens in their various combinations with oxygen, nitrogen and sulphur.

The results, some of which are given in Table III, show that these halogens can be determined simultaneously with an accuracy of ±0.15%.

TABLE III

Compound	*Sample weight in mg*	*% Bromine*		*% Iodine*	
		found	*calculated*	*found*	*calculated*
2:4:6-tribromoiodobenzene	7.376	54.41	54.40	28.81	28.79
	9.122	54.56		28.88	
o-bromoiodobenzene	11.025	28.29	28.25	45.01	44.86
3:5-diiodo-2-hydroxybenzoic acid	5.024				
+ *m*-bromonitrobenzene	4.550	39.42	39.56	64.96	65.09
trimethyl ammonium iodide	4.423				
+ *p*-bromophenacyl bromide	5.616	57.44	57.50	62.97	63.12
7-iodo-8-hydroxyquinoline-5-sulphonic acid	8.554				
+ *p*-bromophenacyl bromide	4.579	57.31	57.50	36.13	36.14

TABLE IV

Compound	*Cl*	*Br*	*I*
1-iodo-2:4-dibromo-6-chlorobenzene			
Halide present (mg)	0.253	1.143	0.907
Halide found (mg)	0.248	1.139	0.905
% theory	8.95	40.33	32.02
% found	8.77	40.18	31.95
p-chloroiodobenzene + p-bromophenacyl bromide			
Halide present (mg)	0.312	1.268	1.118
Halide found (mg)	0.305	1.265	1.119
% theory	14.87	57.50	53.22
% found	14.53	57.33	53.26
o-iodobenzoic acid + p-bromobenzene sulphonyl chloride			
Halide present (mg)	0.285	0.643	1.376
Halide found (mg)	0.281	0.639	1.369
% theory	13.87	31.17	51.17
% found	13.71	31.10	51.00
6-chloro-2:4-dibromoaniline + 7-iodo-8-hydroxyquinoline-5-sulphonic acid			
Halide present (mg)	0.306	1.382	0.785
Halide found (mg)	0.314	1.385	0.786
% theory	12.42	56.01	36.14
% found	12.72	56.16	36.21

Simultaneous determination of chlorine, bromine and iodine

The combustion products were absorbed in alkaline bisulphite solution. The absorption solution had to be divided into three aliquots for the subsequent finishes which involved determination of the iodide by the Leipert method, the total iodide and bromide by the hypochlorite oxidation procedure and the total halide by the method of Vieböck[10]. The chlorine was then determined by the comparison titration method, after deducting the acid equivalents for iodine and bromine. Because all three titrimetric procedures used are unaffected by sulphate and/or nitrate ions, this method is of general applicability.

The three aliquot procedure reduces very considerably the effective halide concentrations in the solutions used for the final titration; but this difficulty can be offset by taking a larger sample weight of the order of 10–12 mg.

The results given in Table IV show that the accuracy for the determinations of bromine and iodine by this method is as good as that reported for their di-halogenated combinations (±0.15%). Not surprisingly, the values for chlorine were the least accurate (±0.30%) though in view of their dependence on the accuracy of the bromine and iodine values, this accuracy must be considered satisfactory.

EXPERIMENTAL

A. The simultaneous determination of chlorine and bromine (in the absence of S)

Procedure

The organic sample (4–8 mg) is burned as described previously[7] and the gaseous products are absorbed in 7–8 ml of 0.1 *N* sodium hydroxide containing 3–5 drops of 35% sodium bisulphite solution. The resulting absorption solution is transferred with the aqueous washings (4 × 3 ml) to a 100-ml lipped, conical flask and boiled for a few minutes with 2–3 drops of M.A.R. 30% hydrogen peroxide to destroy all excess of bisulphite. The solution is cooled, neutralised with 0.1 *N* sulphuric acid in presence of 3 drops of aqueous methyl red indicator solution and then made up to 50 ml in a graduated flask.

Two aliquots of 20 ml are taken for the two halogen determinations.

Bromine determination

The aliquot is placed in a 250-ml stoppered conical flask and analysed by the hypochlorite oxidation procedure (= b ml)[6,9].

Total halide determination

The second aliquot is transferred to a 100-ml conical flask and neutralised in presence of a definite amount of methyl red–methylene blue indicator solution (6–8 drops). After the solution has been treated with 10 ml of 2% mercuric oxycyanide solution (measured accurately), the alkali liberated is titrated with standardised 0.01 *N* sulphuric acid (= a ml).

Chlorine evaluation

In a matched 100-ml conical flask is placed an equal volume of neutral, distilled water and screened indicator solution, together with 10 ml of the mercuric oxycyanide solution and the amount of 0.01 *N* sulphuric acid which is calculated as equivalent to the chloride content ($a - b/3$). Finally, the comparison solution is titrated with 0.005 *N* sodium chloride solution until the colours in the two flasks are again matched.

Blank determination

It is essential to carry out a blank determination on all reagents, preferably using a sample of benzoic acid.

Calculations

Total halide titre: a ml of 0.01 N H_2SO_4
mg of Br^- found in aliquot = b ml of 0.02 N $Na_2S_2O_3 \times 0.26639$
Cl^- acid equivalent = $(a - b/3)$
mg of Cl^- found in aliquot = c ml of 0.005 N NaCl × 0.1773

B. Chlorine and bromine (in the presence of S)

Procedure

The combustion is carried out as before but 7–8 ml of 0.1 *N* sodium hydroxide and 0.5 ml of 30% hydrogen peroxide are used as absorbent. The excess of peroxide is removed by boiling for several minutes in a 100-ml lipped conical flask. The solution is then cooled, neutralised with 0.1 *N* sulphuric acid in presence of aqueous methyl red solution and made up to 50 ml in a standard flask. The two halogen determinations are carried out exactly as described above with two separate aliquots of 20 ml.

C. The simultaneous determination of chlorine and iodine (in the presence or absence of N and/or S) (a general method)

Procedure

The decomposition of the sample and treatment of the absorption solution are exactly as described under (*A*). Two aliquots of 20 ml are then taken.

Determination of iodine

A 20-ml aliquot is placed in a 250-ml stoppered, conical flask, treated with 5 ml of 24% potassium dihydrogen phosphate solution and 1.0–1.5 ml of saturated bromine water and allowed to stand stoppered for 5 min. The destruction of the excess bromine and iodometric titration is as described previously[7].

Total halide determination

After addition of a known amount of screened indicator to the 20-ml aliquot in a 100-ml conical flask, the solution is neutralised and treated with exactly 10 ml of mercuric oxycyanide solution. The released hydroxyl ions are titrated with 0.01 *N* sulphuric acid (= *a* ml). The chloride is evaluated as described under (*A*).

Calculations

Total halide titre = a ml of 0.01 N H_2SO_4
mg of I^- found in aliquot = b ml of 0.02 N $Na_2S_2O_3 \times 0.4231$
Cl^- acid equivalent = $(a - b/3)$
mg of Cl^- found in aliquot = c ml of 0.005 N NaCl × 0.1773

D. The simultaneous determination of bromine and iodine (a general method)

Procedure

7–8 ml of 1 *N* sodium hydroxide containing 3–5 drops of 35% sodium bisulphite solution are used as absorbent. Excess of bisulphite is removed by boiling the resulting solution with 2–3 drops of M.A.R. 30% hydrogen peroxide. The cooled solution is neutralised with 1 *N* phosphoric acid in presence of aqueous methyl red indicator solution and then diluted to 50 ml in a standard flask. Two aliquots of 20 ml are taken for the separate halogen evaluations.

Determination of iodine

The aliquot is placed in a 250-ml stoppered flask treated with 1.0–1.5 ml of saturated bromine water and allowed to stand for 5 min. The subsequent treatment and titration procedure is exactly as described previously. Mg of I^- in aliquot = a ml of 0.02 N $Na_2S_2O_3 \times 0.4231$.

Determination of total iodine and bromine

The 20-ml aliquot is subjected to the hypochlorite oxidation procedure and the total halate is evaluated iodometrically with 0.02 N thiosulphate (b ml).

Calculation

$$\text{mg of Br}^- \text{ found in aliquot} = (b - a) \text{ ml of } 0.02\ N\ \text{Na}_2\text{S}_2\text{O}_3 \times 0.26639.$$

Blank determination

The blank on all reagents must be checked preferably by burning a sample of benzoic acid or sucrose.

E. The simultaneous determination of chlorine, bromine and iodine (in the presence or absence of N and/or S) (a general method)

Procedure

The sample (10–12 mg) is burned as usual and the combustion products are absorbed in 7–8 ml of 0.1 N sodium hydroxide solution containing 3–5 drops of 35% sodium bisulphite solution. After transference to a 100-ml conical flask, excess of bisulphite is destroyed by heating with 1–2 drops of M.A.R. 30% hydrogen peroxide. The cooled solution is neutralised with 0.1 N sulphuric acid, using aqueous methyl red as indicator and then made up to 50 ml in a graduated flask.

Three aliquots of 15 ml are required for the evaluation procedures, two being transferred to 250-ml stoppered, conical flasks and the third to a 100-ml conical flask.

The iodine, total bromine and iodine and total halide determinations are then carried out as already described for the di-halogenated combinations. The chlorine is evaluated by the comparison titration procedure after deducting the acid equivalents for bromine and iodine.

SUMMARY

The absorption of the gaseous combustion products from the rapid, empty tube combustion procedure has been studied. Organic compounds containing any combination of chlorine, bromine, and iodine as well as oxygen, nitrogen and sulphur have been examined. Several methods based on established titration procedures have been developed for the simultaneous microdetermination of any two or all three halogens in organic materials.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'absorption des produits de combustion gazeux et proposent des méthodes titrimétriques pour le microdosage des halogènes dans des substances organiques, par le procédé de combustion rapide.

ZUSAMMENFASSUNG

Beschreibung von Titrationsverfahren zur gleichzeitigen Bestimmung verschiedener Halogene in organischen Substanzen nach Verbrennung mit Sauerstoff im leeren Rohr.

REFERENCES

[1] R. STREBINGER AND L. POLLAK, *Mikrochemie*, 3 (1925) 38.
[2] L. MOSER AND R. MIKSCH, *Mikrochemie, Pregl-Festschrift*, (1929) 293.
[3] C. MAHR AND H. OTTERBEIN, *Z. anal. Chem.*, 140 (1953) 261.
[4] R. BERG, *Z. anal. Chem.*, 69 (1926) 369.
[5] A. S. VOROB'EV, *Zhur. Anal. Khim.*, 12 (1957) 395.
[6] R. BELCHER, A. M. G. MACDONALD AND A. J. NUTTEN, *Mikrochim. Acta*, (1954) 104.
[7] J. E. FILDES AND A. M. G. MACDONALD, *Anal. Chim. Acta*, 24 (1961) 121.
[8] T. LEIPERT, *Mikrochemie, Pregl-Festschrift*, (1929) 266.
[9] I. M. KOLTHOFF AND H. YUTZY, *Ind. Eng. Chem., Anal. Ed.*, 9 (1937) 75.
[10] F. VIEBÖCK, *Ber.*, 35 (1932) 493.
[11] J. H. VAN DER MEULEN, *Chem. Weekblad*, 36 (1939) 414.

ON THE CONCENTRATION AND SEPARATION OF THE TRACE ELEMENTS: Fe, Cu, Zn, Mn, Pb, Mo and Co*

I. ION EXCHANGE METHODS

P. C. VAN ERKELENS

Research Institute for Animal Husbandry, Schoonoord, Utrecht (The Netherlands)

(Received September 28th, 1960)

GENERAL INTRODUCTION

Owing to the increasing demand for rapid results in analytical chemistry, there is a general trend to automation, but at the same time the problems posed become more and more complex. It is thus impossible to do without classical chemical methods and separation techniques, such as ion exchange, solvent extraction and paper chromatography (*cf.* WHITE[1]). This statement is certainly true for trace analysis, where automation is only possible to a very small extent. Only in a limited number of cases (for instance, in some activation methods and in X-ray-fluorescence) is the determination of micro constituents feasible without any classical chemical treatment. Generally, some pretreatment is inevitable, and usually involves concentration of the traces, separation from the macro-constituents and mutual separations. In fact, the development of the separation techniques mentioned above has been greatly stimulated by the importance of trace analysis.

A satisfactory pretreatment should (*1*) concentrate the trace elements to a level at which they can be determined with the accuracy required, (*2*) separate the ions to be analysed from interfering constituents and (*3*) not introduce any compound interfering with the subsequent quantitative determination(s). In some radiochemical separations, a rapid method is required, owing to the short half-lives of the nuclides concerned.

This study is restricted to ion exchange (part I), solvent extraction (part II) and paper chromatography (part III), the results being compared at the end of part III. Elegant solutions of the problem are of course also offered by other methods, but none of these techniques has been so generally accepted as the three mentioned above (*cf.* NORRIS[2]; COOKE[3]). Precipitation must be rejected because of the adsorption-, occlusion- and coprecipitation-effects involved.

A further restriction is made to the ions of iron(III), copper(II), zinc(II), manganese (II), lead(II), molybdate and cobalt(II), while sodium, potassium, calcium, magnesium, phosphate and sulfate ions are considered to be macro-constituents (this classification refers to the situation in the animal field. Application of our results to other fields is of course possible in many cases).

---

* Publication No. 128^a of the Research Institute for Animal Husbandry "Schoonoord", Hoogt 10bis, Utrecht (The Netherlands).

Separations are primarily considered in connection with radiometric determinations of the trace elements, but they are also applicable to other quantitative techniques.

INTRODUCTION TO ION EXCHANGE STUDY

Many new techniques have been developed since RICHES[4] and LUR'E AND FILIPPOVA[5] carried out their experiments on the concentration of trace elements by ion exchange. Apart from more efficient concentration techniques, separations of many inorganic ions have been developed. Reviews have been given by ABRAHAMCZIK[6], KRAUS[7], KUNIN[8,9] and HUDGENS[10].

Three different approaches to the problem can be distinguished*:

(1) Specific ion exchange materials were developed as a parallel to the natural occurring specific metal-complexes. SPECKER *et al.*[11,12] separated iron(III) from other cations and also separated Cu, Zn, Mn, Pb, Co, Ca and Mg from alkali metals; CORNAZ AND DEUEL[13] devised a selective method for iron(III); BAYER[14] obtained a separation of copper and cobalt from zinc, magnesium and barium; KULČICKYJ[15] prepared a selective exchange material for copper. GRIESSBACH[16], TROSTYANSKAYA AND TEVLINA[17] and KUNIN[18] have reviewed the field.

Future developments will be of considerable interest but a solution to our problem on this basis seemed to be rather improbable.

(2) Specific complexing agents, added either to the sample solution, to the eluant, or to the column itself, have been used by many authors and remarkable results have been obtained, *e.g.* in the separation of the rare earth elements. Unfortunately, many complexes interfere with (most of) the subsequent quantitative determinations and thus one of the major advantages of ion exchange is lost. The negatively charged chloro-, bromo-, and fluoro-complexes do not suffer from this disadvantage. A separation of many metals by anion-exchange of their chloro-complexes is possible, as was shown by MOORE AND KRAUS[19]. A review of the extensive literature with Dowex 1 X 10 has been given by KRAUS AND NELSON[20] while results with Wofatit-150 have been reviewed by JENTZSCH[21]. Alcohol–hydrochloric acid mixtures were used by WILKINS *et al.*[22] and by BERG AND TRÜMPER[23]. Unfortunately, with the ashes of biological samples, precipitates of the major constituents are obtained in concentrated solutions of chloride or bromide, thus this method can only be used when the major constituents have been previously removed.

(3) Specific elution of cation-exchange columns with organic solvents has been practised by only a few authors: KEMBER *et al.*[24] separated copper from iron and nickel on Zeocarb 225-H with mixtures of acetone, hydrochloric acid and water. Later these authors[25] recommended Amberlite IR-112. IONESCU *et al.*[26] and BUZNEA *et al.*[27] separated copper and zinc with a similar solvent on the ion-exchange materials KU-2 and R-21.

As this method does not suffer from the disadvantage mentioned above, it was chosen for our experiments. Radioactive tracers were used to facilitate the evaluation of the results.

EXPERIMENTAL

Materials

Choice of the resin. Many resins collapsed in the elution mixtures. Amberlite IR-112

---

* Other ion exchange procedures, *e.g.* electro ion exchange are not considered here.

and Amberlite XE-100 (which according to the manufacturer, Rohm and Haas, Philadelphia (U.S.A.), have the same properties) were the most satisfactory.

Chemicals (not radioactive). Ion exchange water was used, which had a resistivity of at least 3 Megohms. The sulfuric, perchloric, hydrochloric and nitric acids and the ammonia were of "AnalaR" quality and had specific gravities of 1.84, 1.54, 1.18, 1.42 and 0.88 respectively. Nitrates and chlorides were used for the inorganic salts; all reagents, including: sodium pyrophosphate, disodium phosphate, hydrogen peroxide (30%), potassium iodide, hydrazine hydrate, methanol, ethanol, chloroform, acetone (containing 1% water), rubeanic acid and titan yellow, were of reagent grade (either AnalaR or Merck *p.a.*).

Radio-active chemicals. Dilutions from a small volume to 1 ml are given and (between brackets) the amounts of the anion or metal used per experiment (in ml, mμC and μg respectively; for molybdenum, which has a short half life, a medium value for the amount in μg is given).

$^{35}SO_4^{-2}$: 66 μC $Na_2{}^{35}SO_4$ (carrier free) in water, diluted with 0.01 *M* sulfuric acid to 1 ml (0.001–66–0.5).

$^{32}PO_4^{-3}$: 17 μC $Na_2H^{32}PO_4$ (carrier free) in water, diluted with 0.01 *N* phosphoric acid to 1 ml (0.001–17–0.33).

^{59}Fe: 150 μC $^{59}Fe^{+3}$ (33 μg) in 1 *N* hydrochloric acid, diluted with the same acid to 1 ml (0.001–160–0.05).

^{65}Zn: 200 μC $^{65}Zn^{+2}$ (1000 μg) in 1 *N* hydrochloric acid, diluted with the same acid to 1 ml (0.001–200–1).

^{210}Pb: 100 μC $^{210}PbCl_2$ (Radium-D in equilibrium with its decay products) in 2.5 *N* nitric acid, diluted with 9 *N* hydrochloric acid to 7 ml; 210 μg of inactive lead was added, the decay products were removed by anion-exchange through a 5-ml column of Dowex 1 X 10, and the eluate was diluted with 9 *N* hydrochloric acid to 10 ml (0.1–1000–0.22)*.

^{99}Mo: 30 μC $(NH_4)_2{}^{99}MoO_4$ (2500 μg Mo) in water, diluted with water to 1 ml (0.005–150–12.5).

^{54}Mn: 10 μC $^{54}MnCl_2$ (carrier free) in 0.1 *N* hydrochloric acid, diluted with 1 *N* hydrochloric acid to 1 ml (0.01–100–10^{-5}).

^{60}Co: 100 μC $^{60}Co^{+2}$ (10 μg) in 1 *N* nitric acid, diluted with this acid to 1 ml (0.001–100–0.01).

^{89}Sr: 1.25 μC $^{89}SrCl_2$ (carrier free) in 0.1 *N* hydrochloric acid, diluted with *N* hydrochloric acid and 10 mg of Sr as $SrCl_2$ added (0.001–800–10).

^{45}Ca: 0.25 μC $^{45}Ca^{+2}$ (0.2 μg) in 0.1 *N* hydrochloric acid, diluted with 1 *N* hydrochloric acid (0.1–26–0.02).

Apparatus

The *column* consisted of a pyrex glass tube (Fig. 1), fitted with a removable funnel (A) and a fused-in filterplate (B).

Measurement of radio-activity was performed with an end-window GM-tube (Philips 18506), a GM-tube for liquid samples (20th Century Electronics M-6) or a well-type NaI-crystal (Philips PW 4111/W), all combined with a scaler (Philips 4022-32-52). With the crystal sometimes a single-channel analyzer was applied (E.K.A.F. 30301-20102).

---

* For details see ref.[28]

Further apparatus: Beckmann-DU spectrophotometer with flame attachment; Photovolt densitometer with scanning attachment; Beckmann-G pH-meter.

Wet ashings were performed with the apparatus shown in Fig. 2. The pyrex glass tubes (A) were cleaned with sulfuric–chromic acid and then with 3% hydrofluoric acid and were kept under 2 *N* nitric acid. These tubes were heated on the aluminium case (B) over an infrared heater (C), fitted with a mirror (D). Reagents were added through (E) and vapors removed through (F).

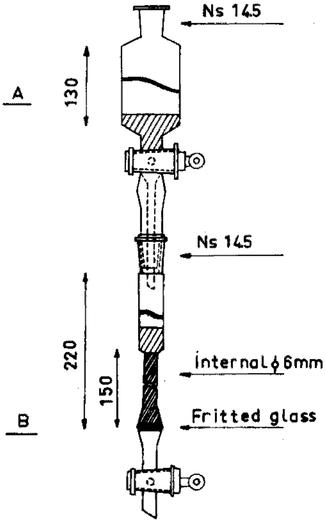


Fig. 1. Ion exchange column.

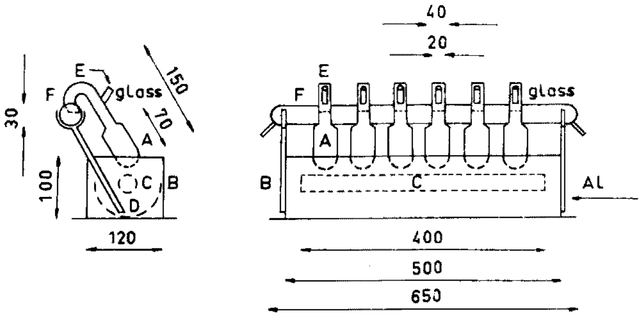


Fig. 2. Ashing apparatus.

Pretreatment of the ion-exchange column and the sample

The ion-exchange material was treated with 0.5 *N* hydrochloric acid and added to the column as a slurry. After a final wash with 10 ml of the 0.5 *N* and acid 10 ml of water, it was ready for use.

The length of the column depended on the amount of cations to be analysed. As the capacity of the wet resin is about 2 milliequivalents per ml and the column can be loaded with cations to about 20% of its capacity, a column of 15 cm (4 ml) is sufficient for 1.6 milliequivalents of cations (or for the ash of 3 g of dry cow liver or 0.8 g of dry grass for instance).

About 1 g of the air-dried sample was ashed with 0.5 ml of sulfuric acid and some nitric acid. Either hydrogen peroxide or perchloric acid was used to clarify the solution. The latter reagent was only added when the mixture contained no coarse particles. After cooling, the solution was diluted with water to 100 ml and added to funnel A of Fig. 1.

Separation technique

The solution of the ash in general had a pH between 1 and 2. Although this value is rather low for sorption by cation-exchange material, it was not increased owing to possible losses of iron(III) at higher pH values. SAMUELSON[29] reported such losses and ascribed them to the formation of colloidal hydroxide*.

Our own experiments, carried out with the ash of 1 g of dry cow liver containing about 300 μg of iron(III) in 100 ml, denoted a loss of: 0, 0.5, 10 and 25% at pH 2.0–2.5, 3.0 and 3.5 respectively.

Sorption was carried out slowly (a flow rate of 10 ml/min/cm^2) in order to obtain homogeneous loading of the column and sharp separations. The last traces of the anions were washed out with 0.01 N hydrochloric acid in order to keep the iron(III) adsorbed on the column.

Before the separation (with the acetone–hydrochloric acid mixtures) the column had to be adjusted to the right acetone concentration with a mixture of acetone and water. Gas bubbles were formed during this treatment (by evaporation of the acetone) but their influence on the efficiency of the separation proved to be small. A cold-water jacket can be used to minimize this effect.

Mixtures of several of the lower esters, alcohols and ketones with aqueous solutions of hydrohalic acids were investigated for the *selective elution*. Acetone–hydrochloric acid was found to be the most satisfactory .Separation into the groups, Fe, Cu, Zn, Pb — Co, Mn — Na, K, Ca, Mg was achieved with acetone–hydrochloric acid mixtures of different composition. The separation of copper and cobalt was the most difficult; separation was obtained more rapidly with a solvent containing acetone–hydrochloric acid–0.01 N potassium iodide (89 : 1 : 10) to which some hydrazine was added to prevent oxidation. The excess of iodide interfered with most subsequent quantitative determinations, hence it had to be oxidised and the iodine boiled out, which made the method more complicated.

With 15-cm columns, 100 ml of acetone–hydrochloric acid was required for each elution; a velocity of 3 to 4 ml/min/cm^2 had to be maintained to achieve sharp separations.

The eluates were collected in "Teflon" dishes and before analysis the acetone was evaporated in a clean atmosphere. The columns were regenerated with 2 N hydrochloric acid, which eluted Na, K, Ca, Sr, Ba and Mg, and were finally washed with water.

---

* The difficulties encountered by HAMM[30] in the sorption of iron(III) were due to the formation of excessive amounts of pyrophosphate in his dry-ashing technique. In wet-ashing only traces of this anion are formed.

Analytical methods

The efficiency of the separation was tested:

(*1*) *With radio-isotopes (see Materials, p. 44).* ^{45}Ca and ^{35}S were measured with the end-window GM-tube, ^{89}Sr and ^{32}P with the M6 GM-tube and the other isotopes with the scintillation counter. With the aid of the single channel analyser several isotopes could be measured simultaneously. All measurements were performed in solution, except for the fractions containing ^{45}Ca or ^{35}S which had to be evaporated in an aluminium dish.

(*2*) *Magnesium* was determined with titan yellow following SANDELL[31]. For *copper* a densitometric method with rubeanic acid was preferred as it allowed the measurement of a large number of samples (parts of the eluates) in one procedure*.

Strips of Whatman No. 1 paper (2.5 × 50 cm) were washed** chromatographically in the descending way with (*a*) 9:1 methanol–hydrochloric acid, (*b*) 9:1 methanol–ammonia and (*c*) 95:5 methanol–water, each washing lasting 24 h. The washed paper had a copper-content of less than 0.01 $\mu g/cm^2$ as was determined by ashing two strips and applying the determination described below.

With a micropipet 0.01 ml of the eluate of the ion-exchange column (or its concentrate***) was placed on a washed paper strip, dried for 2 h, neutralized by placing for 1 h in ammonia vapor and sprayed with a 0.5% solution of rubeanic acid in ethanol on both sides. The spray was of an ordinary type, the current of air being delivered automatically in order to obtain a steady stream of the reagent. The paper strip was moved by hand, but as continuously as possible, before the sprayer at a distance of about 20 cm. This spray was repeated 2 or 3 times. The dried spots were measured with the Photovolt densitometer, a slit of 0.1 × 0.6 cm and a color filter with a maximum at 630 mμ being used. Beer's law was followed from 0.1 to 2.0 μg of copper/0.01 ml.

When standards were placed between the samples the standard deviation was 8% and 4% for the ranges of 0.1–1.0 and 1.0–2.0 μg of copper respectively. Microgram amounts of cobalt and nickel interfered; a reagent-blank had to be subtracted.

(*3*) Finally, *sodium and potassium* were analysed by flame photometry, with which less than 0.004 and 0.2 μg per ml of the respective elements could be determined.

RESULTS

The figures given in Tables I, II and III were all found as a mean of 4 experiments with the ash of 1 g of dry cow liver. Table I shows the separation of cobalt from Cu, Fe, Zn and Pb (manganese behaves similarly to cobalt). It is clear that the mixture 93–1–6 is to be preferred (the acetone contained an additional 1% of water).

Table II shows the separation of cobalt and manganese from calcium (the other

---

* A similar method using either 8-hydroxyquinoline or 7-iodo-8-quinolinol-5-sulfonic acid proved to be suitable for the determination of 0.1 μg of iron in 0.01 ml: a 1% solution of the reagent in ethanol–chloroform (1:1) and a color filter with a maximum at 570 mμ were used. When more than a few mg of sulfate or phosphate was present per ml, the latter reagent is to be preferred (see also ZIEGLER[32]).

** The choice of this purification method was justified in a more extensive consideration of the problem[28].

*** Concentrated in a "Teflon" dish, by evaporation, following the method of THIERS *et al.*[33].

alkaline earth metals behaved similarly and the alkali metals slightly better). It is clear that the mixture 93–5–2 is to be preferred. Table III shows the complete separation with the mixtures selected above.

TABLE I

SEPARATION OF Co FROM Cu, Fe, Zn AND Pb

(Percentages found in the first acetone–hydrochloric acid–water eluant)

Metal	*Eluant*[a]					
	89–1–10[b]	*89–1–10*	*91–1–8*	*92–1–7*	*93–1–6*	*94–1–5*
Co	0.0	0.1	0.3	0.4	1.4[c]	36.5
Cu	99	77	89	96	98	99
Fe, Zn, Pb[d]	99	94	96	98	99	100

[a] Volume percentages of acetone, hydrochloric acid and water respectively.
[b] 10% 0.01 *N* potassium iodide instead of water.
[c] Standard deviation 0.5.
[d] Mean values for the 3 elements are given.

TABLE II

SEPARATION OF Mn AND Co FROM Ca

(Percentages found in the second acetone–hydrochloric acid–water eluant)

Metal	*Eluant*[a]							
	98–1–1	*97–1–2*	*96–2–2*	*95–3–2*	*94–4–2*	*93–5–2*	*92–6–2*	*92–5–0*
Mn	79	76	86	90	93	94	94	96
Co	90	89	93	94	95	97	97	98
Ca	1.5	<1	1.5	1.5	2.0	2.5[b]	3.0	3.5

[a] Volume percentages of acetone, hydrochloric acid and water respectively.
[b] Standard deviation 0.6.

TABLE III

COMPLETE SEPARATION OBTAINED BY CATION-EXCHANGE

(in percentages)

Fraction[a]	*Ion*			*Ion*				*Ion*		*Ion*		
	MoO_4^{-2}	SO_4^{-2}	PO_4^{-3}	Fe^{+3}	Zn^{+2}	Pb^{+2}	Cu^{+2}	Co^{+2}	Mn^{+2}	Ca^{+2}	Mg^{+2}	Sr^{+2}
First effluent	96	96	96	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Washing liquid	2	3	4	0	0	0	0	0	0	0	0	0
93–1–6	<1	<0.5	<0.5	99	99	99	98	1.5	1.0	0	0	0
93–5–2				<0.5	<0.5	<0.5	2.5	97	94	2.5	1.5	2.0
2 *N* HCl and H_2O								<1	4	97	98	98

[a] See procedure below; the 93:7 acetone–water contained none of the ions to an appreciable extent; less than 0.5 or 1.0% of the respective ions was found in the column after the final treatment with 2 *N* hydrochloric acid and water.

CONCLUSIONS

(*1*) The most important separations: Fe–Mn; Fe–Mo; Fe–Co; Cu–Co and Mn–Zn are all established. The trace elements are separated from the macro constituents and concentration is easily accomplished. No interfering complexes are introduced.

(*2*) Further separations of the groups Co–Mn and Fe–Cu–Zn–Pb are possible, *e.g.* by applying anion exchange to the evaporated eluants (concentrated hydrochloric acid).

(*3*) The solvent 93 : 1 : 6 acetone–hydrochloric acid–water (in fact 92–1–7) is better suited for the separation of copper and cobalt than that used by KEMBER *et al.*[24,25] (89 : 1 : 10 of the same constituents), which is however excellent when potassium iodide is added to the water to give a 0.01 *N* solution.

(*4*) The behaviour of the molybdate is in contradiction with the results of SAMUELSON[29].

Recommended procedure

Wet-ash 1 g of air-dried material with 0.5 ml of sulfuric acid and an adequate amount of nitric acid using hydrogen peroxide or perchloric acid if necessary. Cool, and dilute to 100 ml. Fill the column (Fig. 1) with a slurry of Amberlite XE-100 in 0.5 *N* hydrochloric acid and wash with 10 ml of the 0.5 *N* acid and 10 ml of water successively. Adsorb the cations during 40–50 min (molybdenum is found in the eluate) and wash with 50 ml of 0.01 *N* hydrochloric acid during 20 min. Condition with 10 ml of 93 : 7 acetone–water during 5 min and elute Fe, Cu, Zn and Pb with 100 ml of 93 : 1 : 6 acetone–hydrochloric acid–water during 100–125 min. Elute Co and Mn with 100 ml of 97 : 5 : 2 acetone–hydrochloric acid–water over a similar period and regenerate with 20 ml of 2 *N* hydrochloric acid and 20 ml of water (eluting Na, K, Ca, (Sr, Ba) and Mg).

ACKNOWLEDGEMENT

The author's thanks are due to Mrs. G. A. OVEZALL-KLAASEN for valuable technical assistance.

SUMMARY

Cation-exchange materials and selective elution with acetone–hydrochloric acid mixtures are used to concentrate the constituents of biological ashes and to separate them into the groups: MoO_4^{-2}, SO_4^{-2}, PO_4^{-3}; Fe^{+3}, Zn^{+2}, Pb^{+2}, Cu^{+2}; Co^{+2}, Mn^{+2}; Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}.

RÉSUMÉ

Au moyen des échangeurs de cations et par des élutions sélectives, il a été possible de concentrer et de séparer divers constituants des cendres biologiques (Fe, Zn, Cu, Mn, Pb, Mo, Co).

ZUSAMMENFASSUNG

Es wird die Anwendung von Kationen-austauschern und selektive Eluierung mit Aceton–Salzsaure Gemischen beschrieben zur Konzentrierung und Trennung der Bestandteile biologischer Aschen in folgende Grüppen: MoO_4^{-2}, SO_4^{-2}, PO_4^{-3}; Fe^{+3}, Zn^{+2}, Pb^{+2}, Cu^{+2}; Co^{+2}, Mn^{+2}; Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}.

REFERENCES

[1] J. C. WHITE, *U.S.A.E.C., 1st Gatlinburg Symposium on the Use of Analytical Chemistry in Nuclear Reactor Technology*, 1958, p. 240.

[2] J. A. NORRIS, *Symposium on Spectrography, Am. Soc. Testing Materials, Spec. Techn. Publ.*, No. 221 (1957) 33.

[3] W. D. COOKE, in W. G. BERL (ed.), *Physical Methods in Chemical Analysis*, Vol. III, Academic Press, New York, 1956, p. 74.

4 J. P. R. Riches, *Nature*, 158 (1946) 96; *Chem. & Ind. (London)*, (1947) 656.
5 Yu. Yu. Lur'e and N. A. Filippova, *Zavodskaya Lab.*, 13 (1947) 539.
6 E. Abrahamczik, *Mikrochim. Acta*, (1956) 651.
7 K. A. Kraus, in J. H. Yoe and H. J. Koch (eds.), *Symposium on Trace Analysis, New York, 1955*, Wiley, New York, 1957.
8 R. Kunin, *Symposium on Ion-Exchange and Chromatography in Analytical Chemistry*, 1956, *Am. Soc. Testing Materials, Spec. Techn. Publ.*, No. 195 (1958).
9 R. Kunin, F. X. McGarvey and D. Zobian, *Anal. Chem.*, 30 (1958) 681.
10 J. E. Hudgens Jr., in *Symposium on Ion-Exchange and Chromatography in Analytical Chemistry, 1956*, *Am. Soc. Testing Materials, Spec. Techn. Publ.*, No. 195 (1958).
11 H. Specker and H. Hartkamp, *Z. anal. Chem.*, 140 (1953) 167; *Naturwiss.*, 40 (1953) 410.
12 H. Specker, M. Kuchtner and H. Hartkamp, *Z. anal. Chem.*, 141 (1953) 33.
13 J. P. Cornaz and H. Deuel, *Experientia*, 10 (1954) 137.
14 E. Bayer, *Experientia*, 12 (1956) 365; *Chem. Ber.*, 90 (1957) 2325, 2785.
15 I. Kulčickyj, *Collection Czechoslov. Chem. Communs.*, 24 (1959) 3903.
16 R. Griessbach, *Angew. Chem.*, 66 (1954) 17.
17 E. B. Trostyanskaya and A. C. Tevlina, *Zavodskaya Lab.*, 23 (1957) 1042.
18 R. Kunin, *Anal. Chem.*, 32 (5) (1960) 68R.
19 G. E. Moore and K. A. Kraus, *J. Am. Chem. Soc.*, 72 (1950) 5792; 74 (1952) 843; 75 (1953) 1460.
20 K. A. Kraus and F. Nelson, in *Symposium on Ion-Exchange and Chromatography in Analytical Chemistry, 1956*, *Am. Soc. Testing Materials, Spec. Techn. Publ.*, No. 195 (1958).
21 D. Jentzsch, *Z. anal. Chem.*, 152 (1956) 134.
22 D. H. Wilkins, G. E. Smith, J. S. Fritz and D. J. Pietrzyk, *Talanta*, 2 (1959) 392.
23 E. W. Berg and J. T. Trümper, *Anal. Chem.*, 30 (1958) 1827.
24 N. F. Kember, P. S. McDonald and R. A. Wells, *J. Chem. Soc.*, (1955) 2273.
25 N. F. Kember, personal communication (1957).
26 S. Ionescu, I. Negoescu and I. Gainir, *Proc. 2nd U.N. Intern. Conf. Peaceful Uses Atom. Energy, Geneva, 1958*, Vol. 20, p. 123.
27 G. Buznea, O. Costantinescu and D. Topor, *Acad. rep. populare Romîne, Studii cercetări chim.*, 6 (1958) 333.
28 P. C. van Erkelens, *Thesis*, Utrecht, 1960.
29 O. Samuelson, *Ion Exchange in Analytical Chemistry*, Wiley, New York, 1952, pp. 85, 136.
30 R. Hamm, *Mikrochim. Acta*, (1956) 268.
31 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2nd ed., Interscience, New York, 1950, p. 425.
32 M. Ziegler, *Microchim. Acta*, (1957) 215.
33 R. E. Thiers, J. F. Williams and J. H. Yoe, *Anal. Chem.*, 27 (1955) 1725.

ANALYSIS OF ARSENIC-IRON ALLOYS

G. R. DUVAL, R. IRONSIDE AND D. S. RUSSELL

Applied Chemistry Division, National Research Council, Ottawa, Ont. (Canada)

(Received December 11th, 1960)

INTRODUCTION

The most accurate method available for the determination of arsenic is probably the titration of As(III) to As(V) with iodine[1]. Indirect iodimetry, the thiosulphate titration of the iodine liberated by iodide ion reduction of As(V) to As(III), is capable of almost equally good results under proper conditions[2]. In order to apply either method to the analysis of arseniferous materials, it is necessary in the practical case to separate the arsenic from the other constituents of the sample. The most generally applicable method of separation is distillation of the arsenic as $AsCl_3$, but as a considerable number of accurate analyses of specially prepared arsenic compositions was required for an X-ray diffraction study of various arsenides, a more expeditious and convenient method was desirable. Separation of the arsenic by ion-exchange as described by ODENCRANTZ AND RIEMANN[3], makes it possible to avoid the distillation altogether and to use the eluate direct from the resin-bed, after pH adjustment, for the titration of the arsenic. These authors obtained the arsenic in the insecticides, which were the subject of their investigation, as H_3AsO_4 by dissolving the sample in HNO_3 and adding $KBrO_3$ before taking to dryness. On taking up with water and HCl sufficient to give a solution 0.3 N in acid and passing through a column of cation-exchange resin in the H-form, they recovered the As(V) in the eluate, all cations present being retained on the resin. The eluate was then made 4 N in HCl and the As(V) determined by indirect iodimetry with KI and thiosulphate.

The procedure just outlined above was adapted to the analysis of alloys of arsenic with cobalt, copper and nickel. Very satisfactory results were obtained. However, when alloys of arsenic with iron were analyzed by the same method, erratic results were obtained. The sum of the arsenic and iron values was invariably less than 100%. The investigation of this interference and the development of a satisfactory procedure for the rapid analysis of iron-arsenic alloys are the subjects of this report.

EXPERIMENTAL

Reagents

Ion-exchange resin. Most of the work was carried out with Dowex 50 W-X8 Analytical Grade 50–100 mesh, Dow Chemical Company. A few tests were repeated on Amberlite IR 120, Analytical Grade, Rohm and Haas Company.

Arsenic standard solution. A 0.1 N sodium arsenite solution was prepared by dissolving 4.9455 g of A.R. grade As_2O_3 in 40 ml of 1 N NaOH solution and diluting to about 900 ml. The solution was made neutral to litmus with HCl and diluted to 1000 ml. The final solution was standardized against N.B.S. Primary Standard As_2O_3 No. 83b by means of an iodine solution in the usual way.

Iron standard solution 1 ml = 0.005 g Fe. Pure iron wire for Standardizing, A.C.S. reagent, was dissolved in 1:1 HNO_3 and evaporated to dryness. The residue was taken up with HCl and water and diluted to volume. The solution was standardized gravimetrically and volumetrically by the Zimmerman-Reinhardt method.

0.1 N Iodine solution. Prepared in the usual way and standardized against the sodium arsenite solution at frequent intervals, as necessary.

0.1 N Thiosulphate solution. Prepared in the usual way and standardized against the freshly standardized iodine solution.

All other reagents mentioned were of analytical reagent quality.

APPARATUS

The ion-exchange columns were of the conventional pattern made from 10-mm i.d. tubing as shown in Fig. 1. The resin bed was about 10 ml in volume. The 125-ml separatory funnels were marked at 15 ml and 50 ml.

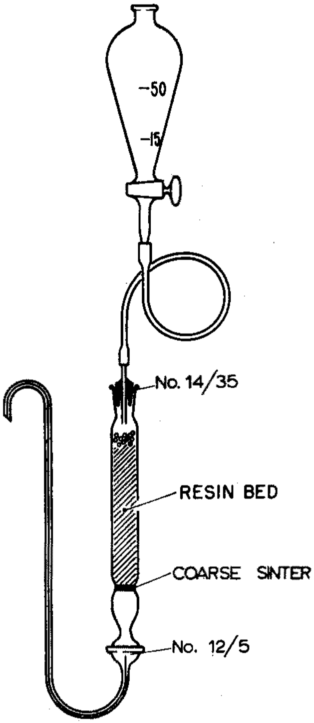


Fig. 1. Convenient rugged column for routine use.

DEVELOPMENT OF METHOD

Procedure I, as applied to alloys of As with Co, Ni or Cu.

About 0.25 g (depending on As content) of the alloy was accurately weighed into a 250-ml beaker and dissolved in 15 ml of 1 : 1 HNO_3, with gentle heating; 10 ml of bromine water was added and the solution evaporated to dryness, finishing on the steam bath. The residue was wetted with about 2 ml of HCl and evaporated again to dryness on the steam bath. This step was repeated once more. The residue was dissolved in 2.5 ml of 1 : 1 HCl and 10 ml of H_2O by gentle warming. When the solution was clear, it was transferred to a separatory funnel marked at 15 ml and 50 ml and made up to a final volume of 50 ml with water. The solution was passed through a column of Dowex 50 W-X8 in the H-form at a rate of approximately 5 ml per min. Three 15-ml portions of 0.3 *N* HCl were then passed through the column, the whole being received in a 500-ml iodine flask. To the nearly 100 ml of eluate in the iodine flask, 60 ml of conc. HCl was added. The solution was cooled to room temperature in a cold water bath and 1 g of $NaHCO_3$ was added in small portions while swirling the solution in the flask. 3 g of KI was added and dissolved and the mixture let stand for 5 min. The iodine was then titrated with 0.1 *N* sodium thiosulphate without added indicator, the final disappearance of the iodine colour being observed against a white background.

The cobalt, copper or nickel on the column was then removed with three 50-ml portions of 2 *N* HCl and determined in any convenient manner.

When As–Fe alloys were treated by this procedure, the iron was determined by precipitation with ammonia and ignition to Fe_2O_3. Reasonable concordance of results was obtained for the iron, but the values for the arsenic were erratic and the sum of Fe plus As was significantly less than 100%. This suggested that the As was not completely removed from the column by the washing sequence of *Procedure I* above. With additional washes of 0.3 *N* HCl, more arsenic(V) was in fact recovered from the column containing the Fe(III), but complete recovery was not obtained even after more than 300 ml of 0.3 *N* HCl had been passed through the column (Fig. 2). Further, the Fe(III) had by then begun to near the break-through point.

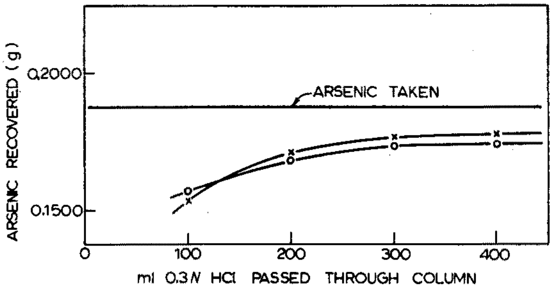


Fig. 2. Recovery of arsenic from synthetic samples containing iron(III) and arsenic(V).

In order to establish that this failure of the H_3AsO_4 to pass freely through the resin bed was due to the presence of Fe(III), synthetic samples were prepared from the solutions described above. 50 ml of the standard 0.1 *N* sodium arsenite was heated with 15 ml of HNO_3 and bromine water was added till in excess (about 20 ml); 20 ml of the standard ferric iron solution was then added and the whole evaporated to dryness, finishing on the steam bath. After twice moistening with HCl and redrying on the steam bath, the residue was taken up with 2.50 ml of 1 : 1 HCl and about 20 ml of water and transferred to the calibrated separatory funnel where it was finally made to 50 ml with water. This gave a solution of As(V) and Fe(III) in 0.3 *N* HCl which was treated by *Procedure I* above. Low values were obtained for the arsenic (Table I).

TABLE I

RECOVERY OF ARSENIC FROM SYNTHETIC SAMPLES OF Fe(III) AND As(V) WITH STANDARD 100-ml WASH

Fe(III) in sample *g*	*As(V) in sample* *g*	*As found* *g*
0.0800	0.1874	0.1657
0.0800	0.1874	0.1625
0.0800	0.1874	0.1538
0.0800	0.1874	0.1571
0.0800	0.1874	0.1532
0.0800	0.1874	0.1550

TABLE II

RECOVERY OF As(III) AND OF As(V) FROM COLUMNS CONTAINING Fe(II) AND Fe(III) WITH STANDARD 100-ml WASH

Fe(II) present in column *g*	*Fe(III) present in column* *g*	*As present as As(III)* *g*	*As found* *g*	*As present as As(V)* *g*	*As found* *g*
0.0800		0.1875	0.1875	0.1875	0.1866
0.0800		0.1875	0.1876	0.1875	0.1874
0.0844		0.1875	0.1875	0.1875	0.1873
0.0844		0.1875	0.1874	0.1875	0.1873
	0.0800	0.1875	0.1875	0.1875	0.1736
	0.0800	0.1875	0.1872	0.1875	0.1721
	0.0800	0.1875	0.1875	0.1875	0.1760
	0.0800	0.1875	0.1872	0.1875	0.1740

TABLE III

RECOVERY OF ARSENIC AND IRON FROM SYNTHETIC SAMPLES CONTAINING Fe(II) AND As(III) WITH STANDARD 100-ml WASH

Fe(II) in sample *g*	*As(III) in sample* *g*	*As found* *g*	*Fe found* *g*	*Total Recovery* %
0.0844	0.1875	0.1875	0.0843	99.96
0.0844	0.0937	0.0935	0.0845	99.94
0.0844	0.0562	0.0564	0.0844	100.14
0.0844	0.0375	0.0377	0.0844	100.16
0.0844	0.0188	0.0189	0.0844	100.09

Similar standard solutions containing As(V) and Fe(III) were tried on Amberlite 120 and again, incomplete recovery of the arsenic was obtained.

Since the method described as *Procedure I* above had succeeded with cobalt, nickel and copper, all divalent ions, the effect of reducing the iron to the divalent state was next tried.

Table II shows the behaviour of As(V) and As(III) on columns in which iron had previously been deposited. Columns containing Fe(II) permitted complete recovery of both As(III) and As(V); columns containing Fe(III) permitted complete recovery of As(III) but showed the expected incomplete recovery of As(V).

Known samples were then prepared containing As(III) and Fe(II) by reducing the standard solution of ferric iron with SO_2 and adding the arsenic(III) as standard arsenite solution. After evaporation to dryness and adjustment to 0.3 *N* as before these solutions were then treated by *Procedure I*. Complete recovery of the As(III) was obtained (Table III).

Thus, it is clear that the ion-exchange separation of pentavalent arsenic from iron is not possible if the iron is in the trivalent state. This specific separation, As(V) from Fe(III), is recommended in a recent text-book of inorganic analysis[4], the paper of ODENCRANTZ AND RIEMANN being cited as source. In fact, ODENCRANTZ AND RIEMANN did not claim to separate As(V) from Fe(III), the only ions mentioned being Cu, Ca, Pb and Mg.

This interference by trivalent iron and not by divalent iron prompted the inclusion of two other trivalent ions, Al(III) and Nd(III) in the synthetic test samples. No interference with the ion-exchange separation in 0.3 *N* HCl solutions of As(V) (as H_3AsO_4) from Al(III) or Nd(III) was observed.

From the foregoing, the following relatively rapid procedure was developed for the analysis of iron–arsenic alloys.

Recommended procedure for arsenic–iron alloys

Weigh accurately into a 250-ml beaker sufficient sample to provide about 125 mg of As. Dissolve in 15 ml of 1 : 1 HNO_3 by gentle heating. Evaporate the solution to dryness finishing on the steam-bath. Wet the residue with about 2 ml of conc. HCl and again evaporate to dryness on the steam-bath. Repeat this treatment once more. Dissolve the residue in 5 ml of 3 *N* HCl and sufficient water to make the volume about 40 ml. Chill the solution in ice and water and saturate with SO_2 gas from a cylinder (Note 1). Allow the closely covered beaker to warm up to room temperature (about 1 h) and expel the excess SO_2 by boiling the solution on a hot plate, taking care to maintain the volume by adding water as necessary (Note 2). No odour of SO_2 should be detectable above the solution at this point. Cool the solution and wash into the dropping funnel adjusting the final volume to 50 ml. Pass the solution through the column of Dowex 50 at a rate of about 5 ml per min, receiving the percolate in a 500-ml iodine flask. Pass 50 ml of 0.3 *N* HCl through the column in at least three portions so as to wash the funnel adequately into the column. To the 100 ml of solution in the iodine flask add 4 g of $NaHCO_3$ a little at a time (Note 3). Observing the solution against a white background, titrate with 0.1 *N* iodine solution to the first detectable yellow tinge (Note 4).

Elute the iron from the column with about 150 ml of 2 *N* hydrochloric acid and determine it gravimetrically or by the Zimmermann-Reinhardt titration.

Notes on the method

(*1*) Sulfur dioxide is the preferred reductant as it avoids the introduction of any other cation into the solution. However, in order to insure the complete reduction of the arsenic(V) the SO_2 concentration in the solution must be maintained at saturation[5]. By chilling the solution to 0° before saturating with SO_2, saturation is maintained as the temperature rises.

(*2*) If the volume is allowed to diminish appreciably, the increase in HCl concentration gives rise to the danger of loss of $AsCl_3$.

(*3*) This amount of $NaHCO_3$ provides for the neutralization of the HCl present and about 1.5 g in excess to maintain the desirable alkalinity for the titration.

(*4*) If there is any doubt as to the completeness of reduction, the percolate may be oxidized by taking to dryness with HNO_3 and bromine and the arsenic determined as in *Procedure I* above.

This procedure has been applied to numerous alloys of arsenic with iron and a sampling of the results obtained is given in Table IV.

TABLE IV

TYPICAL RESULTS OBTAINED BY RECOMMENDED PROCEDURE

Sample number	*Arsenic* %	*Iron* %	*Cobalt* %	*Nickel* %	*Total* %
15	72.10	27.92			100.02
	72.14	27.88			100.02
FM-21	57.04	42.81			99.85
	57.12	42.83			99.95
CAF-3	76.12	9.82	13.94		99.88
	76.16	9.85	13.98		99.99
NF-7	79.29	15.55		5.16	100.00
	79.33	15.54		5.19	100.06

SUMMARY

Contrary to expectation and to published recommendation it is not possible to separate Fe(III) quantitatively from As(V) on a cation-exchange resin. Ion-exchange can however be utilised for the analytical separation of iron and arsenic if the iron is reduced to Fe(II) before the mixture is passed through the cation-exchange column.

RÉSUMÉ

Une méthode est proposée pour l'analyse rapide des alliages arsenic-fer. L'arsenic est séparé au moyen d'un échangeur de cations, après avoir préalablement réduit le fer à l'état bivalent, la séparation fer(III) et arsenic(V) n'étant pas possible.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur raschen Analyse von Eisen-Arsen Legierungen. Die Trennung erfolgt mit einem Kationenaustauscher; Eisen muss in zweiwertiger Form vorliegen.

REFERENCES

[1] W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. I. HOFFMANN, *Inorganic Quantitative Analysis*, Wiley, New York, 1953, p. 266.

[2] I. M. KOLTHOFF AND R. BELCHER, *Volumetric Analysis*, Vol. III, Interscience, New York, 1957, p. 316.

[3] J. ODENCRANTZ AND W. RIEMANN, *Anal. Chem.*, 22 (1950) 1066.

[4] G. CHARLOT AND D. BEZIER, transl. by R. C. MURRAY, *Quantitative Inorganic Analysis*, Wiley, New York, 1957, p. 338.

[5] R. GROS, *Bull. soc. chim. France*, 8 (1941) 521.

CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, USING AQUEOUS ETHANOL AS SOLVENT

II

ERIC JOHN SINGH AND ARUN K. DEY

Chemical Laboratories, University of Allahabad (India)

(Received November 4th, 1960)

Complex formation plays an important role in the chromatographic separation of ions as pointed out by POLLARD *et al.*[1,2], who observed that it was essential for the separation of metal ions on filter paper. We have already studied[3-5] the separation of several ions in the presence of varying concentrations of different complexing agents using aqueous alcohol as solvent. In this paper we describe the separation of metallic ions of the same group in the presence of oxalate, tartrate and citrate.

EXPERIMENTAL

Solutions of the sulphates of iron, aluminium, chromium, zinc, manganese, cobalt and nickel, and of the nitrates of barium, strontium, calcium, magnesium, sodium, potassium and ammonium, and of potassium oxalate, sodium citrate and sodium tartrate were prepared using reagent grade chemicals and standardised by the usual methods. Ascending filter paper strip chromatography as described by GAGE, DOUGLASS AND WENDER[6] was applied. Various concentrations of ethanol were examined but only those which gave good results are recorded here. Series of mixtures were prepared by taking equal concentrations of metals and adding varying quantities

TABLE I

SEPARATION OF METALLIC IONS

No.	*% of ethanol used as solvent*	*Systems investigated (sequence of separation without adding complexing agents)*	*Complexing agent added (equivalents up to which separation is possible)*			*Sequence of separation (Complexing agent added)*
			$C_2O_4^{-2}$	*Tart.$^{-2}$*	*Cit.$^{-3}$*	
1	75	Cr–Fe–Al	—	0.35	0.48	Cr–Fe–Al
			0.16 to 0.20	—	—	Al–Cr–Fe
2	50	Co–Mn–Zn	—	0.32	0.32	Co–Mn–Zn
3	75	Zn, Ni, Mn	0.20	0.96	0.40	Only Zn is separated
4	90	Ca–Sr–Ba	0.20	0.32	0.32	Ca–Sr–Ba
5	90	Mg–NH_4–K	0.32	0.32	0.32	Mg–NH_4–K
6	90	Mg–NH_4–Na	0.32	0.20	0.32	Mg–NH_4–Na

of complexing agent, the total volume being kept constant. The ratio of the total molar concentration of metals to the concentration of the complexing agent is mentioned below. The mixtures were spotted on Whatman filter paper No. 1 and the chromatograms run at constant temperature in a temperature controlled room at 27°. The time allowed for the movement of ions was 1.5 h. In ternary mixtures, the final concentration of each of the metal ions was 0.033 *M*.

Various mixtures [Fe(III), Al(III) and Cr(III); Zn, Mn(II), Ni and Co; Ba, Sr and Ca; Mg, Na, K and NH_4] were studied and some of the results are summarised in Table I.

It can be noted that the separation of Fe(III), Al(III) and Cr(III) ions is possible up to the addition of 0.35 and 0.48 equivalents of tartrate and citrate respectively as complexing agent; the sequence of separation is Cr(III)-Fe(III)-Al(III). The sequence of separation becomes Al(III)-Cr(III)-Fe(III) with the addition of 0.16 to 0.20 equivalents of oxalate. The complexing agent was added to the solvent by previous workers but in the present work it was added to the solution of the metal itself. In general, for good separation of the ions, the addition of a complexing agent is essential, otherwise in many cases no satisfactory separation can be obtained. With higher concentrations of the complexing agent than those mentioned above the separation is not possible.

SUMMARY

The separation of Al, Cr(III), Fe(III), Zn, Mn(II), Ni, Co, Ba, Sr, Ca, Mg, Na, K and NH_4 in ternary mixtures with or without the addition of complexing agents (oxalate, tartrate and citrate) by filter paper strip chromatography has been studied with aqueous ethanol as solvent.

RÉSUMÉ

Les auteurs ont effectué une étude sur la séparation des ions Al, Cr(III), Fe(III), Zn, Mn, Ni, Co, Ba, Sr, Ca, Mg, Na, K et NH_4, en présence d'oxalate, de tartrate et de citrate, par chromatographie sur papier, en utilisant des mélanges eau-éthanol comme solvants.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung von Al, Cr(III), Fe(III), Zn, Mn, Ni, Co, Ba, Sr, Ca, Mg, Na, K und NH_4 in Gegenwart von Oxalat, Tartrat und Citrat durch Papierchromatographie mit einem Wasser-Alkohol Gemisch als Lösungsmittel.

REFERENCES

[1] F. H. Pollard, I. I. M. Elbeih and J. F. W. McOmie, *Discussions Faraday Soc.*, 7 (1949) 183.
[2] F. H. Pollard, J. F. W. McOmie and I. I. M. Elbeih, *J. Chem. Soc.*, (1951) 466, 470.
[3] E. J. Singh and A. K. Dey, *J. Indian Chem. Soc.*, 37 (1960) 235.
[4] E. J. Singh and A. K. Dey, *J. Chromatog.*, 3 (1960) 146.
[5] E. J. Singh and A. K. Dey, *Anal. Chim. Acta*, 24 (1961) 444.
[6] Th. B. Gage, C. D. Douglass and S. H. Wender, *J. Chem. Educ.*, 27 (1950) 159.

MICRODOSAGE COLORIMÉTRIQUE DU BORE DANS LES ACIERS PAR L'EMPLOI DU RÉACTIF À L'AZOMÉTHINE H

R. CAPELLE

Paris (France)

(Reçu le 4 octobre 1960)

Le bore introduit dans l'acier en vue d'augmenter la trempabilité se partage au moins entre les trois formes différentes suivantes dont l'existence est très généralement admise: une forme combinée avec l'oxygène, une forme combinée avec l'azote, le reste enfin se trouvant soit à l'état dissous (état souvent dit libre), soit sous forme de combinaison métallique (borure). Il est souhaitable pour le métallurgiste de pouvoir connaître les proportions de chacune de ces trois formes de bore.

Toutes les techniques publiées procèdent en fait de la manière suivante. Après attaque de l'acier par un acide minéral étendu, généralement de l'acide sulfurique ou chlorhydrique à 20% ou 25% en volumes, une partie du bore passe en solution dans l'acide, et il reste une partie insoluble qui est séparée par filtration. On a donc été amené empiriquement à faire une distinction entre le bore soluble et le bore insoluble dans les acides.

Il résulte de l'ensemble des données de la littérature et d'études personnelles, que si le bore insoluble correspond assez sensiblement à la fraction du bore qui est combinée à l'azote, en revanche il n'apparaît qu'une corrélation assez vague entre la teneur en bore soluble et l'augmentation de la trempabilité de l'acier.

Lors de l'attaque de l'acier par un acide étendu, en effet, passent en solution non seulement le bore métallurgiquement actif du point de vue de la trempabilité (bore libre ou à l'état de borure), mais encore le bore oxydé, qui est sans action sur la trempabilité, tandis que seul le bore combiné à l'azote reste inattaqué.

Dans ces conditions, la teneur en bore soluble doit permettre une appréciation d'autant plus significative de l'amélioration de la trempabilité d'un acier que la proportion de bore oxydé est plus faible. C'est pourquoi il a été souvent constaté que la teneur en bore soluble se montre assez étroitement liée à l'amélioration de la trempabilité dans le cas des aciers où l'addition de bore a été faite après désoxydation très poussée du bain (calmage préalable à l'aluminium et au titane en particulier), alors qu'au contraire il n'existe pratiquement aucune corrélation entre la teneur en bore soluble et l'amélioration de trempabilité, si la désoxydation préalable du bain n'a pu être poussée aussi loin, par exemple si le calmage a été fait au moyen de siliciure de calcium.

DOSAGE DU BORE SOLUBLE ET DU BORE INSOLUBLE DANS LES ACIERS

Le réactif à l'azométhine H[1] a été appliqué au dosage du bore dans les aciers. Il est nécessaire que soient analytiquement éliminés différents éléments gênants dont la présence dans les aciers doit être envisagée comme possible, sinon constante. Outre le fer, on a donc admis que doivent être séparés les éléments suivants: aluminium, titane, vanadium, zirconium, chrome, nickel, molybdène, manganèse, cuivre, etc.

Méthode proposée

Microdosage du bore dans les aciers après extraction des ions gênants au moyen d'une résine échangeuse d'ions.

Domaine d'application

La présente méthode de dosage convient pour les aciers dont la teneur en bore est inférieure à 0.0500%, c'est-à-dire ceux dans lesquels le bore est introduit pour augmenter la trempabilité. La méthode pourrait cependant être adaptée pour des aciers ayant une teneur en bore plus élevée, soit en prenant une prise d'essai plus faible, soit en prélevant un volume partiel plus faible de liqueur.

Principe

Après mise en solution de l'acier par de l'acide sulfurique au quart, la liqueur obtenue est filtrée pour séparer le "bore insoluble" du "bore soluble" dans les acides.

Dosage du bore soluble. Le filtrat qui contient le bore soluble est étendu avec de l'eau distillée, puis passé sur une résine échangeuse d'ions du type sulfonique, afin d'éliminer certains ions gênants dont le fer, l'aluminium, le titane, le vanadium, le zirconium, etc. Après lavage de la résine, le filtrat est neutralisé, puis concentré. Après filtration sur papier pour éliminer les dernières traces d'éléments gênants restés en solution, la liqueur est complétée à un volume connu. Une partie aliquote de liqueur est prélevée et après addition d'acétate d'ammonium, le pH est amené à 5.2 avec de l'acide acétique. Le réactif à l'azométhine H est alors ajouté et la coloration est développée à l'obscurité.

Dosage du bore insoluble. Le filtre qui retient le bore insoluble est incinéré en creuset de platine; puis le résidu est fondu avec du carbonate de sodium. Le culot de fusion est remis en solution par de l'acide sulfurique au quart, et le dosage est continué comme pour le bore "soluble".

Réactifs

(*1*) Acide sulfurique ($d = 1.83$) au quart (1 : 3); (*2*) Solution d'hydroxyde de sodium 2 N; (*3*) Acide acétique pur cristallisable; (*4*) Solution d'acétate d'ammonium à 500 g/l; (*5*) Réactif à l'azométhine H*: azométhine H, 6 g, acide ascorbique, 20 g, eau q.s.p., 1 l; (*6*) Eau distillée obtenue au moyen d'un alambic en cuivre étamé ou mieux d'un appareil distillatoire en silice; à l'exclusion d'eau désionisée obtenue par passage d'eau ordinaire sur des colonnes de résines cationique et anionique; (*7*) Solution titrée de bore: *Solution A* (1 ml = 1 mg de bore). Peser 5.7135 g d'acide borique cristallisé,

---

* L'azométhine H étant légèrement hygroscopique doit être conservé en flacons émeri soigneusement bouchés. Il est néanmoins nécessaire de sécher le produit de temps à autre, à l'étuve chauffée à 100–110°, pendant deux heures, et de garder si possible les flacons contenant le produit dans une enceinte (cage vitrée, dessiccateur, etc.) dans laquelle on aura placé une substance desséchante (acide sulfurique concentré, actigel, etc.). Moyennant cette recommandation les résultats obtenus sont très réguliers et reproductibles.

L'azométhine H doit être pesé très exactement.

séché au dessiccateur à acide sulfurique. Dissoudre le produit dans de l'eau distillée et compléter à 1 l en fiole jaugée avec de l'eau distillée. *Solution B* (1 ml = 0.01 mg de bore). Diluer au centième la solution précédente avec de l'eau distillée en s'aidant d'une fiole jaugée; (*8*) Résine cationique Dowex 50, X4, 100–200* (Voir remarques ci-dessous concernant l'emploi de la résine); (*9*) Carbonate de sodium pur anhydre.

Matériel

(*1*) Appareil pour l'attaque comprenant un ballon de 70 ml avec réfrigérant ascendant à eau relié au ballon par raccord émeri. Le ballon est muni d'un entonnoir à robinet placé latéralement (Fig. 1). Dans cet appareil le ballon, le tube intérieur du réfrigérant, le raccord émeri et l'entonnoir latéral sont obligatoirement en silice; (*2*) Béchers en silice de 600 ml; (*3*) Béchers de 100 ml (de préférence en silice); (*4*) Entonnoirs pour filtres de 70 mm (de préférence en silice); (*5*) Fioles jaugées de 100 ml (de préférence en silice); (*6*) Extracteur en plexiglass (Fig. 1)**; (*7*) Filtres en papier sans cendres (bande bleue) de 70 mm. Avant emploi les filtres seront lavés plusieurs fois avec de l'acide sulfurique à 5% en volume, puis, à fond, à l'eau distillée; (*8*) Creusets en platine de 30 ml.

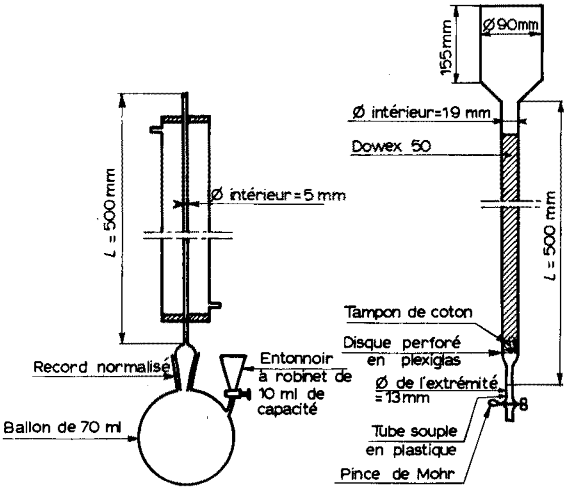


Fig. 1. Appareil pour l'attaque (à gauche). Le ballon, le tube intérieur du réfrigérant, le raccord normalisé et l'entonnoir sont en silice. La gaine extérieure du réfrigérant à eau est en verre ordinaire. Extracteur en plexiglas (à droite).

Remarques très importantes

(*a*) Faire très attention aux pertes possibles en bore par entraînement à la vapeur d'eau, en milieu acide.

---

* Ou tout autre résine du type sulfonique équivalente à la précédente, ayant même capacité d'échange, même granulométrie, même pourcentage de "cross-linkage", etc.

** Les extracteurs que nous avons utilisés ont été construits par les Etablissements Jahan, 24, Rue des Gravilliers, Paris (3°).

(*b*) à froid (températures inférieures à 30°), les solutions et liqueurs peuvent être manipulées sans inconvénient dans des récipients en verre boro-silicaté. Par contre, à chaud il est absolument indispensable d'opérer dans du matériel en silice. Dès 45°, le verre boro-silicaté introduit des quantités de bore incompatibles avec l'ordre de grandeur des quantités à doser. C'est ainsi que l'acide sulfurique ($d = 1.83$) dilué au cinquième servant à l'attaque sera à préparer obligatoirement dans du matériel en silice.

(*c*) Bien que la verrerie boro-silicatée puisse être utilisée pour les manipulations effectuées à froid, comme il est précisé ci-dessus, il n'est pas moins vrai que l'emploi d'un matériel entièrement en silice (ou à défaut en verre ordinaire exempt de bore) reste cependant beaucoup plus recommandable.

Mode opératoire

Prise d'essai: 1 g ± 0.001.

(*1*) Introduire la prise d'essai dans le ballon en silice de 70 ml de l'appareil d'attaque. Mettre en place le réfrigérant (également en silice). Par l'entonnoir latéral à robinet du ballon introduire 5 ml d'acide sulfurique ($d = 1.83$) dilué au quart. Fermer le robinet. Chauffer au bain-marie à 80° pour attaquer le métal. Après attaque complète, laisser refroidir la solution. Rincer le réfrigérant avec quelques ml d'eau distillée, puis l'enlever. Filtrer la liqueur d'attaque sur un filtre sans cendres (bande bleue) de 70 mm. Recevoir le filtrat dans un bécher en silice de 600 ml. Rincer le ballon et laver le filtre avec environ 150 ml d'eau distillée. Compléter le volume du filtrat à 250 ml avec de l'eau distillée et mettre de côté le filtre qui retient le "bore insoluble".

(A) Dosage du "bore soluble"

(*2*) Verser avec précaution la liqueur précédente dans l'entonnoir d'un extracteur en plexiglass préalablement garni avec 150 ml* de Dowex 50, X4, 100–200. Disposer un bécher en silice de 600 ml sous l'extracteur, et ouvrir le robinet inférieur de l'extracteur de façon que le débit d'écoulement soit de 2–3 ml/min.

(*3*) Quand les dernières portions de liqueur surnageante affleurent le niveau supérieur de la colonne de résine, verser immédiatement avec précaution dans l'entonnoir de l'extracteur 250 ml d'eau distillée et maintenir le débit d'écoulement à la même valeur que précédemment.

(*4*) Après écoulement complet des eaux de lavage, enlever le bécher, et neutraliser le filtrat en versant goutte à goutte une solution d'hydroxyde de sodium 2 *N* (essai à la touche en présence de phénolphtaléine ou d'un papier de tournesol).

(*5*) Evaporer doucement la liqueur (éviter l'ébullition) sur plaque chauffante et concentrer jusqu'à un volume de 50 ml environ. Laisser refroidir.

(*6*) Filtrer la liqueur sur filtre sans cendres (bande bleue) de 70 mm, l'entonnoir qui porte le filtre étant disposé au-dessus d'une fiole jaugée de 100 ml. Rincer le bécher et laver le filtre avec le minimum d'eau distillée. Compléter le volume du filtrat à 100 ml avec de l'eau distillée. Agiter.

(*7*) Prélever 50 ml de cette liqueur et introduire ce volume dans un bécher de 100 ml. Ajouter 10 ml de solution d'acétate d'ammonium à 500 g/l. Ajuster le pH à 5.2 avec

---

* Ce qui correspond très sensiblement à 110 grammes de résine humide essorée à fond sur entonnoir de Buchner.

de l'acide acétique. (Contrôle à l'électrode de verre). Transvaser la liqueur dans une fiole jaugée de 100 ml. Rincer le bécher avec quelques ml d'eau distillée. Ajouter 10 ml de réactif à l'azométhine H et compléter le volume à 100 ml avec de l'eau distillée. Agiter. Laisser la coloration se développer pendant 18 h à l'obscurité, à une température de 20° ± 5°*.

(*8*) Mesurer la coloration, à 415 mμ, par rapport à celle du terme zéro de la gamme d'étalonnage.

Tracé de la courbe d'étalonnage du "bore soluble"

Dans une série de béchers en silice de 600 ml verser 5 ml d'acide sulfurique ($d = 1.83$) au quart, puis: 0, 1, 2, 3, 4, 5 . . . 10 ml de solution B de bore, correspondant à: 0, 0.0010, 0.0020, 0.0030, 0.0040, 0.0050 . . . 0.0100% de bore dans l'acier pour une prise d'essai d'un gramme. Diluer chacune des solutions à 250 ml avec de l'eau distillée et passer chacune d'elles à travers 150 ml de Dowex 50, X4, 100–200 contenu dans un extracteur identique à celui utilisé pour les essais. Puis continuer comme pour les essais et mesurer la coloration de chacun des termes, à 415 mμ, par rapport à celle du terme zéro de la gamme.

(B) Dosage du "bore insoluble"

(*2'*) Sécher le filtre qui a été mis de côté après séparation du "bore soluble", puis l'introduire dans un creuset en platine de 30 ml. Ajouter sur le filtre 0.500 g de carbonate de sodium anhydre. Chauffer avec précaution pour incinérer le filtre, puis augmenter progressivement le chauffage pour fondre la masse et atteindre une température de 800–1000° qu'on maintient pendant 15 à 20 min. Remuer doucement le creuset pendant ce temps en le tenant avec une pince. Retirer le creuset du feu et le laisser refroidir.

(*3'*) Placer le creuset dans un bécher en silice de 600 ml. Ajouter 10 à 15 ml d'eau distillée et 5 ml d'acide sulfurique ($d = 1.83$) au quart. Laisser digérer pendant quelques heures (une nuit si possible). Enlever le creuset à l'aide d'une pince et le laver soigneusement à l'eau distillée. Diluer la solution à 250 ml avec de l'eau distillée.

(*4'*) Passer la solution à travers 150 ml de Dowex 50, X4, 100–200 dans les mêmes conditions que pour le dosage du bore soluble; laver la résine avec 250 ml d'eau distillée. Neutraliser le filtrat avec la solution d'hydroxyde de sodium 2 *N*. Concentrer la liqueur à 50 ml environ; filtrer et continuer comme pour le dosage du "bore soluble". Mesurer la coloration finale par rapport au terme zéro de la gamme d'étalonnage.

Tracé de la courbe d'étalonnage du "bore insoluble"

Dans une série de creusets en platine de 30 ml introduire 0, 1, 2, 3, 4 . . . 10 ml de solution B et correspondant à: 0, 0.0010, 0.0020, 0.0030, 0.0040 . . . 0.0100% de "bore insoluble" pour une prise d'essai d'un gramme d'acier. Ajouter 1 goutte de solution d'hydroxyde de sodium 2 *N* (2). Evaporer à sec au bain-marie. Puis introduire dans chaque creuset un filtre de 70 mm identique à celui utilisé pour les essais. Ajouter 0.500 g de carbonate de sodium anhydre. Chauffer avec précaution pour incinérer le filtre, puis

---

* L'intensité de la coloration est assez sensible à l'influence de la température. Si les conditions précédentes ne peuvent être respectées, il vaut mieux tracer une nouvelle gamme d'étalonnage dont la coloration aura été développée à la même température que celle des essais à mesurer.

augmenter progressivement le chauffage pour fondre la masse et atteindre une température de 800°–1000° qu'on maintient pendant 15 à 20 min environ. Remuer doucement le creuset en le tenant avec une pince. Puis continuer comme pour le dosage du "bore insoluble" (voir ci-dessus). Développer finalement la coloration dans les mêmes conditions que celles indiquées précédemment, et mesurer la coloration de chacun des termes de la gamme, à 415 mμ, par rapport à celle du terme zéro.

Remarque. En principe les deux courbes d'étalonnage du "bore soluble" et du "bore insoluble" sont identiques.

Remarques importantes concernant l'emploi de la résine

(*1*) Si la résine est neuve, elle doit subir avant tout emploi le traitement préliminaire suivant qui est très important:

(*a*) *Épuisement par de l'acide chlorhydrique au tiers.* Pour 500 g de résine humide placée dans un bécher de 2 l, ajouter 700 ml environ d'acide chlorhydrique (d = 1.19) au tiers. Agiter mécaniquement pendant une heure, puis laisser reposer. Décanter l'acide et le remplacer par un même volume d'eau distillée. Agiter mécaniquement pendant quelques minutes pour laver la résine, puis laisser reposer et éliminer l'eau de lavage par décantation. Ajouter à nouveau 700 ml environ d'acide chlorhydrique (d = 1.19) au tiers et continuer comme ci-dessus. Recommencer 15 fois de suite ce même traitement, au bout duquel l'acide doit être presque incolore.

(*b*) *Traitement alterné au chlorure de sodium et à l'acide chlorhydrique.* Après le dernier lavage à l'eau distillée, verser sur la résine un litre environ de solution de chlorure de sodium à 30 g/l. Agiter mécaniquement pendant une heure. Puis laisser reposer. Vider par décantation la solution qui surnage et la remplacer par un litre d'eau distillée. Agiter mécaniquement pendant quelques minutes pour laver la résine. Puis laisser reposer. Décanter l'eau qui surnage et la remplacer par un litre environ d'acide chlorhydrique (d = 1.19) au tiers. Agiter mécaniquement pendant une heure, puis laisser reposer. Vider par décantation l'acide qui surnage et le remplacer par un litre environ d'eau distillée. Agiter mécaniquement pendant quelques minutes pour laver la résine, puis laisser reposer. Recommencer deux autres fois le traitement alterné précédent au chlorure de sodium et à l'acide chlorhydrique. En fin d'opération et avant emploi la résine est lavée à fond à l'eau distillée, puis filtrée et essorée à la trompe sur entonnoir de Buchner.

(*2*) *Garnissage de l'extracteur.* (*a*) Dans une éprouvette de 250 ml contenant 100 ml d'eau distillée introduire par petites portions successives une quantité de résine telle que son volume soit sensiblement égal à 150 ml (ce qui correspond à 110 g environ de résine humide).

(*b*) Faire passer peu à peu ce volume de résine dans l'extracteur en l'entraînant par un courant d'eau distillée. Faire très attention à ne pas entraîner de bulles d'air au sein de la masse de résine introduite dans l'extracteur.

(*c*) Quand la totalité de la résine a été introduite dans l'extracteur, attendre quelques minutes pour que la résine se tasse légèrement et prenne sa place. Puis éliminer l'excès d'eau qui surnage en ouvrant légèrement le robinet d'écoulement de l'extracteur. Arrêter l'écoulement quand le niveau de l'eau dépasse de 5 mm environ le niveau supérieur du lit de résine.

(*3*) *Régénération de la résine après emploi.* Bien que cette opération puisse être effectuée directement dans l'extracteur, il est cependant préférable de la réaliser dans un bécher en opérant de la façon suivante: (*a*) Verser 30 ml environ d'eau distillée dans le réservoir de l'extracteur. Secouer l'appareil pour mettre en suspension la partie supérieure du lit de résine. En renversant rapidement le réservoir au-dessus d'un bécher de 2 l, on fait passer dans ce dernier une partie de la résine contenue dans l'extracteur. On répète plusieurs fois de suite cette opération et on arrive ainsi à faire passer peu à peu toute la résine dans le bécher.

(*b*) Quand ce résultat est atteint, laisser la résine se déposer pendant quelques minutes, puis décanter avec précaution l'eau qui surnage.

(*c*) Verser sur la résine environ 500 ml d'acide chlorhydrique ($d = 1.19$) au tiers. Agiter mécaniquement pendant 30 min, puis arrêter l'agitation et laisser la résine se déposer. Décanter l'acide qui surnage et le remplacer par un même volume d'acide chlorhydrique ($d = 1.19$) au tiers. Recommencer 6 fois de suite ce même traitement.

(*d*) Après quoi la résine est lavée à fond six fois de suite avec 500 ml d'eau distillée à chaque fois. On opère comme pour le traitement à l'acide en remplaçant simplement celui-ci par de l'eau distillée. La résine traitée est prête pour un nouvel usage.

(*4*) Si la résine n'est pas utilisée immédiatement elle doit être conservée à l'état humide et de préférence sous de l'eau distillée rendue légèrement chlorhydrique. Comme la plupart des résines cationiques cèdent au bout d'un certain temps une petite quantité de matière soluble colorée en jaune dans l'eau distillée, il est alors nécessaire de relaver à fond la résine à l'acide chlorhydrique au tiers, puis à l'eau distillée au moment de s'en servir.

A titre d'exemple, la Fig. 2 représente la courbe d'étalonnage obtenue pour le bore soluble et le bore insoluble, avec le Spectrophotomètre Jean et Constant, en cuves de 2 cm, à $\lambda = 415$ mμ.

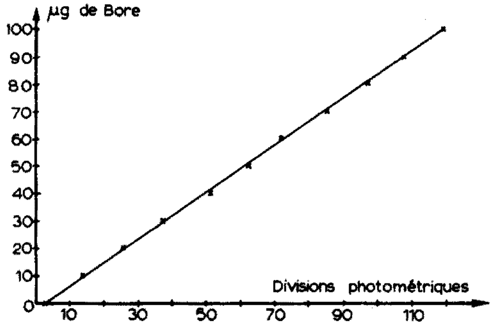


Fig. 2. Courbe d'étalonnage avec le réactif à l'azométhine H.

Vérification de la méthode

La vérification de la méthode a été effectuée d'une part à l'aide de divers aciers-étalons, dont la teneur en bore total avait été déterminée par spectrographie, les uns d'origine anglaise de la série des British Chemical Standards (BCS), les autres d'origine américaine, étalonnés par le Bureau of Standards.

L'ensemble des résultats obtenus avec ces aciers-étalons se trouve résumé dans le Tableau I.

TABLEAU I

	Teneur en bore total annoncée (%)	*Résultats obtenus avec la méthode proposée*		
		Teneur en bore soluble (%)	*Teneur en bore insoluble (%)*	*Teneur en bore total (%)*
Acier-étalon (BCS)				
SS11	0.010	0.0063	0.0039	0.0102
SS12	0.004	0.0032	0.0006	0.0038
SS13	0.002	0.0024	0.0004	0.0028
		0.0023	0.0005	0.0028
SS14	0.009	0.0089	0.0009	0.0098
		0.0082	néant	0.0082
		0.0085 (moyenne)	0.0005 (moyenne)	0.0090 (moyenne)
SS15	<0.001	0.0006	0.0002	0.0008
SS16	0.005	0.0025	0.0025	0.0050
SS17	<0.001	0.0007	0.0008	0.0015
		0.0006	0.0010	0.0016
Acier-étalon (Bureau of Standards)				
425	0.0006	0.0003	0.0005	0.0008
426	0.0011	0.0008	0.0005	0.0013
428	0.0059	0.0036	0.0020	0.0056
429	0.0091	0.0050	0.0044	0.0094
430	0.0190	0.0116	0.0072	0.0188

TABLEAU II

Acier No.	*Mode d'introduction du bore dans l'acier*	*Dosage du bore par la quinalizarine*			*Dosage du bore par l'azométhine H*		
		Bore soluble (%)	*Bore insoluble (%)*	*Bore total (%)*	*Bore soluble (%)*	*Bore insoluble (%)*	*Bore total (%)*
1301-2	Grainal 79	0.0020	0.0005	0.0025	0.0017	0.0006	0.0023
1301-3	d°	0.0015	0.0005	0.0020	0.0014	0.0003	0.0017
1301-4	d°	0.0013	0.0002	0.0015	0.0012	0.0003	0.0015
1301-5	d°	0.0005	0.0003	0.0008	0.0004	0.0003	0.0007
1328	d°	0.0018	0.0001	0.0019	0.0021	0.0001	0.0022
1331	d°	0.0013	0.0002	0.0015	0.0012	0.0001	0.0013
1340	d°	0.0023	0.0001	0.0024	0.0023	0.0001	0.0024
1383-2	d°	0.0013	0.0005	0.0018	0.0010	0.0002	0.0012
1383-3	d°	0.0005	0.0004	0.0009	0.0004	0.0002	0.0006
1383-4	d°	0.0001	0.0003	0.0004	0.0002	0.0004	0.0006
1383-5	d°	0.0001	0.0003	0.0004	0.0002	0.0003	0.0005
1388-2	Manganèse bore à 20%	0.0035	0.0044	0.0079	0.0032	0.0036	0.0068
1388-4	d°	0.0015	0.0020	0.0035	0.0015	0.0022	0.0037
1397-2	Grainal 79	0.0010	traces	0.0010	0.0010	0.0002	0.0012
1400-2	d°	0.0010	0.0002	0.0012	0.0010	0.0003	0.0013
1421-4	Laitier boraté	0.0028	0.0022	0.0050	0.0020	0.0027	0.0047

Ce tableau montre que la teneur en bore total trouvée pour les divers aciers-étalons avec la technique proposée correspond en général bien à celle qui est annoncé sur les certificats d'analyse.

Seuls les résultats trouvés pour les deux aciers-étalons anglais SS13 et SS17 semblent quelque peu élevés; puisque pour des teneurs en bore total annoncées respectivement comme égale à 0.002% et inférieure à 0.001%, il a été trouvé, par des essais faits en double: 0.0028% et 0.0015%; encore faut-il noter que les certificats d'analyse indiquent seulement les unités de la troisième décimale, et ne font nullement mention de la quatrième.

D'autre part, la vérification de la méthode a également été effectuée à l'aide d'un certain nombre d'aciers dont la teneur en bore soluble et en bore insoluble avait été déterminée par la quinalizarine. Les résultats obtenus figurent dans le Tableau II.

A signaler, que les résultats trouvés par la méthode à la quinalizarine d'une part, et par la méthode à l'azométhine H d'autre part, ont été obtenus en partant de prélèvements effectués en deux points différents d'une même barre d'acier laminé. Les différences observées entre les chiffres obtenus par chacune des deux méthodes n'ont rien d'exagéré: elles sont du même ordre de grandeur que les différences normalement observées dans la répartition du bore dans la masse d'acier. On peut donc admettre que les chiffres trouvés par l'une ou l'autre des deux méthodes sont pratiquement identiques.

Remarques

(*1*) *Autre technique envisagée.* Une technique ne faisant pas appel à séparation sur résine échangeuse d'ions avait été envisagée. Son principe était le suivant: après mise en solution de l'acier par de l'acide sulfurique ($d = 1.83$) dilué au cinquième, puis filtration, le filtrat est d'abord électrolysé dans une cellule à cathode de mercure, en silice. Puis, après traitement de la liqueur d'électrolyse par la dithizone et par l'oxine, le "bore soluble" est finalement dosé par le réactif à l'azométhine H.

Pour le "bore insoluble", après incinération du filtre qui retient le "bore insoluble", puis fusion avec du carbonate de sodium, et remise en solution acide, le traitement à la dithizone et à l'oxine est effectué, et finalement le "bore insoluble" est dosé par la réaction à l'azométhine H.

Cette technique s'est montrée à l'expérience assez peu fidèle, une perte de 20% en bore pouvant être observée. Pour cette raison elle ne sera pas développée ici.

(*2*) *Remarques concernant l'emploi de la verrerie boro-silicatée et le chauffage des solutions contenant du bore.* Au cours de la présente étude des essais ont été effectués pour déterminer dans quelle mesure la verrerie boro-silicatée peut être utilisée, et, si par chauffage des solutions contenant du bore, il se produit réellement une perte en bore entraînée par la vapeur d'eau.

Les conclusions de ces observations sont les suivantes: A froid, en milieu acide même concentré, le verre boro-silicaté ne cède pas de bore aux solutions. Du matériel en verre boro-silicaté peut donc être envisagé pour la manipulation à froid des solutions. Par contre, par chauffage, il introduit dès 45–50° des quantités de bore absolument prohibitives (plusieurs microgrammes). Du matériel en silice ou en verre rigoureusement exempt de bore doit donc être recommandé. Par chauffage, une quantité assez importante de bore peut être perdue par entraînement à la vapeur d'eau si le pH de la solution boratée que l'on évapore est franchement acide (pH < 3.7); en revanche l'expérience a montré que la perte est nulle si le pH est > 4.9. Il est donc conseillé de ne chauffer les solutions acides contenant du bore que dans des récipients en silice et sous réfrigérant à reflux.

DISCUSSION

(*1*) La distinction classique du bore soluble et du bore insoluble étant loin d'être satisfaisante pour l'aciériste, il a été recherché une voie tendant à doser sélectivement la partie du bore soluble qui est combinée au métal sous forme de borure, seul actif sur la trempabilité, à l'exclusion du bore sous forme d'oxyde.

Le dosage des inclusions par la méthode à l'iode alcoolique[2-6] pourrait à la rigueur donner une mesure du bore oxydé, qu'il suffirait de retrancher du chiffre trouvé pour le bore soluble (bore des borures, plus bore oxydé) pour obtenir le bore à l'état libre ou à l'état de borure. Il résulte en fait de plusieurs mesures effectuées par cette méthode de séparation, le bore étant dosé par la méthode à l'azométhine H, que des résultats nets ne peuvent pas être retenus comme valables pour mesurer le bore actif.

(*2*) Des essais tendant à dégager, par attaque en milieu acide et anhydre le bore des borures (bore actif) à l'état de borane, se sont soldés par un échec; ce n'est pas surprenant, vu l'extrême aisance avec laquelle les boranes s'oxydent et s'hydrolysent.

Force est donc d'en rester à la notion classique de bore soluble et de bore insoluble, avec toute l'imprécision que comporte le premier quant à l'action de ce bore sur la trempabilité de l'acier.

RÉSUMÉ

Le dosage du bore soluble et du bore insoluble dans les aciers est traité au moyen d'une séparation préalable sur résine échangeuse d'ions, suivie de l'application de la réaction colorimétrique à l'azométhine H.

SUMMARY

A method is described for the determination of soluble and insoluble boron in steels based on preliminary separation with ion-exchange resin and colorimetric determination by means of azomethine-H.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von löslichem und unlöslichem Bor in Stählen durch Behandlung mit einem Austauscherharz und colorimetrische Bestimmung des Reaktionsproduktes mit Azomethin H.

BIBLIOGRAPHIE

[1] R. Capelle, *Anal. Chim. Acta*, 24 (1961) 555.

[2] F. Willems, *Arch. Eisenhüttenw.*, 1 (1927) 655.

[3] T. E. Rooney et A. G. Stapleton, *J. Iron Steel Inst., (London)*, 131 (1935) 1, 249–54.

[4] P. G. Ward, *J. Inst. Metals*, 37 (1927) 89.

[5] T. E. Rooney, W. W. Stevenson et T. Raine, *Seventh Report on the Heterogeneity of Steel Ingots*, Iron Steel Inst., Spec. Rept. No. 16 (1937) 109, 112, 117.

[6] J. E. Garside, T. E. Rooney et J. J. J. Belli, *J. Iron Steel Inst., (London)*, 185 (1957) 1, 95.

CRITICAL FACTORS IN THE COLORIMETRIC DETERMINATION OF SILICA*

G. J. S. GOVETT

Geology Division of the Earth Sciences Branch, Research Council of Alberta, Edmonton (Canada)

(Received November 21st, 1960)

INTRODUCTION

During the course of a comprehensive research programme aimed at a better understanding of the controlling factors in the dissolution of natural silicates and the formation of secondary products in aqueous solution under normal temperature and pressure conditions, it became necessary to undertake a large number of determinations for both soluble and total silica. A brief survey of the literature revealed a large number of analytical methods based upon the formation of silicomolybdate complexes. As routine analyses proceeded, it became clear that lack of understanding of controlling factors and the mechanism of formation of these complexes prevented any adaptation of the method to suit the circumstances and still obtain reliable results. Accordingly, an intensive search of the available literature was undertaken, accompanied by detailed experimental work, to determine the optimum operating conditions. Standard commercial reagent-grade chemicals were used throughout, and hence no great accuracy is claimed for the results presented; moreover, the substance of this paper is only a side-issue of a much more comprehensive project. Inasmuch as geological work is now making increasing demands upon chemical and physical techniques, it is felt desirable to record the results obtained.

Silica in aqueous solution

Silica in "solution" exists in a number of different forms: in the pH range 1–8 and in concentrations less than about 110–140 p.p.m., the stable form is the monomeric molecule $Si(OH)_4$[1]; above pH 9 the solubility of amorphous silica rises sharply due to the formation of the silicate ion, thus:

$$Si(OH)_4 + (OH)^- \rightarrow SiO(OH)_3^- + H_2O$$

The silicate ion will exist in solution together with $Si(OH)_4$. At very low pH solubility of silica may be increased by acids, such as HF to form silicofluoride anions. In solutions more concentrated than 110–140 p.p.m. SiO_2, polymerization occurs giving rise to polysilicic acids, and ultimately a colloid, gel, or a precipitate. Polymerization of two $Si(OH)_4$ molecules may lead to the formation of dimeric silicic acid where each of the two silicons is surrounded octahedrally by 6 OH ions; further polymerization will lead to the formation of trimeric silicic acid, whilst condensation and elimination of water will lead to branched-chain and ring polymers[2]. Continued increase in size will give rise to the formation of colloidal particles and, under suitable conditions, a gel.

---

* Research Council of Alberta, Contribution no. 144.

ILER[2] states that monosilicic acid is most stable at a pH of 1–3, and least stable between pH 5 and 6. According to ALEXANDER[3] monosilicic acid in 0.1 M solution at 2° polymerizes almost instantly at pH 6, and is most stable at pH 3.2; the polymerization below pH 3.2 is a third order reaction, giving linear or openly branched polysilicic acid chains, whilst above pH 3.2 the polymerization is a second order reaction and depolymerization-polymerization rearrangement of polymers gives rise to cyclic or cross linked polymers. ALEXANDER[3] also stated polysilicic acid diluted to 40 p.p.m. depolymerizes at room temperature at a pH of 1.0, but the rate is slow compared with the rate of polymerization. The rate of polymerization at room temperature of polysilicic acid is approximately proportional to the square of the concentration of silica[4].

Reaction of silica with molybdic acid

DIENERT AND WANDENBULCKE[5] in 1923, and HARMON[6] in 1927, showed that only "soluble" silica will react with molybdic acid to form a yellow silicomolybdate complex, and that colloidal silica is unreactive. This reaction has been the basis of very many colorimetric methods for the quantitative determination of silica, either by measurements of the intensity of the yellow silicomolybdate complex or the reduced blue complex. This reaction was further clarified by WEITZ, FRANK AND SCHUCHARD[7] who demonstrated that monomeric silicic acid will react completely in about 75 sec, disilicic acid in about 10 min, whilst higher polymers take even longer. This reaction has been confirmed by ALEXANDER[8] and RICHARDSON AND WADDAMS[9] although, as seen later, it is only true under certain experimental conditions.

In 1952 STRICKLAND[10] published a series of three papers in which he demonstrated that there exists at least two forms of silicomolybdic acid in solution, both having the formula $H_4(SiMo_{12}O_{40})$ and both yellow in color, but having quite different light-absorbances. The stable form was designated as α-silicomolybdic acid which is the predominant form in solutions acidified with up to 1.5 equiv. of acid per mole MoO_4^{-2}. The other form, β-silicomolybdic acid, is formed in quantity when more than 1.5 equiv. of acid per mole MoO_4^{-2} is present, and the yellow complex has an absorbance of about twice that of α-complex. The β-acid changes spontaneously to the α-form, a change which is hastened when the pH is raised above 2.5, by heating, and in the presence of excess electrolyte. The change is retarded, even under the latter conditions, when molybdate is present in excess of that required to react with silica. STRICKLAND[10] suggested that the β-acid is an unstable polymer of the α-acid, the spontaneous β to α change having the characteristics of an irreversible depolymerization.

Published analytical methods for the determination of silica have been based upon the formation of the β-acid, although there have been two recent methods[11,12] based upon the formation of the α-complex. Despite STRICKLAND's[10] detailed investigation of the conditions of formation of silicomolybdic acids, his work has been largely ignored or apparently misinterpreted. Most published data place great emphasis upon the pH and give scant attention to the ratio and type of acid to molybdate, nor to the particular species of molybdate added to the reaction — although both of these factors are important as STRICKLAND's[10] work showed. Data are presented in the following paragraphs which confirm or expand some of STRICKLAND's[10] fundamental observations; the conditions to be considered when designing an analytical method for silica to suit particular circumstances are also outlined.

EXPERIMENTAL RESULTS

It has been asserted by RINGBOM *et al.*[11] that pH is the major variable determining the development of the yellow silicomolybdate complexes; these writers published an absorbance–pH curve showing a plateau of constant absorbance values between pH 2 and 4 which they equated with formation of α-silicomolybdic acid. The initial experiments were designed to compare the results obtained by RINGBOM *et al.*, who used monochloracetic acid as the acidifying agency, with results obtained when using sulphuric acid. The same concentration of ammonium molybdate recommended by RINGBOM *et al.* was used, and the change in absorbance was measured at intervals of 2 min to 96 h over the pH range 0.5 to 5.5.

Method

An aliquot of standard SiO_2 solution in a 50-ml volumetric flask was acidified with a suitable mixture of either sulphuric acid and ammonium hydroxide, or mono-

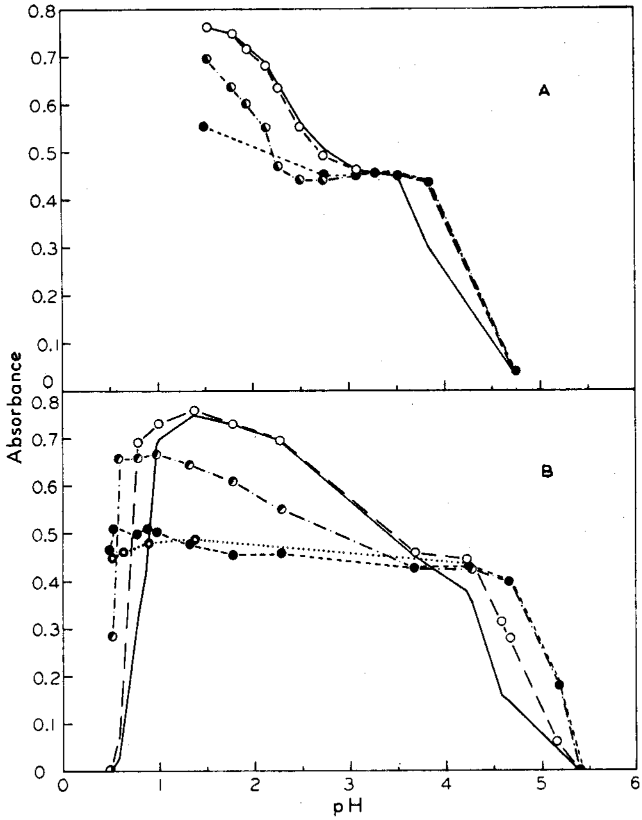


Fig. 1. Variation of absorbance of silicomolybdate solutions due to pH and time, and comparison of results obtained with monochloracetic acid and sulphuric acid. A, solutions acidified by mixtures of 2 *M* monochloracetic acid and ammonium hydroxide. B, solutions acidified by mixtures of 1 *N* sulphuric acid and ammonium hydroxide. ——— absorbance measured 2 min after start of reaction; ○ — — ○ absorbance measured 10 min after start of reaction; ◐·—·—◐ absorbance measured 5 h after start of reaction; ● - - - - ● absorbance measured 24 h after start of reaction; ◎ ...... ◎ absorbance measured 48 h after start of reaction.

chloracetic acid and ammonium hydroxide. This was diluted to about 35 ml with distilled water; 10 ml of ammonium molybdate 0.2 *M* with respect to MoO_4^{-2} was added (0.04 *M* strength in reaction), and then diluted to volume with distilled water. The reaction was timed from the addition of ammonium molybdate solution, and the absorbance in this series of experiments measured on a Beckman Model B spectrophotometer at a wavelength of 400 mμ.

Some of the results obtained in this comparative series of experiments are recorded in Fig. 1. The main conclusions to be noted at this stage are:

1. When sulphuric acid is used, maximum absorbance is attained within 10 min over the pH range 0.75 to 4.25 (within 2 min at pH 1.75 to 2.25), thereafter decreasing to the same constant value over a period of 48 h, the decrease being most rapid in the more acid range. Above pH 4.75 values increase with time, very slowly above pH 5.0; below pH 0.75 absorbance either continues to increase up to 5 h and then decreases or, at pH 0.5, continues to increase with time.

The maximum values (corresponding to the formation of predominantly β-silicomolybdic acid) occur between pH 1.0 and 2.5, but with no well defined plateau of constant values; the low plateau observed after 10-min reaction time between pH 3.75 and 4.25 probably corresponds to the formation of dominant α-silicomolybdic acid, all higher values at higher acidities tending to decrease to this level, and all lower values at lower acidities tending to increase to this level.

2. Whereas the same general pattern is discernible when monochloracetic acid is used, there is one important difference: the whole curve is shifted towards lower pH values compared with that obtained with sulphuric acid. Moreover, the rates of formation and decay of the complexes at any particular pH differ compared with the sulphuric acid reaction.

Clearly, pH is not entirely responsible in determining the formation of the silicomolybdate complexes; the acidifying agency itself appears to affect the rate of formation of the complexes, and the relative amounts of α- and β-silicomolybdic acid at any particular pH. The remainder of the experiments described and reported below were aimed at understanding better the factors controlling the formation of these complexes. All these subsequent experiments were performed with a Beckman Model DU spectrophotometer at a wavelength of 400 mμ and constant slit width of 0.04 mμ.

Variation in absorbance depending upon concentration of ammonium molybdate, and pH of stock solution of ammonium molybdate

The effect upon the rate of formation and the relative amounts of α- and β-silicomolybdic acid over a pH range of 0.5 to about 5.0 caused by variation in the concentration of molybdate and the pH of the stock solution, was investigated for concentrations of ammonium molybdate from 0.01 *M* to 0.1 *M* with respect to MoO_4^{-2} in the reaction. It was found that unless the pH of the stock solution was kept above about 7.0, reproducible results were not obtained using ammonium molybdate solutions more than 12 h old. Solutions which had a pH of greater than 7.0 (pH adjusted with NaOH) gave reproducible results for at least one week after preparation.

Partial results of these determinations are shown in Fig. 2 from which it is clear that the most useful concentration is 0.06 *M* with respect to MoO_4^{-2} in reaction, the stock solution being at a pH of about 7.0. With this concentration of ammonium molybdate, complete reaction within two minutes to give the same absorbance value occurs over the pH range of 1.1 to 1.6 (corresponding to the addition of 5.0 to 2.7 equiv. of acid per mole MoO_4^{-2}), whilst complete reaction to give a constant absorbance in 10 min occurs in the pH range 0.9 to 1.6 (corresponding to 6.7 to 2.7 equiv. of acid per mole MoO_4^{-2}). Variation in concentration of molybdate when considered in relation to pH exerts a considerable effect upon the absolute value of absorbance attained in a given time and, whereas the pH of the stock solution affects the absolute value, its greatest effect is upon the rate of formation of the silicomolybdate complexes.

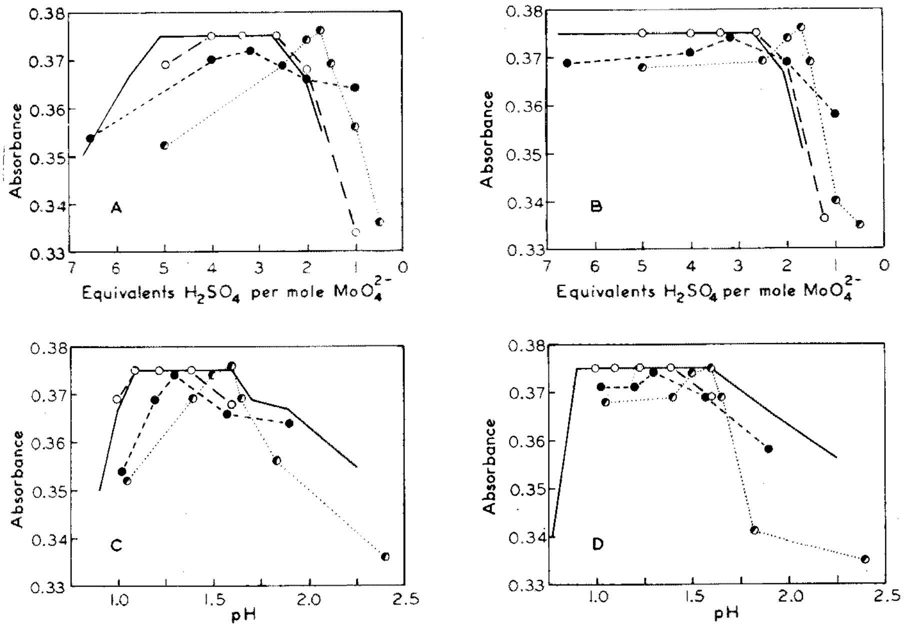


Fig. 2. Comparison of the variation in absorbance of silicomolybdate solutions with acidity and time due to variation in the concentration of molybdate. Sulphuric acid is used to acidify, and the results are shown as a function of both pH and equivalents of acid per mole MoO_4^{-2}. ——— 0.06 *M* with respect to MoO_4^{-2} in reaction. Stock solution 0.3 *M*, pH 7.3; ○— — ○ 0.06 *M* with respect to MoO_4^{-2} in reaction. Stock solution 0.3 *M*, pH 6.2; ◐......◐ 0.04 *M* with respect to MoO_4^{-2} in reaction. Stock solution 0.2 *M*, pH 5.2; ●— — — —● 0.03 *M* with respect to MoO_4^{-2} in reaction. Stock solution 0.5 *M*, pH 5.2. A, absorbance measured 2 min after start of reaction. B, absorbance measured 10 min after start of reaction. C, absorbance measured 2 min after start of reaction. D, absorbance measured 10 min after start of reaction.

Variation in absorbance due to sulphuric and hydrochloric acids

Two series of experiments over a pH range of 0.5 to 5.5 were run using 1 *N* H_2SO_4 and 1 *N* HCl respectively. In such series various strengths ammonium molybdate were used, and results for 0.3 *M* stock solution at pH 7.3 (0.06 *M* in reaction with respect to MoO_4^{-2}) are recorded in Figs. 3 and 4. In Fig. 3, where absorbance is plotted against pH, it is seen that the absorbance at any pH is greater for the HCl series compared with the H_2SO_4 series, a difference which becomes more prominent below a pH of 1.0. Although the pattern of the curve for H_2SO_4 and HCl is the same, the plateau of high values for HCl is displaced to the acid side compared with H_2SO_4.

In Fig. 4 the absorbance is plotted against equiv. of acid per mole MoO_4^{-2}. The absorbance after 10 min shows no significant difference between HCl and H_2SO_4 until more than 1.5 equiv. acid per mole MoO_4^{-2} have been added; at higher concentrations of acid the absorbance for HCl attains a constant greater value than for corresponding concentrations of H_2SO_4. The absorbance values for HCl in the plateau area show a small variation, and are not as consistent as those obtained with H_2SO_4.

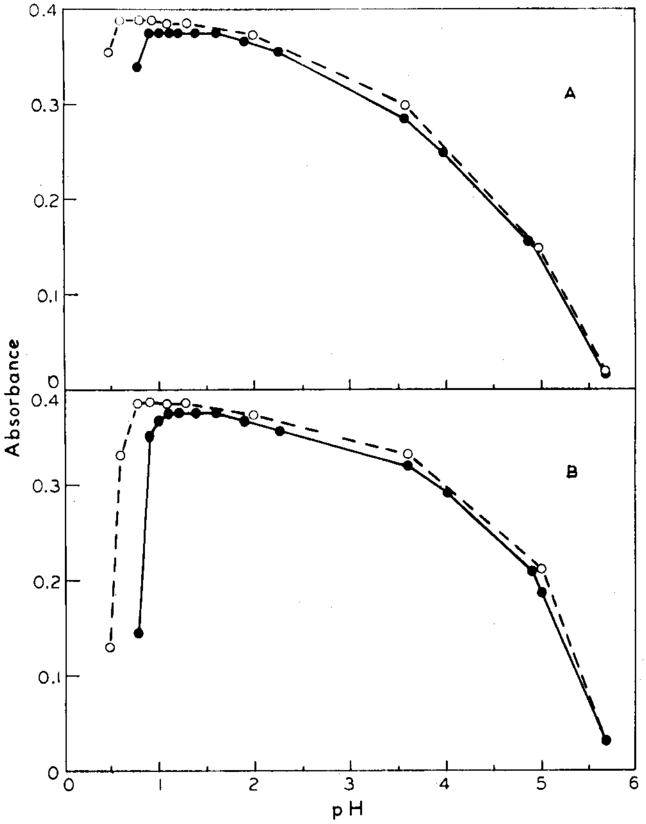


Fig. 3. Comparison of the variation in absorbance of silicomolybdate solutions due to sulphuric and hydrochloric acid as acidifying agencies. Absorbance shown as a function of pH. A, absorbance measured 10 min after start of reaction. B, absorbance measured 2 min after start of reaction. ●———● acidified with H_2SO_4; ○ – – – ○ acidified with HCl.

DISCUSSION

Variation in pH is clearly an important, but not an exclusively responsible, factor in the variation in the development of yellow silicomolybdate complexes. This variation is due to the effect of pH upon the state of the molybdate ions and, as pointed out by MULLIN AND RILEY[13], the rate of formation of silicomolybdate is dependent upon the degree of polymerization of molybdate from which it is formed.

RINGBOM *et al.*[11] quoted LINDQVIST[14] as saying that MoO_4^{-2} ions are stable at pH greater than 6.5, that around pH 4.5 paramolybdate ions ($Mo_7O_{24}^{-6}$) are formed which are transformed into octomolybdate ions ($Mo_8O_{26}^{-4}$) at a pH of 1.5 to 2.9. RINGBOM *et al.*[11] believed that the low-absorbance α-acid is formed from the paramolybdate ion, and the high-absorbance β-acid from the octomolybdate ion. STRICKLAND[10] suggested that concentration must be considered together with acidity: thus, at suitable acidities, and solutions more dilute than 0.01 M with respect to MoO_4^{-2},

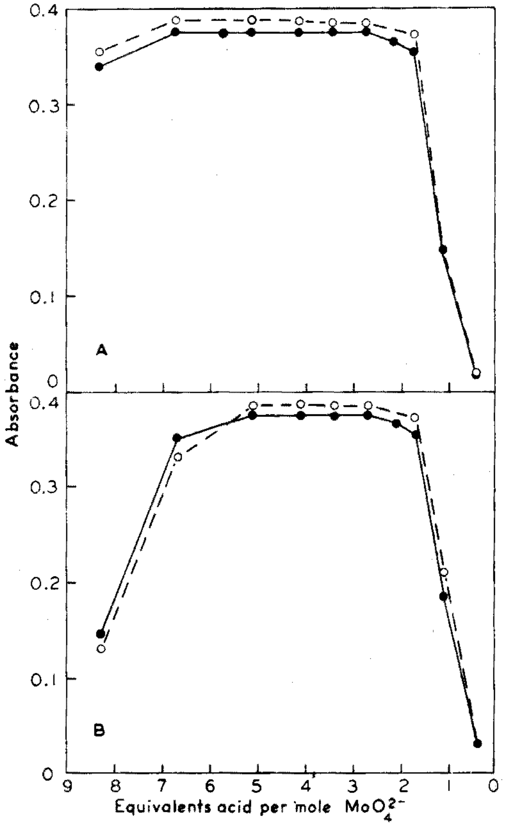


Fig. 4. Comparison of the variation in absorbance of silicomolybdate solutions due to sulphuric and hydrochloric acid as acidifying agencies. Absorbance shown as a function of equivalents acid per mole MoO_4^{-2}. A, absorbance measured 10 min after start of reaction. B, absorbance measured 2 min after start of reaction. ○– – – ○ H_2SO_4; ●———● HCl.

$$4\,MoO_4^{-2} + 6\,H^+ \rightleftharpoons Mo_4O_{13}^{-2} + 3\,H_2O$$

whilst at higher concentrations,

$$5\,MoO_4^{-2} + 4\,Mo_4O_{13}^{-2} \rightleftharpoons 3\,Mo_7O_{24}^{-6}$$

In solutions more concentrated than 0.05–0.1 M, and acidified with 1–1.5 equiv. acid,

$$2\,Mo_7O_{24}^{-6} + 4\,Mo_4O_{13}^{-2} \rightleftharpoons 5\,Mo_6O_{20}^{-2}$$

STRICKLAND[10] correlated the β-forming species with the meta ion, $Mo_4O_{13}^{-2}$, but failed to identify the α-forming species. Therefore, the amount of β-silicomolybdic acid formed, and the rate of formation, will depend upon the amount of β-forming species in the molybdate added, and the rate of change of the molybdate at the dilution and acidity in the reaction vessel. This is further complicated by the spontaneous and irreversible change of β-silicomolybdic acid to α-silicomolybdic acid. Thus, if the molybdate is added in such a form and under such conditions that its change to the β-forming species is very slow, then the earlier-formed β-acid will have changed to the α-acid before all the silica has reacted. This will give low results if the β-acid is being measured; they will be even lower if some α-forming species is initially present in the molybdate added.

Obviously, if the solution chemistry of molybdic acid, and the ion-form of molybdate which reacts with silica to form the various silicomolybdic acids, were completely understood, the molybdate should be added in the form, and into the correct conditions, to yield the form of silicomolybdic acid desired. Inasmuch as solutions of ammonium molybdate made up at a pH of less than 6.5 polymerize with time, and because the chemistry of molybdate in solution is so imperfectly known, it is analytically safer to add molybdate in the form of the simple MoO_4^{-2} ion in solutions of pH greater than 6.5. To allow any latitude in the aliquot of silica solution used the quantity of molybdate added must be comparatively small, and consequently there will be considerable change in the concentration in the reaction vessel compared with the stock solution. For example, adding ammonium molybdate solution at its natural pH of about 5.2 and in such amounts that its concentration in the reaction is 0.03 M with respect to MoO_4^{-2}, considerable variation in absorbance was found depending upon whether the solution was diluted to volume (less volume of ammonium molybdate) before addition of molybdate, or all dilution reserved until after addition of molybdate. When using ammonium molybdate from stock solutions at pH 7.3 and in such quantities as to give a concentration of 0.06 M in the reaction, the broad pH zone over which the same constant values are obtained (Fig. 2) results in there being no difference in absorbance due to differences in initial and final acidity in the reaction vessel.

The much reduced rate of reaction between silica and molybdate solutions at acidities greater than pH 1.0 was suggested by MULLIN AND RILEY[13] to be due to polymerization of silicic acid. This is demonstrably not so in solutions less concentrated than about 100 p.p.m. SiO_2. An impressive number of workers[1,9,15-17] have shown that monosilicic acid solutions are quite stable up to concentrations of 100 to 150 p.p.m. irrespective of pH. To prove the point, a solution containing 1 mg monosilicic acid at a concentration of about 50 p.p.m. was allowed to stand at a pH of 0.3 for 24 h. This solution was then brought up to a pH of 1.5 and ammonium molybdate added. The absorbance was found to be the same as when the same total reagents were used but the silica added at a pH of 1.5. For these reasons it is believed that STRICKLAND'S[10] contention that non-reaction or very slow reaction at high acidities is due to the presence of a non-reactive form of molybdate is correct. STRICKLAND[10] postulated that at very high acidities molybdate is present in a γ-form, probably as the cationic ion MoO_2^{+2} formed from β-molybdate. The γ-molybdate is said to be completely unreactive towards silica, but the slow reaction noted at high acidities is due to a transient stability of the β-form before its conversion to γ-molybdate. It may be noted that polymers of silica smaller than 20 mμ are depolymerized to the monomeric form in the presence of ammonium molybdate[18].

The effect of sulphate ion, as pointed out by STRICKLAND[10] is to cause the development of more α-acid (*i.e.* lower absorbance) than a corresponding amount of chloride ion (Figs. 3 and 4). The stability of β-acid seems to be greater, however, when H_2SO_4

is used as the acidifying agent; the maximum color development (in the range 2.7 to 5.0 equiv. acid per mole MoO_4^{-2}) is attained within 2 min and remains stable for at least 20 min. Absorbance obtained with HCl shows a slight variation after 2 min in the same acidity range and, unlike H_2SO_4, is not exactly the same value over this range. Clearly, although H_2SO_4 causes a small reduction in absorbance compared with HCl due to the formation of α-acid, the sulphate ion appears to stabilize the β-acid formed.

Increase in temperature accelerates the change β- to α-acid[10], and boiling temperatures were utilized in the analytical method of RINGBOM *et al.*[11] to ensure the rapid and complete formation of α-silicomolybdic acid. There is also a positive temperature–absorbance coefficient for both α-acid[11] and β-acid[10]. A high temperature factor of 0.004 absorbance units per degree centigrade was reported for α-acid. The maximum variation found by the writer in admittedly few experiments was 0.001 absorbance units per degree centigrade up to 35°; above 35° the positive variation was offset by the formation of significant amounts of α-acid.

ANALYTICAL CONSIDERATIONS

In formulating a method for the determination of silica, it is desirable that conditions be such that the color is reproducible, stable over a reasonable period of time, relatively insensitive to pH variation, in some cases capable of measuring total and soluble silica, and be as rapid as possible.

It cannot be denied that the observation by RINGBOM *et al.*[11] that the best analytical conditions are obtained by the development of the stable α-silicomolybdic acid is most logical. The necessity of boiling the solutions to promote complete formation of the α-acid is, however, time-consuming, and leads to complications when it is desired to estimate the amount of monosilicic acid as well as total silica in aqueous samples. Moreover, the sensitivity of the test using the α-acid is considerably reduced compared with the β-acid.

It is believed that the present work completely vindicates STRICKLAND's[10] suggestions that to ensure development of β-acid it is necessary that the concentration of molybdate be such that $[Mo] = 0.05$ after the silica has combined, and that there should be 3 to 5 gram equiv. of hydrogen ion per gram ion MoO_4^{-2}. Whereas most published analytical techniques have strived after the formation of the β-acid, the lack of concordance between authors and dissatisfaction with the methods (as evidenced by the large number of published works on molybdate methods for determining SiO_2) is due to lack of appreciation of the fact that two forms of silicomolybdic acid exist, and insufficient precautions to ensure constant development of one of these forms. Thus, the concentration of ammonium molybdate in the reaction proposed by BUNTING[19] is barely enough to react with 2 mg SiO_2 and in no way constitutes an excess as defined by STRICKLAND[10]; the practice of strongly acidifying the ammonium molybdate stock solution allows uncontrolled and unknown polymerization to take place. Methods which advise waiting "about an hour" for the full development of color are clearly open to great variation, whilst heating the sample under conditions of dominant β-acid formation can only lead to the formation of variable amounts of α-acid.

The knowledge that ammonium molybdate reacts rapidly only with monosilicic acid, and the fact that monosilicic acid present in concentrations much above 100 p.p.m.

will polymerize makes the initial treatment of solid samples — and aqueous samples of high silica concentration — of critical importance. It is, therefore, necessary to use weights and volumes such that the concentration of silica in the final sample solution should not be greater than 100 p.p.m. CARRERO AND RAMALLO[20] stated that quartz could be accurately brought into solution at reasonable temperatures and within a reasonable time only with NaOH; the writer has found that Na_2CO_3 fusions are liable to give low results, and that solid NaOH should be used for both solid and high-silica aqueous samples.

The interference of other ions has not been investigated during the present study. MULLIN AND RILEY[13] reported upon the interference of a comprehensive list of cations and anions. The most important source of interference likely to be encountered in most geological work is from iron and phosphorous. MULLIN AND RILEY[13] found that by reducing iron with hydroxylamine hydrochloride, 0.2 p.p.m. Si can be determined in the presence of 100 p.p.m. ferric iron with an error of less than 1%; suppression of phosphorous was achieved by addition of oxalic acid after a method by SCHWARTZ[21], allowing 0.2 p.p.m. Si to be determined in the presence of 5 p.p.m. of phosphate with no error. RINGBOM *et al.*[11] recommended the use of EDTA to avoid the formation of precipitates during the dissolution of silicate melts, and although the iron–EDTA complex has a small absorbance at 400 mμ, this can be corrected by a blank; tartaric acid was found to be the best agent to mask phosphorous, but the masking was apparently not complete at 390 mμ. LINDSAY AND BIELENBERG[22] used sodium citrate to destroy the phosphomolybdate complex, whilst BUNTING[19] employed tartaric acid for the dual purpose of suppressing both iron and phosphorous.

The employment of the reduced blue silicomolybdate complex offers a number of analytical advantages — there is no temperature coefficient and it has greater sensitivity — but suffers the disadvantage of being time-consuming and not well suited if it is desired to estimate the proportion of monosilicic acid as well as total silica in aqueous samples. The success or failure of the reduction method depends upon the same factors as when employing the unreduced complex, although the reducing agent may be of importance in some cases[13]. As determined by STRICKLAND[10], formation of a mixture of α- and β-silicomolybdic acids either initially or by rapid change of β- to α-acid, will give on reduction a mixture of α-silicomolybdous (greenish-blue) and β-silicomolybdous (royal blue) acid which have markedly different absorbance at wavelengths used, *i.e.* above 625 mμ.

Method adopted

Preparation of sample. Solid samples should be fused with solid NaOH (in the ratio of about 3 g NaOH to 0.1 g sample) in nickel crucibles for at least 10 min. The melt is leached into a plastic beaker and acidified with sufficient 1 *N* sulphuric acid to give a pH of about 1.5 to the final solution. The total dilution will depend upon the amount of silica anticipated in the sample; the dilution may be achieved by diluting to volume in 500- or 1,000-ml volumetric flasks or, for greater accuracy, by diluting by weight in the plastic beaker. It must be stressed that the sample solution must not be strongly alkaline when added to glassware, for silica will be dissolved leading to erroneous results.

When it is desired to determine total silica in aqueous samples, a suitable aliquot should be boiled with solid NaOH in a nickel beaker, and then diluted as above. No treatment is necessary for determination of soluble silica.

Procedure. A suitable aliquot of sample solution is added to a 50-ml volumetric flask, acidified with 10 ml 1 *N* H_2SO_4, and followed by 10 ml of 0.3 *M* (with respect to MoO_4^{-2}) ammonium molybdate. The latter solution is prepared by dissolving 52.97 g of crystalline $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ in one litre of water with sufficient sodium hydroxide to give a pH of not less than 7.0. The sample is diluted to 50 ml with distilled water. The absorbance is measured at 400 mμ (at a slit width of 0.04 mμ when using a Beckman Model DU spectrophotometer). The reaction with monosilicic acid is complete within 2 min and if the proportion of monosilicic acid is to be determined in an aqueous sample, the reading should be taken at 2 min; if total silica is being determined (which, of course, will be present as monosilicic acid after sample treatment) the reading should be taken not sooner than 2 min nor later than 10 min after addition of ammonium molybdate.

Calculation of the silica content is made by reference to a standard curve. Standard silica solutions may be prepared either directly by dissolving sodium metasilicate ($Na_2SiO_3 \cdot 9\ H_2O$) in distilled water acidified with H_2SO_4 so that the final pH is about 1.5 (about 60 ml 1 *N* H_2SO_4 per litre) or by fusion of standard felspar or pure quartz in the same manner as outlined for preparing solid samples for silica determinations. The concentration of the stock solution should not be greater than 100 p.p.m. SiO_2; 50 p.p.m. SiO_2 was found to be suitable. Aliquots of the standard solution are used to prepare a standard curve for concentrations up to about 2 mg SiO_2 per 50 ml. It is important that the standard determinations should be made with the same reagents present in the same amounts as the unknown samples.

Treatment of glassware. Dirty glassware should be thoroughly cleaned with chromic acid cleaning solution, followed by washing, and then a further cleaning with 1 : 1 HCl, and a final wash with distilled water. If the glassware is regularly cleaned, it is sufficient to wash with 1 : 1 HCl. The writer confirmed the observation by MULLIN AND RILEY[13] that if glassware is allowed to dry, even after the most stringent washing, it has an appreciable solubility under the conditions of the test. It was found convenient to leave the 50-ml volumetric flasks standing in an acid-bath containing 1 : 1 HCl, and wash well with distilled water just before use.

Replicate determinations with a standard silica solution showed a maximum standard deviation of 0.002 absorbance units in the range 0.1 to 1.0 mg silica per 50 ml. Maximum deviation occurred in the range 0.1 to 0.2 and again in the range 0.7 to 1.0 mg SiO_2 per 50 ml. The higher deviation in the lower range is attributed to pipetting error, whilst in the higher range it is probably due to lack of instrument-reading sensitivity. These determinations were carried out by the method outlined above with no special temperature control, and the standard deviation found does not include errors due to weighing or diluting of the sample; nevertheless, it is believed that it represents an adequate degree of accuracy.

ACKNOWLEDGEMENTS

This paper results from an investigation of the dissolution of silicate minerals in aqueous solution being conducted in co-operation with Dr. C. P. GRAVENOR, whose comments and advice are appreciated. Thanks are extended to Dr. T. RIGG (Research Council of Alberta) and Drs. D. A. W. SHARP AND N. A. GILL (Department of Chemistry, Imperial College, London, U.K.) for their helpful advice on the manuscript.

SUMMARY

The development of rapid colorimetric analytical techniques for silicates has catalysed many fundamental research programs in the geological sciences. Despite a multitude of papers on the silicomolybdate colorimetric technique for the analysis of silica which appear in the journals of nearly all sciences, it was found extremely difficult to adapt any published method for a particular purpose, and obtain reliable results. This is due to a lack of appreciation of the factors which control the silicomolybdate reaction. Data are given which indicate that the major factors are the polymer species of molybdate, which is controlled largely by the pH of molybdate stock solution; the concentration of molybdate; the ratio of acid to molybdate in reaction; and the type of acid used in the reaction. The effect of these variables is outlined, and an analytical procedure for both "soluble" and total silica outlined.

RÉSUMÉ

Une étude critique a été effectuée au sujet du dosage colorimétrique de la silice sous forme de silicomolybdate. Divers facteurs ont été examinés et la méthode, finalement adoptée, pour le dosage de la silice "soluble" et de la silice totale est décrite.

ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über die colorimetrische Bestimmung von Kieselsäure als Silikomolybdat. Unter Berücksichtigung des Einflusses der verschiedenen Faktoren (pH, Konzentration etc.) wird ein Verfahren zur Bestimmung von löslicher und Gesamtkieselsäure angegeben.

REFERENCES

[1] G. B. Alexander, W. M. Heston and R. K. Iler, *J. Phys. Chem.*, 58 (1954) 453.
[2] R. K. Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, 1955.
[3] G. B. Alexander, *J. Am. Chem. Soc.*, 76 (1954) 2094.
[4] R. K. Iler, *J. Phys. Chem.*, 57 (1953) 604.
[5] F. Dienert and F. Wandenbulcke, *Compt. rend.*, 176 (1923) 1478.
[6] R. W. Harmon, *J. Phys. Chem.*, 31 (1927) 616.
[7] E. Weitz, H. Frank and M. Schuchard, *Chemiker-Ztg.*, 74 (1950) 256.
[8] G. B. Alexander, *J. Am. Chem. Soc.*, 75 (1953) 5655.
[9] E. Richardson and J. A. Waddams, *Research (London)*, 7 (1954) 542.
[10] J. D. H. Strickland, *J. Am. Chem. Soc.*, 74 (1952) 862, 868, 872.
[11] A. Ringbom, P. E. Ahlers and S. Siitonen, *Anal. Chim. Acta*, 20 (1959) 78.
[12] L. H. Andersson, *Acta Chem. Scand.*, 12 (1958) 495.
[13] J. B. Mullin and J. P. Riley, *Anal. Chim. Acta*, 12 (1955) 162.
[14] I. Lindqvist, *Nova Acta Regiae Soc. Sci. Upsaliensis*, 15 (Ser. IV), No. 1 (1950) 23 pages.
[15] K. B. Krauskopf, *Geochim. et Cosmochim. Acta*, 10 (1956) 1.
[16] Y. V. Morachevsky and M. M. Piryutko, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. S.S.R. (English Translation)*, No. 4 (1956) 917.
[17] D. E. White, W. W. Brannock and K. J. Murata, *Geochim. et Cosmochim. Acta*, 10 (1956) 27
[18] G. B. Alexander, *J. Phys Chem.*, 61 (1957) 1563.
[19] W. E. Bunting, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 612.
[20] J. G. Carrero and O. C. Ramallo, *Anales real soc. españ. fís. y quím. (Madrid), Ser. B*, 54 B (1958) 190; In *Anal. Abstr.*, 6 (1959) 3921.
[21] M. C. Schwartz, *Ind. Eng. Chem., Anal. Ed.*, 14 (1942) 893.
[22] F. K. Lindsay and R. G. Bielenberg, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 460.

THE SPECTROPHOTOMETRIC DETERMINATION OF STRONTIUM WITH MUREXIDE (AMMONIUM PURPURATE)*

D. S. RUSSELL, J. B. CAMPBELL AND S. S. BERMAN

Division of Applied Chemistry, National Research Council, Ottawa (Canada)

(Received November 17th, 1960)

There have been comparatively few procedures recommended for the spectrophotometric determination of strontium. Of three that have been developed, that involving chloranilic acid as the reagent[1] is an indirect method of low sensitivity. The others, both produced by POLLARD AND MARTIN[2], use murexide and *o*-cresolphthalein complexone respectively as the reagents. Unfortunately, the experimental results upon which these two methods are based were not recorded by the authors.

Attempts in this laboratory to utilize the murexide procedure in order to determine μg-quantities of strontium were unsuccessful. This was apparently due to the instability of both the murexide reagent solution and the strontium-murexide complex produced when the recommended procedure was followed. As a result we have made a further study of the spectrophotometric determination of strontium with murexide and this communication describes a modified method which we have found useful for determining small amounts of strontium.

Murexide is a highly coloured substance which forms chelates with many metal ions. These metal chelates differ in colour with the strength of binding and the pH of the solution. The material has found wide use as a metal indicator in complexometric titrations, especially for the EDTA titration of calcium. It has been used by several workers for the photometric determination of macro quantities of this metal in neutral solution[3,4], and μg amounts in alkaline medium[5,6]. The latter procedure[6] employing a solution of the dye in 70% (v/v) ethanol was adapted for the determination of strontium by POLLARD AND MARTIN[2] by increasing the reagent concentration and taking precautions to minimize the differential errors between the blank and sample solutions due to the high rate of decomposition of the murexide reagent.

We have found that a solution of murexide in 80% (v/v) ethylene glycol results in a reagent of greatly enhanced stability, and addition of ethylene glycol to the reaction mixture results in a stable strontium-murexide complex.

EXPERIMENTAL

Photometric measurements were made with a Beckman Model DU spectrophotometer and optically matched 1.00-cm cells. A constant slit width of 1.0 mm was used since the reagent blank was quite optically dense and small variations in slit at the wavelength employed (510 mμ) resulted in substantial variations in absorbance. Spectral curves of the coloured solutions were made with a Beckman Model DK-1 recording spectrophotometer.

---

* N.R.C. publication No. 6279.

Murexide was obtained from two sources: J. T. Baker Chemical Co. ("Baker Analyzed" Reagent) and Siegfried Chemicals and Pharmaceuticals, Switzerland. All chemicals used were of analytical reagent or C.P. grade. One batch of ethylene glycol was found to be contaminated with a small amount of calcium and was redistilled before use.

Development of the procedure

Initially, attempts were made to stabilize the reagent solution and the colour system by varying some of the conditions recommended by POLLARD AND MARTIN[2]. These included (*i*) varying the percentage of ethanol in the reagent, (*ii*) adding ethanol in various proportions to the reaction mixture, (*iii*) varying the pH slightly by the addition of more or less 0.05 *M* sodium hydroxide solution, (*iv*) varying the reagent concentration and (*v*) keeping the reagent and samples at 0° in an ice-water bath before mixing and cooling the cell compartment of the spectrophotometer to less than 20° by passing cold water through a pair of thermospacers bracketting the compartment. These were all unsuccessful, although enhanced stability was obtained with the cold solutions.

BRUNISHOLZ *et al.*[7] had reported that a saturated solution of murexide in anhydrous ethylene glycol provided a fairly stable dye solution for use as a metal indicator. A solution of this type was prepared and found to be very stable when kept refrigerated. However, it was found difficult to reproduce these solutions as the murexide concentration varied widely from batch to batch. Solutions of murexide in 80% (v/v) ethylene glycol were found to be of equal stability, and could be easily prepared at a given concentration. A 0.05%-solution of the dye in this medium was chosen as the reagent. One batch of this reagent was used over a period of six weeks with no apparent deterioration.

In experiments to find optimum conditions for the colour reaction the following basic procedure was followed. A solution containing 93.8 μg of strontium as the chloride was transferred to a 25-ml volumetric flask, and ethylene glycol and 0.05 *M* sodium hydroxide were added. The solution was well mixed and set in an ice-water

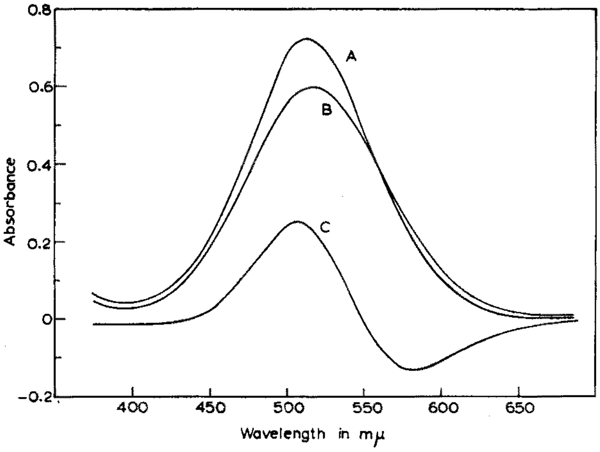


Fig. 1. Typical spectra of murexide and the strontium complex. A, reagent blank against water. B, reagent plus strontium against water. C, reagent plus strontium against a reagent blank.

bath to cool. After cooling, the cold reagent was added, the solution was made up to volume with water, shaken, and the absorbance measured against a reagent blank which was simultaneously prepared.

The preparation of simultaneous blanks is essential. Although the murexide reagent is quite stable when refrigerated, it decomposes slowly at room temperature. Any differential errors due to this decomposition are minimized by this precaution. The rate of reagent deterioration can be reduced appreciably by cooling the cell compartment, but this was not deemed necessary.

Typical spectra of the reagent and strontium-murexide complex are shown in Fig. 1. Since the absorbance of the reagent is relatively high, curves A and B which represent absorbance curves of the reagent blank and of a sample respectively measured against water, have been reduced in size so that a better comparison can be made with curve C which represents a sample measured against a reagent blank. The absorbance maximum of curve C was found to be at 510 mμ.

The stability of the coloured complex was directly proportional to the quantity of ethylene glycol added to the system (Fig. 2). 15 ml was chosen for all subsequent determinations.

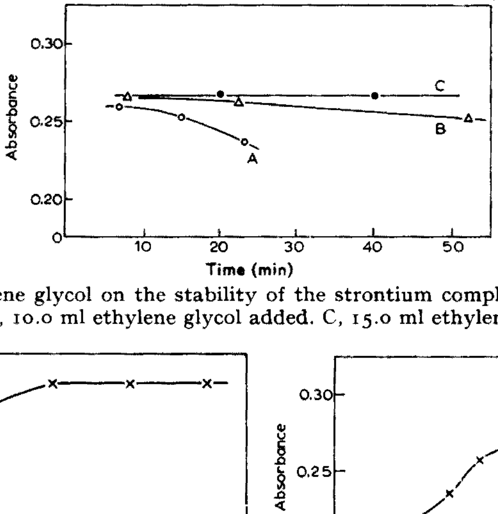


Fig. 2. Effect of ethylene glycol on the stability of the strontium complex. A, 5.0 ml ethylene glycol added. B, 10.0 ml ethylene glycol added. C, 15.0 ml ethylene glycol added.

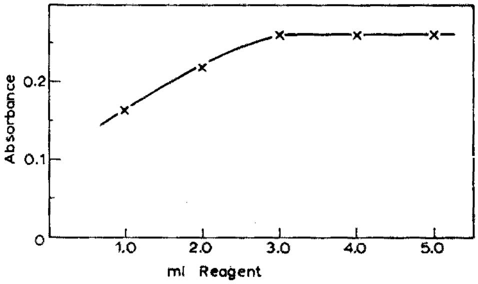


Fig. 3. Effect of varying amounts of reagent.

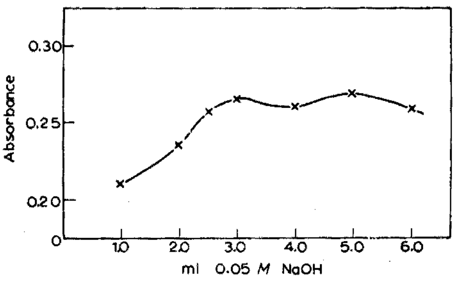


Fig. 4. Effect of varying amounts of sodium hydroxide solution.

The absorbance increased with the quantity of reagent added until a maximum was reached at 3.0 ml (Fig. 3).

Also, with 3.0 ml of reagent, the absorbance increased with the quantity of 0.05 *M* sodium hydroxide added, levelling off at about 3.0 ml (Fig. 4). Although a slight increase in sensitivity may have been obtained at 5.0 ml, 3.0 ml was chosen as the optimum amount in order to keep the pH as low as possible, enhancing the stability of the coloured species. The pH of this solution was found to be 11.3.

Beer's law is followed up to approximately 8 μg per ml, after which the slope of the absorbance curve steadily decreases with increasing strontium concentration. Increasing the quantity of reagent had no effect on this curve.

Six replicate samples, each containing 93.8 μg of strontium in a final volume of 25 ml gave a mean absorbance of 0.265 with an average deviation of 0.003 or 1.1%.

Experiments showed that most elements usually associated with strontium interfere in this determination, even when present in very small amounts. For example, the following quantities in μg produce an approximately 5% increase in the absorbance due to 93.8 μg of strontium; Mg: 300, Ca: 2, Ba: 50, Li: 75, K: 150, Ag: 10.

These interferences can generally be removed by ion exchange[8,9] or paper chromatography[10]. In our own case where we were interested in the analysis of small quantities of silver-strontium alloys used in X-ray diffraction work a micro precipitation of silver as silver chloride served to reduce the silver concentration to below the level of interference.

Recommended procedure

Reagent: Prepare the 0.05%-murexide reagent by dissolving 125 mg of the dye in 50 ml of water and adding 200 ml of anhydrous ethylene glycol. Allow the solution to stand overnight in a refrigerator and filter cold through a Whatman No. 42 paper. Keep the solution in an ice-water bath when in use and store under refrigeration.

Method. Evaporate the strontium sample to dryness and transfer with a few ml of water to a 25-ml volumetric flask. Add 15.0 ml of ethylene glycol and 3.0 ml of 0.05 *M* sodium hydroxide solution. Dilute with water to about 22 ml. Mix well and cool the solution in an ice-water bath. Add 3.0 ml of the murexide reagent and dilute to volume. Shake well and measure the absorbance in matched cells at 510 mμ against a reagent blank which has been prepared simultaneously with the sample.

SUMMARY

A procedure for the spectrophotometric estimation of μg-quantities of strontium with murexide is described. Conditions for the optimum stability of the coloured strontium complex have been determined, the main feature being the addition of large quantities of ethylene glycol to the system. Most elements interfere so that it is necessary to isolate the metal before the determination.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du strontium au moyen de murexide. De nombreux éléments gênant, une séparation préalable est nécessaire.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Bestimmung von Strontium mit Murexid. Wegen des störenden Einflusses der meisten anderen Elemente ist eine Abtrennung erforderlich.

REFERENCES

[1] P. J. LUCCHESI, S. Z. LEWIN AND J. E. VANCE, *Anal. Chem.*, 26 (1954) 521.
[2] F. H. POLLARD AND J. V. MARTIN, *Analyst*, 81 (1956) 348.
[3] H. OSTERTAG AND E. RINCK, *Chim. Anal.*, 34 (1952) 108.
[4] J. RAAFLAUB, *Helv. Physiol. et Pharmacol. acta*, 9 (1951) 33.
[5] L. E. TAMMELIN AND S. MOGENSEN, *Acta Chem. Scand.*, 6 (1952) 988.
[6] M. B. WILLIAMS AND J. H. MOSER, *Anal. Chem.*, 25 (1953) 1414.
[7] G. BRUNISHOLZ, M. GUNTON AND E. PLATTNER, *Helv. Chim. Acta*, 36 (1953) 782.
[8] M. W. LERNER AND W. RIEMAN III, *Anal. Chem.*, 26 (1954) 610.
[9] O. SAMUELSON AND E. SJÖSTROM, *Anal. Chem.*, 26 (1954) 1908.
[10] F. H. POLLARD, J. F. MCOMIE AND J. W. MARTIN, *Analyst*, 81 (1956) 353.

SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF ALCOHOLS

M. STILLER

Department of Analytical Chemistry, Atomic Energy Commission Laboratories, Rehovoth (Israel)

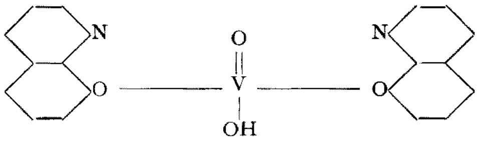
(Received November 26th, 1960)

INTRODUCTION

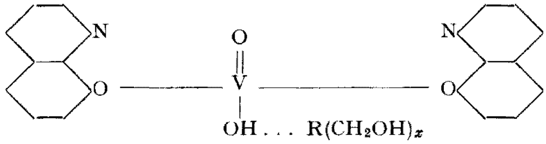
When organic solvents are used in extraction processes, it is often necessary to determine small amounts of esters or alcohols in the organic or aqueous phases.

FEIGL[1,2] mentions a spot test for alcohol as follows: vanadium(V) forms a complex with oxine[3,4] in an acetate medium, the ratio of vanadium to oxine being 1 : 2. The complex is insoluble in water and acetic acid but dissolves in benzene, chloroform, acetone, alcohol and trichlorethylene, giving a dark greyish-green colour to the organic phase.

If alcohol is added to the suspension of the vanadium complex in water and an extraction with benzene is carried out, the organic layer appears red. It is presumed that a second complex with the alcohol is formed (II) which is more stable than the initial vanadium oxine complex (I).



I



II

This secondary complex (II) is formed with primary, secondary and tertiary alcohols but not with alcohols containing a phenolic or carboxylic group (citric or lactic acid, phenol) except where the carboxylic group has undergone esterification *e.g.*, the ester of lactic acid.

BUSCARONS, MARIN AND CLAVER[5] examined the colours obtained by dissolving vanadium oxinate in a long series of organic compounds. They found that the reddish colour is given only with alcohols. These authors report a sensitivity limit of 1.5%–2.5% alcohol in a mixture of organic solvents and 2.5%–5% alcohol, when testing an aqueous solution.

If the aqueous phase (pH 3.5–5) contains insufficient alcohol together with the precipitate of vanadium oxinate, two colours are observed on extraction in the benzene layer:

1. the reddish colour of the alcoholic vanadium-oxinate complex.

2. the grey-black colour of the excess vanadium oxinate.

If it were possible to eliminate the vanadium-oxinate complex (I) from the organic phase leaving only the complex (II), a quantitative determination of small amounts of alcohol would be feasible. Such a method is described here.

When the organic coloured layers are washed with *N* sodium hydroxide solution, the vanadium oxinate is transferred to the aqueous phase, while the alcohol complex remains in the organic phase along with part of the excess oxine.

EXPERIMENTAL

Absorption as function of wavelength

Determination of the absorption of the alcohol complex in benzene solution at various wavelengths was carried out at a concentration of 1.8 mmole of alcohol; methyl, ethyl, butyl and amyl alcohols were tested (see Fig. 1). In these experiments only one benzene extraction was done. Similar curves were obtained for the four alcohols. The highest absorption was obtained with amyl alcohol; absorption decreased through butyl and ethyl to methyl alcohol. In all four spectra two flat areas (plateaux) were found in the two regions, 370–400 mμ and 450–480 mμ.

In Fig. 1, it is difficult to see the flattened areas of the methyl alcohol complex

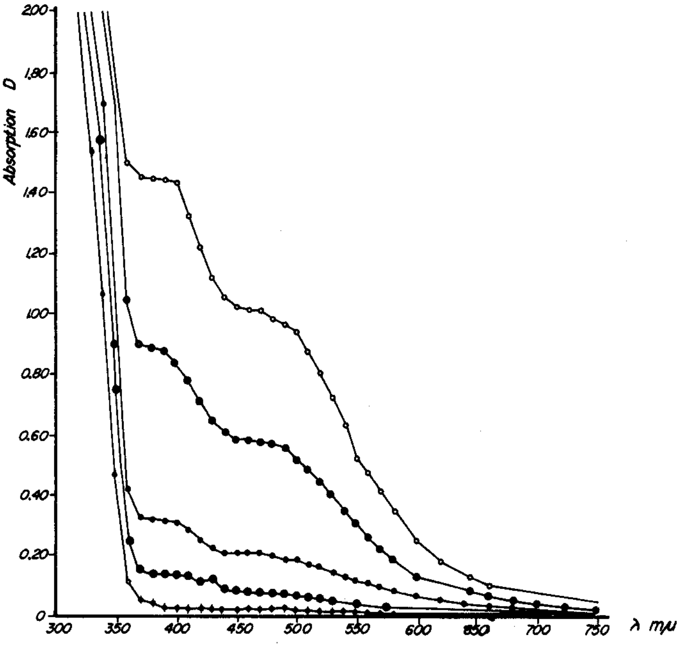


Fig. 1. Absorption of alcoholic vanadium-oxinate complexes as function of wave-length (Beckmann DU spectrophotometer). ○ amyl alcohol complex; ◎ butyl alcohol complex; ● ethyl alcohol complex; ◉ methyl alcohol complex; ϕ without alcohol.

but when the above experiment was repeated with large quantities of methyl alcohol the curve was the same as for the other alcohols.

A control containing all the reagents used, but no alcohol, was also examined.

The spectrum of the control is apparently given by oxine (which is present in excess) and which remains partly soluble in benzene even after the extraction of the vanadium oxinate with alkali from the organic phase. The spectrum found for the control has the same features as that found by MOELLER[6] for oxine (see ϕ in Fig. 1). It can be seen that the first flat area of the spectrum is an area of maximum absorption for the vanadium-oxinate-alcoholate complex. For quantitative determinations therefore, a wavelength of 390 mμ was chosen. At this wavelength, sensitivity is highest and the influence of oxine on the readings very small.

Reagents

(*1*) Solution of ammonium vanadate containing 1 mg of vanadium per ml.
(*2*) 2.5% solution of 8-hydroxy-quinoline in 6% acetic acid.
(*3*) Buffer solution of acetic acid-sodium acetate, pH = 4 (100 ml of acetic acid and 53.5 g of sodium acetate).
(*4*) Benzene, Baker analytical reagent.

The two phases were kept at fixed relative volumes, the ratio of the organic to aqueous phase being 2 : 1.

Procedure

1 ml of ammonium vanadate solution and 1 ml of the oxine solution were added to the sample under test (containing 50-500 μg of alcohol) followed by buffer solution to a volume of 7 ml.

The mixture was shaken in a Burrell wrist action shaker with 15 ml benzene for 20 min. After separation of the phases, extraction from the aqueous phase was repeated twice with fresh quantities of benzene and the other reagents.

The benzene extracts were collected and, after washing with 10 ml of *N* sodium hydroxide solution, the optical density was read in the spectrophotometer; a Coleman universal spectrophotometer or a Beckman DU quartz spectrophotometer was used.

RESULTS

Fig. 2 shows the relationship between the concentrations of four different alcohols in the benzene solution and the optical density of the complex at 390 mμ after correction for the blank. As might be surmised from Fig. 1, the sensitivity increases with the molecular weight. The maximum deviation in results is ± 2.5%. The relative mean deviation is usually 2%. The smallest quantities of alcohol which could be detected are shown in Table I.

TABLE I

	Concentration in the final benzene solution, µg/ml	*Concentration in the original sample, µg/ml*
Butyl or amyl alcohol	1	10
Ethyl or methyl alcohol	2-3	20-30

The proportionality of optical density to concentration was checked up to a concentration of 16–20 μg of alcohol per ml of the final benzene solution (see Fig. 2).

From Fig. 2 it also appears that the sensitivity of the amyl alcohol complex is less than that of the butyl alcohol. If the amounts of alcohol are calculated in mmoles

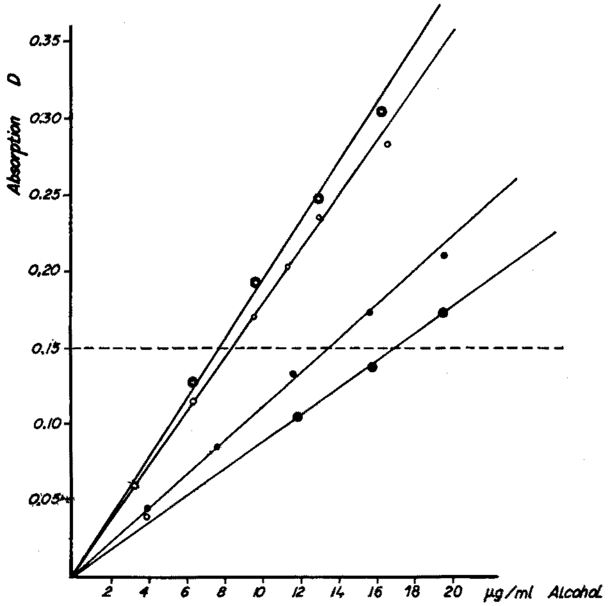


Fig. 2. Absorption as function of alcohol concentration (weight units), $\lambda = 390$ mμ. Coleman Senior spectrophotometer. ○ amyl alcohol complex; ◎ butyl alcohol complex; ● ethyl alcohol complex; ◉ methyl alcohol complex.

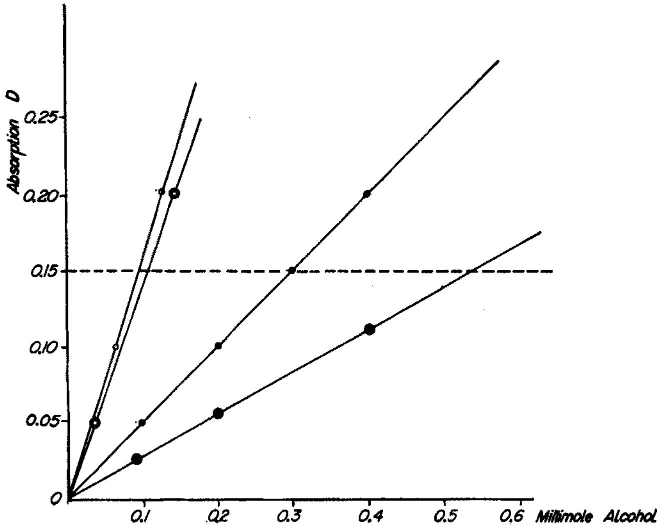


Fig. 3. Absorption as function of alcohol concentration in molar units ($\lambda = 390$ mμ). Coleman Senior spectrophotometer. ○ amyl alcohol complex; ◎ butyl alcohol complex; ● ethyl alcohol complex; ◉ methyl alcohol complex.

at the same optical density of 0.15, for example, the curve for the amyl complex appears higher than that for the butyl complex.

This is clearly seen in Fig. 3 where curves are given of optical density as a function of molar concentration of alcohol.

In Table II, some physical constants of the alcohols are given.

Possible cation interferences have not been studied but data collected from the literature[6–8] shows that the metals extracted with oxine at pH 4–5 are: Al, Bi, Cu, Fe, In, Mo, Ni, Ru(III), Pu(IV, VI), Sn(IV), Ti, V, W, Zn. Of these metals, only copper is totally extracted at pH 14, while no aluminium or iron and probably no molybdenum, nickel, titanium or vanadium is extracted.

TABLE II

PHYSICAL CONSTANTS OF ALCOHOLS

Alcohol		*Mol. wt.*	*Dielectric constant of the alcohol*	*Molecular extinction coefficient of vanadium-oxinate complex (according to Beer's law)*
Methyl	(CH_3OH)	32	32.6	175
Ethyl	(C_2H_5OH)	46	24.3	312
Butyl	(C_4H_9OH)	74	17.1	890
Amyl	($C_5H_{11}OH$)	88	13.9	1000

ACKNOWLEDGEMENT

The author wishes to thank Dr. J. Yofe, Head of the department, for advice and assistance in this work.

SUMMARY

A spectrophotometric method for the determination of small amounts of methyl, ethyl, butyl and amyl alcohols is described. The sensitivity of the method is of the order of 10 μg/ml of test solution in the case of butyl and amyl alcohols and 20–30 μg/ml in the case of ethyl and methyl alcohols. The molar extinction coefficient rises with the molecular weight of the alcohol. The nature of the alcoholic complex is not yet known.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage des alcools méthylique, éthylique, butylique et amylique. On observe que le coefficient d'extinction moléculaire augmente avec le poids moléculaire de l'alcool.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung kleiner Mengen Methyl-, Aethyl-, Butyl- und Amylalkohol mit Hilfe des Vanadiumoxinat Komplexes. Es wurde festgestellt, dass der molekulare Extinktionskoeffizient mit zunehmenden Molekulargewicht des Alkohols grösser wird.

REFERENCES

[1] F. Feigl, *Spot tests in Organic Analysis*, 5th ed., Translated by R. E. Oesper, Elsevier, Amsterdam, 1957.
[2] F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949.
[3] N. A. Talvitie, *Anal. Chem.*, 25 (1953) 604.
[4] M. Borrel and R. Pâris, *Anal. Chim. Acta*, 4 (1950) 280.
[5] F. Buscarons Ubeda, J. L. Marin Malumbres and J. Claver, *Anal. Chim. Acta*, 3 (1949) 310.
[6] T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 364.
[7] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957.
[8] R. G. W. Hollingshead, *Oxine and its Derivatives*, Butterworths, London, 1958.

SPECTROGRAPHIC DETERMINATION OF BORON IN NUCLEAR GRAPHITE

F. GIANNI AND F. POTENZA

Laboratori Riuniti Studi e Ricerche S.p.A., S. Donato Milanese, Milan (Italy)

(Received December 21st, 1960)

The use of graphite as a power reactor moderator necessitates a study of analytical methods for the determination of very low concentrations of those elements which show a high neutron cross section. Amongst these elements is boron, which is usually present in graphite and for which normal purification processes are ineffective. The chemical determination of boron at the concentrations which do not affect the reactor performance requires difficult and time-consuming techniques.

The purpose of this work was to develop a method for the spectrographic determination of the boron content of nuclear graphite at concentrations between 0.1 and 1.0 p.p.m. Such a method had to be, moreover, rapid and economical, *i.e.* properly developed for low-cost routine analysis on thousands of samples.

It was deemed advisable, due to cost problems, to eliminate the use of boron-free graphite for the electrodes. For this reason, among the methods in the literature we excluded the possibility of adapting the methods of FELDMAN AND ELLENBURG[1], RÜSSMANN[2], SHUGAR[3], GARTON[4] or LEPPLA AND MARKEL[5]. Some of these methods were also excluded because the sensitivity indicated by their authors did not meet our requirements.

The addition of substances as internal standards and their accurate mixture — as far as graphite is concerned — are rather tedious operations (as RÜSSMANN[2] points out). Therefore the possibility was studied of using the background as an internal standard with considerable time saving in the preparation of analysis samples. The selection of background as internal standard proved to be quite satisfactory and effectively allowed the use of the sample itself without any handling other than shaping.

APPARATUS

A "Hilger" medium quartz spectrograph (type E 498; dispersion at 2500 Å approx. 9 Å/mm) was employed for the determinations. For a rapid consumption of the sample, an arc source of 380 V d.c. and delivering a 20-A maximum output, was constructed. For the direct sample support, metallic (brass) electrode holders were adopted. Ilford ordinary plates were used and were developed by Ilford ID2.

EXPERIMENTAL

For the preliminary work we considered the possibility of analysing both block and powder samples. Of course it is easy to obtain cylindrical sticks from blocks for the formation of the two electrodes. On the other hand, powder samples require working up and moulding.

For this purpose we adapted the method used by GARTON[4] to prepare graphite pellets suitable for insertion on the end of his boron-free graphite electrodes.

The method was as follows: to 5 parts of finely powdered sample (approximately 100 mesh), one part of bakelite solution was added (we used the SUPERBOL product of Monti & Martini Co. which blank tests showed to be boron-free). The substances were mixed thoroughly and accurately and the mixture was dried at 110°. The sample was subjected at 150° to a pressure of 14,000 p.s.i. Rectangular rods which were 5 mm wide and 20–25 mm high were obtained. Such electrodes were used with a 17-A arc. In order to obtain sufficiently intense boron lines, a rather high sample consumption and relevant exposure time were required. On the other hand it was necessary to prevent the background from reaching prohibitive values; for this purpose the spectrograph was illuminated by an intermediate image of the arc from which the electrode image was removed by masking. The electrode spacing was maintained during exposure at 4 mm and the slit width was 5 μ.

Before exposure, electrodes were arced for a few seconds in order to eliminate any traces of volatile and easily inflammable bakelite residues. The arc was then re-lighted for 3 min for the exposure. Electrode masking allowed such a long exposure time without excessive background values around the two boron lines. Plate calibration was made by the two-step filter method on an iron spectrum.

As the boron analytical line, we used BI 2497.73, on which no interference has been noted by the elements present as impurities in nuclear graphite. As background value the minimum blackening value between B 2496.78 and B 2497.73 lines was employed.

RESULTS

The calibration curve was plotted by starting with two analyzed powdered graphite samples containing 1.05 and 0.10 p.p.m. of boron respectively. By mixing the first with Ringsdorff RWD graphite powder (boron-free), two other samples were obtained containing 0.525 and 0.210 p.p.m. of boron. Once the electrodes had been obtained and arced as described above, the calibration curve was determined (Fig. 1). The abscissa values indicate the boron concentration in the initial sample, *i.e.* before bakelite mixing.

Boron lines proved to be easily measurable for concentrations ranging from 0.2 to 1.0 p.p.m.; between 0.1 and 0.2 p.p.m., insufficient blackening against the background allows only a semiquantitative estimation.

The points shown on the calibration curve are the average of three relatively consistent values.

When a series of electrode couples containing 0.525 p.p.m. of boron were arced twelve times in the same plate, the reproducibility of the method proved to be $\sigma\% = 9.8$, which was quite suitable for our purposes, especially if the data are used as the average of 3 or 4 determinations.

Different values for samples of the same concentration, were found only when the results were obtained with electrodes which were considerably different in geometric size from couple to couple, or when the same couple was used for more than one exposure.

For samples directly cut from blocks of the same boron content, the line-to-background ratio was found to depend on material aggregation and other uncontrollable factors. For this reason, the direct arcing of solid samples (cut from blocks) was impracticable because it would have been necessary to prepare as many calibration curves as the types of graphite to be tested.

CONCLUSIONS

The method described is of practical and economic value for the analysis of a large number of powdered or pulverizable samples. The precision of the method is sufficient for the concentration range under consideration. The time required for analysis of at least 10 samples, each being analyzed three times and the calibration curves being replotted on each plate, is approximately 1 sample/2 h/worker; this includes all operation times from preparing the samples to the final calculation. The method is therefore suitable for graphite stock analysis for nuclear reactor purposes.

A much more detailed account of this work will be published in Italian in *Metallurgia Italiana*.

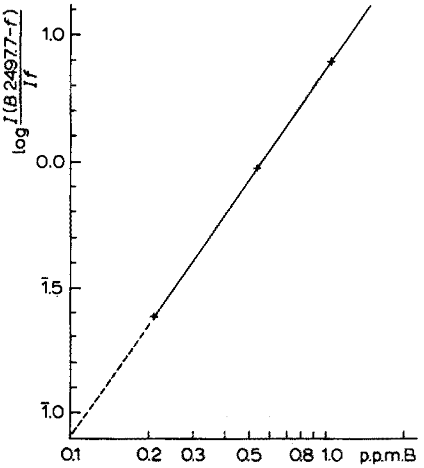


Fig. 1. Calibration curve for boron in graphite.

SUMMARY

A spectrographic method is described for the determination of boron (0.2–1.0 p.p.m.) in nuclear graphite and for the estimation of 0.1–0.2 p.p.m. of boron. Neither boron-free graphite electrodes nor additional foreign substances as internal standard are required. Both the electrodes consist of sample powder, properly bakelite-processed. The standard deviation is 10%.

RÉSUMÉ

Une méthode spectrographique est décrite pour le dosage du bore dans le graphite destiné à l'usage nucléaire, pour des teneurs de 0.2 à 1.0 p.p.m. Les deux électrodes sont constituées par la poudre de l'échantillon à analyser comprimée et durcie par "bakélisation".

ZUSAMMENFASSUNG

Beschreibung einer spektrographischen Methode zur Bestimmung von sehr kleinen Mengen Bor in Kernreaktionen-Graphit, wobei die Elektroden aus dem zu untersuchenden Graphit mit Bakelit als Kittsubstanz bestehen.

REFERENCES

[1] C. Feldman and J. Y. Ellenburg, *Anal. Chem.*, 27 (1955) 1714.
[2] H. H. Rüssmann, *Paper read at a Conference held in Praha*, 19th Oct., 1956, and kindly supplied by the author.
[3] D. Shugar, *Bull. centre phys. nucléaire univ. libre Bruxelles*, No. 34 (1952).
[4] F. W. J. Garton, *Spectrochim. Acta*, 9 (1957) 297.
[5] P. W. Leppla and R. F. Markel, *Great Lakes Carbon Corporation*, F. Process – Contract AT (45-1) – 259, Final Report, 15th March 1951.

PILOT-ION COULOMETRY WITH DROPPING MERCURY ELECTRODES

RICHARD E. COVER AND LOUIS MEITES

Department of Chemistry, Polytechnic Institute of Brooklyn, N.Y. (U.S.A.)

(Received December 5th, 1960)

INTRODUCTION

Coulometric measurements with dropping mercury electrodes have been employed to determine polarographic n-values in three different ways.

One[1-3] involves the periodic measurement of the diffusion current of the substance in question during a prolonged electrolysis of a known volume of solution with a dropping electrode, and the calculation of n from the slope of a plot of log i_d *versus* electrolysis time. In another[2], the number of coulombs flowing during such an electrolysis is measured and compared with the change of diffusion current that occurs: if the amount of material originally present is known, and if the fraction of it that is reduced is calculated from the ratio of diffusion currents before and after the electrolysis, n can be obtained from Faraday's law. In the third[4], the electrolysis current is passed through a second dropping electrode in a solution containing a known amount of a reducible substance (*e.g.*, cadmium ion) for which n is known: if the diffusion currents in the two electrolysis cells are measured separately before and after the electrolysis, it is possible to obtain the ratio of the number of moles of unknown substance reduced to the number of moles of standard substance reduced by the same quantity of electricity, and this immediately gives the ratio of n-values.

Each of these techniques involves the danger of mechanical loss of an appreciable fraction of the small volume of solution that must be employed. The first also involves errors due to local depletion of the solution around the tip of the dropping electrode; the others involve other errors which are associated with the explicit or implicit measurement of the quantity of electricity consumed during the electrolysis. These and other errors have been studied by WEAVER AND WHITNACK[5].

This communication describes a fourth technique, which requires the use of only a single dropping electrode, does not involve the use of any external apparatus for current integration, and avoids many of the errors encountered in these other techniques.

THEORY

Assume that a solution contains two reducible substances, A and B, which yield polarographic waves corresponding to the half-reactions

$$A + n_A e \rightarrow A'$$
$$B + n_B e \rightarrow B'$$

Assume that the waves are sufficiently well separated on the polarogram to permit their diffusion currents to be measured separately. If the solution is electrolyzed with a dropping electrode whose potential is maintained at a value on the plateau of the total combined wave, a current will flow which is the sum of the diffusion currents of A and B, and each of these will be reduced at a rate proportional to its own diffusion current. If it is further assumed that the diffusion current of each is proportional to its concentration by a proportionality constant k, then the rate of change of concentration of A will be given by

$$-\frac{dC_{\mathrm{A}}}{dt} = \frac{i_{d_{\mathrm{A}}}}{n_{\mathrm{A}} F_y V} = \frac{k_{\mathrm{A}} C_{\mathrm{A}}}{n_{\mathrm{A}} F_y V} \tag{1}$$

Integration and obvious substitutions yield

$$\log\left(i_{d_{\mathrm{A}}}/i^{0}_{d_{\mathrm{A}}}\right) = -\frac{0.4343\, i^{0}_{d_{\mathrm{A}}}}{n_{\mathrm{A}} F_y V C^{0}_{\mathrm{A}}}\, t \tag{2}$$

where superscript zeros refer to the initial solution. Dividing this by the corresponding equation for B and rearranging,

$$\frac{\log\left(i^{0}_{d_{\mathrm{A}}}/i_{d_{\mathrm{A}}}\right)}{\log\left(i^{0}_{d_{\mathrm{B}}}/i_{d_{\mathrm{B}}}\right)} = \frac{i^{0}_{d_{\mathrm{A}}} n_{\mathrm{B}} C^{0}_{\mathrm{B}}}{i^{0}_{d_{\mathrm{B}}} n_{\mathrm{A}} C^{0}_{\mathrm{A}}} \tag{3}$$

in which the units are obviously immaterial as long as they are consistent. As the volume of solution does not appear in this equation, it need not be known, and losses (*e.g.*, by entrainment into the gas stream used for deaeration and stirring) are without effect. Errors due to local depletion of the solution around the capillary tip are nearly eliminated by the fact that they will affect A and B about equally.

What is required experimentally is that a solution containing known concentrations of a substance, A, for which n is to be determined, and of a second substance, B, for which n is known, be electrolyzed with a dropping electrode at a potential on the plateau of the second wave for a length of time sufficient to decrease both concentrations appreciably. The diffusion currents of A and B are measured initially and again at the end of the electrolysis, and n_{A} is then calculated from eqn. (3). This is a considerably simpler technique than any of those previously proposed.

The crucial chemical requirement is that neither of the products of the electrode reactions must be capable of reacting with either of the starting materials in any way that will lead to a change in the measured diffusion currents. In practice, this includes (but is not limited to) a requirement that the second wave be totally irreversible; satisfactory results are often impossible, and always difficult, to secure if this is not the case. Several examples of chemical interactions between products and starting materials that lead to erroneous results will be cited below, and it will be apparent that a judicious selection of the "pilot" ion is essential to success.

EXPERIMENTAL

Solutions containing known concentrations of two reducible substances were prepared from stock solutions which had been standardized by conventional methods.

From 0.25 to 0.50 ml of a mixture was placed in the dropping-electrode compartment of a micro H-cell[6] and deaerated with a slow stream of prepurified nitrogen which had been scrubbed with chromous chloride and then with water. When deaeration was judged to be complete, the dropping electrode was inserted and a polarogram was recorded. By appropriate adjustment of the bridge of the polarograph, a potential was then applied which was near the center of the plateau of the second wave on the polarogram, and the electrolysis was allowed to proceed for 1–2 hours with a stream of nitrogen flowing over the surface of the solution. At the end of this time, the solution was stirred briefly with nitrogen, and a second polarogram was recorded.

During the recording of each polarogram there is an interval during which only the substance responsible for the first wave is being reduced. As this is not taken into account in the derivation of equation (3), it causes the calculated value of n for that substance to be a little too high. Hence the electrolysis interval should be much longer than the time during which the first wave is recorded on the polarogram. Moreover, the logarithmic nature of eqn. (3) is such that the normal experimental errors of measuring the diffusion currents will lead to a fairly large relative error in the calculated value of n unless the electrolysis is allowed to proceed until at least about 50% of each reducible substance has been consumed.

A conventional pen-and-ink recording polarograph was used; in view of the considerations just outlined, care was taken to obtain all polarograms as rapidly as possible. All measurements were made at 25.00 ± 0.01°.

DATA AND DISCUSSION

A typical example of a successful application of the proposed technique is that in which the two reducible substances are thallium(I) and nickel(II). In one experiment a solution containing 2.05 mM thallous ion, 1.99 mM nickel ion, 0.005% gelatin, and 1 F sodium perchlorate was electrolyzed for 60 min at —1.4 V *vs.* S.C.E. During this time the diffusion current of thallous ion decreased from 12.65 to 6.75 μA, while that of nickel ion decreased from 14.51 to 9.84 μA. Substituting these values, together with $n_{\mathrm{Tl}} = 1$, into equation (3) yields $n_{\mathrm{Ni}} = 1.91$. A similar experiment with an ammoniacal ammonium chloride supporting electrolyte gave $n_{\mathrm{Ni}} = 1.95$. The small deviations from the expected value of 2 can be attributed to errors of the order of ±1% in the measurements of the four diffusion currents. As is usually the case in coulometric experiments with dropping electrodes, the precision of the result increases with increasing extent of depletion of the solution; hence it is advantageous to prolong the electrolysis as much as possible.

An example of an interaction between starting material and electrolysis product that does not affect the calculated n-value is that which occurs in the following experiment. A solution initially containing 2.00 mM copper(II) and 2.04 mM iodate in 0.1 F ammonia —0.1 F ammonium oxalate was electrolyzed at —1.40 V *vs.* S.C.E. for 2 h. The total diffusion current of the double wave representing reduction of copper to the amalgam decreased from 15.35 to 9.70 μA, while the diffusion current of iodate decreased from 46.9 to 29.3 μA. These data give $n_{\mathrm{IO_3^-}} = 5.82$. However, both the polarogram and the color of the solution at the end of the electrolysis indicated that the reaction Cu(Hg) + Cu(II) → 2 Cu(I) between the amalgam and the copper(II) which escaped electrolytic reduction had occurred to a considerable extent. The nearly correct value of n obtained from the experiment reflects the fact that the copper(I) produced by this reaction gave a diffusion current almost identical with the diffusion current of the copper(II) that the reaction consumed.

At the other extreme, an interaction that does alter the *n*-value was encountered in experiments with solutions containing lead and cadmium ions. When a solution containing 3.97 m*M* lead and 5.00 m*M* cadmium was electrolyzed for 1 h at a potential on the plateau of the cadmium wave, the diffusion current of lead ion decreased from 40.0 to 13.5 μA while the diffusion current of cadmium ion decreased from 44.8 to 36.0 μA. Taking $n_{Cd} = 2$, these data give $n_{Pb} = 0.45$. The error is due to the reaction $Cd(Hg) + Pb^{++} \rightarrow Cd^{++} + Pb(Hg)$, which occurs primarily, though not exclusively, at the surface of the dilute cadmium amalgam that collects at the bottom of the cell. When the experiment was repeated with a layer of chloroform to protect the amalgam, and when the tip of the dropping electrode was placed almost in contact with the surface of the chloroform, a value of 1.97 was obtained for n_{Pb}. On the other hand, with the tip of the dropping electrode 1 cm above the chloroform, the value obtained was $n_{Pb} = 1.81$, showing that the above reaction occurs to an appreciable extent during the brief interval between the detachment of a drop from the capillary tip and its entrance into the protective layer of chloroform. Protecting the pool of reaction product with a layer of chloroform is a simple and useful expedient in dealing with metal amalgams; unfortunately it is useless when, as is true in organic systems, the products of the electrode reactions remain in the solution phase.

It is clear that much discretion must be exercised in choosing the pilot substance and in guarding against deleterious side reactions. When this is done, however, the convenience of the technique and its comparative immunity to mechanical sources of error should commend it to the attention of those seeking to determine polarographic *n*-values by electrolyses with dropping mercury electrodes.

SUMMARY

The theory and the experimental and chemical requirements of pilot-ion coulometry with the dropping mercury electrode are outlined, and several examples are given of its application to the determination of *n*-values for half-reactions occurring in polarographic experiments.

RÉSUMÉ

Une nouvelle méthode par mesures coulométriques ("pilot-ion coulometry") est décrite pour la détermination des valeurs de *n* en polarographie, avec électrode à gouttes de mercure.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über "Pilot-Ion" Coulometrie mit einer Quecksilbertropfelektrode. Das Verfahren dient zur Bestimmung polarographischer *n*-Werte.

REFERENCES

[1] B. A. Loveridge and J. J. Lingane, private communication.
[2] S. Bogan, L. Meites, E. Peters and J. M. Sturtevant, *J. Am. Chem. Soc.*, 73 (1951) 1584.
[3] G. A. Gilbert and E. K. Rideal, *Trans. Faraday Soc.*, 47 (1951) 396.
[4] T. De Vries and J. L. Kroon, *J. Am. Chem. Soc.*, 75 (1953) 2484.
[5] R. D. Weaver and G. C. Whitnack, *Anal. Chim. Acta*, 18 (1958) 51.
[6] T. Meites and L. Meites, *Anal. Chem.*, 23 (1951) 1893.

Book reviews

Gas Chromatography, 1960, by R. P. W. SCOTT (Editor), Butterworths, London, 1960, xvii + 466 pp., 95s.

This volume contains the proceedings of the third symposium organised by the Society for Analytical Chemistry and the Gas Chromatography Discussion Group of the Institute of Petroleum, held in Edinburgh in June 1960. Twenty-nine papers were presented at the symposium. Many of these describe developments in the theory of, and construction of, capillary columns and of sensitive detectors, and demonstrate the significant advances made in these fields since the previous symposium. About half the papers describe the application of gas chromatography to specific problems, and their titles indicate the widespread appreciation of the value of gas chromatography in most branches of chemistry. Although the emphasis of the conference lay, not unreasonably, on the use of chromatography for analysis, it is encouraging to note one paper discussing factors involved in the construction of columns for preparative-scale chromatography.

This book should be available to all who are interested in gas chromatography, and in these days this means the majority of chemists. It is to be regretted, of course, that the proceedings of these excellent symposia as separate volumes has become established practice. The papers could more appropriately be published in available journals, as this would cause less confusion in an already overloaded literature.

C. R. PATRICK (Birmingham)

Anal. Chim. Acta, 25 (1961) 97

Qualitative Analysis and Electrolytic Solutions, par EDWARD J. KING, Harcourt, Brace and Company, New York, 1959, xxi + 641 pp., $ 7.25.

Le livre, que nous avons le plaisir de présenter aux lecteurs des "*Analytica Chimica Acta*", est composé des chapitres suivants: Water; An Introduction to Solutes and Solutions; Ionic Reactions and Ionic Equations; The Concentration of Substances in Solution; More About Solutes and Solutions; Coordination Compounds; Reaction Rates and Chemical Equilibria in Solution; Precipitates and Colloidal Suspensions; The Direction of Reversible Ionic Reactions; An Introduction to Calculations with Equilibrium Constants; Acids and Bases; The Common Ion Effect, Buffer Solutions, Indicators; Solutions Containing Several Weak Acids and Bases; The Dissociation of Complex Ions; Electric Cells; The Laboratory Work in Qualitative Analysis; Cation Group 1; Cation Group 2; Cation Group 3; Cation Group 4; Cation Group 5; The Properties of Anions; The Identification of Anions; The Analysis of Solids for Cations and Anions; Special Methods of Qualitative Analysis; Appendixes.

La parution d'un nouveau manuel d'analyse qualitative pourrait laisser nos lecteurs

Anal. Chim. Acta, 25 (1961) 97–98

quelque peu indifférents, vu le nombre de publications déjà existantes dans ce domaine. Or, précisément, le livre en question est à prendre sérieusement en considération, étant donné son originalité.

En ce qui concerne la partie théorique, nous nous plaisons à reconnaître que, peu à peu et en partant des notions les plus simples, l'auteur a su construire un édifice harmonieux qui s'érige jusqu'aux niveaux élevés de la chimie physique. (Nous ne citerons ici en exemple que le calcul des produits de solubilité à partir des énergies libres de formation). D'autre part, de bonnes références bibliographiques permettent aux étudiants intéressés d'étendre les connaissances acquises par la lecture de cet ouvrage. Des nombreux schémas et illustrations aident le lecteur à se faire une idée plus tangible des notions théoriques. Grâce à de petits artifices d'écriture l'étudiant se rend compte quels sont les facteurs importants et quels sont les facteurs secondaires dans un calcul. Des exemples de calculs approximatifs et exacts sont également donnés avec une clarté qui est tout à l'honneur de M. KING.

Quant à la partie pratique, elle est aussi satisfaisante. Elle est essentiellement classique, avec quelques heureuses modifications dictées par les acquisitions récentes de l'analyse chimique.

L'impression du livre est impeccable et en facilite grandement la lecture. Nous recommandons donc vivement cet ouvrage dont l'introduction aux Universités Européennes serait à souhaiter.

I. KAPÉTANIDIS (Genève)

Anal. Chim. Acta, 25 (1961) 97–98

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. GAUTIER, 8e série, 148 pages (16.5 × 25), 14 figures et 8 tableaux, Masson et Cie, Paris, 1960, 26 NF.

La collection dont je lis et analyse régulièrement les Conférences, continue sa bonne voie. Avec un recul de 8 ans, on se rend compte qu'elle répond à un réel besoin. Le succès est dû, nous le savons, au choix des sujets traités et, naturellement, de la notoriété des conférenciers, à la bibliographie intelligente et à une présentation agréable.

Cet ouvrage annuel contient cette fois une mise au point de P. CHOVIN sur la chromatographie en phase gazeuse (appareillage, bases théoriques, température, phase stationnaire, etc.). L'auteur cite quelques applications corps gras, hydrocarbures, matières colorantes, aromes. La deuxième Conférence due à A. DESVIGNES a pour titre: Les possibilités de l'analyse par voie microbiologique. Les micro-organismes se comportent comme de véritables réactifs spécifiques dont on peut suivre la multiplication ou l'inhibition, la modification des activités métaboliques (dosage des hormones). L'auteur insiste sur les difficultés opératoires: choix et conservation des souches. Ensuite, P. DEVILLERS décrit en détail l'analyse bactériologique des sucres; il fait la critique des résultats, précise les normes, les origines et les remèdes aux contaminations. Puis, F. PERCHERON expose les méthodes chimiques et physiques de dosage des groupements C-méthyle et l'identification des chaînes alcoylées dans les matières organiques. L'ouvrage se termine par une intéressante étude de G. LE

Anal. Chim. Acta, 25 (1961) 98–99

Moan (avec 232 références) des problèmes posés par l'emploi des pesticides en agriculture. L'auteur donne le dosage de résidus toxiques dans les aliments et les sols et celui d'un grand nombre de pesticides minéraux et organiques.

Cl. Duval (Paris)

Anal. Chim. Acta, 25 (1961) 98–99

The Identification of Organic Compounds by Stig Veibel, 5th Ed., 2nd English Ed., G.E.C. Gad, Copenhagen, 1961, xvi + 426 pp.

It is just over six years since the first English edition of this book appeared. During this time, many new developments have been made in the field of study covered by this book and it is proper that a new edition should now have been prepared.

Professor Veibel's work in the field of organic functional group analysis needs no elucidation or recommendation from this reviewer; his active researches in this branch of organic analysis have earned him a world-wide reputation which this new edition can only enhance. The book retains the form and system of the 1954 edition, but it has undergone appreciable revision, particularly with regard to the use of new and better reagents for several functional groups, and the means of determining the equivalent weights of the various derivatives used to establish the identity of the unknown compounds. The extended use of non-aqueous titrimetry has led to the improvement of many procedures for the determination of organic compounds. Many of these are now incorporated in the present text. The major part of the book is concerned with the identification of functionality in organic compounds through the formation of specific derivatives and their quantitative analysis — an approach to the subject of organic analysis at which Professor Veibel excells. In contrast, however, the early chapter on ultimate analysis, both qualitative and quantitative, lacks details or even mention of the many excellent new tests and analytical methods which have come to the fore in recent years. Obviously these aspects of organic analysis form a minor part in the purpose of the present text.

In conclusion, this book cannot be too strongly recommended to all interested in organic analysis. It contains a wealth of information (over 400 pages of text in what appears to be a very modestly sized book), and it is well indexed. The errors which have been noted are mainly typographical and in no way alter the chemical sense of the text.

W. I. Stephen (Birmingham)

Anal. Chim. Acta, 25 (1961) 99

Die Flammenspektralanalyse, von W. Schuhknecht, Bd. 48 der Reihe: *Die chemische Analyse*, Ferdinand Enke, Stuttgart, 1961, 258 Seiten, 42 Abbildungen, 67 Tabellen.

Die spektrochemische Analyse mit Flammenanregung, an sich seit mehr als 100 Jahren bekannt, hat in den letzten 15 Jahren eine stürmische Entwicklung durchgemacht. Nicht nur die Anwendungsmöglichkeiten und die Leistungsfähigkeit der auf diesem Prinzip beruhenden Verfahren, sondern auch die Zahl derer, die sich dieser Methoden bedienen haben sich in dieser Zeit erheblich vergrössert. Neben

Anal. Chim. Acta, 25 (1961) 99–100

einer grossen Zahl von Einzelveröffentlichungen über dieses Gebiet, die wohl über 3000 liegen dürfte, sind auch eine Reihe zusammenfassender Darstellungen und Bücher erschienen, welche dem Bedürfnis derer Rechnung tragen, die sich neu in flammenspektralanalytische Verfahren einarbeiten wollen. Auch das hier vorliegende Buch von SCHUHKNECHT ist nicht als vollständige und erschöpfende Darstellung des Gesamtgebietes gedacht sondern als Einführung in und als Hilfe für das praktische Arbeiten. Dementsprechend steht die Beschreibung und Diskussion der wesentlichen Vorgänge, Einrichtungen, Arbeitsprinzipien und Fehlermöglichkeiten im Vordergrund, in einem Umfange, wie es für ein verständnisvolles Arbeiten erforderlich ist und nicht die referierende Behandlung der Literatur. Dabei ist weitgehend auf die eigenen Arbeiten des Verfassers Bezug genommen worden, der sich seit mehr als 25 Jahren mit der Flammenspektralanalyse praktisch beschäftigt und wesentliche Beiträge zur Entwicklung der Methode geliefert hat, die besonders auf apparativem Gebiet und im Bereich der Anwendung auf praktische Fragen liegen aber auch dem Studium einiger theoretischer Fragen gewidmet sind.

Zunächst werden die Zerstäuberbrenner und ihr Betrieb (30 Seiten) und die Anregung in der Flamme (34 Seiten) besprochen, danach Bau und Arbeitsweise der Flammenphotometer und Flammenspektralphotometer (33 Seiten), wobei ihre Vor- und Nachteile gegeneinander gehalten werden. Es folgt eine allgemeine Beschreibung der Arbeitstechnik und -methodik (21 Seiten). Besonders ausführlich ist das Kapitel Flammenphotometrische Arbeitsvorschriften gehalten (74 Seiten), in welchem die Bestimmung der Alkali- und Erdalkalimetalle unter Verwendung des vom Verfasser entwickelten Gerätes in verschiedenen Materialien in allen Einzelheiten beschrieben wird und Hinweise für die Bestimmung anderer Elemente, auch eniger Nichtmetalle, gegeben werden. Ein Abschnitt über Flammenspektrographie (18 Seiten) und ein Literaturverzeichnis (496 Zitate) schliessen das Buch ab.

Das Buch kann als gute Grundlage zur Einarbeitung in die Flammenspektralanalyse empfohlen werden, aber auch dem Erfahreneren wird mancher aus der Praxis gegebene Hinweis von Nutzen sein.

H. BODE (Hannover)

Anal. Chim. Acta, 25 (1961) 99–100

Publications received

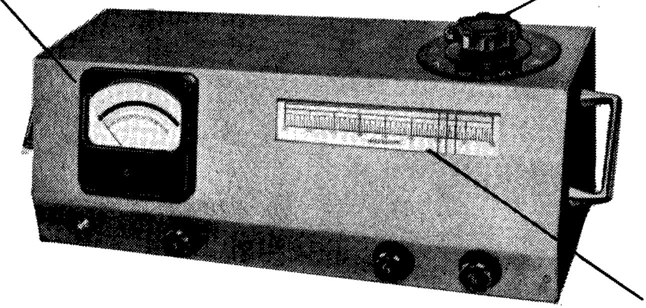
1. *Contributi Teorici e Sperimentali di Polarografia*, Vol. V, 1960, Supplement to *La Ricerca Scientifica*, A cura del Centro di Studio per la Polarografia, Price: 2500 lire, 315 pp.

2. *Bibliografia Polarografica (1922–1959)*, Part I (1958) and Part II (1960), Supplement to *La Ricerca Scientifica*, A cura del Centro di Studio per la Polarografia, Price: 800 lire and 1,000 lire, 80 and 63 pp.

3. *Reagent Chemicals: American Chemical Society Specifications, 1960*, prepared by the 1960 Committee on Analytical Reagents (chairman: W. STANLEY CLABAUGH), Applied ublications, American Chemical Society, Washington, D.C., 1961, xv+564 pp.

4. *Chimie générale et abrégé de Chimie minérale*, par P. COLMANT, Masson et Cie, Paris, 1960, 566 pp., 96 figs., Price: NF 45.

Anal. Chim. Acta, 25 (1961) 100



Elsevier Monographs

...expert knowledge in compact form...

Gas Chromatography

E. BAYER
Institute of Organic Chemistry, Technical University, Karlsruhe (Germany)

5 × 7½" xii + 240 pages 28 tables 88 illus. 420 refs. 1961

Although compact, this monograph contains sufficient detail to be valuable both as a general laboratory manual and as a work to which reference may be made when specific problems arise. Particular attention has been paid to a comprehensive account of applications while the apparatus used is described in detail.
There are over 400 literature references and the appendix contains tables of retention volumes (over 2000) and selectivity coefficients.

CONTENTS:
1. Introduction. 2. Theoretical Treatment. 3. Separatory Columns for Gas Chromatography. 4. Apparatus for Gas Chromatography. 5. Practical Applications of Gas Chromatography. 6. Design and Mode of Action of Detectors.

Principles and Applications of Paper Electrophoresis

CH. WUNDERLY
Medical University Clinic, Zürich (Switzerland)

5 × 7½" xii + 255 pages 33 tables 73 illus. 1721 refs. 1961

An up-to-date review of principles and applications of paper electrophoresis was urgently needed. This completely revised translation of the very successful German edition will fill this need. It gathers together in one compact volume information which is scattered throughout many publications of greater or less accessibility. Only that information which the very experienced author felt to be utterly reliable has been included. The large number of results considered and the carefully compiled list of references (1721) will make this a standard monograph in the field.

CONTENTS:
1. Introduction. 2. Theoretical Foundations. 3. Methods. 4. Technique. 5. Results (about 100 pages devoted to chapter 5).

ELSEVIER PUBLISHING COMPANY
SPUISTRAAT 110-112
AMSTERDAM

Eastman Organic Chemicals around the world

Workers in the countries served by these distributors of Eastman Organic Chemicals can avoid the paperwork involved in importing. Some of these distributors maintain their own rather substantial stocks from which they can fill orders immediately. All can give you the benefit of the consolidated orders they place.

Among the 3900 Eastman Organic Chemicals these firms distribute are uncommon ones as well as uncommonly pure ones—organics that are often more economical to purchase than to make. These firms make it easier to purchase them. Find yours among them and ask for details.

Distillation Products Industries
Eastman Organic Chemicals Department
Rochester 3, N. Y., U.S.A.

DPi

Distributors

AUSTRALIA
H. B. Selby & Co. Pty. Ltd.
35 York Street
Sydney, N.S.W.

H. B. Selby & Co. Pty. Ltd.
393 Swanston Street
P. O. Box 409G
Melbourne, C.1

H. B. Selby & Co. Pty. Ltd.
Box 606J, G.P.O.
Brisbane, Queensland

AUSTRIA
Heilmittelwerke Wien
G.m.b.H.
III/40, Rennweg 12
Vienna

W. J. Rohrbecks Nachf.
Wehrgasse 18
Vienna V

BELGIUM
Analis, S. A.
14, Rue Dewez
Namur

DENMARK
H. Struers Chemiske
Laboratorium
38, Skindergade
Copenhagen K

FINLAND
G. W. Berg & Co.
Fabiansgatan 14
Helsinki

Havulinna Oy
P. O. Box 468
Helsinki

FRANCE
Touzart & Matignon
3, Rue Amyot
Paris V°

Substantial stocks maintained

GERMANY
Serva-Entwicklungslabor
Romerstrasse 45
Heidelberg

GREAT BRITAIN
Kodak Limited
Kirkby
Liverpool

Substantial stocks maintained

HOLLAND
N. V. Holland Indonesia
Agenturen Mij.
HIAM
139 De Ruyterkade
Amsterdam C

INDIA
The Andhra Scientific Co., Ltd.
4, Blacker's Road,
Mount Road
Madras

Raj-Der-Kar & Co.
Sadhana Rayon House
Dr. D. Naoroji Road
Bombay

INDONESIA
N. V. Chemicalienhandel
Rathkamp and Co.
18 Djalan Madja Pahit
Djakarta

ITALY
Prodotti Gianni, s.r.l.
Via Mecenate, 30/14
Milano

JAPAN
Asano Bussan Company
New Kaijo Building
6 Marunouchi I-Chome,
Chiyoda-ku
Tokyo

NEW ZEALAND
Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 1495
Wellington, C.1

Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 319
Dunedin, C.1

NORWAY
Nerliens Kemisk-Tekniske
Aktieselskap
Tollbodgt. 32
Oslo

PORTUGAL
Soquimica, Sociedada de
Representacoes de
Quimica, Lda.
Rua dos Correeiros, 113-3°
Lisbon

SOUTH AFRICA
Kodak (South Africa) (Pty.)
Limited
"Kodak House"
45 Shortmarket Street
Cape Town

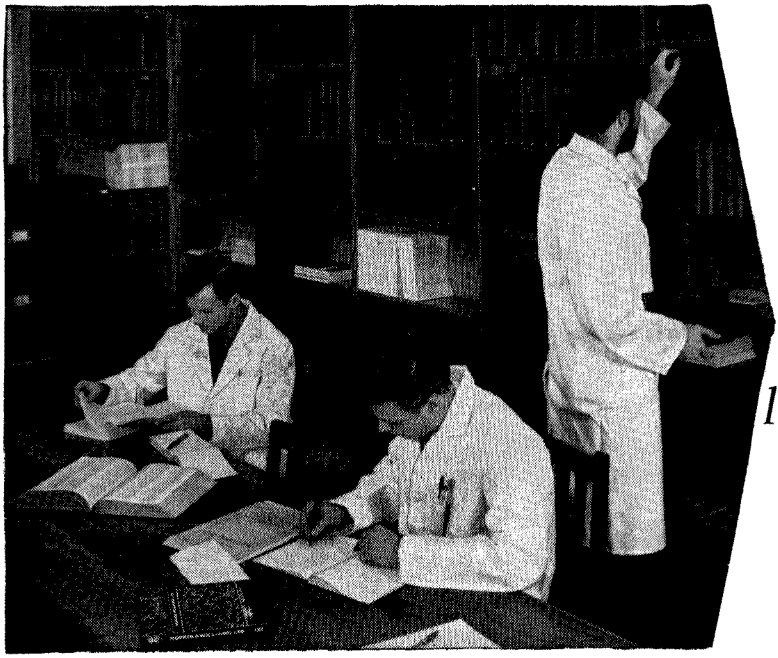
SWEDEN
Rudolph Grave A/B
Box 3082
Stockholm 3

SWITZERLAND
Dr. Bender & Dr. Hobein AG.
Riedtlistrasse 15a
Zurich 6

Distillation Products Industries *is a division of* **Eastman Kodak Company**

Incidental information

No. 15



Items of interest from our laboratory notebooks

▶ Acid radicles by colorimetry

This method, depending on the liberation from chloranilates of an equivalent amount of highly coloured chloranilic acid, is continually gaining in scope as the appropriate chloranilates become available.

We now prepare and supply from stock:—

▶ **Barium chloranilate** for **sulphate**

(J. E. Barney and R. J. Bertolacini, *Anal. Chem.* **30**, 202 (1958)).
CODE 1909 Price—5g: 10/9, 10g: 20/-

▶ **Mercuric chloranilate** for **chloride**

(the above paper and *idem, ibid.* **29**, 1187).
CODE 5541 Price—5g: 10/6, 10g: 19/6

▶ **Lanthanum chloranilate** for **fluoride**

(K. Hayashi *et al., Talanta,* **4**, 126 (1960)) and for **phosphate** (*idem, ibid.*, **4**, 244 (1960)).
CODE 5002·5 Price—5g: 11/9, 10g: 22/-

▶ For analysis and production

1:10-Phenanthroline, a sensitive reagent that gives a stable colour with ferrous ions, can be used to mask Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} in the complexometric titration of Pb^{2+} and Al^{3+} with EDTA. (R. Pribil and F. Vydra, *Coll. Czech. Chem. Commun.*, **24**, 3103 (1959) (in German): *Anal. Abs.* 2668 (1960)). It is also a **dryer-catalyst** and, in conjunction with manganese, can shorten the drying time of printing ink on 'acid' papers (W. H. Canty *et al., Ind. Eng. Chem.*, **52**, 67 (1960)). We offer in bulk for industrial use at considerably reduced prices.
CODE 6580 Price—1g: 6/-, 5g: 23/3

▶ Greater selectivity

As our metal indicator **Xylenol Orange** is used in acid solution, the EDTA titration is unaffected by some common metal ions that do not form EDTA complexes at low pH. Selectivity can be increased still further by using **acetylacetone,** which will mask Fe^{3+}, Al^{3+}, Be^{2+}, Pd^{2+} and UO_2^{2+} in, for instance, the determination of Zn^{2+} or Pb^{2+} (W. Z. Jablonski and E. A. Johnson, *Analyst*, **85**, 297 (1960)).

The above are further examples from the great range of up-to-date reagents made available by Hopkin & Williams Ltd.

H & W
TRADE MARK

CHEMICALS

for research, analysis and industry

HOPKIN & WILLIAMS LTD., CHADWELL HEATH, ESSEX, ENGLAND
Branches: London, Manchester, Glasgow
Agents throughout U.K. and all over the world
TAS/HW.14

VOL. 25 NO. 1 ANALYTICA CHIMICA ACTA JULY 1961

CONTENTS

ELSEVIER PUBLISHING COMPANY, AMSTERDAM
Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH