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| | | |
|---|---|---|
| Vol. **68**, No. 1 | January 1974 | |
| Vol. **68**, No. 2 | February 1974 | **(completing Vol. 68)** |
| Vol. **69**, No. 1 | March 1974 | |
| Vol. **69**, No. 2 | April 1974 | **(completing Vol. 69)** |
| Vol. **70**, No. 1 | May 1974 | |
| Vol. **70**, No. 2 | June 1974 | **(completing Vol. 70)** |
| Vol. **71**, No. 1 | July 1974 | |
| Vol. **71**, No. 2 | August 1974 | **(completing Vol. 71)** |
| Vol. **72**, No. 1 | September 1974 | |
| Vol. **72**, No. 2 | October 1974 | **(completing Vol. 72)** |
| Vol. **73**, No. 1 | November 1974 | |
| Vol. **73**, No. 2 | December 1974 | **(completing Vol. 73)** |

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# the role RNA in reproduction and development

**Proceedings of a Symposium of the American Association for the Advancement of Science, Washington, D. C., December, 1972, sponsored by the Division of Developmental Biology, American Society of Zoologists.**

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CONTENTS:

Session 1: RNA Metabolism in Developing Embryos and Organs. Gene transcription and gene expression during sea urchin development (P. R. Gross and K. W. Gross). Unbalanced growth and cell determination in frog embryos (R. A. Flickinger). Ovalbumin mRNA, complementary DNA and hormone regulation in chick oviduct (R. T. Schimke, R. E. Rhoads, R. Palacios and D. Sullivan). Regulation of albumin synthesis in cultured mouse hepatoma cells (J. Papaconstantinou and B. E. Ledford). Session 2: RNA Programmed Protein Synthesis in Cell-Free Systems. Session 3: RNA Effects on in vivo Synthesis of Specific Proteins. A hormone-controlled RNA fraction regulating enzyme development in plant cells (S. Sawhney and A. Galston). Effects of exogenous RNA on steroid metabolism in adrenals and gonads (D. Villee and A. Goswami). Thyrotropin-like activity of thyroid RNA in vitro (J. Mu). In vivo uptake of RNA and its function in castrate uterus (M. C. Niu, L. C. Niu and S. F. Yang). Injection of messenger RNA into living cells and its application to the study of gene action in Xenopus laevis (J. S. Knowland, J. Gurdon and R. A. Laskey). Session 4: Transfer of Tissue Specificity. The role of macrophage RNA in the immune response (M. Fishman). Biological potentiality of testis-RNA. I. Induction of axial structures in whole and excised chick blastoderms (H. Lee and M. C. Niu). Biological activity of RNA from estrogen-stimulated uterus (P. Galand and N. Dupont). Effects of exogenous polynucleotides on uterine enzymes (C. Villee). The role of RNA in the differentiation of presumptive ectoderm from urodele embryos (N. Sasaki and M. C. Niu). Session 5: Nucleic Acid-Induced Changes in Living Systems. Transforming RNA as a template directing DNA and RNA synthesis in bacteria (M. Beljanski and M. Plawecki). RNA mediated transformation in Pneumococcus (A. Evans). Requirement of informational molecules in heart formation (A. K. Deshpande, L. C. Niu and M. C. Niu). Intercellular communication during odontogenic epithelial-mesenchymal interactions (H. C. Slavkin and R. Croissant). Nucleic acid induced changed in Neurospora (N. Mishra, G. Szabo and E. L. Tatum). Specific and heterospecific transfer of hormone action by mRNA (S. J. Segal, R. Ige, M. Burgos, P. Tuohimao and S. S. Koide). Session 6: Mechanism of RNA Action. Appearance and decay of RNA in cytoplasm of sallivary gland cells of Chironomus tentans (J. E. Edström). Sequence composition and organization of the genome and of the nuclear RNA of higher organisms: an approach to understanding gene action (D. Homes and J. Bonner). Nonhistone proteins as gene de-repressor molecules (T. Y. Wang and N. C. Kostraba). RNA in gene de-repression (J. H. Frenster and P. R. Herstein). RNA directed DNA synthesis in normal cells (C. Y. Kang and H. Temin). Index.

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*Analytica Chimica Acta*, 72 (1974) 1–29

# THE SIMULTANEOUS DETERMINATION OF 20 TRACE ELEMENTS IN TERRESTRIAL, LUNAR AND METEORITIC MATERIAL BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

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(Received 12th February 1974)

In a planned investigation of lunar material, two groups of trace elements appeared to be of unusual interest: volatiles and siderophiles[†]. Volatile depletion in many meteorite types relative to solar composition apparently reflects the conditions in the nebula at the time of accretion[1]. Since even highly differentiated rocks show vestiges of the Earth's volatile depletion pattern, it was clearly important to gather analogous data for the Moon. Siderophile elements, particularly the platinum metals, are strongly depleted in the Earth's crust and are good indicators of extra-terrestrial infall[2–4]. If the Moon were a differentiated body (as proved to be the case), these elements could provide valuable clues concerning the influx of meteoritic material. Abundances for volatile and siderophile elements were expected to be present in the range $10^{-8\pm4}$ g g$^{-1}$, and experience with meteorites had shown that important trends may become manifest from differences of a factor of 2 or less. In addition, the material to be investigated was scarce and generally irreplaceable, and sample sizes were generally restricted to 1–100 mg. It was important that all elements be determined simultaneously on the same sample to conserve material and to ensure that interelement correlations and ratios were realistic. At present, no purely instrumental analytical technique has the required sensitivity, and radiochemical neutron activation analysis is the only appropriate method currently available.

The initial list of elements comprised Ag, Au, Bi, Br, Cd, Co, Cs, Cu, Ga, In, Ir, Pd, Rb, Te, Tl, and Zn. Later Pd and Cu were dropped and Ge, Ni, Re, Sb, Se, and U were added. The method described below simultaneously determines these 20 elements with sensitivities in the following ranges, in ng g$^{-1}$, assuming a 100-mg sample:

$$10^3 > \mathrm{Ni} > 10^2 > \mathrm{Rb} > 10^1 > \mathrm{Br} > 10^0 > \mathrm{Co, Cs, Ga, Se, Te, U, Zn} > 10^{-1}$$

$$10^{-1} > \mathrm{Ag, Bi, Cd, Ge, In, Sb, Tl} > 10^{-2} > \mathrm{Au, Ir} > 10^{-3} > \mathrm{Re} > 10^{-4}$$

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[†] Denotes iron-loving, *i.e.*, those elements which are strongly concentrated in the Ni–Fe phases of meteoritic (and by analogy, also of planetary) material.

It has enabled actual values (rather than upper limits) to be reported for almost all of the elements sought in 70 meteorites[5–8], 45 terrestrial rocks and 230 lunar samples[9–16]

*Nuclear data*

The relevant data for these determinations are given in Table I. The more likely interferences are also listed.

*Irradiation*

Irradiations were made in batches generally consisting of 12 samples with appropriate standards. The number of samples was largely governed by manpower and equipment limitations; more samples (up to 16) were irradiated when fewer elements were sought. Most runs utilized the reactor at NASA Lewis Research

TABLE I

RELEVANT NUCLEAR DATA

| *Stable isotope (% Abundance)* | *Cross-section barn* | *Isotope produced* | *Half-life (Decay mode)* | *γ-Energy (keV) (% Branching ratio)* | *Interference* |
|---|---|---|---|---|---|
| $^{197}$Au (100) | 98.8 | $^{198}$Au | 2.69 d($\beta^-$) | 412 (95%) | $^{198}$Hg (n, p) |
| $^{109}$Ag (48.65) | 3.0 | $^{110m}$Ag | 255 d ($\beta^-$) | 658 (96%) | $^{110}$Cd (n, p)<br>$^{113}$In (n, $\alpha$) |
| $^{209}$Bi (100) | 0.015 | $^{210}$Bi | 5.01 d($\beta^-$) | — | — — |
| $^{81}$Br (49.48) | 3.0 | $^{82}$Br | 35.3 h ($\beta^-$) | 554 (66%)<br>619 (41%) | $^{82}$Kr (n, p)<br>$^{85}$Rb (n, $\alpha$) |
| $^{114}$Cd (28.86) | 1.1 | $^{115}$Cd | 53.5 h ($\beta^-$) | 335 ($^{115m}$In) | $^{235}$U (n, f) |
|  | 0.14 | $^{115m}$Cd | 43 d ($\beta^-$) | 485 (31%) | $^{115}$In (n, p)<br>$^{118}$Sn (n, $\alpha$) |
| $^{59}$Co (100) | 19 | $^{60}$Co | 5.26 y ($\beta^-$) | 1173 (100%)<br>1332 (100%) | $^{60}$Ni (n, p)<br>$^{63}$Cu (n, $\alpha$) |
| $^{133}$Cs (100) | 28 | $^{134}$Cs | 2.05 y ($\beta^-$) | 605 (98%)<br>796 (99%) | $^{134}$Ba (n, p) |
| $^{63}$Cu (69.1) | 4.5 | $^{64}$Cu | 12.8 h (EC,$\beta^+$) | 511 ($\beta^+$) | $^{64}$Zn (n, p) |
| $^{71}$Ga (39.8) | 5.0 | $^{72}$Ga | 14.1 h ($\beta^-$) | 835 (96%)<br>630 (27%) | $^{72}$Ge (n, p)<br>$^{75}$As (n, $\alpha$) |
| $^{70}$Ge (20.55) | 3.2 | $^{71}$Ge | 11.4 d (EC) | Ga x-ray | $^{74}$Se (n, $\alpha$) |
| $^{113}$In (4.23) | 8.0 | $^{114m}$In | 50 d (IT, EC) | 192 (17%) | $^{114}$Sn (n, p) |
| $^{191}$Ir (37.3) | 750 | $^{192}$Ir | 74.2 d ($\beta^-$) | 317 (81%)<br>468 (49%) | — —<br>— — |
| $^{58}$Ni (67.76) | 4.4 | $^{59}$Ni | 8 × 10$^4$ y (EC) | Co x-ray |  |
| $^{85}$Rb (72.15) | 0.9 | $^{86}$Rb | 18.7 d ($\beta^-$) | 1078 (8.8%) | $^{86}$Sr (n, p)<br>$^{89}$Y (n, $\alpha$) |
| $^{185}$Re (37.07) | 110 | $^{186}$Re | 88.9 h ($\beta^-$) | 137 (9%) | $^{186}$Os (n, p) |
| $^{123}$Sb (42.75) | 3.3 | $^{124}$Sb | 60.3 d ($\beta^-$) | 603 (97%) | $^{124}$Te (n, p)<br>$^{127}$I (n, $\alpha$) |
| $^{74}$Se (0.87) | 30 | $^{75}$Se | 120 d (EC) | 136 (57%)<br>265 (60%) | $^{78}$Kr (n, $\alpha$) |
| $^{122}$Te (2.46) | 1.0 | $^{123m}$Te | 117 d (IT) | 159 (84%) | $^{126}$Xe (n, $\alpha$) |
| $^{203}$Tl (29.5) | 11 | $^{204}$Tl | 3.8 y ($\beta^-$) | — | $^{204}$Pb (n, p) |
| $^{235}$U (0.72) | 579 (n, f) | $^{132}$Te | 78 h ($\beta^-$) | 230 (90%) |  |
| $^{64}$Zn (48.89) | 0.47 | $^{65}$Zn | 245 d (EC,$\beta^+$) | 1115 (49%) |  |

Center, Plumbrook Station, Sandusky, Ohio. The irradiation time was generally 10 days. A typical dosimetry analysis is given below.

| *Cycle* | *Thermal* | *Fast(> 2.9 MeV)* | *Fast(> 1.0 MeV)* | *Fast(> 0.1 MeV)* |
|---|---|---|---|---|
| 107 | $8 \cdot 10^{19}$ | $1.5 \cdot 10^{18}$ | $4 \cdot 10^{18}$ | $9 \cdot 10^{18}$ |
| 109 | $1.1 \cdot 10^{20}$ | $1.7 \cdot 10^{18}$ | $5 \cdot 10^{18}$ | $1.0 \cdot 10^{19}$ |

These values were calculated assuming a fission spectrum for neutron energies above 1 MeV (Gary Snyder, written communication).

More recently, samples were irradiated at the National Bureau of Standards reactor in Washington, D.C. which yields a dose of *ca.* $5 \cdot 10^{19}$ n in a 10-day irradiation. Samples containing high abundances of the required elements, (*e.g.*, chondritic meteorites) were irradiated for shorter periods at the CP-5 reactor at Argonne National Laboratory in a thermal flux of $10^{13}$ n cm$^{-2}$ s$^{-1}$.

In some cases (Br, Ge, Ir), chemical yields were measured by reactivation with a 10-min irradiation in CP-5.

*Outline of chemical procedure*

After irradiation, samples are fused, in the presence of carriers, in zirconium crucibles with a sodium peroxide–sodium hydroxide mixture. The fusion cake is dissolved in water and sodium sulfide is added.

The precipitate of mixed hydroxides and sulfides contains Ag, Au, Bi, Cd, Co, Cu, In, Ir, Ni, Tl, Zn, some Te, and occasionally some Sb. These are converted to chlorides (Ag precipitates and is removed and purified[17]) and loaded onto an anion-exchange column in 0.75 *M* hydrochloric acid containing cerium(IV). The initial effluent contains Co, Cu, In, Ni, and Te. The tellurium in this fraction is precipitated as metal with sulfur dioxide before further processing of the accompanying elements[18–23]. The tellurium precipitate is combined with other Te fractions before final purification[18,24]. The elements (Zn, Cd, Bi, Tl, Au, and Ir) remaining on the column are then eluted sequentially[18,25,26]. Zinc and cadmium are further decontaminated by a second anion-exchange step: the subsequent processing of thallium and bismuth is based on procedures described by Laul *et al.*[27,28]. The purification of iridium is achieved by hydrolytic precipitation and a cation-exchange step[29]. Gold is twice precipitated with hydroquinone.

The supernate contains Br, Cs, Ga, Ge, Re, Sb, Se, and the remaining Te. After removal of excess sulfide as CdS, gallium is precipitated at pH 6–7 and purified by solvent extraction[30]. (Some Ge and Te are also present in this fraction). Following an iron(III) hydroxide scavenge (which coprecipitates some Re, Sb, and Se), alkali metals are precipitated with tetraphenylboron, and Rb and Cs are determined by the procedure of Tomura *et al.*[31]. After removal of excess tetraphenylboron, the supernate is combined with the iron(III) hydroxide precipitate. The acidity is adjusted to *ca.* 10% sulfuric acid, and Re, Sb and Se are precipitated as sulfides. The supernate is made 3 *M* in sulfuric acid and $GeS_2$ is precipitated. Bromine is recovered from the supernate by solvent extraction into carbon tetrachloride[32]. The $GeS_2$ and CdS precipitates are combined and Ge distilled as $GeCl_4$[33]. Germanium is further purified by solvent extraction[34]. Metallic tellurium is precipitated by sulfur dioxide from the distillation residue and is combined with the other major Te fraction. From the supernate, Re, Sb and Se are recovered as sulfides and combined with the other sulfide fraction containing the same elements. After dissolving the sulfides, antimony is extracted into ether and then purified following procedures given by Tanner and Ehmann[35]. Selenium is precipitated by sulfur dioxide as metal[36], and the rhenium purification is based on the method described by Morgan[37]

## EXPERIMENTAL

### *Samples*

Use powdered and finely divided material (*e.g.*, U.S.G.S. standard rock powders or < 1 mm lunar fines) as received, without further treatment. Other samples should be coarsely crushed to < 2 mm size in an agate mortar; really fine grinding is not recommended, since this greatly increases the likelihood of contamination at the submicrogram level. Prepare irradiation vials (*ca* 8 cm long) from high-purity silica tubing, 3 mm internal diameter with 1 mm wall (*e.g.* Suprasil quartz tubing, Amersil, Inc., Hillside, New Jersey.). Clean in hot nitric acid and then aqua regia, and wash at least 6 times with distilled water. Drain out as much water as possible. Dry in an oven, cool and weigh. Load the sample into a weighed tube, reweigh and seal the vial.

TABLE II

PREPARATION OF MONITOR SOLUTIONS

| *Element* | *Weighing form* | *Treatment* | *Final solution* |
|---|---|---|---|
| Ag | Ag metal[a] | Conc. $HNO_3$ | 7 $M$ $HNO_3$ |
| Au | Au metal[b] | Aqua regia | 1 $M$ HCl |
| Bi | $Bi(NO_3)_3 \cdot 5H_2O$[c] | | 2 $M$ $HNO_3$ |
| Br | $NaBrO_3$[c] | | $H_2O$ |
| Cd | Cd metal[a] | 1:1 $HNO_3$ | 0.1 $M$ HCl |
| Co | Co metal[c] | $HNO_3$ | 1.5 $M$ $HNO_3$ |
| Cs[f] | CsCl[b] | | $H_2O$ |
| Cu | Cu metal[b] | 1:1 $HNO_3$ | $H_2O$ |
| Ga | $Ga(NO_3)_3 8H_2O$[b] | | 0.5 $M$ $H_2SO_4$ |
| Ge | $(NH_4)_2Ge(C_2O_4)_3 4H_2O$[b] | | $H_2O$ |
| In | In metal[d] | 7.5 $M$ $HNO_3$ | 1.5 $M$ $HNO_3$ |
| Ir | $(NH_4)_2IrCl_6$[b] | | 0.2 $M$ HCl |
| Ni | Ni metal[e] | $HNO_3$ | 3 $M$ $HNO_3$ |
| Rb[f] | RbCl[b] | | $H_2O$ |
| Re | $KReO_4$ | | $H_2O$ |
| Sb | $K(SbO)C_4H_4O_6\frac{1}{2}H_2O$[c] | None | $H_2O$ |
| Se | $H_2SeO_3$[b] | | 0.5 $M$ $HNO_3$ |
| Te | Te metal[b] | 7.5 $M$ $HNO_3$ | 1.5 $M$ $HNO_3$ |
| Tl | $TlNO_3$[b] | | 0.2 $M$ $HNO_3$ |
| U[f] | | | |
| Zn | Zn metal[e] | Dil.HCl | 0.1 $M$ HCl |

[a] Matheson, Coleman and Bell.
[b] Johnson-Matthey 'Specpure', spectrographically pure.
[c] Fisher certified.
[d] Tadanac, high-purity.
[e] Baker analyzed.
[f] BCR-1 used as monitor for these elements.

*Standards*

Prepare stock solutions which contain appropriate concentrations (typically 0.5–5 mg $ml^{-1}$ except for nickel which should be about 10 times higher) of the required elements. Typical gravimetric forms used in this work are given in Table II. In order to maximize use of the space in the irradiation capsule it is convenient to prepare mixed monitors. (Some typical combinations used in this work are Ag–Ni–Se, Au–Cd–Zn, Bi–In–Te–Tl, Ir–Co, Ge–Re–Sb; for Rb, Cs, and U, BCR-1 U.S.G.S. standard basalt may be used as a monitor if high accuracy is not required.) Prepare a dilute solution containing a combination of elements in appropriate concentrations, *i.e.*, in the 1 $\mu g\ g^{-1}$–1 mg $g^{-1}$ range. Weigh 0.05–0.10 g of solution into clean silica vials. Add 20–50 mg of "Specpure" magnesium oxide to each vial. (This inert diluent reduces recoil and self-shadowing problems during irradiation). Evaporate the solutions to dryness in an oven, initially at 60°C and gradually increasing the temperature to 80–90°C when nearly dry. Seal the vials.

*Carriers*

Prepare carriers for all elements to be determined (except for uranium which is determined via fission tellurium). The weighing forms used for monitor preparation are suitable, but cheaper analytical-grade chemicals are adequate if available. The carrier solution should be just sufficiently acidic to prevent hydrolysis (except for Br, Ge and Sb which should be in neutral solution if the weighing forms from Table II are used). Typical concentrations of carrier solutions are as follows (in mg $ml^{-1}$ of the element): Ag 15, Au 15, Bi 15, Br 20, Cd 12, Co 15, Cs 10, Cu 15, Ga 15, Ge 5, In 15, Ir 2, Ni 10, Rb 10, Re 5, Sb 15, Se 20, Te 20, Tl 15, Zn 10. In addition, the Cs carrier should contain *ca.* $10^4$ c.p.m. (on Ge[Li] detector) of $^{137}$Cs tracer.

*Preliminary treatment of samples*

Into an appropriate number of zirconium crucibles pipet suitable aliquots of carrier solution, in order of increasing acidity. After the addition of each carrier, add a slight excess of 6 *M* sodium hydroxide, and evaporate to dryness under a heat lamp. Store the crucibles under vacuum in a desiccator until required.

When the irradiated samples are ready for opening, clean each vial in turn in aqua regia and wash with distilled water. Add 5 g of sodium peroxide and 2 g of sodium hydroxide pellets to each zirconium crucible. Open the vial and transfer the sample to the crucible. Add a further 5 g of sodium peroxide and cover the crucible with a zirconium lid, allowing a gap of *ca.* 3 mm at one side. Heat over a Meker burner at very low heat for about 5 min until all water is driven off. (If the crucibles have been stored for several days in a vacuum, this step proceeds very smoothly.) Close the crucible completely, gradually heat to a dull red color, and fuse for about 45 min, swirling the melt every few minutes to assist in dissolution and mixing. Allow to cool for 10 min.

Remove the lid from the crucible and wash with water, allowing the washings to run into a 250-ml beaker. Wash the outside of the crucible, and discard the washings. Stand the crucible in the beaker and cover the latter with a watch glass. Add *ca.* 50 ml of distilled water to the crucible and allow the reaction to subside. Remove the crucible from the beaker and wash carefully inside and outside with water, allowing the washings to run into the beaker. Add *ca.* 3 ml of (1+1) sulfuric acid to the crucible and heat to white fumes over a burner. Cool, dilute with 10 ml of water, and transfer this solution to the beaker. (This solution is usually blue owing to iridium.)

Cover the beaker and warm the contents for 15 min. Add sufficient 10% (w/v) sodium sulfide solution (typically 10–20 ml) to precipitate the insoluble sulfides completely. Heat the solution for a further 15 min. Cool in a cold water bath.

Transfer the solution and precipitate to a 250-ml centrifuge tube and spin down. Transfer the supernate to a clean centrifuge tube and keep both fractions for further treatment. The mixed sulfide–hydroxide precipitate contains Ag, Au, Bi, Cd, Co, Cu, In, Ir, Ni, Tl, and Zn together with *ca.* 50% of the Te and some Sb. The supernate contains Br, Cs, Ga, Ge, Rb, Re, Se, and the remaining Sb and Te.

*Initial separation of Ag, Au, Bi, Cd, Ir, Tl, Zn, and of the Co, In, Ni, Te fraction*

Transfer the sulfide–hydroxide precipitate to a 250-ml beaker using 30 ml of aqua regia. Wash the centrifuge tube with a few ml of hydrochloric acid*. Digest the precipitate for several hours, add 20 ml of hydrochloric acid, and then allow to go to near dryness. Add 5 ml of hydrochloric acid and again evaporate to near dryness. (Repeated evaporation is needed to decompose nitrosyl complexes with iridium, which seriously affect the behavior of this element in the anion-exchange step.)

Prepare an anion-exchange column, 1 cm × 10 cm, using Bio-Rad AG 1-X10 resin, 100–200 mesh, chloride form. Condition the column with *ca.* 100 ml of 0.75 *M* hydrochloric acid–0.004 *M* cerium(IV) solution.

Dissolve the residue from the hydrochloric acid evaporation in 25 ml of 0.75 *M* hydrochloric acid by warming on a hot plate for a few minutes. A white precipitate of silver chloride (and some silicic acid) forms at this point. Cool and add 1 ml of 10% (w/v) ammonium hexanitratocerate(IV) solution. Centrifuge and filter the supernate onto the prepared anion-exchange column. Collect the eluate which contains Co, Cu, In, Ni and some Sb and Te. Wash the silver chloride precipitate with 25 ml of 0.75 *M* HCl–0.004 *M* cerium(IV) solution, and centrifuge. Retain the precipitate for the silver determination. Filter the supernate and transfer to the anion-exchange column. Wash the column with 25 ml of 0.5 *M* hydrochloric acid, and 25 ml of 2 *M* hydrochloric acid. Further separation of the combined eluate is described under *Preliminary treatment of Co–In–Ni–Te fraction* (below).

Elute zinc with 200 ml of 0.1 *M* hydrochloric acid.

Elute cadmium with 200 ml of 0.002 *M* hydrochloric acid.

Elute bismuth with 200 ml of 1 *M* sulfuric acid containing 0.2% cerium(IV) sulfate.

Wash the column with 10 ml of water. Elute thallium with 100 ml of 1 *M* sulfuric acid which has been saturated with sulfur dioxide. Some iridium is eluted in this fraction. Add 2 ml of 1 *M* potassium iodide to precipitate TlI. Centrifuge and retain the precipitate for thallium determination. Reserve the supernate for the iridium determination.

Wash the column with 10 ml of water. Treat the column with 25 ml of

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* All acids used are concentrated unless otherwise specified.

aqua regia. (This is necessary to redissolve gold which was reduced to metal by sulfur dioxide during the Tl elution.) Wash the column with 20 ml of 2 *M* hydrochloric acid. Some iridium is removed from the column during this step and the eluates should be retained.

Wash the column with 10 ml of water and elute gold with 200 ml of 0.1 *M* HCl–0.1 *M* thiourea.

Elute the major iridium fraction with 200 ml of 6 *M* hydrochloric acid.

*Preliminary treatment of Co–In–Ni–Te fraction*

To the first eluate of the initial ion-exchange procedure (above), add sufficient hydrochloric acid to make 2 *M*. Pass sulfur dioxide through the solution for 10 min to precipitate tellurium metal. Centrifuge and retain the precipitate for processing with other Te fractions. Transfer the supernate, which contains Co, Cu, In, Ni and rare earth elements, to a beaker (see Note) and evaporate to dryness.

Prepare a cation-exchange column (1 cm × 25 cm) with Dowex 50W-X8 resin, 50–100 mesh, hydrogen form. Condition the column with 50 ml of 0.1 *M* hydrochloric acid.

Dissolve the dried residue in the minimal volume of 0.1 *M* hydrochloric acid and load onto a prepared cation-exchange column.

Elute indium with 100 ml of 0.5 *M* HCl–40% acetone mixture.

Remove iron from the column with 100 ml of 0.5 *M* HCl–80% acetone mixture.

Elute cobalt with 300 ml of 0.5 *M* HCl–90% acetone mixture. Continue elution until the eluant has become colorless.

Elute nickel with 50 ml of 3 *M* hydrochloric acid. (This fraction also contains rare earth element activity.)

*Note*: If copper is to be determined, boil off sulfur dioxide and precipitate CuS from 2 *M* hydrochloric acid solution. After centrifuging, continue the main procedure with the supernate. Wash the precipitate in 2 *M* hydrochloric acid and redissolve in 3 *M* nitric acid. Add As, Co, and Cr holdback carriers, and remove nitrogen oxides. Dissolve in 2 *M* hydrochloric acid and precipitate CuS. Repeat the sulfide cycle twice. Redissolve CuS and scavenge once with iron(III) hydroxide and twice with lanthanum hydroxide from ammoniacal solution. Finally precipitate CuSCN from 0.5 *M* hydrochloric acid in the presence of sulfite.

The procedure for copper is not given in detail since it was used for comparatively few samples and is not as highly evolved as those for other elements. Occasionally significant contamination (*i.e.* 10–20% of the initial $^{64}$Cu activity) is found in low level samples, apparently because of $^{60}$Co.

*Initial separation of Br, Cs, Ga, Ge, Rb, Re, Sb, Se, and Te*

*Removal of sulfide*. The supernate from the initial hydroxide–sulfide precipitation contains Br, Cs, Ga, Ge, Rb, Re, Se, most of the Sb and about 50% of the Te. Add *ca.* 20 g of cadmium sulfate as a saturated solution to remove excess of sulfide. The CdS precpitate contains about 50% of the germanium, and significant but variable amounts of Re, Sb, and Se. Centrifuge and transfer the supernate to a 250-ml centrifuge tube.

Add 15 ml of 6 *M* hydrochloric acid to the cadmium sulfide precipitate, stir well and set aside for distillation of germanium (see below).

*Precipitation of Ga–Te fraction.* Adjust the acidity of the clear colorless supernate from the removal of sulfide to pH 6–7 using (1 + 1) sulfuric acid. A mixed precipitate of $Ga(OH)_3$ and Te metal (reduction by hydrogen peroxide) is formed, which also contains about 10% of the germanium. Centrifuge and transfer the supernate to a 250-ml centrifuge tube. Retain the precipitate for further processing for Ga and Te.

*Iron scavenge.* Acidify the supernate with 10 drops of (1 + 1) sulfuric acid and add 20 mg of iron(III) holdback carrier (as $FeCl_3$ in 2 *M* hydrochloric acid). Stand the solution overnight to allow radiochemical equilibration.

Adjust to above pH 12 with 6 *M* sodium hydroxide. The resulting iron(III) precipitate removes $^{59}$Fe which would otherwise interfere with the rubidium determination. This precipitate also contains some Re, Sb, and Se. Centrifuge and filter the supernate into a 250-ml centrifuge tube.

Dissolve the iron(III) hydroxide precipitate in the minimal volume of (1 + 1) sulfuric acid and retain for recovery of Re, Sb, and Se (see below).

*Isolation of Rb–Cs fraction.* Adjust the acidity of the filtrate to 0.05 *M* in sulfuric acid. Add an excess (*ca.* 2 g) of sodium tetraphenylboron, (freshly prepared reagent in water). Centrifuge and filter the supernate into a 250-ml centrifuge tube. Reserve the precipitate for Rb–Cs analysis.

Add sufficient saturated potassium sulfate solution in water to the supernate in order to remove all of the excess of tetraphenylboron. Centrifuge and filter. Discard the precipitate.

*Sulfide precipitation of major Re–Sb–Se fraction.* Add the above retained solution of the iron(III) hydroxide to the filtrate. Adjust the acidity to *ca.* 10% in sulfuric acid. Allow the solution to cool to room temperature. Add 10 ml of 5% (w/v) thioacetamide solution, stir well and allow to stand overnight. Centrifuge and reserve the sulfide precipitate for Re–Sb–Se analysis.

*Sulfide scavenge of Ge.* Adjust the acidity of the supernate to 3 *M* in sulfuric acid. Cool the solution and add 50 mg of bismuth(III) holdback carrier. Add 5 ml of 5% thioacetamide solution, stir well and allow to stand overnight. The $Bi_2S_3$ precipitate scavenges the germanium (*ca.* 30%) remaining in the solution. Centrifuge and reserve the supernate for bromine determination. Add 15 ml of 4 *M* hydrochloric acid to the $Bi_2S_3$ precipitate and stir well.

To the hydrochloric acid solutions of CdS (*Removal of sulfide*) and $Bi_2S_3$, add about 20 mg of potassium chlorate to dissolve the sulfides. Allow to stand until clear, pale-green solutions are obtained. Combine the solutions and transfer to a 100-ml round-bottomed shortneck distillation flask using 15 ml of concentrated hydrochloric acid.

*Distillation of germanium.* Use a simple one-piece distillation unit made from 6 mm i.d. glass tubing, attached to the flask with a (24/40) ground-glass joint. An air inlet passes down the center of the flask, with 5-mm clearance at the bottom. An outlet tube from the top of the flask has a 20-cm section inclined at +15° to the horizontal, running into a vertically downward arm 35 cm long. The latter has a water-cooled section 15 cm long near the top. Distil at a rate of 1–2 ml $min^{-1}$ in a flow of air and collect the distillate in a boiling tube containing 10 ml of water (cooled in an ice bath). Continue until *ca.* 10 ml of solution is left in the distillation flask. Reserve the distillate for germanium determination.

*Recovery of second tellurium fraction.* To the solution in the distilling flask immediately add 80 ml of 2 *M* hydrochloric acid, and stir to dissolve the residue. Pass sulfur dioxide for 10 min to precipitate tellurium. Centrifuge and retain the black precipitate for Te determination (*ca.* 50% of Te in this fraction). The supernate contains *ca.* 50% of Re, Sb, and Se fractions.

*Recovery of second Re, Sb, and Se fraction.* Transfer the supernate to a 150-ml beaker, cover with a watch glass and boil off sulfur dioxide. Evaporate to *ca.* 50 ml and allow to cool. Add 10 ml of 5% thioacetamide solution, stir well, and allow to stand overnight. Centrifuge and discard the supernate. Wash with 3 *M* hydrochloric acid twice, and twice with water. Reject the washings. Combine the precipitate with sulfide precipitate of the major Re–Sb–Se fraction and retain for Re–Sb–Se determinations.

### *Treatment of Re–Sb–Se fraction*

Dissolve the combined sulfides of the Re–Sb–Se fraction in 10 ml of aqua regia. Evaporate to near dryness in a water bath.

*Extraction of Sb.* Dissolve the residue in 25 ml of 8 *M* hydrochloric acid and transfer the solution to a 125-ml separatory funnel. Add saturated potassium permanganate solution until there is a permanent brown coloration. (This ensures oxidation to antimony(V)). Extract with an equal volume of isopropyl ether (previously equilibrated with 8 *M* hydrochloric acid). Wash the organic phase with 10 ml of 8 *M* hydrochloric acid and combine the aqueous phases. Reserve the ether phase for antimony determination.

*Separation of Se and Re fractions.* Immediately after extraction, pass sulfur dioxide through the aqueous phase to precipitate selenium. (If the solution is allowed to stand for 1 h or more before passing sulfur dioxide, a small amount of selenium precipitates spontaneously, but the remainder cannot be precipitated even by prolonged treatment.) Centrifuge. Reserve the precipitate for selenium determination, and the supernate for rhenium determination.

### *Purification of individual elements*

*Antimony.* Add 5 ml of 2 *M* hydrochloric acid to the isopropyl ether extract containing Sb, and evaporate the ether in a warm (not hot!) water bath. Dilute the aqueous residue to 15 ml with 2 *M* hydrochloric acid and warm slightly if necessary to obtain a clear solution. Add 2 ml of 5% thioacetamide solution and warm until the orange precipitate coagulates. Cool and centrifuge. Wash the precipitate with 2 *M* hydrochloric acid and with water.

Transfer the precipitate to a 100-ml beaker using 20 ml of water. Add 5 ml of hydrochloric acid and mix well. Add 0.5 g of potassium chlorate, cover with a watch glass and digest until the solution is clear and colorless. Add 5 mg each of $Zn^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $La^{3+}$, and $Cu^{2+}$ holdback carriers. Digest for a few minutes and filter.

Add 5 ml of 5% thioacetamide solution to the filtrate and digest to coagulate the precipitate. Cool and centrifuge. Wash the precipitate with 2 *M* hydrochloric acid and water. Add 10 ml of freshly prepared 3 *M* potassium hydroxide solution saturated with $H_2S$, and warm to dissolve $Sb_2S_3$. Centrifuge and filter. To the filtrate add hydrochloric acid drop by drop until the solution is slightly acidic. (Caution: $H_2S$ evolution can be very vigorous as solution becomes acidic.) Centrifuge and wash the $Sb_2S_3$ precipitate with water.

Repeat from * to *, omitting the addition of holdback carriers.

Add 10 ml of chromium(II) chloride solution to the filtrate; antimony precipitates. Filter onto a glass fiber disk and wash with water and methanol. Dry at 110°C. Allow 2.8-day $^{122}Sb$ to decay before counting. (Sources for $\gamma$-ray counting are mounted on aluminum plates with double-sided scotch tape, and covered with mylar film.)

*Bismuth.* * Evaporate the 200-ml Bi fraction to a low volume. Cool and dilute to 100 ml. Add 5 ml of 5% thioacetamide solution and digest for 10 min on a hot plate. Centrifuge the $Bi_2S_3$ precipitate and reject the supernate. Wash the precipitate with water and reject the washings.

Dissolve the $Bi_2S_3$ in 5 ml of hydrochloric acid. Boil off the hydrogen sulfide. Reduce the volume to 0.5 ml and precipitate BiOCl by addition of water. Centrifuge and reject the supernate.*.

Add 5 ml of hydrochloric acid and 2 ml of nitric acid to the BiOCl precipitate. Add 5 mg of Fe, Cr, Co, Al, Te, Sb, Sn, Ir, Cu, Cd, Zn, Se, and Hg holdback carriers. Evaporate the mixture to dryness overnight in a water bath. Dissolve the residue in 10 ml of 2 *M* hydrochloric acid and add 2 ml of 10% ammonium hexanitratocerate(IV) solution. If the solution becomes cloudy, add a few drops of hydrochloric acid to dissolve the turbidity.

Prepare an anion-exchange column, 1 cm × 10 cm, using Bio-Rad AG 1-X10 resin, 100–200 mesh, chloride form. Condition the column with *ca.* 100 ml of 0.5 *M* HCl–0.004 *M* cerium(IV) (prepared immediately before use) followed by 50 ml of 2 *M* hydrochloric acid. Load the above solution onto the column. Wash the column with 100 ml of 2 *M* HCl, 200 ml of 0.1 *M* HCl and 200 ml of 0.002 *M* HCl. A white band forms as BiOCl precipitates on the column. Reject the washings.

Elute bismuth with 200 ml of 1 *M* sulfuric acid containing 0.2% cerium(IV) sulfate. Repeat the procedure from * to *.

Dissolve BiOCl in 10 ml of 2 *M* hydrochloric acid. Dilute to 15 ml with water. Heat the solution and add 10 mg of Ag carrier. Allow to cool, and centrifuge. Filter the supernate. Reject the AgCl precipitate.

Add dilute ammonia solution to the filtrate until bismuth hydroxide precipitates. Cool and centrifuge. Reject the supernate. (Check the $\gamma$-activity of the precipitate at this stage. It should be less than 20 c.p.m. above background with a 3 × 3 in. NaI(Tl) detector with a threshold of 100 keV.)

Dissolve the bismuth hydroxide in 30 ml of 6 *M* hydrochloric acid. Transfer the solution to a separatory funnel and shake with an equal volume of methyl isobutylketone (MIBK). Reject the organic phase. Add another 30-ml portion of MIBK and 0.5 g of solid sodium iodide. Extract bismuth iodide into the organic phase. Reject the aqueous phase. Wash the organic phase with 30 ml of 6 *M* hydrochloric acid containing 0.5 g of sodium iodide. Discard the washings. Add 15 ml of 6 *M* hydrochloric acid and 0.5 g of sodium nitrite. When the reaction has ceased, back-extract bismuth into the aqueous phase (the organic phase should be yellow and the aqueous phase colorless).

Add ammonia solution to the aqueous phase to precipitate bismuth hydroxide. Allow to cool, and centrifuge. Reject the supernate. Wash the precipitate with water. Discard the washings.

Dissolve the bismuth hydroxide precipitate in 2 ml of nitric acid and dilute to 10 ml. Warm the solution and add 0.5 g of trisodium phosphate. Boil and dilute to 40 ml. Allow to cool and let the bismuth phosphate settle. Centrifuge and discard the supernate.

Dissolve the precipitate by warming with 2 ml of hydrochloric acid. Add 6 *M* sodium hydroxide solution to precipitate bismuth hydroxide. Cool and centrifuge. Discard the supernate. Dissolve the precipitate in 10 ml of 2 *M* hydrochloric acid and filter into a *new* centrifuge tube. Add ammonia solution to precipitate bismuth hydroxide.

Dissolve this precipitate in 1 ml of hydrochloric acid. Add water until the first turbidity appears. Allow to stand. Add water from time to time until precipitation of bismuth oxychloride is complete.

Filter onto a paper filter disk (lower background than glass fiber filter) and wash with water and methanol. Dry in an oven at 110°C.

Mount on a low-background stainless steel disk and cover with mylar film. Count the $^{210}$Bi $\beta$-activity in a low background (*ca.* 0.2 c.p.m.) $\beta$-proportional counter. Correct the activity for self-absorption (Fig. 1).

*Bromine.* Add excess of Bi holdback carrier to the bromine fraction to precipitate excess of sulfide. Filter into a 1-l separatory funnel and add a slight excess of permanganate. Add 200 ml of carbon tetrachloride and extract bromine (organic phase gives a golden color).

Drain off the organic phase and wash with 100 ml of water. Discard the washings. Back-extract bromide into 100 ml of water containing a slight excess of sodium sulfite.

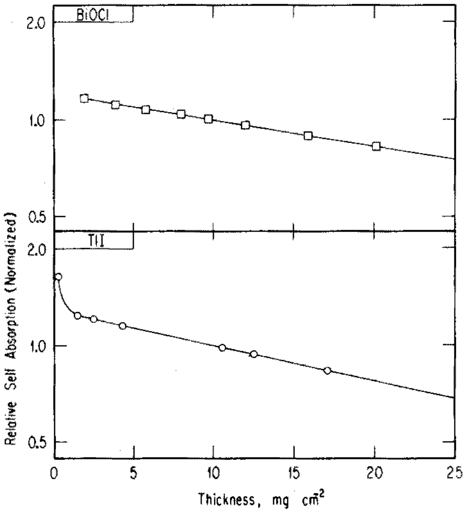

Fig. 1. Beta self-absorption for $^{210}$Bi in BiOCl and for $^{204}$Tl in TlI. Recalculated from curves given by Laul (1969)[38] using a source area[27] of 3.08 cm$^2$. The data were arbitrarily normalized to a source thickness of 10 mg cm$^{-2}$.

[Optional step: Make the solution 2 *M* in sulfuric acid. Add a slight excess of permanganate and extract bromine with 100 ml of carbon tetrachloride. Wash with 50 ml of water. Discard the washings. Back-extract into 50 ml of water containing a very slight excess of sulfite.]

Make the aqueous phase 3 *M* in nitric acid. Heat to boiling and add silver nitrate solution to precipitate silver bromide. Filter onto a glass fiber filter and wash with water and acetone. Dry for 30 min at 110°C. If the optional step has been omitted, the chemical yield of AgBr should be checked by re-irradiation, since silver sulfite may be present.

*Cadmium.* To the 200-ml cadmium fraction, add 5 mg each of $Fe^{3+}$, $Zn^{2+}$, $Cr_2O_7^{2-}$, $Sc^{3+}$ and $Co^{2+}$ holdback carriers. Evaporate the solution to dryness.

Prepare an anion-exchange column, 1 cm × 10 cm, using Bio-Rad AG 1-X10 resin, 100–200 mesh, chloride form. Condition the column with 100 ml of 1 *M* hydrochloric acid before use. Dissolve the residue in 15 ml of 1 *M* hydrochloric acid, warming the solution if necessary. Add titanium(III) chloride solution to reduce iron(III) and dichromate (test for iron(III) with thiocyanate to verify complete reduction). Load onto the prepared anion-exchange column. Wash the load solution through the column with 20 ml of 1 *M* hydrochloric acid containing a few drops of titanium(III) solution. Wash the column with 100 ml of 1 *M* hydrochloric acid and 300 ml of 0.1 *M* hydrochloric acid. Reject the washings.

Elute cadmium with 200 ml of 0.002 *M* hydrochloric acid. Evaporate to dryness. Dissolve the residue in 15 ml of water and a drop of hydrochloric acid. Add 5 ml of 3 *M* ammonium chloride and warm gently. Add 5 ml of 1.5 *M* diammonium hydrogenphosphate dropwise to precipitate $Cd(NH_4)PO_4$. Allow the mixture to stand for an hour. Filter onto a glass fiber disk. Wash with water and acetone. Dry at 110°C.

Allow the 4.5-h $^{115m}In$ daughter to come to secular equilibrium with 54-h $^{115}Cd$ before counting.

*Cesium and rubidium.* Transfer the tetraphenylboron precipitate from the centrifuge tube to a 150-ml beaker. Add approximately 25–30 ml of 4 *M* nitric acid and 10 mg of iron(III) carrier. Cover the beaker with a watchglass and heat the mixture overnight (*ca.* 16 h). Add 2 ml of 70% perchloric acid and digest until the solution is a clear yellow. Add 6 *M* sodium hydroxide to precipitate iron(III) hydroxide. Filter and discard the precipitate. Acidify the filtrate and evaporate to 15 ml. Transfer the liquid into a standard glass counting vial.

Count on a Ge(Li) spectrometer: use the 600-keV peak for $^{134}Cs$, 662-keV peak for $^{137}Cs$ tracer added, and the 1085-keV peak for $^{86}Rb$.

Some $^{137}Cs$ is produced by fission of $^{235}U$ in the sample. For the present irradiation and counting conditions even as much as 1 $\mu$g U produces only *ca.* 1 c.p.m. $^{137}Cs$ which is completely swamped by *ca.* $10^4$ c.p.m. $^{137}Cs$ added as tracer. It is necessary to ensure that the $^{137}Cs$ tracer used does not contain appreciable $^{134}Cs$ activity.

*Cobalt.* Evaporate the pure cobalt fraction (*viz.* the middle fraction from the green band) to a small volume. Precipitate cobalt hydroxide with 10 *M* potassium hydroxide. Centrifuge and discard the supernate. Dissolve the precipitate in 6 *M* acetic acid. Dilute the solution to *ca.* 3 *M* acetic acid and warm on a water bath.

Add solid chunks (not powder) of potassium nitrite to precipitate

$K_3[Co(NO_2)_6]H_2O$. (Add the chunks in small amounts to avoid frothing.) Filter on a glass fiber disk and wash with water and alcohol. Dry at 110°C.

*Gallium.* The gallium fraction also contains some Ge, Te and $SiO_2$. Add 10 ml of 2 *M* hydrochloric acid to dissolve $Ga(OH)_3$ and $GeO_2 \cdot x H_2O$. Centrifuge and reserve the black metallic tellurium residue for further analysis.

Add 5 mg of iron(III) holdback carrier and adjust to above pH 12 with 6 *M* sodium hydroxide ($Ga(OH)_3$ redissolves in strongly alkaline solution). Centrifuge and filter. [This fraction contains a small amount (about 10%) of germanium, which can usually be neglected. If it must be recovered, gallium can be extracted from 5.5 *M* hydrobromic acid, instead of hydrochloric acid, in the following step and germanium then recovered from the aqueous phase, as described by Wasson and Baedecker[44].] Discard the iron(III) hydroxide precipitate.

Adjust the acidity of the supernate to 6 *M* hydrochloric acid, and extract gallium twice with equal volumes of isopropyl ether. Wash the organic phase twice with 6 *M* hydrochloric acid and back-extract gallium into water by 3 successive extractions. Add 5 mg of iron(III) to the aqueous phase and repeat the addition of sodium hydroxide and centrifugation.

Acidify the filtrate to pH 1. Heat the solution to 80°C and add 5 ml of 5% (w/v) 8-quinolinol (oxine) reagent in 2 *M* acetic acid. Precipitate gallium oxinate by dropwise addition of 6 *M* ammonium oxalate (precipitation starts at pH 2). Filter, wash the precipitate with water (not acetone or alcohol) and dry at 110°C.

*Germanium.* To the germanium fraction (distillate), add 10 ml of 5% thioacetamide reagent and seal the tube with plastic stretchfilm (Parafilm). Allow to stand for at least 24 h ($GeS_2$ tends to be colloidal and very difficult to centrifuge unless it is given several hours to coagulate). Centrifuge and reject the supernate. Dissolve the precipitate in 5 ml of ammonia liquor. Stir well and centrifuge. Transfer the supernate to a centrifuge tube. Leach the residue with another 5-ml portion of ammonia liquor. Centrifuge and combine the supernates. Reject the yellowish-white sulfur residue.

Evaporate the solution to dryness on a water bath. Dissolve the residue in 5 ml of 4 *M* hydrochloric acid containing 10 mg of potassium chlorate. Allow to stand for 24 h. (The resulting solution should then be clear and colorless.) Add 20 ml of hydrochloric acid and extract with two 15-ml portions of carbon tetrachloride. Wash the combined organic phase twice with 15 ml of 10 *M* hydrochloric acid. Reject the washings. Back-extract with two 10-ml portions of 1 *M* hydrochloric acid. Acidify the combined aqueous phase to 6 *M*. Saturate the solution with $H_2S$, seal the tube, and allow to stand for 24 h. Filter onto a paper disk. Wash with water and dry at 105°C. Mount the x-ray sources on scotch tape only, and cover with mylar. Count the 9.3-keV Ga-*K* x-ray of 11-day $^{71}$Ge using a Si(Li) high-resolution, low-background detector.

The chemical yield is determined by re-irradiation via the 266-keV $\gamma$-photopeak of 82-min $^{75}$Ge.

*Gold.* Evaporate the gold fraction (200 ml of 0.1 *M* HCl–0.1 *M* thiourea) to dryness. Cover the beaker with a watch glass and cautiously add 15 ml of nitric acid to the residue dropwise. Warm on a hot plate. Use great care since the destruction of thiourea by nitric acid is very violent. When the reaction has ceased, add 15 ml of hydrochloric acid, and evaporate to near dryness. Repeat the evaporation three times. Do not evaporate to dryness completely, because gold may be reduced to the metal. Dissolve the residue in 30 ml of 2 *M* hydrochloric acid.

⋆Filter the solution into a 40-ml centrifuge tube. Heat this solution in a *boiling* water bath and add hydroquinone (20 g) to precipitate metallic gold. (The water bath must be boiling to coagulate gold sufficiently for quantitative decantation.) Stir well and digest for 30 min. Decant the solution while hot and discard the supernate after making sure that no gold has been carried over. Digest with 30 ml of water to dissolve any hydroquinone, and decant the supernate. Digest with a second 30-ml portion of water.⋆ Centrifuge and discard the supernate.

Dissolve the gold by warming with 2 ml of aqua regia. Remove nitrogen oxides by boiling with hydrochloric acid. Dilute with 30 ml of 2 *M* hydrochloric acid and repeat from ⋆ to ⋆.

Filter onto a glass fiber disk using ethanol to transfer the precipitate quantitatively. Dry at 110°C. Use antistatic spray on mylar film before covering the gold precipitate.

*Indium.* Evaporate the 100-ml 0.5 *M* HCl–40% acetone fraction to a small volume. Add 10 mg of $La^{3+}$, $Fe^{3+}$, $Cu^{2+}$, $Co^{2+}$ holdback carriers, evaporate and adjust the acidity to 10 *M* in hydrochloric acid.

Prepare an anion-exchange column, 1 cm × 30 cm, using Bio-Rad AG 1-X10 resin, 100–200 mesh, chloride form. Condition the column with 100 ml of 10 *M* hydrochloric acid until the yellow color of copper appears in the eluate (typically 400 ml). Evaporate the solution to near dryness.⋆ Add a few drops of bromocresol purple indicator. Add dilute ammonia solution until the pH is 6.3–6.8 to precipitate $In(OH)_3$ and $La(OH)_3$. Centrifuge, and discard the supernate. Dissolve the mixed hydroxide precipitate in a few drops of hydrobromic acid. Add 30 ml of 4.5 *M* hydrobromic acid and extract indium twice into an equal volume of equilibrated isopropyl ether. (If diethyl ether is used, only a single extraction is necessary.) Discard the aqueous phase. Wash the combined organic phases 3 times with 4.5 *M* hydrobromic acid. Reject the washings. Back-extract indium into three 20-ml portions of 6 *M* hydrochloric acid.⋆ Evaporate the aqueous phase (6 *M* hydrochloric acid) to near dryness. Add 10 mg of lanthanum carrier and repeat the procedure from ⋆ to ⋆.

Evaporate the final indium fraction to near dryness. Add 50 ml of water and adjust the acidity to pH 1 with hydrochloric acid. Heat the solution to 60–80°C. Precipitate indium oxinate following the procedure used for gallium; precipitation begins at pH 2.7.

*Iridium.* The iridium appears in three fractions from the initial anion-exchange procedure. Evaporate the 200 ml eluate of 6 *M* hydrochloric acid to near dryness. (This generally contains most of the iridium.) Add the combined eluate of the aqua regia treatment to the same beaker and evaporate to near dryness. Finally, add the 1 *M* $H_2SO_4$–$SO_2$ (+KI) supernate from thallium iodide precipitation and evaporate to fumes of sulfur trioxide.

Add 10 ml of nitric acid, cover the beaker with a watch glass, and digest on a hot plate until the solution turns an intense blue color. (It may take 24–36 h for the color to develop fully, and more nitric acid or (1+1) sulfuric acid may be added as required).

Add 1 mg of Ru (as chloride) and 10 mg of Cr (as dichromate) holdback carriers. Digest on a hot plate until the brown colour disappears and the solution turns deep blue. Dilute to 50 ml with water and filter into a 250-ml beaker. Discard the residue which may contain some anion-exchange resin, metallic gold and possibly silver chloride.

Neutralize the filtrate with solid sodium hydrogencarbonate and adjust to pH 6–7 with 1 *M* sulfuric acid. Digest for a few minutes and check the pH. Add 0.5 g of sodium bromate. Digest on a hot plate for about 1 h, checking the pH from time to time. (The resultant mixture should have a dark brown to black precipitate and a yellow supernate.) Cool and centrifuge. Discard the supernate. Wash the precipitate with water, centrifuge and discard the washings.

Dissolve the precipitate in 5 ml of hydrochloric acid by heating over a bunsen flame. Add 1 mg of Ru and 10 mg each of Cr (as $Cr_2O_7^{2-}$), $Fe^{3+}$ and $Co^{2+}$ holdback carriers. Add 10 ml of hydrochloric acid and evaporate slowly to dryness overnight (chromium is reduced to $Cr^{3+}$). Add 10 ml of 0.03 *M* hydrochloric acid (pH 1.5) and warm over a flame to dissolve the residue. (A white precipitate of AgCl usually forms at this stage.) Cool and centrifuge. Prepare a cation-exchange column, 1 cm × 10 cm, using Bio-Rad AG 50W-X12, 200–400 mesh, hydrogen form. Wash the column with water until the eluate is colorless (initially it is orange to pink). Load the sample solution onto the column and collect the eluate. Hexachloroiridate(IV) passes through the column while $Cr^{3+}$, $Co^{2+}$ and $Fe^{3+}$ are retained. Wash the column with 0.03 *M* hydrochloric acid until the eluate becomes colorless (typically 10 ml is required).

Add 10 mg of Cr holdback carrier and neutralize the eluate with solid sodium hydrogencarbonate. Adjust the acidity to pH 6–7 with 1 *M* hydrochloric acid. Add 0.5 g of sodium bromate and digest until the black precipitate of $IrO_2 \cdot xH_2O$ coagulates. Cool and centrifuge. Discard the supernate. Wash the precipitate with water, and discard the washings.

Dissolve the precipitate by heating with 5-ml portions of hydrochloric acid over a bunsen flame. (This may require several additions and a drop of nitric acid may assist.) Evaporate to near dryness and dissolve in 3 ml of 1 *M* hydrochloric acid. Centrifuge and transfer the supernate to a weighed 2-dram screw-top glass vial. Make up to volume with 1 *M* hydrochloric acid, mix well and reweigh. Take an aliquot of about 10% by weight for chemical yield determination by re-irradiation.

Count the 470 keV $\gamma$-ray of 70-d $^{192}$Ir with a Ge(Li) spectrometer.

The same radionuclide may be used for the yield determination. A very small correction may be necesary for the original $^{192}$Ir activity in the aliquot before re-irradiation. (There is little advantage in using 17-h $^{194}$Ir, because of its lower $\gamma$-branching ratio and production rate).

*Nickel.* Evaporate the nickel fraction to about 15 ml. Add excess of ammonia solution to precipitate insoluble hydroxides. Nickel goes back into solution as an ammine complex. Centrifuge and reject the precipitate.

To the supernate, add 15 ml of dimethylglyoxime (1% in 95% ethanol). Extract with 500 ml of chloroform. Wash the organic phase twice with water containing a drop of ammonia liquor. Back-extract nickel into 80 ml of 6 *M* hydrochloric acid. Evaporate the aqueous phase to dryness. Add 40 ml of water and heat to 80°C. Add excess of ammonia and precipitate nickel by the addition of dimethylglyoxime solution. Filter onto a glass fiber disk. Wash with water and methanol. Dry at 110°C. Count the 7.5-keV Co x-ray from $8 \cdot 10^4$-y $^{59}$Ni using a high-resolution, low-background Si(Li) detector.

*Rhenium.* Filter the rhenium fraction and boil off sulfur dioxide. Adjust the acidity to 8 *M* hydrochloric acid. Add 5 ml of 5% thioacetamide solution, stir well and allow to stand overnight. Centrifuge and reject the supernate.

Dissolve the $Re_2S_7$ precipitate in 3 ml of nitric acid. Warm in a water bath for a few minutes. Add a total of 1 ml of hydrobromic acid dropwise, making sure each one has reacted completely before further addition. Evaporate to near dryness in the water bath. (Do not heat too strongly since many rhenium compounds are volatile.)

Cool and dissolve the residue in 5 ml 1 *M* $H_2SO_4$–0.4% hydrazine sulfate. Extract rhenium with 10 ml of isoamyl alcohol for 10 min. Repeat the extraction with a 5-ml portion of isoamyl alcohol. Combine the organic extracts and wash with 3 ml of 1 *M* $H_2SO_4$–0.4% hydrazine sulfate. Centrifuge and transfer the organic phase to a clean separatory funnel. Back-extract twice for 5 min with 5-ml portions of 5 *M* sodium hydroxide. Combine the aqueous extracts and add 5 mg of $Fe^{3+}$ holdback carrier (as $FeCl_3$ in 1 *M* hydrochloric acid). Add a slight excess of the acid to redissolve iron(III) hydroxide. Cool and add ammonia solution to precipitate the iron(III). Centrifuge and filter.

Add 2 ml of 0.05 *M* tetraphenylarsonium chloride dropwise to the filtrate. Cool the mixture in an ice bath and allow the perrhenate precipitate to settle. Filter onto a glass fiber disk and wash with ice cold water. Dry at 110°C. Count the $\beta^-$-activity of 89-h $^{186}$Re in a low-background $\beta$-proportional counter.

*Selenium.* Wash the selenium metal precipitate twice with 8 *M* hydrochloric acid and once with water. Centrifuge each time and discard the washings. Dissolve selenium by heating with a few drops of nitric acid and continue heating to remove excess of acid.

Add 20 ml of 8 *M* hydrochloric acid to take up selenium. Centrifuge the solution and filter the supernate through a Whatman 541 paper into a clean centrifuge tube. Pass sulfur dioxide through the filtrate until selenium coagulates. Filter onto a glass fiber disk. Wash with 8 *M* hydrochloric acid, water and methanol.

*Silver.* Add 20 ml of ammonia liquor to the silver chloride–silica immediately after precipitation. Stir well and warm to dissolve silver as its ammine complex. Centrifuge and discard the residue. (If barium analysis is required, barium sulfate may be recovered almost quantitatively from this residue.)

⋆Dilute the supernate to 40 ml with water and pass $H_2S$ to precipitate black $Ag_2S$. Centrifuge and discard the supernate. Dissolve $Ag_2S$ by heating with 1 ml of nitric acid. Add 5 mg of iron(III) (as $FeCl_3$ in 1 *M* hydrochloric acid) and warm the mixture; AgCl precipitates. Add 20 ml of (1+1) ammonia solution to dissolve the white precipitate. Centrifuge and filter. Discard the residue.⋆ Repeat the procedure from ⋆ to ⋆. Add 2–3 ml of 6 *M* hydrochloric acid to the supernate and acidify with nitric acid to precipitate silver chloride. Filter immediately onto a glass fiber disk. Wash with water and acetone. Dry at 110°C.

*Tellurium (and uranium).* Combine the tellurium precipitates and dissolve in

3–5 ml of nitric acid. Centrifuge. Wash the sulfur residue with a further 3 ml of nitric acid. Combine the nitric acid fractions, add 5 mg of Se holdback carrier and evaporate to dryness in a waterbath. Dissolve the residue in a few drops of 6 *M* hydrochloric acid and make the solution up to 20 ml in 3 *M* hydrochloric acid.

Prepare an anion-exchange column, 1 cm × 5 cm long, using Bio-Rad AG 1-X10, 100–200 mesh, chloride form. Condition with 100 ml of 3 *M* hydrochloric acid. Load the solution onto the column, and wash with 70 ml of 3 *M* hydrochloric acid. Discard the washings. Elute tellurium with 20 ml of 0.25 *M* hydrochloric acid.

Adjust the acidity of the eluate to 2 *M* hydrochloric acid and pass sulfur dioxide for at least 5 min. Centrifuge and discard the supernate.

★To the precipitate, add 10 drops of nitric acid and 5 mg of selenium. Boil the mixture to near dryness 5 times with the addition of 2 ml of hydrobromic acid. (This step volatilizes any remaining selenium contamination.) Take up the residue in 10 ml of 2 *M* hydrochloric acid and pass sulfur dioxide for at least 5 min.★ Centrifuge the precipitate and repeat the procedure from ★ to ★.

Filter the tellurium precipitate onto a glass fiber disk, and wash with water and acetone. Dry at 110°C. Use antistatic spray during mounting. Count the 228-keV $\gamma$-ray of 78-h $^{132}$Te for the uranium determination. After a delay of 4–6 weeks to allow $^{132}$Te to decay, count the 159-keV $\gamma$-ray of 120-d $^{123m}$Te for the tellurium determination.

*Thallium.* Wash the thallium iodide precipitate with water and reject the washings. Dissolve it in 2 ml of nitric acid and 4 ml of hydrochloric acid. Add 5 mg each of Ir, Te, Sb, Sn, Se, Al, Cu, Cd, and Zn holdback carriers. Digest for several hours on a water bath to ensure equilibration of the carriers, and then evaporate to dryness. Add 10 drops of hydrobromic acid to the residue and evaporate to near dryness on a water bath, to oxidize thallium(I).

Dissolve the residue in 3 ml of hydrobromic acid. Dilute the solution with 30 ml of water (*ca.* 1 *M* hydrobromic acid) and immediately extract thallium into 30 ml of diethyl ether, pre-equilibrated with 1 *M* hydrobromic acid. (If the extraction is not carried out immediately, an insoluble precipitate forms.) Discard the aqueous phase and wash the ether phase three times with 30 ml of 1 *M* hydrobromic acid. Transfer the organic phase to a 40-ml centrifuge tube containing 5 ml of water. Evaporate the ether phase gently with a heat lamp.

Add 2 ml of 2 *M* hydrochloric acid to the remaining water in the tube and mix well. Precipitate brown $Tl(OH)_3$ by the addition of excess of 6 *M* sodium hydroxide. Cool, centrifuge and discard the supernate.

Redissolve the $Tl(OH)_3$ precipitate in 10 ml of 1 *M* sulfuric acid (saturated with sulfur dioxide), warming gently to obtain a clear solution ($Tl^{3+} \rightarrow Tl^{+}$). Add 5 mg of aluminium(III) carrier and mix well. Add ammonia solution dropwise until $Al(OH)_3$ precipitates (thallium stays in solution). Cool, centrifuge and filter the supernate.

To the filtrate add 5 ml of 1 *M* sulfuric acid ($+SO_2$) and mix well. Precipitate thallium(I) iodide by addition of 2 ml of 1 *M* potassium iodide solution. Allow the precipitate to settle for 30 min.

Filter the precipitate onto a paper disk and wash with water and methanol. Dry at 110°C. Count the $^{204}$Tl $\beta^{-}$-activity in low-background, $\beta$-proportional counter. Correct the activity for self-absorption (Fig. 1). If the activity is sufficiently high, the Hg-*K* X-ray following electron capture (2.1% branching ratio) may be counted.

*Zinc.* To the 200-ml zinc fraction, add 5 mg each of $Fe^{3+}$, $Co^{2+}$, Cr (as $Cr_2O_7^{2-}$), and $Sc^{3+}$ holdback carriers. Evaporate to dryness. Dissolve the residue in 15 ml of 2 *M* hydrochloric acid. Add sufficient titanium(III) chloride solution to reduce all iron(III) (test with 10% thiocyanate solution).

Prepare an anion-exchange column as in the cadmium procedure. Condition with 100 ml of 2 *M* hydrochloric acid. Load the zinc solution onto the column. Wash with 100 ml of 2 *M* hydrochloric acid and 300 ml of 1 *M* hydrochloric acid. Discard the washings. Elute zinc with 150 ml of 0.1 *M* hydrochloric acid. Evaporate to dryness. Dissolve the residue in 20 ml of 2 *M* hydrochloric acid and add 10 mg of $Fe^{3+}$ holdback carrier. Precipitate iron(III) hydroxide by adding an excess of carbonate-free sodium hydroxide. Cool and centrifuge. Filter the supernate into a centrifuge tube.

Acidify the supernate by the dropwise addition of 6 *M* hydrochloric acid until the zinc hydroxide precipitate has redissolved. Add 5 ml of saturated sodium carbonate solution and centrifuge. Discard the supernate.

Dissolve zinc carbonate in 1 *M* hydrochloric acid, add 1 ml of saturated oxalic acid and cool the solution in ice. Add 5 ml of $K_2Hg(SCN)_4$ (39 g KCNS + 27 g $HgCl_2$ in 1000 ml of water) and allow the mixture to stand for 1 h to precipitate $ZnHg(SCN)_4$. Filter the precipitate onto a glass fiber disk. Wash with water and acetone. Dry at 110°C.

## DISCUSSION

### *Precision*

Analyses were not routinely replicated, because of the large effort required for each sample (about 1.5 man-weeks) and the rarity of meteoritic and lunar material. In every irradiation, however, a sample of the US Geological Survey standard BCR-1 (Columbia River basalt) was included as a safeguard against gross monitor errors. Not all elements were analyzed in every run, for two reasons. Firstly, the meteorite studies have largely been concerned with the volatile elements and on these occasions the refractory elements were not analyzed. Secondly, in the lunar work, the suite of elements was modified as only the most informative were recognized, and included. Since BCR-1 is a well-mixed powder of a fine-grained rock, the sampling error is small, and the observed error is largely due to between-irradiation variations (*e.g.*, secular changes in neutron spectrum and spatial flux distribution, and monitor errors). The BCR-1 results to date are summarized in Table III.

Previous analyses of C1 (*i.e.*, Type 1 carbonaceous) chondrites have shown large variations, particularly in trace elements[39], and it was generally supposed that these meteorites were inhomogeneous at the scale sampled (typically 0.1–1 g). As verification, chips from different specimens of two C1 chondrites (Ivuna and Orgueil) were analyzed. All C1 samples were irradiated together to minimize between-irradiation errors. (Several replicate analyses of L (*i.e.*, low-iron) chondrites were the first made by an early version of the procedure. These were much less precise than

TRACE ELEMENTS IN U.S.G.S. STANDARD BASALT BCR-1

(p.p.b. except Co, Ge, Ni, Rb, Zn, p.p.m.)

| *Run* | *Ir*[a] | *Re* | *Au* | *Ni* | *Sb* | *Ge* | *Se* | *Te* | *Ag*[a] | *Br* | *In* | *Bi* | *Zn* | *Cd*[a] | *Tl* | *Rb* | *Cs* | *Co* | *Ga* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11-1 | | | 0.43 | | | | | | 26.4 | 97 | 96 | 40 | 127 | 99 | 274 | 44 | 930 | 35.4 | 20.1 |
| 11-2 | | | 1.33 | | | | | | 26.7 | 152 | 107 | 44 | 126 | | 283 | 48 | 920 | 36.7 | 22.5 |
| 12-1 | BCR not irradiated | | | | | | | | | | | | | | | | | | |
| 12-2 | (0.012) | | 0.84 | | | | 95 | | 31.5 | | 91 | 46 | 118 | 124 | 278 | 45 | 890 | 36 | 22 |
| 12-3 | (4.0) | | 0.41 | | | | 94 | | 26.3 | 31 | 96 | 49 | 116 | 127 | 290 | 46 | 925 | 35 | 21 |
| 12-4 | | | | | | | 80 | | 24.3 | | 80 | 46 | 116 | 129 | 289 | | | | |
| 12-5 | (0.058) | | | | | | 85 | | 25.5 | 60 | 88 | 46 | 130 | 120 | 282 | 46 | 900 | 37 | 22 |
| 12-6 | (0.048) | | 0.35 | | | | 95 | | | | | | 108 | 140 | | 47 | 910 | 28 | — |
| 12-7 | 0.0067 | | 0.44 | | | | 90 | | 26.3 | | 91 | 48 | 108 | 134 | 270 | 47 | 930 | 38 | 22 |
| 14-1 | | | | | | | 94 | | 24.8 | | 97 | 44 | 175 | 145 | 300 | | | | |
| 14-2 | | | | | | | | | 27.1 | | 105 | 46 | | | 283 | | | | |
| 14-3 | (≤0.009) | | 0.77 | | | | 86 | | 25.8 | | | 47 | 141 | | 300 | | | | |
| 14-4 | 0.006 | 0.71 | 0.75 | | 480 | | 77 | | 26.5 | | | 46 | | | 300 | | | | |
| 14-5 | 0.001 | 0.71 | 0.74 | | 520 | | 85 | | 26.0 | 60 | 88 | 46 | 110 | 141 | 300 | | | 36 | 22 |
| 14-6 | (≤0.002) | 0.64 | 0.43 | | 460 | | 80 | | 27.1 | | | 46 | 134 | 107 | 300 | | | | |
| 14-7 | (≤0.002) | 0.79 | 0.41 | | 556 | | 92 | | 25.2 | | | 47 | | 135 | 280 | | | | |
| 14-8 | 0.004 | 0.81 | 0.47 | | 556 | 1.31 | 81 | | 25 | 110 | 88 | 46 | 143 | 142 | 305 | | | 35.7 | |
| 15-1 | 0.012 | 0.82 | 0.77 | | 588 | 1.56 | | 5.2 | 25.2 | 68 | | 46 | 150 | 141 | 360 | | | | |
| 15-2[b] | (0.113) | 0.85 | 0.66 | | 543 | 1.46 | 80 | | (145) | 35 | 92 | 42 | | | 302 | | | | |
| 15-3 | 0.0011 | 0.90 | 0.99 | | 616 | 1.35 | 78 | 7.8 | 24.7 | 76 | 90 | 56 | 125 | (530) | 365 | | | | |
| 15-4 | 0.0023 | 0.78 | 0.59 | | 613 | 1.61 | 87 | 4.6 | 31.3 | 84 | 90 | 47 | 140 | 115 | 339 | | | | |
| 16-1 | 0.0023 | 0.92 | 0.58 | | 542 | 1.52 | 97 | 4.3 | 35.7 | 97 | | 51 | 139 | 180 | 302 | | | | |
| 16-2 | 0.0034 | 0.87 | 0.48 | 12.5 | 592 | 1.58 | 90 | 4.6 | 31.3 | 117 | | 50 | 147 | 142 | 359 | | | | |
| 16-3 | 0.0022 | 0.89 | 0.57 | 10.3 | 508 | 1.44 | 78 | 8.2 | 31.5 | 81 | | 39 | 127 | 156 | 252 | | | | |
| 16-4 | (≤0.0116) | 0.95 | 0.89 | 9.2 | 609 | 1.62 | 84 | 4.7 | 30.0 | 72 | | 46 | 135 | 136 | 290 | | | | |
| 17-1 | (≤0.015) | | 0.46 | 10.9 | | 1.53 | 78 | 10 | 24.1 | | | 46 | 132 | 149 | 246 | | | | |
| 17-2[b,c] | (≤0.076) | 1.00 | 0.79 | | 420 | 1.66 | 78 | | | | | | | | | | | | |
| 17-3 | (≤0.002) | 1.01 | 0.78 | 7.3 | 547 | 1.57 | 89 | 5.7 | 24.6 | 50 | | 42 | 129 | 144 | 283 | | | | |
| 17-4 | 0.0038 | 1.06 | 0.38 | 13 | 550 | 1.52 | 83 | 2.7 | 29.5 | 87 | | 46 | 139 | 144 | 269 | | | | |
| 17-5 | 0.0025 | 0.97 | 0.60 | 9.2 | 650 | 1.47 | 77 | 3.1 | 23.6 | 66 | | 42 | 128 | 162 | 269 | | | | |

[a] Underlined values are probably contaminated; values in parentheses excluded from mean (Table IV).

[b] Low flux CP-5 irradiation.

[c] Changed to different batch of BCR-1.

the C1 analyses, partly because of sampling problems, but mainly because of a lower neutron flux and poorer radiochemical purity.)

A few lunar analyses were replicated, when one or more elements were lost initially, or when unusually interesting or suspicious results were obtained. These replicates were irradiated in different batches. Most of the elements examined here are very low in lunar rocks relative to C1 chondrites (except for Rb, Cs, and U) and BCR-1 (except for Ir). Lunar soils are enriched in some elements by meteoritic influx[9–16], and, more rarely, by fumarolic activity[40]. Standard deviations for a single determination ($s$) for each replicate set are plotted in Fig. 2, arranged in increasing

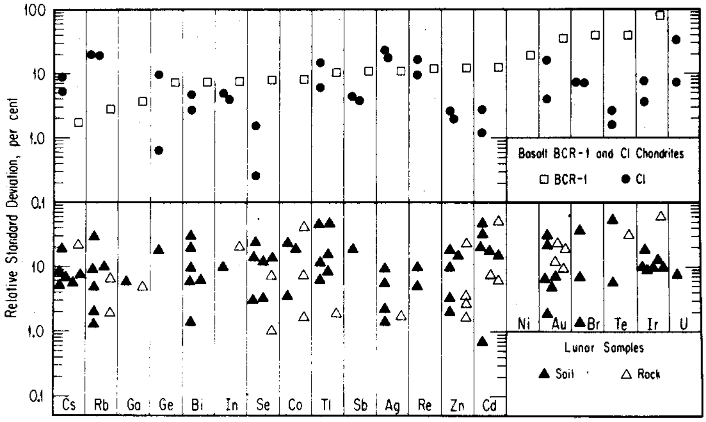

Fig. 2. Relative standard deviations for a single determination ($s$) for replicate determinations of trace elements in U.S.G.S. standard basalt BCR-1, C1 (*i.e.*, type 1 carbonaceous) chondrites[8] (upper) and in lunar rocks and soils[9–16] (lower). Elements are arranged in order of increasing $s$ for BCR-1. Uranium was arbitrarily put last since no independent determinations of the element were made in BCR-1.

order for BCR-1. In BCR-1, Cs, Rb, and Ge are determined to better than ± 5%, in part reflecting their residence in a major mineral phase (feldspar). Apparently, flux inhomogeneity and variations between runs at worst introduce only a few percent error. For C1 chondrites the alkali analyses are less precise, presumably a result of the strange mineralogy of these meteorites (clay minerals, water-soluble phases). Five elements, Ge, Bi, In, Se, and Co, have standard deviations of between 5% and 10% in BCR, and are as well, or better, determined in C1 chondrites. Relative standard deviations of BCR-1 measurements lie between 10% and 20% for Tl, Sb, Ag, Re, Zn, Cd, and Ni. For nickel, the counting statistics alone account for much of the error. The standard deviation for 3 copper values for BCR-1 is also about 10%. For three of these elements (Cd, Sb, Zn), the better precision in C1 chondrites than in BCR-1 may reflect their chalcophilic nature, since sulfides are more abundant (and probably more homogeneously distributed) in the chondrites than in the basalt. The precision for thallium and rhenium in C1 chondrites, is similar to that in BCR-1, but silver is worse by a factor of two, perhaps as the result of a real inhomogeneity in C1 chondrites. The nickel content of C1 chondrites is well established[39] and was not measured again here. Three of the remaining four elements, Te, Au and Br, have relative standard deviations between 35% and 40% in BCR-1, and for Te and Br much of the error is due to the low abundance. In the case of gold, however, the method has the sensitivity to allow precise determination at the BCR-1 level (0.65 p.p.b.) and there appear to be real variations similar to those found in replicates of other terrestrial basalts[41]. In C1 chondrites, these three elements are much more precisely determined, although the precision for gold in Ivuna is worse than one might expect and probably reflects a real sampling variation. Iridium in BCR-1 shows a large scatter mainly because of the extremely low abundances (0.01–0.001 p.p.b.) which approach the detection limit. Some higher values may be due to inactive contamination in sample preparation or radioactive contamination by long-lived $^{192}$Ir. The C1 chondrite results indicate the iridium procedure is reproducible to better than ±10%. Uranium was not determined in BCR-1 here, since this powder was used as the standard. The precision for uranium in Orgueil is only ±7%, but in Ivuna, is ±30% owing to one high value which may possibly reflect contamination. In previous studies of uranium in chondrites[39,42] about 20% of the samples studied appeared to be contaminated, probably because uranium in common terrestrial crustal rocks is $10^2$–$10^3$ times higher than in chondrites, and even more highly enriched in the uranium-bearing minerals seen in many museums.

The relative standard deviations for lunar samples (Fig. 2, lower) have a contribution from between-run errors (probably less than ±5% judging from Rb, Cs, and Ga in BCR-1) in addition to any sampling errors. For Cs, Rb, Ga, In, Ag, Re, Br, and U, the precision is generally about ±10%, and is similar to, or better than, that for BCR-1 or Cl chondrites. The siderophiles iridium and gold do not enter the major silicate in lunar rocks and accordingly are much less abundant, and far less uniformly distributed. In lunar soils their variability probably reflects the distribution of meteoritic Ni–Fe. (The variability in Ge, Ni, and Re is probably similar but far fewer replicates have been analyzed). The occasionally large standard deviations for Tl and Cd (and to a lesser extent Bi, Zn and perhaps Sb) may be the result of small additions of highly enriched material of probably fumarolic origin. Two other volatile elements Se and Te in lunar rocks are determinable with precision similar to that for BCR-1.

To summarize, the method described above can produce results with a precision of about ±10% (one standard deviation for a single determination) for well mixed samples, even when replicates are run in different irradiations, provided that the abundance levels do not approach too nearly the limit of sensitivity.

### *Accuracy*

The results obtained for BCR-1 are compared with those from other laboratories (using chiefly neutron activation and stable isotope dilution) in Fig. 3. Intercomparison data are largely taken from Flanagan's compilation[43] and more recent determinations from the Lunar Science Proceedings[44–46]. Elements are arranged in order of absolute abundance. For those where many data are available, only mean values have been plotted for analyses determined by the same method in a single laboratory. Where the standard deviation of the present determinations exceeds the size of the symbol, error bars have been plotted. No comparison was possible for tellurium, since apparently no other laboratory has analyzed BCR-1

TABLE IV

PRECISION OF TRACE ELEMENT DETERMINATIONS IN TERRESTRIAL, METEORITIC (p.p.b. except Ni, Co, Ge, Zn, Ga, Rb, p.p.m.)

| | *Ir* | *Re* | *Au* | *Ni* | *Co* | *Sb* | *Ge* | *Se* | *Te* |
|---|---|---|---|---|---|---|---|---|---|
| *Terrestrial* | | | | | | | | | |
| BCR-1[a] | 0.004 | 0.86 | 0.64 | 10.3 | 35.3 | 550 | 1.51 | 85 | 5.5 |
| | ±0.003[b] | ±0.12 | ±0.23 | ±2.0 | ±2.9 | ±60 | ±0.10 | ±7 | ±2.2 |
| *Meteorites* | | | | | | | | | |
| Ivuna (3)[a] | 521 | 31.1 | 172 | | | 134 | 31.3 | 19500 | 3080 |
| | ±35 | ±5.2 | ±28 | | | ±6 | ±0.2 | ±300 | ±50 |
| Orgueil (4) | 515 | 37.6 | 150 | | | 130 | 31.3 | 19200 | 2990 |
| | ±19 | ±3.6 | ±6 | | | ±5 | ±3.0 | ±50 | ±80 |
| *Lunar* | | | | | | | | | |
| 10084,49 (4) | 7.6 | 0.71 | 2.9 | | 28 | 2.2 | | 300 | 30 |
| | ±0.8 | | ±1.0 | | ±1 | | | ±42 | |
| 12032,33 (3) | 4.0 | | 1.4 | | 42 | | | 195 | 20 |
| | ±0.4 | | ±0.1 | | ±8 | | | ±7 | |
| 12033,20 (3) | 3.9 | | 1.5 | | 34 | | | 175 | 40 |
| | ±0.5 | | ±0.1 | | ±8 | | | ±21 | |
| 12037,25 (3) | 4.2 | 0.25 | 1.8 | | | 0.77 | | 192 | 40 |
| | ±0.8 | | ±0.4 | | | | | ±27 | |
| 14163,57 (2) | 12.7 | 1.0 | 5.4 | | | 5.7 | | 343 | 50 |
| | ±1.3 | ±0.1 | ±0.1 | | | | | ±11 | ±28 |
| 15401,26 (2) | 2,1 | 0.20 | 1.03 | | 59 | 0.85 | 220 | 197 | 17 |
| | ±0.2 | ±0.01 | ±0.05 | | | ±0.16 | ±40 | ±49 | ±1 |

[a] Number of determinations in parentheses, see Table III for BCR-1 replicates.

[b] Standard deviation for a single determination. No entry indicates only one determination.

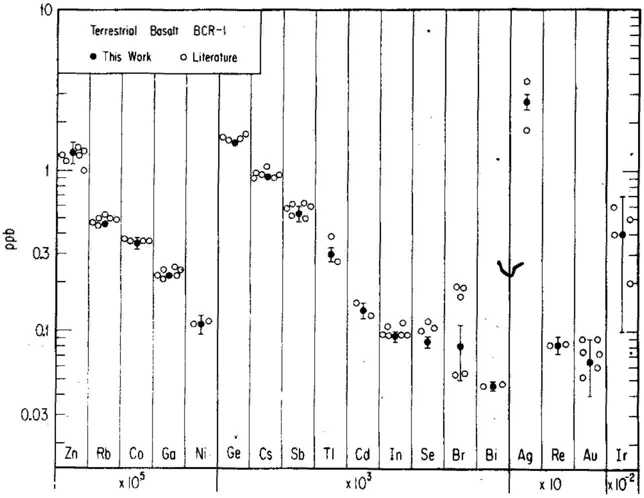

Fig. 3. Comparison of the present BCR-1 trace element results with (mainly) neutron activation and isotope dilution analyses selected from the literature[43–46]. Where there are many data determined by a single method in the same laboratory, only mean values are shown. Error bars are shown for our determination when *s* exceeds the size of the symbol.

AND LUNAR MATERIAL

| *Ag* | *Br* | *In* | *Bi* | *Zn* | *Cd* | *Tl* | *Ga* | *Rb* | *Cs* | *U* |
|---|---|---|---|---|---|---|---|---|---|---|
| 27.1 | 79 | 93 | 45.9 | 131 | 137 | 295 | 21.7 | 46 | 915 | |
| ±3.0 | ±30 | ±7 | ±3.4 | ±15 | ±18 | ±30 | ±0.8 | ±1.3 | ±16 | |
| | | | | | | | | | | |
| 150 | 2350 | 82 | 112 | 304 | 677 | 160 | | 1.850 | 194 | 10.3 |
| ±35 | ±180 | ±4 | ±3 | ±8 | ±8 | ±24 | | ±0.36 | ±17 | ±3.5 |
| 200 | 1450 | 76 | 107 | 303 | 661 | 134 | | 1.99 | 191 | 8.2 |
| ±35 | ±110 | ±3 | ±5 | ±6 | ±18 | ±8 | | ±0.40 | ±10 | ±0.6 |
| | | | | | | | | | | |
| 8.8 | 85 | | 1.6 | 20 | 44 | 1.6 | 5.1 | 3.0 | 99 | |
| ±0.2 | ±6 | | ±0.1 | ±2 | ±9 | ±0.1 | ±0.3 | ±0.3 | ±5 | |
| 3.2 | 180 | 10 | 0.52 | 5.4 | 17 | 1.9 | 5.1 | 7.6 | 385 | |
| ±0.3 | | ±1 | ±0.16 | ±1.0 | ±8 | ±0.9 | | ±0.7 | ±21 | |
| | 130 | | 0.35 | 5.0 | 26 | 1.9 | 4.7 | 8.3 | 400 | |
| | | | ±0.07 | ±0.1 | ±4 | ±0.3 | | ±0.4 | ±28 | |
| | 115 | | 0.71 | 6.1 | 46 | 3.9 | 3.4 | 5.0 | 230 | |
| | ±35 | | ±0.01 | ±0.2 | ±15 | ±1.8 | | ±0.1 | ±44 | |
| 18 | 490 | | 1.7 | 31 | 140 | 33 | | 16.0 | 690 | |
| ±1 | | | ±0.1 | ±0 | ±1 | ±4 | | ±0.2 | ±60 | |
| 60 | 74 | | 1.03 | 59 | 91 | 4.7 | | 3.7 | 185 | 915 |
| ±1 | ±1 | | ±0.10 | ±9 | ±16 | ±0.4 | | ±1.1 | ±14 | ±7 |

for this element.

For Rb, Co, Ga, Ni, Ge, Cs, In, Bi, and Re, the scatter of the literature values is small and they agree well with the present values. The scatter is larger for Zn and Sb but again the overall agreement is satisfactory. There are fewer and more scattered data for Tl, Cd, and Ag, but the present mean value lies well within the range of other analyses. (The mean value found for copper in BCR-1 (17 p.p.m.) lies well within the range given by Flanagan[43].) BCR-1 is clearly not a very good choice for intercomparison of Au and Ir but the present results resemble those from the literature in both variability and absolute value. (Only the iridium values of Greenland *et al.*[47] have been plotted. The values of Baedecker and co-workers[44–46] and certain other groups have been omitted since they are high and probably reflect contamination.) In BCR-1, the present selenium values appear to be low by about 15–20%; this is puzzling since the C1 chondrite values agree with other analyses. Perhaps more BCR-1 analyses from other laboratories may clarify the situation, since for many elements, the number of analyses made in this laboratory exceeds those previously published. There appears to be a problem with bromine. Three closely-grouped literature values are more than twice as high as the present mean (which admittedly shows considerable scatter), whereas two precise unpublished values by O. Müller are lower by a factor almost as large although still within the range of the present results. The C1 chondrite results have recently been compared with those from other laboratories by Krähenbühl *et al.*[8] and their conclusions are briefly restated here. There is excellent agreement for Cs, Bi, Ge and Tl. (The Tl values reported by the Purdue group[28] contain a numerical error, but agree well with present values when corrected.) Agreement is almost as good for In, Re and U if some suspect literature values are ignored. The present iridium values for Orgueil agree reasonably with most other determinations, and similar results were obtained for Ivuna. The present Ivuna values, however, are about 20% higher than the literature abundances for the same meteorite. The present antimony results are more precise than those reported in the literature, but appear to be significantly lower. This trend is also seen in BCR-1. We have yet to discover the cause of this apparent discrepancy. In this laboratory Zn, Cd, Te, and Se were determined precisely, but the literature values have large scatter. The determinations lie rather centrally within the range of the previous analyses.

The remaining elements, Rb, Ag, and Br, show large variance, which perhaps indicates some analytical problems. In the proposed method, the radiochemical yield of Rb and Cs was determined with $^{137}$Cs tracer. If insufficient reagent is added during the tetraphenylborate precipitation (due to variable potassium impurity in the fusion mixture), Rb and Cs may fractionate, leading to erroneous rubidium values. Apparently, the possibility of fractionation is reduced if Rb and Cs carriers are not added (H. Higuchi, personal communication). Nevertheless, the rubidium values largely overlap those reported previously, and there seems to be no significant systematic error. The variation in silver abundances may be genuine, since silver radiochemistry is well-defined. The present values are lower than the literature results, yet these BCR-1 analyses indicate that a systematic monitor error is unlikely. Alternatively, the few C1 chondrite silver values reported by other groups could be high because of contamination. The bromine C1 chondrite results look suspicious. There are lower by a factor of 2 or 3 than the literature values. Krähenbühl *et al.*[8] suggested that active bromine may be preferentially lost from organic compounds as a result of hot atom chemistry, which may lead to the low results.

For the intercomparison of lunar data, the Apollo 11 soil 10084, which has been extensively studied by many other laboratories[44–46], was selected. The analyses are plotted in Fig. 4 in order of abundance. (The indium values have not been plotted because of massive contamination from NASA's indium alloy gaskets).

Of the six most abundant elements, five (Co, Zn, Ga, Rb, and Cs) are very well determined, and agree well with the many literature values. Two other elements, Bi and Re, are in good agreement with the only other available determinations. For three elements, Se, Ir, and Au, values scatter badly by the following factors; Au 12, Se 4, and Ir 3. The present results lie well within these ranges but the comparison is scarcely rigorous. For the remaining elements, Ag, Br, Cd, Sb, and Tl, the present values are substantially lower than those of other groups. For silver at least some of the high literature values are the result of contamination, since silver is a component of the infamous indium alloy gaskets. In the case of Cd, Sb, and Tl we are more inclined to believe the present results, in view of the consistency of the BCR-1 and C1 analyses. For bromine, the situation is unclear. For C1 chondrites, where bromine may partly reside in organic compounds, there may be losses. Experi-

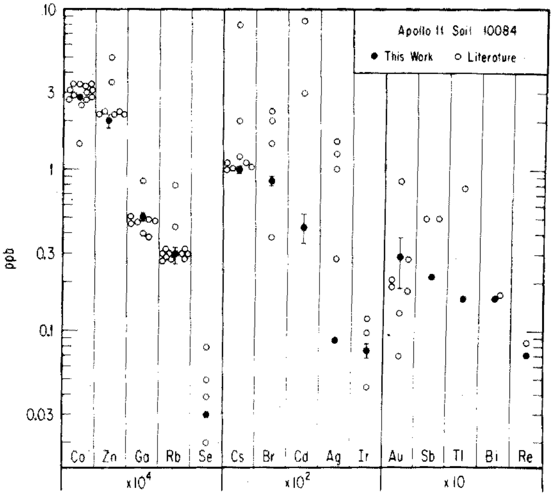

Fig. 4. Comparison of the present results for Apollo 11 soil (< 1 mm fines) 10084 with literature values[44–46] (see Fig. 3 caption for other details). Indium values have not been used because of massive contamination from indium alloy gaskets. There are no literature values for Te; Ge, Ni, and U were incorporated into the scheme after 10084 analyses were complete.

ments with BCR-1, however, indicate that less than 1% of bromine is lost from the rock during irradiation, and that no significant amount is lost during transfer and fusion. One may reasonably expect the same to be true for lunar rocks. In lunar soils, however, bromine may occupy less tightly bound sites, since many elements appear to be surface-correlated[12].

Comparisons in 10084 cannot be made for Ge, Ni, Te, and U. There appear to be no literature values for tellurium. The other three elements were incorporated into the scheme after completion of the 10084 analyses. (The 10084 Ni value of 150 p.p.m., reported in the Luna 16 paper[48] was made via $^{58}$Co and is probably no better than ±25%. The newer x-ray method currently used is vastly superior). In other lunar material the present Ge, Ni, and U values agree well with those from other laboratories.

## APPLICATIONS

### *Cosmic abundances*

C1 chondrites play a central role in cosmochemistry since five lines of evidence suggest that they closely approximate the condensible fraction of primordial solar system material[49]. The most recent "cosmic"* abundance table[51] is based largely on C1 chondrites. Nevertheless, the abundances of several elements showed considerable scatter (*e.g.*, factors of 3–5 for Cd and Te), perhaps indicating real compositional variations. In 8 C1 chondrite samples analyzed here, the standard deviations of a single measurement for 13 elements (Bi, Cd, Cs, Ge, In, Ir, Re, Sb, Se, Te,

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* Although these abundances are based solely upon solar system material, the term "cosmic" is quite valid, since 95% of all stars have essentially solar composition[50].

Tl, U, and Zn) lie between 2 and 14%[8]. For 4 remaining elements, they are: Au ±18%, Ag ±22%, Rb ±19%, and Br ±33%. The first two probably reflect contamination and/or sample heterogeneity; the last two, analytical error. Clearly C1 chondrites are compositionally far more uniform than previously supposed. The new C1 data indicated significant revisions in cosmic abundances for the following elements (old values in parentheses): Zn 1250 (1500), Cd 1.51 (2.12), Ir 0.72 (0.43) atoms/$10^6$ Si atoms.

### *Fractionation in chondrites*

C1 chondrites provide a datum line for interpreting the composition of other chondrite classes. The depletion of volatile elements can be understood in terms of two components; high-temperature, volatile-poor chondrules and low-temperature, volatile-rich matrix[52,53]. The precise elemental complement of each component reflects its temperature of condensation from a cosmic gas. This model predicts that elements which condense above the condensation temperature of the matrix but below that of the chondrules will be depleted by a constant factor. Highly volatile elements will be strongly depleted since they will be only partially condensed even in the matrix. From a critical evaluation of existing data Larimer and Anders[54] verified the two-component model, although there were some irregularities in the depletion pattern. New data from both this laboratory[5,7,8] and others[55] have smoothed the data considerably. The mean depletion of volatile elements (Sb, Rb, Cs, Ge, Se, Te, Ag, Bi, In, Tl, Zn, and Cd) in C2 (Type II carbonaceous) chondrites is 0.51±0.04 (*i.e.*, ratio of C2 to C1 abundance), which implies that the matrix ceased to equilibrate with the cosmic gas below 400°K and chondrules at about 1100°K. For ordinary chondrites, only elements condensing between 550°K and 950°K show constant depletion [0.23±0.03 for H (high iron) chondrites], setting the upper limit of condensation for the matrix and the lower limit for chondrules. Elements condensing between 400°K and 550°K are depleted by variable and usually larger factors, implying that the matrix ceased equilibration with cosmic gas in this temperature range[5,8,55].

### *Meteoritic material on the Moon*

From trace element analyses of lunar soils and rocks, the composition and amount of two types of meteoritic material have been determined: micrometeorites, and ancient planetesimal debris from the early intense bombardment of the Moon[56] The micrometeorite component is uniformly distributed over the front side of the Moon and is seen most clearly in *mare* soils. It resembles C1 chondrites in trace element composition, and comprises 1–1.5% of mature lunar soils. The ancient component is seen in lunar highland breccias and soil older than $3.9 \cdot 10^9$ y, and is depleted in volatile elements relative to siderophiles. The siderophile elements Ir, Re, Au, Ni, and Ge are the most reliable indicators of meteoritic material, and their relative distribution has allowed 6 ancient component groups to be distinguished. The most common of these are characteristically depleted in refractory siderophiles (Re, Ir) relative to normal siderophiles (Au, Ni).

### *Accretion of the Moon*

Most lunar rocks are strongly depleted in volatile elements relative to meteoritic or terrestrial material[9–11]. On the Moon, Tl (a very volatile element), Rb, and Cs (moderately volatile), and U (refractory) are strongly correlated over an abundance range of 3 orders of magnitude. All four elements are lithophilic (stoneloving, *i.e.*, are concentrated in the silicate), form large ions and are not separated from potassium or each other by igneous rock-forming processes. The lunar Tl/U ratio of $(2.8 \pm 1.0) \cdot 10^{-3}$ is well below the terrestrial ratio of 0.27 or cosmic ratio of 17. Without pursuing the model in detail, it appears that the Moon comprised perhaps up to 0.50 of its mass of a Ca–Al early condensate[57], highly enriched (*ca.* 22 times C1 abundance) in refractory trace elements, compared to 0.06 for the Earth[15]. The early condensate seems to have formed the nuclei for accretion of Earth and Moon. Since the Earth is 81 times heavier than the Moon, the Earth's nucleus would have been 10 times larger, and accreted lower temperature material far more efficiently.

### *Lunar highland vulcanism*

Anorthositic rocks* from highland regions (Apollo 15 and 16) often have very anomalous volatile contents, deviating by factors of $10^{-2}$ to $10^4$ from the almost constant Tl/Cs and Tl/U ratios seen in other lunar rocks[15]. The highest enrichment of 6 volatiles (Cd, Ge, Sb, Se, Tl, and Zn) was found in a unique rock which contained goethite (FeOOH). Apparently, vulcanism in the lunar highlands involved the release of water and other volatiles. All highland soils have systematically higher Tl/U than average rocks, which indicates widespread volatile enrichment.

We thank Edward Anders for advice and discussion during the course of this work and for a critical reading of the manuscript. Hideo Higuchi ably contributed to some of the experimental aspects. This work was supported in part by NASA Grant NGL 14-001-167. Some of the counting equipment had been provided by the AEC under Contract AT(11-1)-382.

## SUMMARY

A radiochemical neutron activation method has been developed and was applied to the determination of Ag, Au, Bi, Br, Cd, Co, Cs, Cu, Ga, Ge, In, Ir, Ni, Rb, Re, Sb, Te, Tl, U, and Zn in 45 terrestrial, 230 lunar and 70 meteoritic samples. The inherent accuracy and precision for most elements is generally 10% or better, as is demonstrated by the results for well-mixed powdered rocks, for example, the U.S.G.S. standard basalt BCR-1.

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* Anorthosites are largely composed of plagioclase which in this special case may be approximated by $CaAl_2Si_2O_8$.

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# SIMULTANEOUS DETERMINATION OF CHROMIUM AND SILICON IN STEEL BY 14-MeV NEUTRON ACTIVATION ANALYSIS

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The determination of silicon in cast iron and steel by 14-MeV neutron activation through the $^{28}Si(n, p)^{28}Al$ reaction has already been investigated[1]. However, high chromium contents interfere in the determination of low levels of silicon. In the present work, it is shown that a suitable correction can be applied if the chromium content is determined simultaneously via the $^{52}Cr(n, p)^{52}V$ reaction.

From a recent bibliography[2], it appears that hitherto the determination of chromium by 14-MeV neutron activation has only been examined thoroughly for nickel and chromium alloy matrices[3–5].

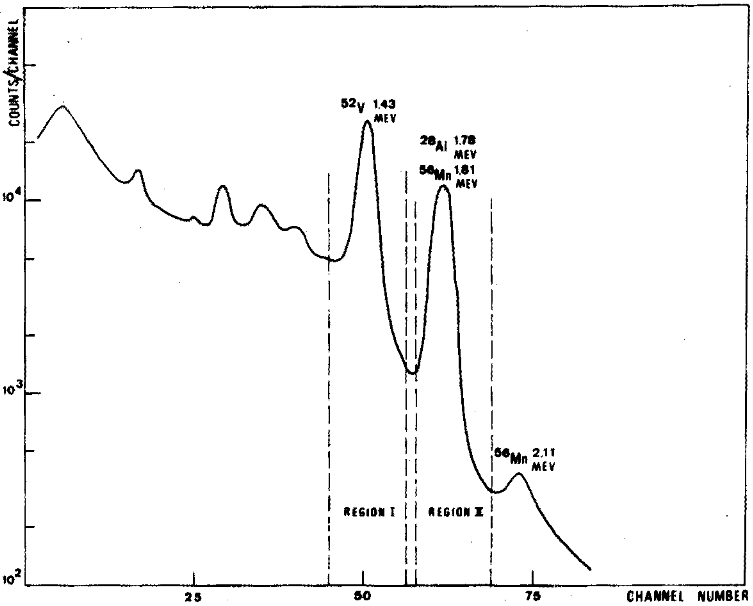

Fig. 1. γ-Ray spectrum of a typical stainless steel sample showing the settings of the two single-channel analysers.

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TABLE I

MAIN REACTIONS OF 14-MeV NEUTRONS WITH CHROMIUM, SILICON AND SOME INTERFERING ELEMENTS

| *Reaction* | *Isotopic abundance (%)* | *Cross-section (mb)* | $t_{\frac{1}{2}}$ | *E(MeV) (% abundance)* |
|---|---|---|---|---|
| $^{28}$Si(n, p)$^{28}$Al | 92.2 | 230 | 2.24 min | 1.78(100) |
| $^{52}$Cr(n, p)$^{52}$V | 83.8 | 90 | 3.76 min | 1.43(100); 1.33(0.9) |
| $^{56}$Fe(n, p)$^{56}$Mn | 91.7 | 110 | 2.58 h | 0.85(99); 1.81(29); 2.11(16); 2.52(1.1); 2.66(0.7) |
| $^{55}$Mn(n, $\alpha$)$^{52}$V | 100 | 40 | 3.76 min | 1.43(100); 1.33(0.9) |
| $^{31}$P(n, $\alpha$)$^{28}$Al | 100 | 130 | 2.24 min | 1.78(100) |

### *Nuclear data*

Figure 1 shows a $\gamma$-ray spectrum obtained from a typical stainless steel sample after a 14-MeV neutron irradiation. The main activities can be attributed to $^{28}$Al(from $^{28}$Si(n, p)$^{28}$Al) and to $^{52}$V (from $^{52}$Cr(n, p)$^{52}$V). Some important features of these reactions and of the main interfering reactions are listed in Table I.

## EXPERIMENTAL

The SAMES J 150-kV neutron generator and associated pneumatic transfer system have already been described in detail[6]. As a flux monitor, a low geometry BF$_3$ long counter was used. Counting was performed with a 3 × 3-in. NaI(Tl) detector coupled to an EMI photomultiplier, a preamplifier NE 5288, an amplifier NE 4603 and two single-channel analysers NE 4602 each connected to a scaler NE 4612. The entire irradiation and counting sequence was controlled by 5 clocks.

An analysis cycle consisted of a 5-s irradiation, during which the neutron output was monitored with the BF$_3$ counter, a 60-s waiting time including the sample transfer to the counting position, a 180-s counting time, an additional 180-s waiting time, and a second 180-s counting time.

The first single-channel analyser was set to span the 1.25–1.60-MeV energy range (region I), while the second one selected the 1.65–2.00 MeV region (region II) as shown in Fig. 1.

### *Calculation of results*

A simultaneous measurement of the activity in the two energy regions allows the determination of both the chromium and silicon content by mixed $\gamma$-spectrometry. The iron matrix, however, produces $^{56}$Mn activity in both energy regions through the $^{56}$Fe(n, p)$^{56}$Mn reaction. This can easily be corrected for by performing two successive countings and assuming the long-lived $^{56}$Mn activity to remain constant during the 360-s time interval between the start of the two countings. The difference in count rates can then be attributed to the decay of the short-lived $^{28}$Al and $^{52}$V activities. It was found that for the analysis cycle used in the case of a typical stainless steel sample, the decay of $^{56}$Mn induced an error of +0.0064% Si and +0.0057% Cr.

The calculation procedure requires the knowledge of the ratios

$$k_{Cr} = \frac{A_{II}(^{52}V)}{A_{I}(^{52}V)} \qquad k_{Si} = \frac{A_{I}(^{28}Al)}{A_{II}(^{28}Al)}$$

where, *e.g.*, $A_I(^{52}V)$ indicates the $^{52}V$ activity in the first energy region.

These ratios can be estimated by measuring the ratio of the activities, in both energy regions, induced in pure silicon and chromium samples. From such experiments, it was found that $k_{Si}$ was independent of the count rate, while $k_{Cr}$ increased as the total induced activity increased (Fig. 2). This can be attributed to pulse pile-up effects in the counting chain. However, when the $^{52}V$ activity in the 1.25–1.60-MeV region was lower than about 4500 c.p.m., the ratio was constant within experimental error. For a typical stainless steel sample, the $^{52}V$ activity could be kept well below this level by limiting the deuteron beam intensity to 60 $\mu$A for a 5-s irradiation. The mean values of $k_{Cr}$ and $k_{Si}$ were 0.0235 and 0.720, respectively, in the conditions used (see Fig. 2).

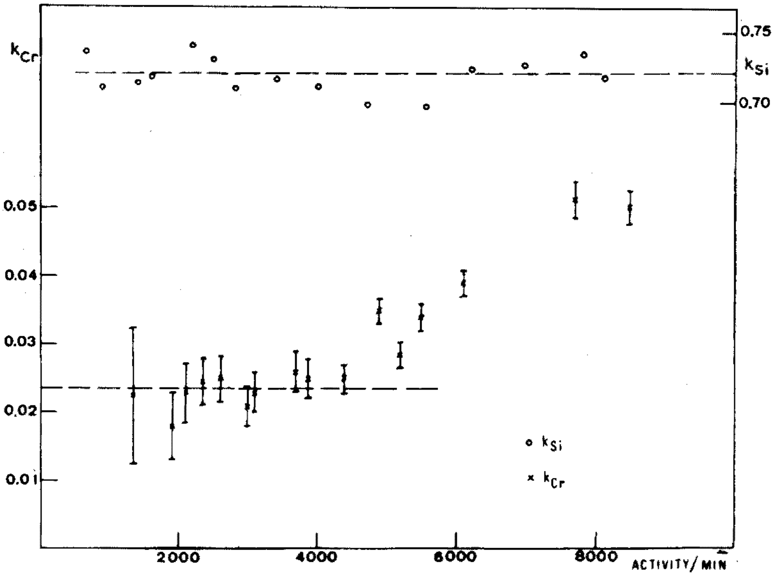

Fig. 2. Dependence of $k_{Cr}$ and $k_{Si}$ on the count rate in the 1.25–1.60 MeV region; (○) $k_{Si}$, (×) $k_{Cr}$.

The chromium and the silicon concentration can then be calculated from the irradiation of a standard and a sample by means of the formulae:

$$(\%\mathrm{Si})_x = \frac{I_{Al,x}}{A_{BF_3} \cdot W_x \cdot K_{Si}} \qquad K_{Si} = \frac{I_{Al,s}}{A_{BF_3} \cdot W_s \cdot (\%\mathrm{Si})_s}$$

$$(\%\mathrm{Cr})_x = \frac{I_{V,x}}{A_{BF_3} \cdot W_x \cdot K_{Cr}} \qquad K_{Cr} = \frac{I_{V,s}}{A_{BF_3} \cdot W_s \cdot (\%\mathrm{Cr})_s}$$

$$I_{Al} = (A_{II,1} - A_{II,2}) - k_{Cr}(A_{I,1} - A_{I,2})$$

$$I_V = (A_{I,1} - A_{I,2}) - k_{Si}(A_{II,1} - A_{II,2})$$

where: % Si, % Cr denotes the weight percent of silicon or chromium;
$A_{BF_3}$, the number of counts recorded with the $BF_3$ counter during the irradiation of the sample or the standard;
$W$, the weight of the standard or sample;
and $A$, the measured activity.

The subscripts x and s indicate, respectively, the sample and the standard, I and II indicate the energy region, and 1 and 2 refer to the first and second counts.

In routine analysis, a standard was irradiated, then five samples, followed by another standard. Results for the samples were calculated from the mean of the surrounding $K$ values.

### *Standards and samples*

The cylindrical steel samples (diam. = 26 mm, thickness = 9 mm) fitted into the rectangular transfer tube. The sample weight was about 36 g.

As standards, steel samples with the same dimensions and similar composition as the samples were used to avoid errors arising from geometry and neutron and $\gamma$-ray attenuation effects. The chromium and silicon contents had been determined by ASTM methods[7]. A typical standard contained 2.79% silicon and 8.83% chromium.

### *Interferences*

Since the analysed samples contain varying amounts of other alloying elements, the possibility of interferences had to be carefully considered. It has been shown that 1% manganese or phosphorus induces an error of +0.31% in chromium or +0.55% in silicon, through the reactions shown in Table I. The resulting corrections for manganese varied from −0.32% Cr (T 60) to −0.04% Cr (W 7). They were deduced from the industrially determined manganese content. Corrections for phosphorus could not be applied since the concentrations were not known. However, in stainless steel the concentration is usually in the 0.015–0.025% P range, hence corrections should be between −0.01 and −0.015% Si.

Interferences caused by other alloying elements (Ti, Mo, Cr, Al, Ni) were found to be negligible.

## RESULTS AND DISCUSSION

Under the described experimental conditions (*i.e.* a 5-s irradiation at 60 $\mu$A deuteron intensity), 1% chromium produces an activity difference ($A_{I,1} - A_{I,2}$) of about 350 counts, and 1% silicon produces an activity difference ($A_{II,1} - A_{II,2}$) of about 2500 counts. The $^{56}$Mn activity from the iron matrix is about 600 counts/180 s in region II and 500 counts/180 s in region I.

Results for 10 steel samples with varying chromium and silicon contents (and with different concentrations of other alloying elements *e.g.* from 20 to 0.2% Ni) are given in Tables II and III.

For the chromium determination, the average relative standard deviation on one determination varied from about 3% for 10–30% Cr, to about 10% in the 2–6% Cr concentration ranges. For silicon, the mean relative standard deviation goes from about 2% to 10% for silicon levels from 1.7 to 0.1%.

TABLE II

DETERMINATION OF CHROMIUM IN STEEL

| *Sample code* | *Industrial analysis (% Cr)* | *Activation analysis (% Cr)* | | | | *Average* | *Relative difference between industrial and activation analysis (%)* |
|---|---|---|---|---|---|---|---|
| H 10 | 31.2 | 32.0 | 31.4 | 31.2 | | 31.6±0.4[a] | +1.1 |
| H 11 | 28.9 | 27.6 | 27.6 | 28.7 | | 28.3±0.6 | −2.0 |
| W 7 | 3.09 | 3.03 | 3.33 | 3.52 | | 3.29±0.24 | +6.5 |
| T 60 | 19.1 | 18.9 | 18.7 | 19.9 | | 19.2±0.6 | +0.5 |
| W 6 | 2.20 | 2.27 | 1.87 | 2.32 | | 2.15±0.24 | −2.3 |
| W 12 | 12.3 | 12.0 | 11.8 | 13.2 | | 12.3±0.8 | −0.3 |
| W 8 | 4.06 | 4.01 | 4.23 | 4.75 | 4.14 | 4.28±0.32 | +5.4 |
| W 9 | 5.84 | 5.29 | 6.06 | 5.25 | | 5.53±0.46 | −5.3 |
| H 2 | 24.2 | 24.7 | 24.4 | 23.8 | | 24.3±0.45 | +0.3 |
| H 8 | 19.3 | 19.0 | 19.9 | | | 19.4±0.6 | +0.7 |

[a] Standard deviation.

TABLE III

DETERMINATION OF SILICON IN STEEL

| *Sample code* | *Industrial analysis (% Si)* | *Activation analysis (% Si)* | | | | *Average* | *Relative difference between industrial and activation analysis (%)* |
|---|---|---|---|---|---|---|---|
| H 10 | 0.37 | 0.35 | 0.35 | 0.39 | | 0.36±0.02[a] | −2.2 |
| H 11 | 0.67 | 0.73 | 0.68 | 0.72 | | 0.71±0.02 | +5.7 |
| W 7 | 0.14 | 0.14 | 0.12 | 0.16 | | 0.14±0.02 | −0.7 |
| T 60 | 0.78 | 0.85 | 0.73 | 0.79 | | 0.79±0.06 | +1.1 |
| W 6 | 0.12 | 0.14 | 0.16 | 0.15 | | 0.15±0.01 | +26 |
| W 12 | 0.29[b] | 0.36 | 0.32 | 0.30 | | 0.33±0.03 | +12 |
| W 8 | 0.26 | 0.28 | 0.27 | 0.28 | 0.26 | 0.27±0.01 | +5.4 |
| W 9 | 0.47 | 0.48 | 0.49 | 0.44 | | 0.47±0.03 | −0.2 |
| H 2 | 0.36 | 0.29 | 0.28 | 0.30 | | 0.29±0.01 | −19 |
| H 8 | 1.66 | 1.70 | 1.67 | | | 1.68±0.03 | +1.5 |

[a] Standard deviation.

[b] Independent chemical analysis 0.30–0.34% Si.

The chromium results agree, within experimental error, with the industrial analyses. The same holds for the silicon results except for two samples (W 6 and H 2).

Attempts to improve the precision of the determination by enhancing the neutron output, resulted in significant errors on the silicon determination for high chromium samples, since $k_{Cr}$ could no longer be regarded as constant, mainly owing to pile-up effects. When more elaborate calculation procedures were used, with the assumption that the pile-up $^{52}$V contribution in the 1.8-MeV energy range was proportional to the $^{52}$V count and to the total count rate, accurate analyses could be performed up to a 10 times higher count rate. However, the necessity of checking several critical constants, measuring the total count rate and calculating the results through an intricate procedure, makes this method less attractive for practical purposes.

## SUMMARY

Chromium and silicon are determined simultaneously in steel by 14-MeV neutron activation analysis. The activities of $^{52}$V ($E_\gamma = 1.43$ MeV, $T_{\frac{1}{2}} = 3.76$ min) from $^{52}$Cr(n, p)$^{52}$V and $^{28}$Al ($E_\gamma = 1.78$ MeV; $T_{\frac{1}{2}} = 2.24$ min) from $^{28}$Si(n, p)$^{28}$Al are evaluated by mixed $\gamma$-ray spectrometry. The influence of manganese and phosphorus, the main interfering elements, is negligible for most stainless steels. The count rate should be limited, to avoid $^{52}$V pulse pile-up effects interfering in the $^{28}$Al energy region. Precisions in the 2–10% range are reached, depending on the concentrations, for a 10-min analysis time. Results for a series of steel samples are compared with industrial analyses.

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*Analytica Chimica Acta*, 72 (1974) 37–48

# STANDARDIZATION OF METHODS FOR THE DETERMINATION OF TRACES OF MERCURY

## PART I. DETERMINATION OF TOTAL INORGANIC MERCURY IN INORGANIC SAMPLES

A REPORT PREPARED BY THE MERCURY ANALYSIS WORKING PARTY OF THE BUREAU INTERNATIONAL TECHNIQUE DU CHLORE*

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(Received 2nd January 1974)

In the last few years, it has become clear that mercury, released into the environment by human activities, may cause problems. In order to control local pollution, both industry and the authorities are interested in analyses for mercury.

It has been clear for some time to the European chlorine manufacturers, co-operating in the Bureau International Technique du Chlore (BITC), that a reliable method for the determination of the total amount of mercury present was necessary, because this gives a first indication and it is known that in the environment mercury and its compounds all participate in chemical reactions[1].

Many articles have recently been published in the literature concerning the determination of mercury (see the review of Reimers *et al.*[2]). Several different methods are used for this determination: for example, the dithizone method[3], atomic absorption spectrometry[4–6], chromatography[7,8], neutron activation analysis[9], *etc.* Chromatography is not very suitable for the determination of the total amount of mercury present, because all mercury compounds have to be converted into one specific compound. Neutron activation analysis is very suitable, but has the disadvantages of long analysis time (a few days) and high cost of apparatus (therefore, the apparatus is not available in most laboratories). The dithizone method is time-consuming and requires more skill than atomic absorption spectrometry; also the reagent is affected by oxidizing reagents and can generate coloured products that interfere with the determination of mercury. Therefore, flameless atomic absorption spectrometry was selected as the best method to determine mercury; the apparatus is available in most laboratories and the method is sensitive and very selective.

In order to carry out the determination, all the mercury compounds present must be converted into metallic mercury. This can be done in several ways, depending on the nature of the sample and the types of mercury compounds present. As a first step, we have standardized a method for the determination of total inorganic mercury

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* The members of the Working Party responsible for the preparation of this report were R. Ankersmit, J. Barjhoux, F. Cappellina, W. T. Carter, A. A. Deetman, W. Dürr, Ch. Killens, J. Lutz, P. Mélard, Sven A. Norberg, F. Nouyrigat, M. Olivier, M. Pouillot, P. Reiners and H. Romeis. This report has been approved by the General Technical Committee of the BITC, which also authorized its publication.

in inorganic samples because the pretreatment is relatively easy. Mercury and its compounds are converted to mercury(II) ions by oxidation with acidic permanganate in the presence of chloride ions, or with aqua regia. The excess of oxidant and the mercury(II) ions are subsequently reduced with hydroxyammonium chloride and tin(II) chloride, respectively. The mercury vapour is removed from the solution in a stream of air which is passed into an absorption cell with windows transparent at 253.7 nm, the wavelength at which the absorption of atomic mercury is measured with a spectrophotometer. The method suffers interference from other volatile compounds which absorb at 253.7 nm and also from substances such as bromide and iodide which inhibit the liberation of mercury vapour from aqueous solution[4, 6].

The method given here resembles the method of the Dow Chemical Company[10].

## METHOD DESCRIPTION*

### *Scope and field of application*

The method can be used for the routine determination of mercury in process streams and wastes of a chlor alkali electrolysis plant (excluding chlorine).

The detection limit depends on the level of the instrument noise and the amount of mercury in the reagent blank, but in general the procedure should be capable of detecting 0.01 μg of mercury in a solution with a (maximum) volume of 40 ml, *i.e.* 0.25 μg Hg $l^{-1}$ (see Note 7, p. 43).

### *Apparatus*

An atomic absorption spectrophotometer with a low-pressure mercury vapour or hollow-cathode lamp, and either a fast-response recorder (full scale deflection in less than 1 s) or a maximum deflection indicator are required.

The apparatus is shown schematically in Fig. 1. This consists of: (a) an aeration flask of 100-ml capacity, marked at 60 ml (several identical aeration flasks are needed for routine determinations, see Note 5); (b) a 4-way tap; (c) a guard flask; (d) a measuring cell with windows transparent to ultraviolet light of 253.7 nm (cells of

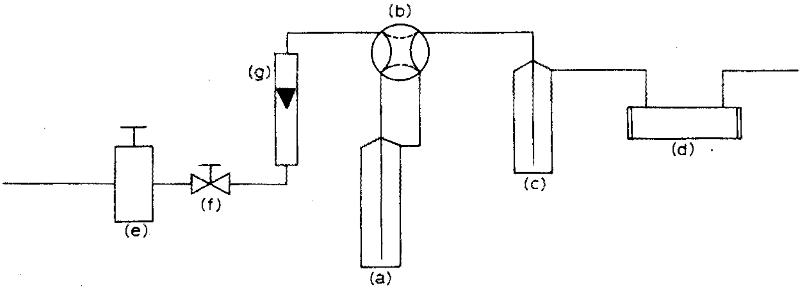

Fig. 1. Schematic diagram of apparatus.

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* For technical reasons, the text of the original method has been modified and shortened in certain places; those interested in the original text can obtain it in French, German or English, on application to the BITC.

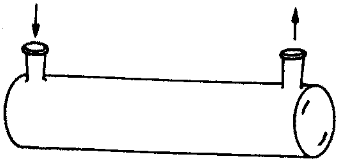

Fig. 2. Measuring cell with windows transparent to 253.7-nm radiation. Pathlength 1 cm and 10 cm.

1-cm and 10-cm pathlengths are necessary), see Fig. 2. A supply of air or nitrogen (e), controlled by a pressure regulator and a needle valve (f) is needed. The flow of gas is measured with a rotameter flowmeter, capacity 0–150 l $h^{-1}$ (g). A wet gas meter and a 1-l bulb with two teflon valves and an injection port, are also required.

*Reagents*

All reagents must be of analytical-reagent grade and must contain only a very low amount of mercury (E. Merck, Darmstadt, Germany, for example, is marketing reagents with guaranteed low mercury contents: potassium permanganate cat. no. 5084; tin(II) chloride cat. no. 7814; nitric acid cat. no. 452; sulphuric acid cat. no. 732; hydrochloric acid Suprapur cat. no. 318 and hydroxyammonium chloride cat. no. 4619. A blank determination must always be done, see below. Common reagents are not listed here.

*Absorbing solution.* Transfer 60 ml of aqueous potassium permanganate solution (40 g $l^{-1}$), and 70 ml of sulphuric acid (1+4) to a 250-ml standard flask. Dilute to volume with distilled water and mix. Prepare fresh daily.

*Reduction solution.* Transfer 25 g of tin(II) chloride dihydrate to a 250-ml standard flask. Add 50 ml of warm, concentrated hydrochloric acid (*ca.* 12 *M*). Swirl to dissolve, dilute to volume with distilled water and mix. Discard the solution if a turbidity appears (see Note 2).

*Standard mercury solutions* (1 g Hg $l^{-1}$, 1 mg Hg $l^{-1}$). Introduce 1.354 g of mercury(II) chloride into a 1-l standard flask. Add 25 ml of concentrated hydrochloric acid (*ca.* 12 *M*) and swirl to dissolve. Dilute to volume with distilled water and mix. From this solution, prepare a solution of 1 mg Hg $l^{-1}$ by dilution. Add 25 ml of concentrated hydrochloric acid per litre (see Note 1).

*Sample preparation for liquids and suspensions*

*Brine and water samples.* If the water samples cannot be analysed straight away, immediately after sampling add 10 ml of concentrated nitric acid and 5 ml of potassium permanganate solution (40 g $l^{-1}$) for each litre of sample. Before removing an aliquot for analysis, treat the whole sample with sufficient hydroxyammonium chloride solution (100 g $l^{-1}$) to dissolve the precipitated $MnO_2$.

The size of sample to be taken for the analysis depends on the expected mercury concentration (see Table I) and on the use of the 1-cm or 10-cm cell.

Weigh the sample in a 100-ml beaker. Add distilled water to a volume of 40 ml. Add 0.5 ml of sodium chloride solution (300 g $l^{-1}$) if the sample does not contain an equivalent amount or more of chloride ions. Neutralize, if necessary, with (1+4) sulphuric acid using phenolphthalein as indicator. Add a 1 ml excess, followed by 1 ml of potassium permanganate solution (40 g $l^{-1}$). Cover the beaker with a watch glass, heat to boiling, boil for a few seconds and cool. Decolourize

TABLE I

DEPENDENCE OF SAMPLE SIZE ON EXPECTED MERCURY CONTENT

| *Sample size (ml)* | *Expected mercury content (mg kg$^{-1}$)* |
|---|---|
| 0.5 | 5–20 |
| 2.0 | 1–5 |
| 10.0 | 0.25–1 |

the solution by the dropwise addition of hydroxyammonium chloride solution (100 g l$^{-1}$). Transfer the solution to an aeration flask, and measure the mercury content by the procedure given under *Determination of mercury content.*

*Sodium hydroxide solutions.* Collect the sample in a polythene bottle containing sufficient solid potassium permanganate to give a final concentration of 0.5 g $KMnO_4$/100 g of sample. Shake vigorously to dissolve the potassium permanganate and allow to stand for at least 30 min before removing an aliquot for analysis.

The size of the aliquot to be taken for the analysis depends on the expected mercury concentration and on the use of the 1-cm or 10-cm cell.

Weigh a quantity of sample between 0.5 and 5 g into a 100-ml beaker. Add distilled water to a volume of 40 ml. Neutralize with (1 + 1) hydrochloric acid. Add 1 ml of (1 + 4) sulphuric acid followed by 1 ml of potassium permanganate solution (40 g l$^{-1}$). Cover the beaker with a watch glass, heat to boiling, boil for a few seconds, and cool. Decolourize the solution by the dropwise addition of hydroxyammonium chloride solution (100 g l$^{-1}$). Transfer the solution to an aeration flask. Measure the mercury content by the procedure given under *Determination of mercury content.*

*Brine purification mud.* Weigh 5 g of mud into a 250-ml beaker. Add 20 ml of aqua regia. Cover the beaker with a watch glass, heat to boiling, boil for a few seconds and cool. Dilute to a suitable volume depending on the expected mercury concentration.

Into an aeration flask, pipette a 25.0-ml aliquot of the clear liquid. Add 0.5 ml of sodium chloride solution (300 g l$^{-1}$). Add 1 ml of (1 + 4) sulphuric acid, followed by 1 ml of potassium permanganate solution (40 g l$^{-1}$).

Decolourize the solution by the dropwise addition of hydroxyammonium chloride solution (100 g l$^{-1}$). Measure the mercury content by the procedure given under *Determination of mercury content.*

*Sample preparation for hydrogen and air*

Two methods are described. The first one, using an evacuated bulb, is more generally applicable than the second which uses washing bottles, although a lower limit of detection can be obtained with the latter.

*Low mercury content (mercury content less than 5 × the limit of detection per litre of sample).* This method can also be used for hydrogen if it has been established that the gas meter is accurate on this gas. The method is not usable when aerosols (resulting from mercury and chlorine) are present.

Transfer 60 ml of the absorbing solution into each of two aeration flasks. Connect these flasks to the sample point using the shortest possible length of plastic tubing. Connect the second aeration flask to a wet gas meter (for the analysis of hydrogen, the gas leaving the meter must be discharged to a vent). Allow the gas to pass at a maximum rate of 50 $\mathrm{l\,h^{-1}}$. The amount of gas to be sampled depends on the expected mercury concentration. Note the sample volume and the atmospheric pressure and temperature.

Add to each aeration flask 0.5 ml of sodium chloride solution (300 $\mathrm{g\ l^{-1}}$). Place the flasks in a boiling water bath for 2 min, and cool. Decolourize the solutions by the dropwise addition of hydroxyammonium chloride solution (100 $\mathrm{g\ l^{-1}}$). Measure the mercury content by the procedure given under *Determination of mercury content.*

*Higher mercury content (more than 5 × the limit of detection per litre of sample).* Evacuate the 1-l bulb, equipped with two teflon valves and an injection port. Note the pressure in the bulb and the temperature. Suck the sample into the bulb. Wait until the temperature of the bulb is in equilibrium with the surroundings. Note the pressure in the bulb.

By means of a syringe, introduce 50 ml of absorbing solution into the bulb via the serum cap. Shake vigorously for 30 min to absorb all the mercury present. Transfer the solution to a 250-ml standard flask, wash the bulb with water, and add the washings to the flask. Add 0.5 ml of sodium chloride solution (300 $\mathrm{g\ l^{-1}}$). Place the flask in a boiling water bath for 2 min, and then cool. Decolourize the solution by the dropwise addition of hydroxyammonium chloride solution (100 $\mathrm{g\,l^{-1}}$). Dilute the content of the flask to 250 ml with distilled water. Depending on the expected mercury content, take a suitable aliquot (max. 50 ml) of the solution and transfer this aliquot into an aeration flask.

Add 1 ml of (1 + 4) sulphuric acid followed by 1 ml of potassium permanganate solution (40 $\mathrm{g\ l^{-1}}$). Decolourize the solution by the dropwise addition of hydroxyammonium chloride solution (100 $\mathrm{g\ l^{-1}}$). Measure the mercury content by the procedure given under *Determination of mercury content.*

*Standardization*

A standard graph is necessary for each type of measuring cell. (See also Note 4.)

*For the 1-cm cell (calibration graph for 0–10 μg Hg).* Into 6 beakers of 100-ml capacity, transfer 0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml of standard mercury solution (1 mg $\mathrm{Hg\ l^{-1}}$). Dilute each solution to 40 ml. Add 0.5 ml of sodium chloride solution (300 $\mathrm{g\ l^{-1}}$). Add 1 ml of (1+4) sulphuric acid, followed by 1 ml of potassium permanganate solution (40 $\mathrm{g\ l^{-1}}$). Cover each beaker with a watch glass, boil for a few seconds and cool. Decolourize each solution by the dropwise addition of hydroxyammonium chloride solution (100 $\mathrm{g\ l^{-1}}$). Transfer each solution into an aeration flask. Measure the mercury content by the procedure given under *Determination of mercury content.* Plot a graph of the measured peak height against amount of mercury.

*For the 10-cm cell (calibration graph for 0–1 μg Hg).* Follow the same procedure as given for the 1-cm cell, using a standard solution of 0.1 mg $\mathrm{Hg\ l^{-1}}$ prepared from the standard solution of 1 mg $\mathrm{Hg\ l^{-1}}$ just before the calibration.

*Instrumental conditions*

Some of the instrumental conditions may be somewhat dependent on the type of apparatus used.

Adjust the spectrophotometer to a wavelength of 253.7 nm. Place the cell in position and adjust it to give the best response. Adjust the air (or nitrogen) pressure regulator to 0.5 bar and the gas flow to 55 $\mathrm{l\ h^{-1}}$.

It is better to use a 10-cm cell than to resort to scale expansion with the 1-cm cell.

*Determination of mercury content*

Add distilled water to the aeration flask containing the solution to be analysed to give a volume of 60 ml. Add 2 ml of tin(II) chloride reducing solution, and swirl to mix. Immediately attach the aeration flask to the apparatus*.

Turn the 4-way tap so that air passes through the flask. Allow the recorder pen to trace out the peak. When it has returned to the base line, turn the tap to isolate the aeration flask. Another determination can now be done.

Measure the height of the peak and read off the mercury content from the calibration graph.

*Blank determination (see Note 7)*

For the analysis of brine and water of various types, the standard containing no added mercury will serve as a blank (see above under *Standardization*). For the analysis of caustic soda it is necessary to add the same quantity of hydrochloric acid as that necessary to neutralize the sample. For the analysis of muds, it is necessary to add to the standard containing no added mercury the same amount of aqua regia as that added to the sample. For the analysis of gases, the blank solution consists of the same volume of absorbing solution as the aliquot of the analysis solution.

*Notes*

*1. Deterioration of solutions of mercury.* Dilute solutions of mercury are not completely stable. Their mercury content tends to diminish with time, the relative loss of mercury being the more pronounced in the diluted solutions. It is advisable to renew the standard 1 g Hg $\mathrm{l^{-1}}$ solution every two months and the dilute standard solutions daily.

Note that it is possible to improve the stability of the standard solutions by the addition of an oxidizing agent.

It is advisable to confirm that the mercury solutions are stable in the type of container in which they are stored (in particular it is necessary to take precautions against adsorption by ordinary glass[11]).

*2. Oxidation of the reduction solution.* Tin(II) ions are oxidized by air to tin(IV) ions. Because of this, the reduction solution is useless after it has become turbid.

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* If the samples are of unknown composition, or if the concentration of the measuring quantity is higher than 2.5 g $\mathrm{Cl^-}$ 60 ml, it is recommended to wait for at least 5 minutes after introduction of the reduction solution and before aeration, and to use the addition method in order to examine a possible matrix effect on the way the mercury comes out.

*3. Cleaning glass-ware.* All glass-ware must be cleaned carefully before use either with aqua regia, nitric acid or chlorine water.

*4. Standardization.* It is assumed that the oxidation procedures are capable of converting all the mercury present to the ionic form and that therefore it is acceptable to use mercury(II) chloride solutions for standardization.

Variations in the composition of the sample can cause changes in the instrument response, resulting in a change of slope of the calibration graph. In order to detect this, it is recommended that whenever unknown samples are being analysed, cross-checks on the normal procedure by the method of standard additions should be carried out.

*5. Gas velocity and glass-ware.* The height of the mercury peak obtained depends on the dimension of the apparatus and the gas velocity. It must be confirmed that changes in the glass-ware, particularly the aeration flasks, do not alter the peak height. Reducing the gas velocity gives shorter, wider peaks. The optimal gas velocity must be determined experimentally and maintained at this value during measurement of sample and calibration.

*6. Sampling.* Taking representative samples for mercury determination can give special problems. No general procedures can be given. One has to pay special attention to the presence of more than one phase (*e.g.* metallic mercury present), to concentration gradients and to variations in concentration with time.

*7. Lower limit of detection.* The lower limit of detection will be taken as equal to or greater than three times the standard deviation of the blank determination[12].

## INTERLABORATORY TESTS AND RESULTS

To test the above-described method, samples were exchanged between many laboratories of the companies that participate in the Bureau International Technique du Chlore. The first samples were artificially made solutions of mercury(II) chloride in nitric acid; thereafter industrial samples of waste water and caustic soda (50% solutions) were analysed. One of the caustic soda samples was specially treated for the sample exchange in order to obtain a low mercury content. Each sample was analysed on one day in a previously agreed period of a few days. This period was selected to allow an interval of approximately one month between the preparation of the samples and the analysis in order to allow adequate time for the distribution of the samples. One analyst in each laboratory carried out three separate analyses of each sample. Different types of sample container were used in some cases because of differing air freight regulations in the countries of origin.

### *Analytical procedures*

Samples were prepared by one of the participating laboratories (a different laboratory for each group of samples). All pretreatments were done in the bulk solutions, which were then divided into samples to be sent to the different laboratories.

The artificial standard samples were prepared by weighing mercury(II) chloride into 2 *M* nitric acid to give solutions of 5.0 and 20.0 mg Hg per kg of solution. Samples of 500 ml were sent in glass bottles to the participating laboratories.

TABLE II

RESULTS OF INTERLABORATORY ANALYSIS FOR MERCURY[a]

| *Laboratory number* | *Standard samples (mg Hg $kg^{-1}$)* | | | | | | *Waste water (mg Hg $kg^{-1}$)* | | | *Caustic soda (μg Hg $kg^{-1}$)* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *5.0 mg Hg $kg^{-1}$* | | | *20.0 mg Hg $kg^{-1}$* | | | | | | *Sample 1* | | | *Sample 2* | | |
| 1 | 4.80 | 4.82 | 4.90 | 20.3 | 20.6 | 20.8 | 3.46 | 3.41 | 3.34 | 25.9 | 24.8 | 24.4 | 116 | 153 | 139 |
| 2 | 5.16 | 5.19 | 5.33 | 20.9 | 20.8 | 21.2 | 3.01 | 2.94 | 2.85 | 26 | 24 | 25 | 183 | 180 | 189 |
| 3 | 4.36 | 4.36 | 4.38 | 19.9 | 20.4 | 19.9 | 2.98 | 3.08 | 2.95 | 22.1 | 22.5 | 26.8 | 244 | 225 | 230 |
| 4 | 5.4 | 5.2 | 5.5 | 20.0 | 19.1 | 21.2 | 3.78 | 3.94 | 4.00 | 20.5 | 22.6 | 24.0 | 206 | 206 | 221 |
| 5 | 5.13 | 4.87 | 4.87 | 19.7 | 19.7 | 20.0 | 3.00 | 3.02 | 3.00 | 19.7 | 19.7 | 19.1 | 194 | 184 | 178 |
| 6 | 5.00 | 4.85 | 4.85 | 19.9 | 19.7 | 20.7 | 3.30 | 3.21 | 3.15 | 25.8 | 26.1 | 25.5 | 154 | 151 | 152 |
| 7 | 4.72 | 4.72 | 4.87 | 19.4 | 19.4 | 19.7 | 3.5 | 3.5 | 3.8 | 91.5 | 94.1 | 92.8 | 180 | 155 | 155 |
| 8 | 5.3 | 5.0 | 5.1 | 19.7 | 20.9 | 21.2 | 2.8 | 2.9 | 2.9 | 20 | 20 | 20 | 236 | 234 | 236 |
| 9 | 5.44 | 5.43 | 5.44 | 21.3 | 21.3 | 22.72 | 3.10 | 3.18 | 3.02 | 28.6 | 22.4 | 24.8 | 220 | 240 | 230 |
| 10 | 5.1 | 5.3 | 5.2 | 21.5 | 21.0 | 21.3 | 3.00 | 2.9 | 2.9 | 17.6 | 18.9 | 19.6 | 276 | 276 | 276 |
| 11 | 5.1 | 5.1 | 5.1 | 20.7 | 20.4 | 21.4 | 3.2 | 3.2 | 3.3 | 18.9 | 18.9 | 18.9 | 185 | 189 | 187 |
| 12 | 5.0 | 4.9 | 5.0 | 20.0 | 20.4 | 20.2 | 3.0 | 3.0 | 3.0 | 19.6 | 19.6 | 19.6 | 230 | 210 | 220 |
| 13 | 4.9 | 4.8 | 5.05 | 19.0 | 20.0 | 20.0 | 3.19 | 3.18 | 3.18 | 18.3 | 20.3 | 19.6 | 230 | 200 | 250 |
| 14 | 5.0 | 4.5 | 5.0 | 18.6 | 18.6 | 19.2 | 2.7 | 2.7 | 2.7 | 26.1 | 26.1 | 13.1 | 189 | 182 | 188 |
| 15 | 5.65 | 5.0 | 4.75 | 19.8 | 19.0 | 21.6 | 3.2 | 3.0 | 3.5 | 20.9 | 18.3 | 17.0 | 197 | 174 | 192 |
| 16 | 5.05 | 5.05 | 5.10 | 20.8 | 20.7 | 20.6 | 3.27 | 3.10 | 3.0 | 22.9 | 24.2 | 32.7 | 189 | 178 | 198 |
| 17 | 5.17 | 5.3 | 5.3 | 20.2 | 19.8 | 20.0 | 2.8 | 2.9 | 2.8 | 20.8 | 20.7 | 20.3 | | | |
| 18 | 5.67 | 5.06 | 5.61 | 18.6 | 19.8 | 20.9 | 3.5 | 3.6 | 3.6 | 20 | 20 | 18 | | | |
| 19 | 5.3 | 5.2 | 5.6 | 21.8 | 20.6 | 20.8 | 3.45 | 3.45 | 3.50 | 28 | 31 | 23 | | | |
| 20 | 5.5 | 5.5 | 5.5 | 21.8 | 22.4 | 22.4 | 3.1 | 3.1 | 3.3 | 26 | 30 | 27 | | | |
| 21 | 4.9 | 5.1 | 5.0 | 19.2 | 19.6 | 20.4 | 3.4 | 3.2 | 3.2 | 17 | 17 | 15 | | | |
| 22 | 4.6 | 4.7 | 4.6 | 19.2 | 17.0 | 18.0 | 3.9 | 3.7 | 3.9 | 36 | 48 | 40 | | | |
| 23 | 5.1 | 5.0 | 4.9 | 21.5 | 21.8 | 19.4 | 2.5 | 2.9 | 2.8 | 27.5 | 27.5 | 27.5 | | | |
| 24 | 5.2 | 4.9 | 5.0 | 19.6 | 20.3 | 20.7 | 3.2 | 2.1 | 2.6 | 15 | 12 | 17 | | | |
| 25 | 5.3 | 5.1 | 5.15 | 20.0 | 19.5 | 19.0 | 3.00 | 2.95 | 2.75 | 24.0 | 20.0 | 20.0 | | | |
| 26 | 4.8 | 4.9 | 5.0 | 21.6 | 21.3 | 21.2 | 2.20 | 2.40 | 2.85 | 9.1 | 8.5 | 9.2 | | | |
| 27 | 4.8 | 4.8 | 4.9 | 22.5 | 20.7 | 21.2 | 2.85 | 2.85 | 2.85 | 26.3 | 27.4 | 27.6 | | | |
| 28 | 5.0 | 4.94 | 5.1 | 20.3 | 20.5 | 20.6 | 3.17 | 3.03 | 3.12 | | | | | | |
| 29 | 4.33 | 4.60 | 5.26 | 19.6 | 19.2 | 22.8 | 3.88 | 3.66 | 3.76 | | | | | | |
| 30 | 4.75 | 5.13 | 4.80 | 21.8 | 21.8 | 19.9 | [b] | | | | | | | | |
| 31 | 5.1 | 4.75 | 5.45 | 19.3 | 21.0 | 17.8 | | | | | | | | | |
| 32 | 4.6 | 4.4 | 4.6 | 17.0 | 21.0 | 19.0 | | | | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 33 | 4.9 | 5.2 | 5.3 | 19.0 | 20.2 | 20.2 |
| 34 | 4.8 | 4.9 | 4.9 | 19.9 | 19.6 | 19.7 |
| 35 | 5.4 | 5.4 | 5.3 | 21.6 | 21.3 | 21.4 |
| 36 | 4.6 | 4.9 | 4.7 | 20.2 | 20.0 | 19.9 |
| 37 | 5.3 | 5.3 | 5.4 | 21.5 | 20.4 | 20.4 |

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[a] Because of technical problems, only the results of 16 laboratories were used for the last interlaboratory test.

[b] One laboratory could not get consistent results.

TABLE III

RESULTS OF STATISTICAL EVALUATION OF INTERLABORATORY ANALYSIS FOR MERCURY

| | *Standard samples* | | *Waste water* | *Caustic soda* | |
|---|---|---|---|---|---|
| | *Ctg. 5.0 mg Hg kg*$^{-1}$ | *Ctg. 20.0 mg Hg kg*$^{-1}$ | | *Sample 1* | *Sample 2* |
| Number of participating laboratories | 37 | 37 | 29 | 27 | 16 |
| Number of laboratories eliminated: | | | | | |
| in advance | 0 | 0 | 0 | 1 | 0 |
| because of lack of repeatability | 0 | 0 | 2 | 3 | 1 |
| because of lack of reproducibility | 0 | 0 | 0 | 0 | 0 |
| Resulting number of laboratories | 37 | 37 | 27 | 23 | 15 |
| Results: | | | | | |
| Arithmetic mean | 5.03 mg kg$^{-1}$ | 20.3 mg kg$^{-1}$ | 3.18 mg kg$^{-1}$ | 21.4 μg kg$^{-1}$ | 201 μg kg$^{-1}$ |
| Repeatability[a] | | | | | |
| Standard deviation | 0.18 mg kg$^{-1}$ | 0.8 mg kg$^{-1}$ | 0.10 mg kg$^{-1}$ | 1.7 μg kg$^{-1}$ | 11 μg kg$^{-1}$ (footnote [b]) |
| Relative standard deviation | 3.5% | 4.0% | 3.1% | 8% | 5.4% |
| Reproducibility[a] | | | | | |
| Standard deviation | 0.30 mg kg$^{-1}$ | 1.1 mg kg$^{-1}$ | 0.34 mg kg$^{-1}$ | 4.8 μg kg$^{-1}$ | 38 μg kg$^{-1}$ (footnote [b]) |
| Relative standard deviation | 5.9% | 5.4% | 11% | 22% | 19% |

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[a] Repeatability means single laboratory, single operator and single apparatus precision; reproducibility means multi-laboratory, multi-operator and multi-apparatus precision.

[b] The results of laboratory 7 (Table II) for the caustic soda sample 2 were not used for the determination of repeatability and reproducibility.

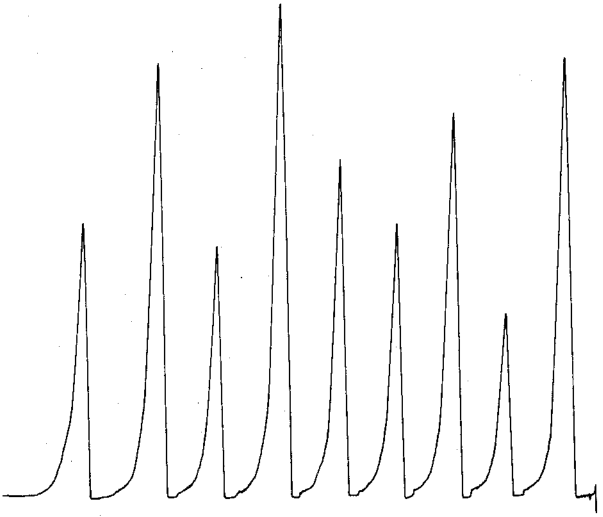

Fig. 3. Example of recorder tracing during routine determinations of mercury. Chart speed 12.5 mm min$^{-1}$.

The samples were analysed according to the procedure given under *Brine and water samples* (p. 39) from "Add 1 ml of potassium permanganate solution (40 g l$^{-1}$)..." For the samples of waste water and caustic soda (50% solutions), one large sample of waste water and one of caustic soda were taken. Each sample was divided in two parts. One of the parts was divided into 250-ml portions (untreated samples) and the other parts were treated with nitric acid and potassium permanganate as described for *Brine and water samples* (for samples that cannot be analysed immediately) or with potassium permanganate as described for *Sodium hydroxide solutions.* After that, the treated parts were divided into 250-ml portions to be sent to the participating laboratories. The samples were sent in polythene bottles. The results obtained are given in Table II; the results of the untreated samples are omitted because they clearly showed that pretreatment is necessary.

### *Statistical procedure*

Each laboratory sent its analytical results (Table II) to one of the participating laboratories for statistical evaluation. All results which were obviously in error were eliminated. It was then established that the distributions of the results could be considered as gaussian, and that the histogram of the distribution of the variances did not present any important anomaly. Cochran's test[13] was applied at a significance level of 1% in order to eliminate laboratories for a lack of repeatability, and Dixon's test[14] was used to eliminate laboratories for a lack of reproducibility. The means, repeatabilities and reproducibilities of the remaining results were calculated and are given in Table III.

### *Conclusion*

The results obtained on the standard samples show that the method described does not suffer from systematic errors, and that both the standard samples and the industrial samples gave a relative standard deviation for repeatability of about 4%

except for the caustic soda sample of very low mercury content. The relative standard deviation of the reproducibility of the standard samples remained at the same level as the repeatability, but a higher value was obtained for the industrial samples indicating that for samples of this type with low mercury contents, problems arise from changes occurring either during transportation or in the rather long period between preparing the samples and analysing them. In normal practice it should be possible to achieve a reproducibility on samples of this type similar to that obtained on the waste water sample.

Nevertheless, the results of the interlaboratory trial clearly indicate the value of the standard procedure used, as described, without any supplementary information.

## FURTHER WORK

Further work is being carried out to devise suitable methods of pretreatment for samples such as chlorinated hydrocarbons, waste water, fish, vegetation, blood and urine which may contain organomercurial compounds or have a high content of organic matter. A method for the determination of mercury in chlorine is also under investigation.

## SUMMARY

A method is described for the routine determination of mercury in the process and product streams of chlor alkali electrolysis plants (with the exception of chlorine) and also in the plant waste waters. The procedure is based on flameless atomic absorption spectrophotometry. Results for interlaboratory trials involving up to 37 participating laboratories are presented. Both synthetic and technical samples were analysed with mercury contents varying between 20 $\mu$g kg$^{-1}$ and 20 mg kg$^{-1}$. Statistical evaluation of the results gave a value of from 4 to 8% for the repeatability and from 6 to 22% for the reproducibility.

## RÉSUMÉ

On décrit une méthode permettant la détermination du mercure en analyse de routine sur les fluides de fabrication (chlore excepté) et les eaux usées des ateliers d'électrolyse de chlorures alcalins. La mesure est effectuée par absorption atomique sans flamme. Pour vérifier la méthode, on a procédé à des essais circulaires auxquels ont pris part jusqu'à 37 laboratoires industriels. Des échantillons synthétiques et industriels couvrant une gamme de concentrations de 20 $\mu$g kg$^{-1}$ à 20 mg kg$^{-1}$ ont été examinés. L'exploitation statistique des résultats a montré que la répétabilité variait de 4 à 8% et la reproductibilité de 6 à 22%.

## ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben zur Routinebestimmung von Quecksilber in Produktstromen und Abwasser der Chloralkalielektrolyse (ausser Chlor). Die Messung erfolgt nach dem Verfahren der flammenlosen Atomabsorption. Zur

Prüfung der Methode wurden Ringversuche durchgeführt, an denen sich bis zu 37 industrielle Laboratorien beteiligten. Es wurden synthetische und technische Proben über einen Konzentrationsbereich von 20 $\mu$g kg$^{-1}$ bis 20 mg kg$^{-1}$ analysiert. Die statistische Auswertung ergab eine Wiederholbarkeit von 4 bis 8% und eine Reproduzierbarkeit von 6 bis 22%.

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# NON-FLAME ATOMIZATION IN ATOMIC ABSORPTION SPECTROMETRY

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Within the last few years probably the most significant developments in atomic absorption spectrometry have been concerned with improvements in atomization techniques. In this area much effort has been centred on the development of non-flame atomizers as substitutes for the conventional flame-based systems. These atomizers have utilized heated graphite tubes[1], rods[2], and crucibles[3], or metallic elements such as platinum[4], tungsten[5], and tantalum[6]. It must be conceded that, at least on the basis of sensitivity, the results obtained with these atomizers are generally superior to those obtained with flame atomization. Other potential advantages claimed for non-flame atomizers are their requirement of very small samples (1–50 $\mu$l) and the possibility of using sequential atomization as a means of performing simultaneous analyses[7] or removing interferences[8]. Until the present time, emphasis in research appears to have been placed on the construction and analytical evaluation of these devices and apart from a brief comment by Amos[9] there is no information on the mechanism of atom formation and only spasmodic reference to interferences. The work reported in this paper was undertaken as an attempt to obtain some understanding of these processes. At the outset it was considered that knowledge of the mechanism of atomization could have some bearing on the control of interferences which appear to be generally more serious than has been observed in flame atomization[10,11].

## EXPERIMENTAL

The non-flame atomizer has been described previously[8]. In order to use tantalum, it was necessary to modify the apparatus in the following way. The stainless steel shields were lengthened so that they reached 10 mm above the carbon rod and a glass plate was placed across them in order that the argon was forced to exit horizontally. Without these modifications the life of the tantalum filaments was extremely short.

The atomizer was used in combination with a Unicam SP90A atomic absorption spectrophotometer. Power was supplied manually through a Variac and transformer. The analytical procedure generally involved a low-voltage drying step followed by an atomization step. Additional steps were introduced where necessary, *e.g.* an after-burn was used to remove magnesium after atomization of zinc in the interference studies. In all cases timing and voltage adjustments were strictly controlled.

Signal integration was accomplished with a digital integrator constructed by the Department's electronics workshop.

Solutions were prepared from analytical reagent-grade sulphates where this was chemically feasible. In the lead–magnesium system, nitrates were used. Chlorides were not used in order to avoid the possible volatilization of anhydrous metal chlorides.

## MECHANISM OF ATOM FORMATION

It was reasoned that in metal-based atomizers, such as those with tantalum strips, the most likely path to the formation of gaseous atoms involves thermal dissociation of the metal salt to the oxide and thence to the metal atom; consequently the atomization behaviour of a metal would be influenced by the thermal stability of the metal oxide. To measure the extent of this influence, several elements were atomized from a tantalum strip, and the lowest temperature at which atomic absorption signals were observed was measured. The data obtained in these experiments are assembled in Table I together with the boiling points of the elements concerned. These data (columns 2 and 3 of Table I) show that some elements, notably silver, gold, and copper, vaporize at temperatures well below their boiling points, while others, notably calcium and magnesium, require temperatures in excess of their boiling points for vaporization. It seems reasonable to infer that the higher the temperature relative to the boiling point at which a metal vaporizes, the greater is the influence of the metal oxide on the atomization process. A more exact measure of this influence was obtained by considering both the vapour pressure at the temperature at which atomization becomes evident, and the values for the free energy for the dissociation of the metal oxides (columns 4 and 5 of Table I). Gold, silver, and copper, which atomize at temperatures at which their vapour pressures are still very low, are elements which are shown by the free energy data to be stable with respect to their oxides at the temperatures in question. For these elements the appearance of gaseous atoms in the optical path is controlled entirely by the vapour pressure of the metal.

The influence of the increasing thermal stability of the metal oxides is evident with the other elements, and reaches its maximum with magnesium and calcium, the oxides of which are thermally very stable even at elevated temperatures and which atomize only when the temperatures have exceeded their boiling points. Unfortunately, a quantitative description of these systems does not appear possible, because they are complicated by the passage of the argon stream around the tantalum strip and because the temperature at which atomization becomes evident is dependent on the sensitivity of the analytical technique for each element.

When graphite is used in the atomizer, a second atomization mechanism is possible, *viz.* the graphite may reduce the metal oxide to the metal. This possibility was examined by determining the lowest temperature at which gaseous atom formation was observed when a carbon rod was used in the atomizer, and by comparing the data with those obtained by atomization from tantalum. The results obtained with carbon are shown in column 6 of Table I.

For the majority of the elements studied, the minimal atomization temperature from tantalum is within 100°C of the atomization temperature from carbon; in these

TABLE I

ATOMIZATION AND VAPORIZATION CHARACTERISTICS

| *Element* | *B.p. (°C)* | *Min. vap. temp. from Ta strip (°C)* | *Vapour press. at min. vap. temp. (Pa)* | *Free energy (kJ)* | *Min. vap. temp. from C rod (°C)* |
|---|---|---|---|---|---|
| Aluminium | 2467 | 1560 | $1.33 \cdot 10^{2}$ | +728 | 1550 |
| Bismuth | 1560 | 820 | $3.54 \cdot 10^{1}$ | +172 | 860 |
| Cadmium | 765 | 300 | 6.65 | +445 | 270 |
| Calcium | 1487 | 1510 | $1.01 \cdot 10^{5}$ | +900 | 1550 |
| Chromium | 2482 | 1330 | $5.32 \cdot 10^{-1}$ | +460 | 1380 |
| Cobalt | 2900 | 1520 | 1.33 | +209 | 1300 |
| Copper | 2595 | 1030 | $1.33 \cdot 10^{-2}$ | + 62 | 1160 |
| Gold | 2966 | 1080 | $1.33 \cdot 10^{-2}$ | − ve | 1080 |
| Iron | 3000 | 1450 | 1.06 | +301 | 1230 |
| Lead | 1744 | 780 | 4.00 | +230 | 860 |
| Magnesium | 1107 | 1170 | $1.01 \cdot 10^{5}$ | +890 | 1300 |
| Manganese | 2097 | 1150 | $4.00 \cdot 10^{1}$ | +556 | 1210 |
| Nickel | 2732 | 1500 | 1.33 | +151 | 1420 |
| Silver | 2212 | 830 | $1.33 \cdot 10^{-2}$ | − ve | 850 |
| Tin | 2270 | 1400 | $1.33 \cdot 10^{1}$ | +293 | 1140 |
| Zinc | 907 | 820 | $4.60 \cdot 10^{4}$ | +482 | 800 |

TABLE II

FREE ENERGIES OF PROBABLE REACTIONS AT CARBON ROD

| *Reaction* | *Temp. (°C)* | *ΔG(kJ)* |
|---|---|---|
| $Al_2O_3 + 3\,C \rightarrow 2\,Al + 3\,CO$ | 1550 | +280 |
| $Bi_2O_3 + 3\,C \rightarrow 2\,Bi + 3\,CO$ | 860 | −377 |
| $CdO + C \rightarrow Cd + CO$ | 270 | + 63 |
| $CaO + C \rightarrow Ca + CO$ | 1550 | +176 |
| $Cr_2O_3 + 3\,C \rightarrow 2\,Cr + 3\,CO$ | 1380 | − 59 |
| $CoO + C \rightarrow Co + CO$ | 1300 | −126 |
| $CuO + C \rightarrow Cu + CO$ | 1160 | −252 |
| $FeO + C \rightarrow Fe + CO$ | 1230 | − 77 |
| $Fe_3O_4 + 4\,C \rightarrow 3\,Fe + 4\,CO$ | 1230 | −352 |
| $PbO + C \rightarrow Pb + CO$ | 860 | − 92 |
| $MgO + C \rightarrow Mg + CO$ | 1300 | +163 |
| $MnO + C \rightarrow Mn + CO$ | 1210 | + 37 |
| $NiO + C \rightarrow Ni + CO$ | 1420 | −176 |
| $SnO_2 + 2\,C \rightarrow Sn + 2\,CO$ | 1140 | −126 |
| $ZnO + C \rightarrow Zn + CO$ | 800 | + 37 |

cases, there is a general tendency for the former temperature to be lower, which is in line with the fact that with tantalum filaments the sensitivity for a given element is usually higher than with graphite. However, the behaviour of four elements—cobalt, iron, nickel and tin—appears to be different, in that the minimal vaporization temperature from carbon is significantly lower than that from tantalum. This suggests that in these four cases the free metal is formed by reduction of the oxide by graphite rather than by thermal dissociation.

This conclusion was checked by use of thermodynamic data in the following manner. The most likely reaction between the metal oxide and graphite was postulated, and the free energy for that reaction was calculated at the temperature at which atom formation was first observed from carbon. These data are presented in Table II. Since these reactions are actually taking place in a stream of argon which removes gaseous products, these free energy values underestimate the extent of the reaction. Nevertheless, they do indicate, at least qualitatively, whether reduction by graphite is thermodynamically possible.

The reactions postulated for aluminium, cadmium, calcium, magnesium, manganese, and zinc all have positive free energies and all show no significant difference in their atomization behaviour between carbon and tantalum, *i.e.* both arguments lead to the conclusion that carbon does not act as a reducing agent in the atomization of these elements.

On the other hand, for the elements cobalt, iron, nickel, and tin, where the minimal atomization temperature from carbon is significantly lower than that from tantalum, the free energy change indicates that reduction of the oxide by carbon is thermodynamically feasible; it can thus be concluded that graphite is active as a reducing agent in these systems.

It is of interest to note that at the observed atomization temperatures from graphite, the partial pressures of cobalt and iron are both approximately $2.6 \cdot 10^{-2}$ pascal while those of nickel and tin are both approximately $2.6 \cdot 10^{-1}$ pascal. The value of $2.6 \cdot 10^{-2}$ pascal is of the same order as those observed for the atomization of silver and gold from tantalum. Since the oxides of silver and gold have no influence on their atomization behaviour, it seems reasonable to conclude that on graphite the oxides of cobalt and iron are reduced to the respective metals at temperatures below those at which the metals commence to vaporize, *i.e.* the formation of gaseous atoms is controlled by the vapour pressures of the elements. That nickel and tin appear as gaseous atoms only when the vapour pressures of the elements are about $2.6 \cdot 10^{-1}$ pascal, may be a consequence of less efficient reduction reactions.

The other four elements bismuth, chromium, copper, and lead are characterized by a third pattern. Their observed atomization behaviour suggests that graphite does not act as a reducing agent despite favourable free energies for the reduction reactions. One possible explanation is that, in these systems, the rate of reduction of the oxides is slow relative to their thermal dissociation, with the consequence that equilibrium is not established in the graphite reduction reaction.

## OBSERVATIONS ON INTERFERENCES

In broad terms, interference may occur either on the surface of the rod or above it in the vapour cloud. In the former case, the extent of interference in a particular system should be independent of the height above the filament at which measurements are made. In the latter case, the extent of interference will probably increase with the distance between filament and optical path; patterns of this type have been reported previously[10].

With the aid of data accumulated in the studies on atomization, a number

TABLE III

INPUT VOLTAGES FOR VAPORIZATION AND ANALYTICAL MEASUREMENT FROM CARBON ROD

| *Element* | *Min. vaporization voltage* | *Anal. signal voltage* |
|---|---|---|
| Copper | 110 | 180 |
| Lead | 110 | 130 |
| Magnesium | 140 | 180 |
| Nickel | 130 | 180 |
| Zinc | 100 | 130 |

of systems was selected for detailed examination of interference patterns. The binary combinations zinc–magnesium and lead–magnesium were chosen as examples of systems in which interference is likely to occur only on the filament, since the optimal input-voltage for measurement of lead and zinc signals is below that at which magnesium began to vaporize (Table III). Binary combinations of magnesium, copper and nickel were chosen to investigate systems in which the elements were atomized more or less simultaneously with the expectation that vapour-phase interference could be studied.

### *The systems lead–magnesium and zinc–magnesium*

Interference patterns for the lead–magnesium and zinc–magnesium systems are shown in Table IV. That the extent of interference is independent of optical height seems to confirm that it originates on the rod in both systems. However, there is a marked difference between the results obtained by peak-height measurement and those obtained by peak-integration measurement; in the latter case, the signals are greater than those observed for pure zinc solutions. The most likely explanation, consistent with these observations, is associated with the relatively slow speed of response of the instrument. If the actual signal becomes broader with lower maximum in the presence of interferent, then the instrument will follow this with greater efficiency than it will follow the signal for the pure element. Thus all observed signals in the presence of interferent will underestimate the true interference, and where integration is used for measurement an apparent positive interference may be observed. The signal broadening itself is probably a function of both the thermal conductivity of the interferent relative to graphite, and the rate of diffusion of the analyte to the surface of the interferent layer in which it is embedded. This is certainly suggested by the observation (Table IV) that interference was reduced when the total amount of material was reduced ten-fold although the ratio of lead to magnesium remained constant.

The extent of interference of zinc on magnesium was studied at an optical height of 1 mm with the peak-height method for measurement. When an input voltage of 180 V was used to atomize magnesium, no interference was observed in the presence of 1000-fold excess of zinc. In view of the difference in atomization temperatures for magnesium and zinc, it would appear that most of the zinc has volatilized before magnesium begins atomizing, *i.e.* this system demonstrates sequential atomization where the interferent is removed before the analyte.

TABLE IV

RELATIVE SIGNAL AS FUNCTION OF OPTICAL HEIGHT FOR LEAD AND ZINC MEASUREMENTS

| *System* | *Optical height (mm)* | *Relative signal*[a] | |
|---|---|---|---|
| | | *Peak height method* | *Integration method* |
| 1 p.p.m. Pb + 1000 p.p.m. Mg | 1 | 63 | |
| | 3 | 77 | |
| | 5 | 75 | |
| | 7 | 73 | |
| 0.1 p.p.m. Pb + 100 p.p.m. Mg | 1 | 88 | |
| 0.1 p.p.m. Zn + 100 p.p.m. Mg | 1 | 56 | 123 |
| | 3 | 54 | 118 |
| | 5 | 47 | 123 |
| | 7 | 62 | 126 |

[a] Observed signal expressed as percentage of signal for pure analyte solution at the same optical height.

TABLE V

INTERFERENCES ON COPPER, NICKEL AND MAGNESIUM SIGNALS

| *System* | *Optical height (mm)* | *Relative signal* |
|---|---|---|
| 1 p.p.m. Cu + 1000 p.p.m. Mg | 1 | 104 |
| | 3 | 104 |
| | 5 | 105 |
| | 7 | 107 |
| 1 p.p.m. Cu + 1000 p.p.m. Ni | 1 | 92 |
| | 3 | 22 |
| | 5 | 4 |
| | 7 | 0 |
| 1 p.p.m. Ni + 1000 p.p.m. Cu | 1 | 87 |
| | 3 | 47 |
| | 5 | 5 |
| | 7 | 0 |
| 1 p.p.m. Ni + 1000 p.p.m. Mg | 1 | 87 |
| | 3 | 68 |
| | 5 | 37 |
| | 7 | 8 |
| 0.1 p.p.m. Mg + 100 p.p.m. Cu | 1 | 78 |
| | 3 | 31 |
| | 5 | 10 |
| | 7 | 0 |
| 0.1 p.p.m. Mg + 100 p.p.m. Ni | 1 | 67 |
| | 3 | 17 |
| | 5 | 7 |
| | 7 | 0 |

### *The systems copper–magnesium, magnesium–nickel, and copper–nickel*

Interference data for these systems are presented in Table V. There are two noticeable features in these data. Firstly, apart from the system copper (1 p.p.m.)–

magnesium(1000 p.p.m.), in which no significant interference was observed, each of these systems is characterized by an increase in the extent of interference with optical height. Secondly, the relative order of interference, which is summarized in Table VI, is Ni > Cu > Mg.

TABLE VI

RELATIVE ORDER OF INTERFERENCE

| *Analyte* | *Interference order* |
|---|---|
| Copper | Nickel > magnesium |
| Magnesium | Nickel > copper |
| Nickel | Copper > magnesium |

If vapour-phase interference is associated with condensation of the gaseous atoms in a manner such that the analyte atoms are occluded in clusters of condensing interferent atoms, then three factors can contribute to the observed pattern:

(1) the volatility of the interferent.

(2) the mutual affinity of the elements for each other,

(3) the tendency of an interferent to recombine with traces of oxygen and thus to condense as the oxide rather than as the metal.

That the order of interference corresponds with the order of the boiling points of the elements suggests that the first of these factors may be the most important. Reasoning based on both relative volatility and mutual affinity (as measured by mutual solubility) suggests that magnesium should be significantly less efficient as an interferent than either nickel or copper. The observations do not demonstrate this unequivocally, and to account for the interference of magnesium on nickel it is suggested that magnesium recondenses as magnesium oxide which has a very much lower volatility than the metal itself. Calculations show that in an argon supply containing 1 p.p.t. oxygen the amount of oxygen is well in excess of the amount of magnesium. Furthermore, the free energy of formation of the oxide at the boiling point of magnesium (1107°C) indicates the likelihood of oxide formation. Whether the equilibrium situation is approached is not clear, since the components are moving at about 20 cm $s^{-1}$ through a very steep temperature gradient[12,13].

## SUMMARY

The role of the metal oxides and the graphite in non-flame atomizers has been examined. It has been concluded that graphite probably acts as a reducing agent in the atomization of cobalt, iron, nickel, and tin. It has also been established that interferences may originate both on the surface of the graphite rod and in the vapour phase immediately above the rod. The origin of these interferences is discussed.

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# THE APPLICATION OF ELECTRODEPOSITION TECHNIQUES TO FLAMELESS ATOMIC ABSORPTION SPECTROMETRY

## PART II. DETERMINATION OF CADMIUM IN SEA WATER

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When conventional atomic absorption spectrometry is used for the determination of trace metals at the p.p.b. level in water, an extraction step is usually employed, to increase the sensitivity of the method. With the introduction of the flameless techniques, the detection limits of atomic absorption spectrometry have been so much improved that the preconcentration step can be eliminated in many cases. However, for the determination of trace metals in sea water by atomic absorption, a separation procedure is always needed, even when a flameless technique is used, in order to eliminate interferences arising from unspecific absorption by light scattering from salt particles in the sample.

Recently, a simple flameless technique has been described[1] where matrix interferences are eliminated by an electrodeposition step, before the flameless atomization. In this paper, the application of this technique to the determination of cadmium in sea water is described.

## EXPERIMENTAL

### *Apparatus*

A double-beam atomic absorption spectrophotometer, Perkin–Elmer 403, and a Hitachi Perkin–Elmer 165 recorder were used. The cadmium hollow-cathode lamp was operated at a current of 12 mA, and the signal was measured at 228.8 nm. The instrument was used in the Concentration mode, with the Recorder Response in position 2. The burner head was replaced by an absorption cell made of glass, with quartz windows. A tungsten filament electrode was placed in the centre of the cell through a glass joint. Details of the filament electrode and absorption cell have already been given[1]. The cell was flushed with nitrogen to prevent oxidation of the filament. The tungsten filament was heated electrically from a simple 30 W power supply, consisting of a Variac and an a.c. transformer.

The controlled potential electrolysis was performed by means of a potentiostat built in this laboratory. A Metrohm EA 880-20 vessel was used as electrolytic cell. The cell was treated with a silicone repellent (dimethyldichlorsilane) to prevent the adsorption of metal ions on the glass walls. The filament electrode served as working electrode; a platinum coil was used as counter electrode. The reference electrode was a saturated Ag/AgCl electrode, which was placed inside a salt bridge filled with the solution to be analyzed.

The solution was stirred during the electrolysis by means of a steady flow of highly purified nitrogen gas through the cell. The flow-rate was controlled by means of a flow-meter. This flow of nitrogen gas also partly removed dissolved oxygen from the solution. It was, however, observed that the presence of oxygen did not have any noticeable influence on the analytical results.

### *Sea water*

The sea water was collected at a depth of 40 m near Drøbak in the Oslofjord. This sea water was filtered through 0.45 $\mu$m Millipore filter and stored in a 5-l polythene bottle, which had been thoroughly cleaned with acid and rinsed with distilled water and sea water. The salinity was 33.75 g $kg^{-1}$ of sea water, which is close to the salinity of oceanic water (35 g $kg^{-1}$).

The pH of the raw sea water was 7.5. When nitrogen was passed through the solution during the electrolysis the pH increased slightly, owing to the removal of dissolved carbon dioxide. After 30 min of nitrogen bubbling, the pH had reached 8.1. For the measurements described in the present paper, the pH was always within the range 7.8–8.1. In this pH region, the hydrogen carbonate–carbonate present in sea water acts as a buffer. (In absence of carbonate the hydrogen carbonate would give rise to a pH of 7.55. This value is found from the equation $pH = \frac{1}{2}(pK_1 + pK_2)$, where $K_1$ and $K_2$ are the apparent dissociation constants of carbonic acid in sea water. At a salinity of 33.75, $pK_1 = 6.00$ and $pK_2 = 9 \cdot 10$ (ref. 4). (A more rigorous mathematical treatment, taking into account the actual concentration of hydrogen carbonate in the sample, gives exactly the same pH value.)

The natural buffer capacity of sea water around pH 8 was found, theoretically as well as experimentally, to be satisfactory for the present analyses. Such a naturally occurring buffer is to be preferred to the addition of chemicals, which will usually contaminate the samples significantly at the p.p.b. level; moreover, the addition of buffers may change the chemical composition of the sample.

The cadmium solution which was used for standard addition to the sea water was nearly neutral, and did not affect the pH of the sample. Owing to the buffer action of hydrogen carbonate, the dilution caused by the addition of a standard would in itself have a negligible effect on the pH, even if the standard solution was added in ml, and not $\mu$l amounts.

### *General procedure*

The electrodeposition was carried out at $-1.0$ V *vs.* Ag/AgCl (corresponding to $-1.04$ V *vs.* a saturated calomel electrode) for 5 min with a sample volume of 20 ml. The solution was stirred by a nitrogen flow of 100 $cm^3$ $min^{-1}$ during the electrolysis. The filament electrode was then removed from the electrolytic cell without disconnecting the electrical circuit, rinsed with distilled water and dried with acetone, and finally placed in the absorption cell. The atomic absorption signal was recorded during the application of a voltage of 4 V to the tungsten filament for 5 s. This voltage gives a filament temperature of 1650°C (ref. 1).

The concentration of cadmium was determined by the method of standard addition. The peak height of the adsorption signal was measured before and after the addition of 20 $\mu$l of a $10^{-5}$ *M* standard solution of cadmium chloride.

## RESULTS AND DISCUSSION

The results of the analyses are given in Table I. All the results refer to the same batch of sea water. For each aliquot, duplicate measurements were carried out before and after the addition of the standard cadmium solution. As can be seen from the Table, the mean value was found to be 0.24 p.p.b. cadmium. The relative standard deviation of the five results given is 10%. The value found for cadmium is in good agreement with recent results obtained by atomic absorption analysis after extraction with APDC into MIBK on samples from the Oslofjord[2]. It is also well within the range 0.1–0.3 p.p.b., which has been given for cadmium in the eastern North Sea[3]. However, the concentration of cadmium in ocean water seems to be somewhat lower, a value of 0.05 p.p.b. being frequently cited[4].

TABLE I

DETERMINATION OF CADMIUM IN SEA WATER

(The results are given in $\mu g\ l^{-1}$ (p.p.b.))

| *Aliquot no.* | | | | | *Average* | $s_r$ *(%)* | *ASV HMDE*[a] | *ASV MFE*[b] |
|---|---|---|---|---|---|---|---|---|
| *1* | *2* | *3* | *4* | *5* | | | | |
| 0.26 | 0.26 | 0.20 | 0.25 | 0.24 | 0.24 | 10 | 0.20 | 0.21 |

[a] ASV, HMDE: Anodic stripping voltammetry with a hanging mercury drop electrode.
[b] ASV, MFE: Anodic stripping voltammetry with a mercury film electrode.

The results of the analysis of the sea water sample by anodic stripping voltammetry are also included in Table I. A hanging mercury drop electrode, as well as a film electrode mercury plated *in situ*, were used for these analyses[5]. Each of the results given represents the mean of six determinations. As can be seen from the Table, the results of the anodic stripping voltammetric experiments agree quite well with the value found by the atomic absorption technique, when the low concentration level is taken into consideration.

By successive additions of standard cadmium solution to the sea water sample it was ascertained that there was a linear relationship between the peak height of the atomic absorption signal and the concentration of the metal in the sample.

For routine analysis, the standard addition technique is usually too time-consuming. A calibration curve, made by adding cadmium to sea water (preferably from the same area as the unknown samples), may be used in this case. Standards made from a cadmium salt dissolved in water should not be used for the construction of the calibration curve, as it was found that the peak height of the absorption signal for a given concentration was approximately 40% lower in sea water than in a solution containing only potassium chloride as supporting electrolyte. This decrease of signal in sea water may be due to complex formation of cadmium in solution, or to some other sort of matrix effect during the deposition or atomization steps. It is, however, not a result of the high salt concentration alone, as the presence of 0.1 *M* potassium chloride does not in itself have this effect on the absorption signal.

In principle, the electrochemical deposition step should discriminate between the various forms of cadmium in solution. In this respect the present technique may be compared to the anodic stripping voltammetric technique, which also involves an electrochemical deposition step. The application of this technique to the characterization of metals in natural waters has been discussed[6,7].

The amount deposited on the filament, and consequently also the peak height of the absorption signal, should be a function of the stability and rate constants of the cadmium complexes in solution. Also the diffusion coefficient of the electroactive species (which in turn depends on the size of the diffusing species) should have an influence on the amount deposited. By the choice of a suitable reduction potential, only the "free" metal ions in solution should be deposited on the filament. Even so, all the metal present in solution as the hydrated ion or as a labile complex would be determined when the standard addition technique is used[6], provided that the complex-forming ligands are present in an excess in the solution, and an equilibrium is attained in the solution after the addition of standard.

In the present investigation, a deposition period of 5 min was necessary, in order to obtain satisfactory peak heights. The total time for a single analysis was then *ca.* 7 min. With a larger electrode area and more effective stirring of the solution, it should be possible to decrease the deposition time further, and still obtain reasonable peak heights. However, the precision of the method is improved when the peak height is increased, as the signal-to-noise ratio then becomes more favourable.

The dependence between the peak height and the deposition time is illustrated in Fig. 1. As can be seen, the peak height increases linearly with the deposition time. However, a deposition time above 10–15 min may be unacceptable for many practical purposes.

The present method compares quite favourably with alternative atomic absorption procedures for the determination of sub-p.p.b. levels of cadmium in sea water. A separation step, preceding the atomization of the sample, is always needed when sea water is analyzed, because of the unspecific absorption by light-scattering

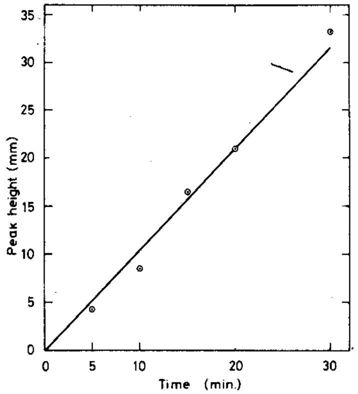

Fig. 1. The dependence of peak height on electrolytic deposition time for cadmium in sea water. Each point represents the mean of two measurements.

from salt particles in the sample. Compared to the commonly used solvent extraction or ion-exchange procedures, the technique proposed here has the advantage of avoiding contamination of the sample by impurities from the organic solvent or ion-exchange resin.

The proposed technique utilizes flameless atomization, which is a great advantage when such low concentration levels must be determined. If conventional atomization in a flame had to be used, a sample volume of 250–500 ml of sea water would be needed for each determination. The proposed method needs a sample volume of 2–20 ml. If such a volume of sample is available, and time can be allowed for the deposition of all the cadmium in solution onto the filament, the detection limit of this method should be better than that of other flameless techniques, as most flameless cells, such as the graphite furnace or the carbon rod, usually employ aliquots of only a few $\mu$l.

It is also an advantage of the technique described here that no drying and ashing steps are needed before atomization. Partly as a consequence of this, the equipment needed is quite cheap, compared to the instrumentation which is commercially available for flameless atomization—no expensive temperature-programming unit or powerful power supply is needed. The filament electrode is easy to make, and it will last for at least 200 atomizations. When the electrode is worn out, only the tungsten spiral needs to be changed (the tungsten filament is taken from a commercially available light bulb[1]). A potentiostat was used for the electrochemical deposition in the present investigation. There seems, however, to be a fair chance that even this equipment can be replaced by a more simple device. A study of this possibility is in progress.

The proposed technique is of course not restricted to the determination of cadmium. Work is in progress on the determination in sea water of other trace metals which can be deposited electrochemically from an aqueous solution.

We are grateful to Dr. Arne Thorvin Andersen at the Institute of Marine Biology and Limnology, University of Oslo, for providing the sea water samples, and to the National Institute of Public Health, for the use of their atomic absorption instrument.

## SUMMARY

Cadmium in sea water at the sub-p.p.b. level has been determined by a simple flameless atomic-absorption technique. The metal is first electrolyzed for 5 min onto a thin tungsten wire, and then atomized by electrical heating of the filament within an absorption cell. The results obtained agree well with data obtained by anodic stripping voltammetry.

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# THE DETERMINATION OF MERCURY IN SOILS AND RELATED MATERIALS BY COLD-VAPOUR ATOMIC ABSORPTION SPECTROMETRY

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Mercury has long been of geochemical interest and more recently it has become important as an environmental pollutant. Atomic absorption and fluorescence by mercury vapour was reported by Wood[1] as early as 1912 and quantitative measurement of mercury absorption by Goos and Meyer[2] and Hughes and Thomas[3] in the 1920s. The first analytical applications of atomic absorption were made by Müller and Pringsheim[4] and Woodson[5] for the determination of mercury in air and gases. Atomic absorption instruments for the determination of mercury have been described[6–11] and many commercial mercury analyzers are available. Atomic absorption methods have been reviewed by Manning[12] and Feklichev and Pashutin[13] and discussed by various authors[14–17]. Following the work of Kimura and Miller[18] and Poluektov and coworkers[19,20] on the reduction–aeration system for the production of mercury vapour, Hatch and Ott[21] developed a sensitive method for soils.

A method for mercury in materials such as soils, peats, rocks and plant materials must take account of the possible presence of organic material. In these circumstances pyrolytic methods for the evolution of mercury are unlikely to be satisfactory, at least with simple apparatus[22]. In this study attention was therefore concentrated on the liberation of mercury from sample solutions by reduction and aeration before determination by cold-vapour atomic absorption spectrometry. The chief difficulty lay in ensuring that all the mercury, organically bound, inorganically bound or elemental, was brought into solution in a form readily released as atomic vapour by reduction and aeration.

Since no suitable reference samples with well-authenticated mercury contents are available, comparative analyses of a wide range of natural samples by radically different methods were considered to be the best criteria for validating the findings. Three sample preparation methods were therefore used: (I) digestion and wet oxidation, (II) digestion and wet oxidation followed by reduction, volatilization and collection in solution, and (III) oxygen flask combustion.

The cold-vapour atomic absorption technique chosen differed from the usual bubbling technique[21] in that the mercury in the sample solution was first partitioned between the liquid phase and a fixed volume of air by agitation, before

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the latter was passed through the measuring cell, as this is shown below to be more reproducible.

Because of the many points at which loss or contamination can occur, the procedures are described in some detail; most techniques previously described in the literature proved unsatisfactory for the types of sample involved.

## PREPARATION OF SAMPLE SOLUTIONS

### *Method I. Acid digestion and wet oxidation*

Several of the numerous digestion procedures described for the determination of mercury in rocks, soils and sediments were tried and rejected. Nitric acid alone[23,24] has been found here and elsewhere[25] to give incomplete oxidation, low recovery and frothing difficulty when aerated. With samples having an appreciable organic matter content, concentrated sulphuric acid produced charred, tarry lumps extremely resistant to further oxidation. Addition of potassium peroxydisulphate after hot acid and permanganate treatment has been reported[26,27] to be necessary for the complete oxidation of some organic mercury compounds, but in this work permanganate alone was found to provide adequate oxidation. Cold mixtures of nitric and sulphuric acids with potassium peroxydisulphate[28] were found to give incomplete oxidation of organic matter and low mercury results. Methods involving hydrogen peroxide[21,35] did not completely oxidize the organic material and were tedious because of the need for repetitive addition.

The procedure adopted, similar to that of Iskander *et al.*[25], employed a nitric and sulphuric acid mixture for digestion followed by potassium permanganate oxidation.

*Equipment cleaning.* Pyrex glassware is washed in tap-water, followed by 6 *M* hydrochloric acid, 8 *M* nitric acid and several rinses in glass-distilled water. Ground-glass stoppered Kjeldahl flasks are rinsed in tap-water, brushed clean using Teepol, then rinsed thoroughly in tap-water before being washed with acid and distilled water as above. Kjeldahl flasks in regular use are soaked once a week, or whenever stains develop, in a solution of Decon 90 (Decon Laboratories Ltd., Portslade, Brighton), rinsed in tap-water and washed in acid and distilled water as above.

*Sample preparation.* The required weight of finely ground (< 150 μm) air-dried (< 30 °C) soil or peat is placed in a 100-ml Kjeldahl flask, 10 ml of a mixture of redistilled nitric acid and concentrated sulphuric (1 + 1) are added and the contents are swirled to wet the sample thoroughly. The weight taken depends on the expected mercury content and amount of oxidizable matter. It is generally 0.5–2.0 g, the sample size being limited by the oxidizing ability of the 40 ml of permanganate solution that the flask can conveniently hold; with peat, for example, 0.5 g is the maximum. The sample is digested unstoppered for 2 h in a water bath at 60°C, with swirling at intervals, only the bulb of the flask being immersed so that its long neck acts as an air condenser. Times of digestion from 1 h to 3 h do not alter the recovery of mercury. The flask is cooled, 20 ml of glass-distilled water is added, the flask is again cooled and 5-ml aliquots of 6% potassium permanganate solution are added until the purple colour is retained for at least 1 h. By grouping samples of similar organic content for analysis, the same volume of potassium permanganate solution can be used for each sample of a set. The sample is then left glass-stoppered at room temperature overnight, and 20% (w/v) hydroxylammonium chloride is added slowly until the brown hydrated manganese oxides and the excess of potassium permanganate are reduced, giving a clear solution with a residue of insoluble material. The unstoppered flask is then left for 1 h to allow the evolved gases to be liberated; no loss of mercury is observed at this stage. This solution is used for the determination of mercury in Method I.

*Standard solutions.* From a 1000 mg $ml^{-1}$ mercury stock solution of mercury(II) chloride in 0.5 *M* sulphuric acid, a 10 mg $ml^{-1}$ mercury solution in 0.5 *M* sulphuric acid, stable for at least one month, is prepared. Solutions containing 0.05, 0.1, 0.2, 0.3 and 0.5 $\mu$g Hg $ml^{-1}$ are prepared daily by repeated dilution of the 10 mg $ml^{-1}$ solution with 0.5 *M* sulphuric acid. Standard samples, analyzed with each set of analysis samples, are prepared by adding 1 ml of these solutions to Kjeldahl flasks with 10-ml aliquots of the nitric/sulphuric acid mixture and 20 ml of water, and digesting in the same manner as the samples, using the same volume of potassium permanganate and hydroxylammonium chloride. Errors arising from volume differences and traces of mercury in the reagents are thus compensated. No loss of mercury was found to occur in the digestion of the standard solutions and the determined mercury contents did not differ from these from undigested standard solutions.

### *Method II. Acid digestion, wet oxidation and collection in potassium permanganate*

In this development of Method I, sample solutions prepared as described above are treated with 5 ml of 20% tin(II) chloride solution in a Kjeldahl flask fitted with a sintered glass bubbler (Quickfit, Porosity 2). By aspirating air at 750 ml $min^{-1}$ through the solution for 30 min, the liberated mercury is transferred to a 60-ml boiling tube, also fitted with a sintered glass bubbler and containing 40 ml of an acidic potassium permanganate collecting solution (see Method III below). The mercury is all trapped here, none being found in a second collecting tube in series with the first. Some of the mercury is retained in the sintered glass bubbler and must be washed into the permanganate collecting solution with 20 ml of a solution consisting of a mixture of 20 ml of 20% $NH_2OH.HCl$, 50 ml of 10% NaCl[29], 10 ml of (1+1) $HNO_3/H_2SO_4$ mixture and 140 ml of distilled water, for subsequent analysis by cold-vapour atomic absorption. The final reduction with tin(II) chloride and the evolution of mercury into the atomic absorption cell can thus be conducted in a matrix of constant composition, which may be expected to eliminate interference effects. This method can readily be adapted for the collection and determination of mercury in air[30] or other gases.

### *Method III. Oxygen flask combustion*

Several methods of direct oxidation of organic material by oxygen at elevated temperatures have been reported for the determination of mercury. The present method is a modified version of the closed oxygen flask combustion technique of Schöniger[31,32] used for mercury by Gutenmann and Lisk[33]. It was developed for the analysis of soils by White and Lisk[34], for grain samples by Pappas and Rosenberg[35], and for other biological and organic samples[36–43], with a variety of techniques for the final mercury determination, including reduction–aeration atomic absorption[42].

Initial trials of the oxygen flask combustion technique, which involved burning a pelleted sample in a platinum basket in an oxygen-filled flask containing a collecting solution to absorb the mercury evolved, gave low mercury recoveries. This was caused by the depressive interference of platinum volatilized from the basket, 5–10 $\mu$g platinum being found in the collecting solution (see *Interference effects* and Fig. 3). A similar effect was produced by adding 10 $\mu$g of platinum to a mercury solution before analysis. The platinum basket was therefore discarded for a perforated tantalum basket in a tungsten wire holder. Neither tantalum nor tungsten interfered in the mercury determination and recoveries of 95–100% were obtained. Figure 1a shows the basket pressed from a 25-mm square sheet of 0.1-mm thick tantalum foil and the tungsten mounting wire attached by an epoxy adhesive to the stopper of the flask. The basket is 4 mm deep and has seven 1 mm holes punched in its base; Fig. 1b shows the sample disk and the mounted basket, while Fig. 1c shows the complete assembly with the filter paper fuse. For these preliminary experiments the collecting solution in the oxygen flask was the acidic permanganate solution used in the final procedure reported below.

Simple collecting solutions have been used by White and Lisk[34] (0.1 *M* hydrochloric acid), Pappas and Rosenberg[35] (1.2 *M* hydrochloric acid), Burnett *et al.*[36] (concentrated nitric acid) and Jones and Schwartzmann[38] (0.5 *M* sulphuric acid). Cellulose pellets (0.5 g) containing 0.10 $\mu$g Hg were burned in a 5-l oxygen flask containing 50 ml of these and other collecting solutions, and the recovery of

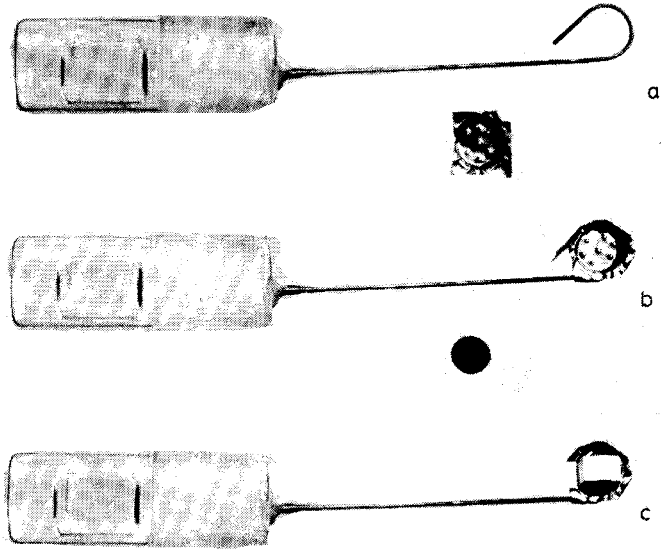

Fig. 1. Sample pellet holder for oxygen flask combustion. (a) Perforated basket pressed from 25-mm square 0.1-mm thick tantalum sheet, before fitting to the tungsten wire (1.5 mm diameter) holder attached to 5-l flask stopper by epoxy resin adhesive. (b) Tantalum basket fitted to tungsten wire holder, with pelletted soil sample alongside. (c) Pellet with filter-paper fuse in sample holder ready for combustion.

mercury was determined by reduction–aeration atomic absorption; mercury standard solutions with a corresponding concentration of the appropriate collecting compound were used. The recoveries are shown in Table I.

It can be seen from Table I that hydrochloric acid at concentrations above 2.5 *M* and a mixture of potassium permanganate with nitric and sulphuric acids both give complete recovery whilst nitric acid, even at 6 *M* concentrations, sulphuric acid, distilled water, and ammonium peroxydisulphate in dilute nitric acid give incomplete recovery. Only acidic potassium permanganate and 2.5 *M* hydrochloric acid were further tested as collecting solutions. Both functioned equally well for standard cellulose pellets containing mercury but with soil and peat samples it was later found that incomplete recovery of mercury was obtained with 2.5 *M* hydrochloric acid, probably because of a waxy film which developed on the inner walls of the combustion flask and was not removed by the acid. Incomplete oxidation of certain materials appeared to occur even in direct combustion with oxygen and further oxidation by potassium permanganate in the collecting solution was necessary to achieve complete extraction of the mercury from the flask.

The oxygen flask combustion method employing an acidic potassium permanganate collecting solution (Method III) is as follows.

The reagents are the same as those described above for the digestion method, with an additional collecting solution made by mixing 50 ml of 6% potassium permanganate solution, 50 ml of a mixture of redistilled nitric and concentrated sulphuric acids (1+1) and 400 ml of distilled water.

*Equipment cleaning.* After each combustion, the 5-l flask is filled completely with tap-water to displace any mercury vapour, drained, washed with 6 *M* hydro-

TABLE I

EFFECTIVENESS OF VARIOUS COLLECTORS OF MERCURY FROM OXYGEN FLASK COMBUSTION OF CELLULOSE PELLET SAMPLES CONTAINING 0.10 μg Hg $g^{-1}$

| *Collector* | *Concentration* | *Recovery of 0.10 μg Hg (%)* |
|---|---|---|
| HCl | 0.05 *M* | <5 |
| | 1 *M* | 53 |
| | 2.5 *M* | 100 |
| | 6 *M* | 100 |
| $HNO_3$ | 0.05 *M* | <5 |
| | 1 *M* | 8 |
| | 2.5 *M* | 18 |
| | 6 *M* | 64 |
| $H_2SO_4$ | 0.05 *M* | 5 |
| | 1 *M* | <5 |
| | 2.5 *M* | <5 |
| | 6 *M* | <5 |
| $(NH_4)_2S_2O_8$ in 0.05 *M* $HNO_3$ | 0.05% w/v | <5 |
| | 1.0% w/v | <5 |
| | 2.5% w/v | <5 |
| $H_2O$ | — | <5 |
| $KMnO_4$ in $HNO_3$/$H_2SO_4$ mixture | 0.6% | 100 |

chloric acid and distilled water, and inverted to drain for at least 2 min. After each day's use, the oxygen flask is soaked overnight with 2% Decon 90, rinsed with distilled water, 6 *M* hydrochloric acid, 8 *M* nitric acid and finally distilled water. After draining, at most only 1 ml remains on the surface of the clean flask so that volume errors are negligible.

*Sample preparation.* 1.000 g of finely ground ($< 150$ µm) air-dried soil or peat (dried at $< 30$ °C) is mixed with 0.500 g of cellulose powder, in a polystyrene tube by a Perspex ball in a vibrating ballmill, for 1 min and pressed into a 12.5-mm diameter pellet at a pressure of 600 MN $m^{-2}$ (40 tons/$in^2$). Other types of sample such as ground rock are generally prepared in a similar way, but peat, coal and plant materials can be pelletted and burned without addition of cellulose powder. Pellets prepared from some inorganic compounds used to test interference effects are difficult to ignite and for these a larger proportion of cellulose and a lower pressure are desirable to ensure ignition.

The pellet is wrapped in an 80 × 10 mm strip of filter paper (Whatman 540) and placed in the tantalum cup with a 30-mm paper tail to act as a fuse (Fig. 1c). A clean 5-l round-bottomed heavy-walled combustion flask is prepared by adding to it 50 ml of the acidic potassium permanganate collecting solution and a 5-cm polypropylene-encapsulated magnetic follower. The flask is flushed with oxygen for 1 min and the tantalum cup with the sample is inserted into the neck of the flask with tail-fuse protruding. The fuse is ignited with a filter-paper spill, the flask closed quickly and placed behind a Perspex safety shield. After burning is complete, the flask is allowed to cool, first in air and then under a running cold-water tap for 5 min. It proved essential to cool the flask to room temperature to prevent losses of mercury on removing the stopper. The sample holder with its ash is removed carefully and the flask stoppered quickly. The collecting solution is then stirred magnetically with maximum splashing for 15 min. After stirring, 2 ml of 20% hydroxylammonium chloride solution is added to reduce the excess of permanganate and any insoluble manganese oxides, the flask is swirled a few times and allowed to drain for 2 min into a 250-ml conical flask which is then stoppered ready for mercury determination by atomic absorption.

*Standard solutions.* Standard pellets are prepared with 0.500 g of cellulose containing 0.0, 0.05, 0.1 and 0.25 µg of mercury added as mercury(II) chloride solutions and analyzed with each set of samples. These are burned immediately after preparation and treated as described for samples. The blank pellet allows a correction to be made for the small mercury content of the cellulose (generally $< 0.008$ µg). A standard mercury solution containing 0.1 µg Hg, with the same reagents but not burned in a pellet in the flask, is used as a check on the system by running it with each set of analyses.

## MEASUREMENT TECHNIQUE

In most cold-vapour, reduction–aeration methods, the mercury is removed from the sample solution, after the addition of tin(II) sulphate or chloride, by continuous bubbling of air or other gas through it into the atomic absorption measuring cell and thence recirculated through the system[21,44] or passed from the cell to an exhaust[25].

Bubbling techniques have two disadvantages. Firstly, frothing can occur, especially when oxidation of organic material is incomplete, as with nitric acid digestion of soil[25, 28]. This results in low mercury recovery and may necessitate complete stripping of the apparatus for cleaning. Secondly, it is necessary to insert a drier containing magnesium perchlorate, calcium chloride or silica gel to remove aqueous spray and vapour; this not only needs frequent changing but, with silica gel, has been found to give rise to variable losses of mercury. Recirculation methods seemed likely to suffer from memory effects in view of the long path length, which includes a pump, and were not investigated. For these reasons, the bubbling technique was replaced by an agitation procedure in which the mercury in the reduced sample solution is partitioned between a fixed volume of air and the liquid phase in a closed vessel by hand-shaking or magnetic stirring. The mercury-laden air is then blown by air at a flow rate of 3 l $\text{min}^{-1}$ directly, without a drier, through the absorption cell for the atomic absorption measurement. Absorption peak-heights by this technique are some 30–40% greater than those obtained with a bubbling system without recirculation, using the same vessel and flow rates, and the absorption pulse is of shorter duration (*ca.* 20 s) and lacks the slow exponential trailing edge produced by bubbling. Similar partitioning techniques have been described by Thorpe[45] and Stainton[46].

### *Method*

*Apparatus.* The apparatus is shown schematically in Fig. 2, where the sample vessel is the long-necked, 100-ml ground-glass stoppered Kjeldahl flask (total volume including the long neck, about 200 ml) in which the acid digestion and wet

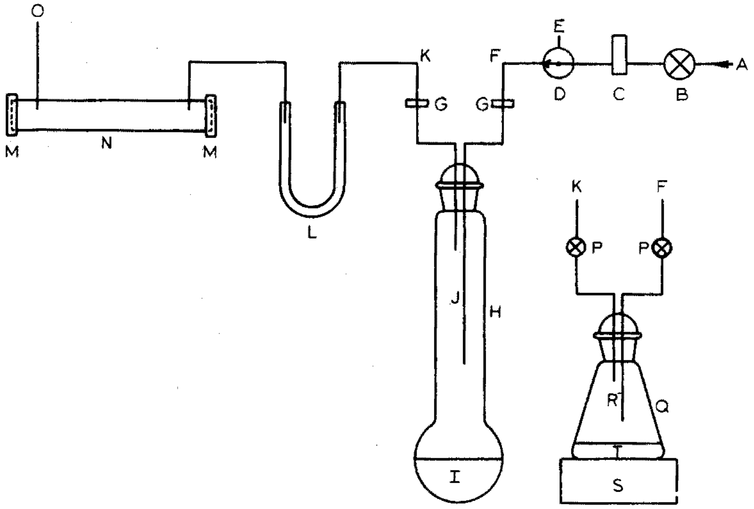

Fig. 2. Apparatus for the determinaton of mercury by cold-vapour atomic absorption. Compressed air line 105 kN $m^{-2}$ (15 $lb/in^2$) A; needle valve B; flow meter C; two-way tap D; vent E; connection points F and K; silicone rubber tubing with Mohr spring-clips G to Kjeldahl flask H; sample I; plain glass tubes, o.d. 0.5 cm J; empty U-tube L; 25-cm Pyrex absorption tube N, o.d. 1.9 cm, with removable fused-silica end windows; O-ring seals M and exhaust O; alternative conical flask Q; plain glass tubes R; nylon stop-cocks P; sample T; and magnetic stirrer S.

oxidation are carried out. The flask is connected to the air-train by flexible silicone-rubber tubing fitted with Mohr spring clips to isolate the sample and the fixed volume of air with which mercury is partitioned by manual shaking of the flask and contents. An empty U-tube is used as a safety trap but no drier is necessary. Sample solutions prepared by the oxygen flask combustion method are decanted into the alternative vessel, a conical flask whose flat bottom makes it convenient to carry out the partitioning operation by magnetic stirring. Isolation of the contents is achieved in this case by nylon stopcocks.

*Operation.* The apparatus is cleaned before use and between samples by attaching the Kjeldahl flask, containing 10–20 ml of distilled water, to the air-train. The clips are attached and the flask is shaken manually. After repeating with a fresh aliquot of distilled water the clips are removed, the two-way tap is opened and air is passed at 10 l $\min^{-1}$ through the flask and measuring system until no absorption is obtained. The air flow is then reduced to 3 l $\min^{-1}$, the two-way tap is set to vent, and the clips are replaced.

The mercury content of a sample is then measured by adding 5 ml of 20% $SnCl_2.2H_2O$ in 6 *M* hydrochloric acid to the sample solution prepared as described above (methods I, II or III) in a Kjeldahl or conical flask, which is immediately fitted to the apparatus to prevent loss of mercury. After agitation for 2 min (manual shaking for Kjeldahl, magnetic stirring for conical flask), the clips are removed (or the stopcocks opened) and air is blown through at 3 l $\min^{-1}$. The absorption is measured at 253.7 nm with a single-beam laboratory-built atomic absorption apparatus of conventional design fitted with a pen recorder with a chart speed of 2.5 mm $\min^{-1}$. Linear calibration curves of absorbance *versus* mercury content are obtained up to about 0.3 $\mu$g, with slight curvature from 0.3 to 0.5 $\mu$g. For a 1-g sample, the analytical range of 0.01–0.5 $\mu$g of mercury corresponds to 0.01–0.5 p.p.m. mercury in the soil.

### *Partition equilibrium*

Time of shaking after addition of tin(II) chloride is not critical. Equilibrium between the phases is obtained in less than 1 min and is unchanged after 4 min of shaking. Absorbance is essentially independent of flow rates between 2 and 4 l $\min^{-1}$ but decreases slightly outside this range. Although the height of the absorbance peak increases with temperature by up to 15% over the temperature range 10–30 °C, no significant errors arise from this cause, since sample and standard solutions analyzed at the same time are at the same temperature.

To confirm that a genuine equilibrium of mercury between the air and the solution is obtained, 5 ml of 20% tin(II) chloride solution were added to 50 ml of a solution containing 0.3 $\mu$g of mercury in a Kjeldahl flask and the mercury was determined after shaking for 2 min. The shaking and measuring process was repeated 10 times with the unchanged solution. The results are shown in Table II. The ratio of mercury in air to mercury in solution is essentially constant for at least 4 shaking cycles. After one shaking, the mercury was partitioned approximately 2 parts in air to 3 parts in solution. The mercury in air thus represented some 40% of the mercury in the original sample and a second partition gave an absorbance of 60% of the first. This was found to be true in general whether the solution was a synthetic standard solution or one derived from a natural soil sample.

TABLE II

RELATIVE MERCURY CONTENTS OF THE LIQUID AND VAPOUR PHASES IN TEN CONSECUTIVE ESTIMATIONS FROM ONE STANDARD SOLUTION CONTAINING 0.300 μg Hg

| *Shake number* $(n)$ | *Hg in air (μg)* $(A_n)$ | *Hg in solution (μg)*[a] $(S_n=0.300-\Sigma_1^n A_n)$ | *(Hg in air)/(Hg in solution)* $(A_n/S_n)$ |
|---|---|---|---|
| 1 | 0.120 | 0.180 | 0.67 |
| 2 | 0.072 | 0.108 | 0.67 |
| 3 | 0.043 | 0.065 | 0.66 |
| 4 | 0.026 | 0.039 | 0.67 |
| 5 | 0.017 | 0.022 | 0.74 |
| 6 | 0.009 | 0.013 | 0.69 |
| 7 | 0.005 | 0.008 | 0.63 |
| 8 | <0.005 | <0.008 | — |
| 9 | <0.005 | <0.008 | — |
| 10 | <0.005 | <0.008 | — |

[a] $\Sigma_1^n A_n$ = Total weight of mercury liberated into air phase after $n$ partitions.

TABLE III

PRECISION OF THE INSTRUMENTAL DETERMINATION OF MERCURY IN STANDARD SOLUTIONS

| *Method of partition* | *Nominal Hg content (μg)* | *Average found*[a] *(μg)* | $s$ *(μg)* | $s_r$ *(%)* |
|---|---|---|---|---|
| 100 ml Kjeldahl flask, | 0.025 | 0.025 | ±0.002 | ±8.0 |
| 2 min manual shaking, | 0.10 | 0.101 | ±0.002 | ±2.0 |
| 60 ml sample volume | 0.20 | 0.201 | ±0.003 | ±1.5 |
| | 0.50 | 0.518 | ±0.011 | ±2.3 |
| 250 ml Conical flask, | 0.05 | 0.052 | ±0.001 | ±2.0 |
| 2 min agitation by | 0.10 | 0.099 | ±0.004 | ±4.0 |
| magnetic stirrer, | 0.20 | 0.200 | ±0.003 | ±1.5 |
| 50 ml sample volume | | | | |

[a] Average of 10 determinations.

Several successive determinations of mercury could thus be made on the same solution, subject only to the limit imposed by the progressive reduction in sensitivity. This is useful in order to obtain a result when the mercury content is initially too high for measurement.

### *Precision*

Reproducibility for standard solutions is shown in Table III, with typical sample volumes, for the two types of vessel, the Kjeldahl flask with manual shaking and the conical flask with agitation by magnetic stirrer. The smaller air/liquid volume ratio in the Kjeldahl flask results in a significantly higher absorbance (0.33 for 0.2 μg Hg) compared with the conical flask (0.23 for 0.2 μg Hg) which was tried out mainly because its flat base is convenient for magnetic stirring.

TABLE IV

REPRODUCIBILITY OF THE COMPLETE ANALYTICAL PROCEDURE BASED ON ACID DIGESTION AND WET OXIDATION (METHOD I)

| | *Sample weight (g)* | *Average Hg found*[a] *(μg)* | *s (μg)* | $s_r$ *(%)* |
|---|---|---|---|---|
| Soil 1 | 1.000 | 0.073 | ±0.005 | ±7 |
| Soil 2 | 1.000 | 0.134 | ±0.008 | ±6 |
| Soil 3 | 1.000 | 0.184 | ±0.012 | ±7 |
| Peat 1 | 0.500 | 0.082 | ±0.004 | ±5 |

[a] Average of 10 determinations.

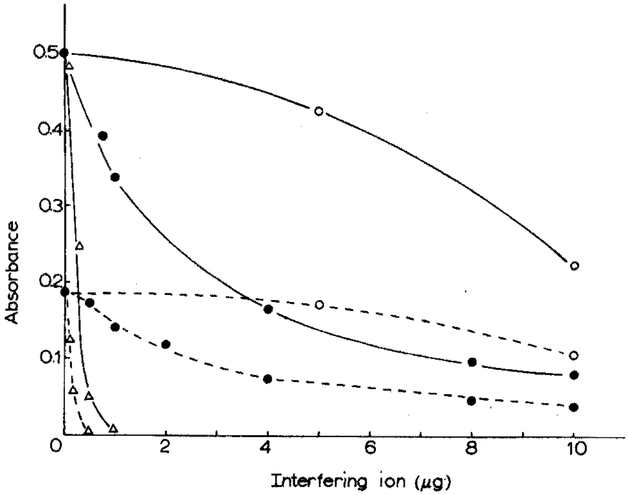

Fig. 3. Interference by gold (○), platinum (●) and palladium (△) on the determination of 0.25 μg (full line) and 0.1 μg (dashed line) of mercury by Method I.

The reproducibility of the complete analytical procedure based on Method I, is shown in Table IV for 10 replicate analyses of 4 samples. The coefficients of variation range from 5% to 7%. The reproducibility of the complete analytical procedure based on Method III, is similar to that obtained with the digestion technique. For ten replicate soil analyses, a mean mercury content of 0.091 μg, a standard deviation of ±0.003 and a relative standard deviation of ±3.3% were obtained with a 1-g sample weight.

## *Interference effects*

No significant (> 5%) interference effects occurred in the determination of 0.1 μg of mercury in solutions prepared by digestion (Method I) or by oxygen flask combustion (Method III), from standard solutions or cellulose pellets containing elements such as aluminium, calcium, iron and magnesium, present in major amounts in soils. The compounds added in approximately 0.5-g quantities were aluminium chloride (Method I), aluminium oxide (Method III), calcium carbonate

(Methods I and III), calcium chloride (Method I), iron(II) sulphate (Method I), iron(III) oxide (Method III) and magnesium oxide (Methods I and III). With phosphorus, added as calcium phosphate (0.5 g), a small ($<10\%$) depressive interference was found in Method I but not in Method III.

With neither preparative method was any interference shown by copper (250 $\mu$g) as copper sulphate, silver (100 $\mu$g) as silver nitrate, or sulphur (1000 $\mu$g Method I, 10,000 $\mu$g Method III) as sodium sulphide. Neither selenium (400 $\mu$g) as selenous acid nor iodine (100 $\mu$g) as potassium iodide interfered when Method III was used. With Method I, selenium as selenous acid interfered with the mercury determination: 400 $\mu$g Se depressed the absorbance for 0.2 $\mu$g Hg by 90% and 40 $\mu$g Se by 8%, but the absorbance was not depressed significantly by 4 $\mu$g Se. Method I was also subject to depressive interference by iodine; 100 $\mu$g of iodine as potassium iodide or as elemental iodine depressed the absorbance of 0.1 $\mu$g of mercury by 10%.

For solutions prepared by Method I, the depressive interference of gold, platinum and palladium, increasing in that order, is shown in Fig. 3 for mercury contents of 0.1 and 0.25 $\mu$g; the effect of palladium was particularly severe. In the oxygen flask combustion method, platinum and gold interfered slightly less than in the digestion method, and palladium (0.6 $\mu$g) did not interfere at all. If the pellet ash after combustion were not removed but deposited in the collecting solution, the interference caused by gold and platinum was enhanced and palladium also showed a depressive effect. The amount of depression caused by gold and platinum was somewhat variable from pellet to pellet and probably reflected the influence of temperature differences in successive burns.

Molecular absorption and light scattering interference effects were found to be insignificant for solutions of 3 soils and 3 rocks prepared by Method I.

## COMPARATIVE ANALYSIS BY THE THREE METHODS

Results are presented in Table V for soils and peats covering ranges of organic matter contents (1–7) and parent materials (8, granitic gneiss; 9, sandstone; 10, olivine gabbro; 11, knotted schist; 12, argillaceous schist; 13, shell-sand) which were analyzed by the different methods of sample preparation already discussed. The excellent agreement obtained between the digestion method (method I) and the oxygen flask combustion method (method III) for mercury contents from 0.09 to 0.26 $\mu g\ g^{-1}$ indicates that these two radically different oxidation procedures are equally effective. A plot (Fig. 4) for 36 soils and peats analyzed by Methods I and III adheres closely to the line for 100% correlation with no evidence of bias. Analyses by the digestion, volatilization and collection method (II) are (Table V) in good agreement with those of methods I and III, which suggests that no significant matrix effects occur.

Further oxidation with potassium peroxydisulphate following the procedure of Method I does not appear to effect any improvement. Table V also shows that the analytical values obtained by a nitric acid digestion alone are considerably lower than those by Methods I, II or III. The failure of hydrochloric acid (2.5 *M*) to collect mercury after oxygen flask combustion, in spite of its promise with standard cellulose pellet samples, is also demonstrated. Recoveries of 0.10 $\mu$g of mercury added as mercury(II) chloride by Method I ranged from 92% to 109%

TABLE V

COMPARATIVE ANALYSIS OF SOILS FOR MERCURY WITH DIFFERENT SAMPLE PREPARATION METHODS

| *Soil no.* | *Loss on ignition (%)* | *Method I*[a] *($\mu g\ g^{-1}$)* | *Method II*[b] *($\mu g\ g^{-1}$)* | *Method III*[c] *($\mu g\ g^{-1}$)* | *Digestion with $K_2S_2O_8$ etc.*[d] *($\mu g\ g^{-1}$)* | *$HNO_3$ digestion ($\mu g\ g^{-1}$)* | *Oxygen flask HCl collecting solution ($\mu g\ g^{-1}$)* |
|---|---|---|---|---|---|---|---|
| 1 | 77 | 0.10 | 0.11 | 0.11 | 0.10 | 0.07 | 0.04 |
| 2 | 63 | 0.14 | 0.14 | 0.13 | 0.14 | 0.10 | 0.04 |
| 3 | 53 | 0.11 | 0.11 | 0.12 | 0.11 | 0.07 | 0.03 |
| 4 | 40 | 0.20 | 0.19 | 0.20 | — | 0.14 | 0.07 |
| 5 | 31 | 0.13 | 0.12 | 0.13 | 0.11 | 0.10 | 0.04 |
| 6 | 20 | 0.15 | 0.14 | 0.15 | 0.14 | 0.11 | 0.06 |
| 7 | 9 | 0.26 | 0.25 | 0.25 | 0.23 | 0.18 | 0.18 |
| 8 | 11 | 0.11 | 0.10 | 0.11 | 0.10 | 0.10 | 0.10 |
| 9 | 10 | 0.09 | 0.08 | 0.08 | — | 0.07 | 0.07 |
| 10 | 15 | 0.15 | 0.14 | 0.14 | — | 0.12 | 0.12 |
| 11 | 14 | 0.12 | 0.12 | 0.12 | — | 0.08 | 0.10 |
| 12 | 10 | 0.14 | 0.13 | 0.14 | — | 0.11 | 0.10 |
| 13 | — | 0.09 | 0.10 | 0.09 | — | 0.08 | 0.09 |

[a] $HNO_3/H_2SO_4/KMnO_4$ digestion.

[b] $HNO_3/H_2SO_4/KMnO_4$ digestion, volatilization and collection.

[c] Oxygen flask, $KMnO_4$ collecting solution.

[d] $HNO_3/H_2SO_4/KMnO_4/K_2S_2O_8$ digestion.

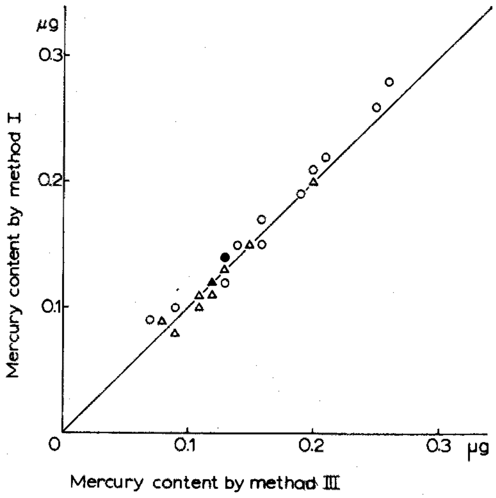

Fig. 4. Correlation of mercury contents in 36 soils and peats determined by acid digestion and wet oxidation (Method I) and oxygen flask combustion (Method III). Mercury content determined in: (○) a single soil, (△) 2 different soils, (●) 3 different soils, (▲) 6 different soils.

TABLE VI

MERCURY CONTENT FOUND IN U.S. GEOLOGICAL SURVEY STANDARD ROCKS BY METHODS I AND III

(Single determinations, 2-g samples)

| *U.S.G.S. standard rock* | *Hg found* ($\mu g\ g^{-1}$) | | *Literature values* ($\mu g\ g^{-1}$) | | |
|---|---|---|---|---|---|
| | *Method I* | *Method III* | [a] | [b] | [c] |
| AGV1 | 0.025 | 0.025 | 0.025 | 0.0016 | 0.004–0.026 |
| BCR1 | 0.050 | 0.025 | 0.018 | 0.006/7 | 0.004–0.018 |
| DTS1 | 0.020 | 0.025 | 0.012 | 0.006/7 | 0.004–0.012 |
| G2 | 0.065 | 0.060 | 0.040 | 0.073 | 0.029–0.120 |
| GSP1 | 0.040 | 0.050 | 0.015 | 0.019 | 0.015–0.041 |
| PCC1 | 0.025 | 0.025 | 0.005 | 0.006/7 | 0.004–0.011 |

[a] Atomic absorption[22].
[b] Emission spectrographic[47].
[c] Atomic absorption and neutron activation: range[48].

and showed no correlation with the values for loss on ignition.

Methods I and III therefore appear to provide accurate analytical values for total mercury in most soils and peats. This conclusion is supported by the analysis of six U.S. Geological Survey standard rocks by Methods I and III. Even at the low levels involved, reasonable agreement between the two methods is found (Table VI) except for BCR1. Only a limited amount of material was available and this difference was not investigated further; repetition of the analyses confirmed that the values were reproducible and that the difference was not due to molecular absorbance in Method I. The very wide range of values reported[22,47,48] for these rocks and the limited number of analyses so far conducted makes it impossible to assign definitive values to their mercury contents.

For the analysis of soils and related materials, the digestion and wet oxidation method (Method I) is preferred, and the oxygen flask method (Method III) is reserved for purposes of confirmation or investigation. Although for a limited number of samples the latter is quicker, the suitability of the digestion method for batches of samples makes it more productive. It has the further advantage that it is suitable for fresh (undried) material. If the presence of significant amounts of selenium or iodine is suspected, Method III should be used.

In addition to the analytical problems considered in this paper, the problem of obtaining a representative sample for analysis, without loss of, or contamination by, mercury, is under investigation.

Preliminary trials indicate that the methods are also applicable to plant materials.

The authors wish to acknowledge the assistance of Miss J. Jackson in the experimental work involved in developing these methods.

## SUMMARY

A method for the determination of mercury in soils and related materials, by the cold-vapour, reduction–aeration absorption technique, is described. The mercury in the reduced sample solution is partitioned, by agitation, between the liquid phase and a fixed volume of air which is then blown through an absorption cell for measurement. Three preparative methods were developed, two of which use acid digestion and wet oxidation and the other direct oxidation in an oxygen-flask combustion technique. Comparative analysis of natural samples by the three methods was used to validate the techniques developed, since no authenticated reference samples were available. For 1-g samples, the analytical range was 0.01–0.5 p.p.m.

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# ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF GALLIUM AND INDIUM IN INORGANIC MATERIALS BY DIRECT ATOMIZATION FROM THE SOLID STATE IN A GRAPHITE FURNACE

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Gallium and indium are not found as major constituents of minerals. The former element is widely distributed in nature, and is found in small quantities in aluminium, iron and zinc minerals. Small amounts of indium occur in many sulfide minerals, and in manganese, iron, tin and tungsten ores. The concentration of gallium in silicate rocks is normally in the range 10–100 p.p.m., while indium is usually found in the p.p.b. range; in sulfide ores indium may be found in p.p.m. amounts. Various instrumental techniques, such as spectrophotometry, neutron activation analysis, emission or X-ray spectrography, and conventional atomic absorption spectrometry have been used to determine gallium in rocks, ores, metals and other inorganic materials; the low contents of indium normally met with in these materials limit the number of useful methods.

Pollock[1] applied atomic absorption spectrometry to determine gallium in limonite, the procedure involving a decomposition and a preconcentration step. Lypka and Chow[2] reported a comparison of the determination of gallium in several ore products by atomic absorption with a solvent extraction technique, and by a spectrophotometric method.

The present paper describes direct-atomization methods for the determination of gallium or indium in bauxite, clay, laterite, sulfide ores and concentrates, alumina, and aluminium metal. For comparison, some sample solutions were also analyzed by atomization in the graphite furnace or in the flame.

Nothing was found in the literature on the use of the present technique for the determination of gallium or indium.

## EXPERIMENTAL

### *Apparatus*

A Perkin–Elmer 303 atomic absorption spectrophotometer equipped with an arc-source deuterium background corrector was used. The high-frequency induction-heated graphite furnace has been described elsewhere[3]. The signals were detected with a 2-channel recorder; one of the channels plotted the peak (in percent absorption), and the other was connected to instrumentation that transformed the signals into absorbance and recorded the integrated peak areas.

Some samples were decomposed in polytetrafluoroethylene-lined aluminium bombs (capacity about 120 ml).

Weighings were made with semi-micro or micro balances.

*Reagents and solutions*

Standard solutions were prepared from Koch–Light gallium rod (99.999%) and indium shot (99.9999%).

The acids employed were of Suprapur quality (Merck).

Primary metal standard solutions (1000 p.p.m. of the element) were prepared by dissolving 1 g of metal in 25 ml of nitric acid (1+1), the solutions being diluted to 1 l. Secondary standard solutions, 100 p.p.m. in gallium and 20 p.p.m. in indium, were prepared by dilution.

*Preparation and decomposition of the samples*

Details of the types and origin of the samples are given in Tables I and II (*vide infra*).

*Aluminium samples.* From the two aluminium ingots, samples for analysis were prepared by drilling. The sample of alumina passed a 100-mesh (149 μm) sieve. The other samples present as powders were ground to pass a 270 mesh (53 μm) sieve.

Solutions to be analyzed in the furnace or in the flame were prepared as follows. For each of the two aluminium samples, five portions of about 0.3 g were dissolved in 10 ml of sulfuric acid (1+3), and the solutions were diluted to 25 ml. From each of the five solutions prepared of the sample Al (1S RX-D), 3 ml were transferred to small sample bottles; 60, 120, 180 or 240 μl of 100 p.p.m. gallium solution were added to four of the bottles by syringe, and water was then added, where required, to give a total volume of 3.240 ml. To the fifth bottle, 240 μl of water were added. 10 μl of each solution were taken for analysis in the furnace.

From the five solutions of Al (99.5%), solutions for analysis were prepared in the same way, except that 30, 60, 90 or 120 μl of 100 p.p.m. gallium solution were added, and all solutions were made up to 3.120 ml. From all bottles, 10 μl were taken for analysis in the graphite tube.

*Bauxite.* For the sample of bauxite, five portions of about 0.5 g were attacked, in polytetrafluoroethylene-lined bombs, by a mixture of 12.5 ml of hydrofluoric acid and 1 ml of nitric acid; the bombs were heated for 1 h at 150°C. After the decomposition, the contents were transferred to platinum dishes and evaporated to dryness. The residues were moistened with water, 2 ml of hydrofluoric and 1 ml of sulfuric acid were added, and the mixtures were again evaporated to dryness. The residues were finally dissolved in 10 ml of sulfuric acid (1+9), and the solutions were diluted to 50 ml.

*Sulfide ore.* Five 0.5-g portions of the ASK sulfide ore were decomposed in the bombs by a mixture of 6.5 ml of hydrofluoric, 5 ml of hydrochloric, 5 ml of nitric and 1 ml of sulfuric acid. After the attack, the contents of the bombs were transferred to platinum dishes and evaporated to dryness. The residues were dissolved in 15 ml of sulfuric acid (1+3), and the solutions were diluted to 50 ml.

From each of the five sample solutions, 3 ml were transferred to sample bottles; to four of these bottles, 30, 60, 90 or 120 μl of 20 p.p.m. indium solution were added, and water was added to all bottles to give a total volume of 3.120 ml. From the bottles, 10 μl were again pipetted for analysis in the graphite furnace.

*Determination of water*

The content of water in the samples of bauxite, flint clay and laterite was determined by drying for 2 h at 140°C; the other samples (with the exception of the metals) were dried for 1 h at 110°C.

*Measurement procedures*

The settings of the spectrophotometer were adjusted as prescribed in the instrument manual. The measurements were made at the wavelengths: 287.4 nm for gallium, and 304.0 nm for indium. The deuterium and hollow-cathode lamps were heated for 1 h before the measurements started.

A 0.5–10-mg portion of the solid sample or standard, with or without added carbon, was weighed in a small tantalum scoop (produced by Perkin–Elmer), and the contents were placed in the middle of the graphite tube by means of a home-made adjustable inserting device; the scoop was reweighed, and the furnace was moved into its preadjusted position.

Gallium was determined without adding carbon to the samples or standard. In the analyses for indium, the beneficial effect of carbon was not pronounced; some samples were analyzed without added carbon, and some were mixed with equal amounts of graphite, but all measurements were made with a standard to which carbon had been added.

When a solid sample was measured against a solid natural standard, five sets of integrated peak areas were produced, each set consisting of one measurement of the sample and one of the standard. The amounts of standard were varied so that a calibration curve could be plotted. The drying and atomization procedures for solid samples were as follows: for gallium, drying at 200°C, atomization at 1900°C and cleaning of the furnace at 1980°C, each operation taking 60 s; for indium, drying at 100°C for 30 s; for the sulfide-containing samples an additional heating period at 700°C for 90 s, and atomization for 60 s at the temperatures indicated in Table II (*vide infra*), with cleaning as for gallium.

Figure 1 shows some characteristic signals, as obtained from gallium in aluminium and bauxite, and from indium in the ASK sulfide ore. As can be seen, the gallium peaks are rather broad; sharper peaks would probably be obtained, if higher atomization temperatures were to be employed.

For indium, two peaks are reproduced, one with and the other without a preliminary heating at 700°C. The small peak appearing before the main peak in

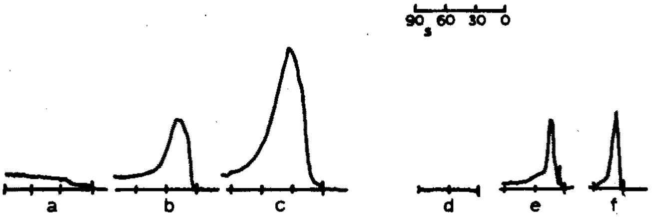

Fig. 1. Typical signals, obtained for gallium from (a) the empty furnace, (b) 0.674 mg of bauxite, (c) 0.821 mg of aluminium (1S RX-D); and for indium from (d) the empty furnace, (e) 2.38 mg of ASK sulfide ore without heating at 700°C, (f) 2.45 mg of the latter sample with preheating at 700°C. The samples (e) and (f) contained 50% of graphite.

samples not preheated is believed to be caused by partial decomposition of the pyrite. The preheating step removes this additional signal.

From the series of solutions prepared for atomization in the furnace by the standard addition technique, 10 μl were introduced by syringe through the radial opening of the furnace, and water was removed by evaporation at about 100°C for 30 s. The residues were then heated for 150 s at 700°C to transform the sulfates to oxides. The further procedure for gallium was as for the solid samples; indium was atomized by heating for 60 s at 1840°C. All atomizations ended with a cleaning step.

The content of gallium in bauxite was also established by aspirating the solutions prepared for the standard addition method in an acetylene–air flame.

The standard addition technique is probably applicable also to the determination of the high amounts of gallium in the aluminium (1S RX-D), but the low concentration in aluminium (99.5%) can only be established with poor precision.

Separate experiments involving aspiration of gallium solutions in the acetylene–air flame, with and without added aluminum demonstrated a depressing effect of the latter metal.

## RESULTS

The feasibility of the proposed technique was demonstrated by analyzing various inorganic materials; the results (reported on a moisture-free basis) are listed in Tables I and II.

In the determination of gallium, the NBS bauxite (sample no. 69A) was used as the solid natural standard. As the certificate from the issuing organization does not indicate the content of gallium (or indium), the concentration of gallium was established by analyzing five sample solutions in the furnace by the standard addition technique; the average was found to be 115 p.p.m. gallium with a standard deviation of 5 p.p.m. and a relative standard deviation of 4%. Table I shows that 110 p.p.m. was established from the conventional flame method; by emission spectrography, the value 111 p.p.m. ($s=7$ p.p.m.) was found. The value 115 p.p.m. gallium was chosen as the standard value.

With the exception of the aluminium sample 1S RX-D, nothing was known about the content of gallium in the materials listed in Table I. The company issuing this reference metal indicates a gallium content of 170 p.p.m.; in this work, direct atomization from the metal and atomization of sample solutions in the furnace gave the values 188 and 174 p.p.m., respectively. Assuming the value 170 p.p.m. to represent the "true" amount, the differences between this and the two other results can be accounted for by the random errors associated with the two proposed methods. The precision of the proposed direct-atomization technique for gallium is satisfactory.

The analytical results for indium are listed in Table II. The solid natural standard in these analyses was the ASK sulfide ore. By analyzing five solutions of this sample in the furnace by the standard addition method, the content of indium was found to be 17.0 p.p.m. Two previous independent analyses[4,5] by neutron activation gave the values 17 and 21 p.p.m., respectively. The value 17.0 p.p.m.

TABLE I

DETERMINATION OF GALLIUM

(Results are given in p.p.m. Unless otherwise stated, five analyses of each sample were made.)

| | *By direct atomization in the furnace* | | | *Atomization of sample solution in the furnace* | | | *Atomization of sample solution in the flame* | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\bar{x}$[a] | $s$ | $s_r$ | $\bar{x}$ | $s$ | $s_r$ | $\bar{x}$ | $s$ | $s_r$ |
| Bauxite (NBS sample no. 69A) | 115[b] | — | — | 115 | 5 | 4 | 110[c] | 15 | 14 |
| Flint clay (NBS sample no. 97) | 70 | 4 | 6 | — | — | — | — | — | — |
| Alumina[d] | 77 | 6 | 8 | — | — | — | — | — | — |
| Aluminium[e] (99.5%) | 79 | 10 | 13 | 70 | 6 | 9 | — | — | — |
| Aluminium[f] (1S RX-D) | 188 | 17 | 9 | 174 | 7 | 4 | — | — | — |

[a] $\bar{x}$, Average; $s$, standard deviation; $s_r$, relative standard deviation. [b] Bauxite was used as the solid standard. [c] Six analyses were made. [d] Reagent-grade alumina (Riedel-de Haën). [e] Technically pure aluminium. [f] Technically pure aluminium; reference sample issued by Alcan Aluminium Ltd., Canada.

TABLE II

DETERMINATION OF INDIUM

(Results are given in p.p.m. Five analyses of each sample were made.)

| *Sample* | *By direct atomization in the furnace* | | | *By atomizing the sample solution in the furnace* | | | *Temperature of atomization from the solid state (°C)* |
|---|---|---|---|---|---|---|---|
| | $\bar{x}$[a] | $s$ | $s_r$ | $\bar{x}$ | $s$ | $s_r$ | |
| Bauxite (NBS sample no. 69A) | 0.11 | 0.02 | 18 | — | — | — | 1900 |
| Flint clay (NBS sample no. 97) | 0.14 | 0.02 | 14 | — | — | — | 1900 |
| Laterite[b] | 0.15 | 0.02 | 13 | — | — | — | 1900 |
| ASK sulfide ore[c] | 17.0[d] | — | — | 17.0 | 0.6 | 3.5 | 1780 |
| Killingdal sulfide ore | 2.9 | 0.3 | 10 | — | — | — | 1900 |
| Mofjell sulfide ore | 0.26 | 0.04 | 15 | — | — | — | 1780 |
| Mofjell zinc concentrate | 5.0 | 0.5 | 10 | — | — | — | 1780 |
| Folldal zinc concentrate | 12.1 | 0.7 | 6 | — | — | — | 1780 |

[a] $\bar{x}$, Average; $s$, standard deviation; $s_r$, relative standard deviation.

[b] A sample from Uganda, East Africa.

[c] The ore contains pyrite, chalcopyrite, sphalerite and galena as essential minerals.

[d] The ASK sulfide ore was used as the solid standard.

was taken as the standard value in the present analyses for indium, which were made only by direct atomization from the solid state. The indium contents of the other samples were too low for atomization of sample solutions to give valid results. The only earlier report on the content of indium in the present type of samples is an analysis by emission spectrography made by Oftedal[6], who gave a concentration of 0.001% in the Folldal zinc concentrate.

By the present technique, the following approximate detection limits were obtained; for gallium, $2.5 \cdot 10^{-9}$ g, and for indium $2.6 \cdot 10^{-10}$ g.

The donation of a reference sample of aluminium from DNN Aluminium A/S, Eydehavn, Norway, and of a sample of laterite from Dr. K. Bjørlykke, Department of Geology, University of Oslo, are gratefully acknowledged.

## SUMMARY

Atomic absorption spectrometric determinations of gallium or indium in alumina, clay, laterite, bauxite, sulfide ores and concentrates, and in aluminium metal, were carried out by atomizing the elements directly from the solid state. Atomizations were made in a high-frequency induction-heated graphite furnace. For comparison purposes, some samples were also decomposed, and analyses made by atomizing sample solutions in the furnace and in the flame.

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*Analytica Chimica Acta*, 72 (1974) 85–90

# THE DETERMINATION OF ARSENIC BY NON-DISPERSIVE ATOMIC FLUORESCENCE SPECTROMETRY WITH A GAS SAMPLING TECHNIQUE

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As discussed by earlier workers[1–7], a non-dispersive system for atomic fluorescence measurements has many advantages such as: (1) greater energy throughput; (2) simple and compact instrumentation; (3) simultaneous detection of multiple lines for the element of interest; and (4) convenience for multi-element analysis. However, this system is subject to the drawback of light-scattering effects caused by particles in atomic clouds. This effect is especially serious when the element of interest is contained in a large amount of matrix.

It is known that arsenic has more than ten atomic fluorescence spectral lines in the ultraviolet spectral region[8]. Therefore, arsenic should be one of the elements most suitable for non-dispersive atomic fluorescence spectrometry. Vickers *et al.*[7] and Larkins[2] have already reported the detection limits of 0.3 $\mu$g ml$^{-1}$ and 6 $\mu$g ml$^{-1}$, respectively, for their non-dispersive atomic fluorescence measurements of arsenic with the solution methods.

Since the report by Holak[9] in 1969, many workers have applied the gas-sampling technique to the determination of arsenic by atomic absorption[10–13] and emission spectrometry[14,15]. The principal advantages of the gas-sampling technique are as follows: (1) arsenic is converted to arsine isolated from the matrix elements; (2) the total amount of arsine evolved is available for atomization; (3) arsine is easily atomized even in a relatively cool flame such as a hydrogen–argon-entrained air flame; and (4) the scattering effects often associated with the ordinary solution method are essentially eliminated. In view of the considerations mentioned above, the gas-sampling technique was employed to eliminate the light-scattering effect in non-dispersive atomic fluorescence measurements of arsenic.

This paper describes the application of the gas-sampling technique to the determination of arsenic by non-dispersive atomic fluorescence spectroscopy; a microwave-excited electrodeless discharge lamp served as a light source and a hydrogen–argon-entrained air flame as an atom reservoir.

## EXPERIMENTAL

The arrangement of the apparatus and the arsine generator used in the experiment are shown in Figs. 1 and 2, respectively. The detector was a solar-blind photomultiplier (HTV R166), which was housed in a detector box of a

Hitachi Spectrophotometer Model 139. A John Fluke Model 412B power supply was used to provide high voltage (700 V) for the photomultiplier. The signals from the photomultiplier were fed into a lock-in amplifier (Princeton Applied Research Corp., Model HR-8) which was phased with a reference signal from a mechanical light chopper (Princeton Applied Research Corp., Model 125, Chopping frequency: 27 Hz), and recorded on a Hitachi Model QPD-54 recorder. To minimize stray light from the light source reaching the detector, a baffle was placed in front of the detector box. The arsenic electrodeless discharge lamp used (EMI Electronics Ltd.) was maintained with a Microtron 200 microwave generator (2450±25 MHz) and a Model 210 resonant cavity (Electro Medical Supplies Ltd.) which was operated at 33 W. The discharge was initiated with a high-frequency Tesla vacuum-tester. A hydrogen–argon-entrained air flame was supported on a specially manufactured three-slot burner head (see Fig. 3) fitted to a Hitachi nebulizer chamber. To obtain the most sensitive results, the light source and the detector box were situated as closely as possible to the flame. The distances from the flame center to the light source and to the detector photocathode were approximately 9.5 cm and 13.5 cm, respectively.

### *Reagents*

*Arsenic stock solution.* A 1000-p.p.m. commercially available standard solution (Kanto Chemical Corp. Inc.) made from sodium arsenite was used. More dilute standard solutions were prepared just before use, by appropriate dilution of the stock solution.

All other reagents used were prepared from analytical reagent-grade chemicals. They were 1% potassium iodide in deionized water, 20% tin(II) chloride in concentrated hydrochloric acid, and 5% sulfuric acid–20% hydrochloric acid (mixed acid) solution.

### *Procedures*

The electro-magnetic valves A, B, and C in Fig. 2 were adjusted to pass argon through a by-pass tube. A sample containing 1 ml of iodide solution, 0.5 ml of tin(II) solution, and 20 ml of mixed acid solution was transferred to a reaction flask. The solution was then diluted to about 50 ml with deionized water. After 1 g of zinc powder had been placed in a glass boat (D in Fig. 2), the atmosphere in the reaction flask was replaced with argon, by adjustment of the valves to pass argon through the reaction flask. The valves were again set at

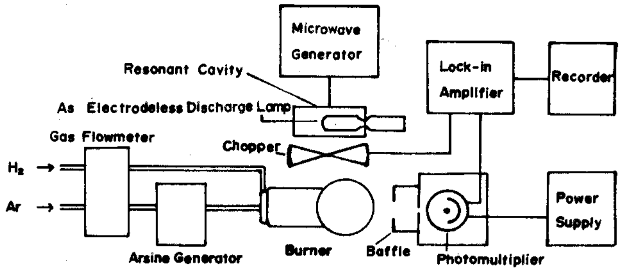
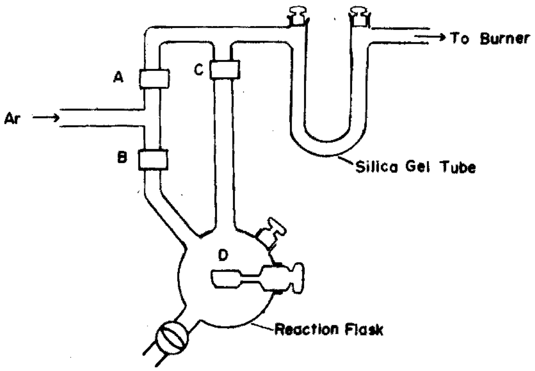


Fig. 1. Schematic diagram of the apparatus.

the initial position to pass argon through the by-pass tube. The zinc powder was then added to the solution and agitated with a magnetic stirrer, and the reaction was allowed to continue for 75 s. The switch of the valves was then turned on, allowing argon to flow through the reaction flask and to carry the arsine evolved into the burner.

The atomic fluorescence signals were recorded, and the peak heights were measured to obtain relative fluorescence intensities for various amounts of arsenic.



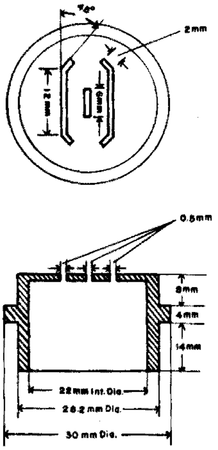


Fig. 2. Arsine generator. A, B, and C, electro-magnetic valves; D, glass boat.

Fig. 3. Manufactured burner head.

## RESULTS AND DISCUSSIONS

### *Effect of the configuration of the burner slots*

As shown in Fig. 3, three slots are cut in the burner head. The configuration of the burner head was changed in three ways as shown in Fig. 4, and the effect on fluorescence intensity was examined. In three different configurations of the burner head, the maximal fluorescence intensity was obtained at the A position, at which the slots were parallel to the incident beam. The intensities obtained at the B and C positions were about 86% and 59% of that at the A. This is possibly related to the decreasing solid angle subtended by the photomultiplier and the increasing re-absorption of fluorescence with the rotation of the burner head from the A to the C position. All further work was carried out at the A position.

### *Effect of the flame composition*

The flame composition was not a critical factor with regard to the fluorescence intensity, when the flow rate of argon was kept constant. However, the noise level was markedly affected by the flame composition, and the signal-to-noise ratio was improved with low flow rates of hydrogen (see Fig. 5). The increase of S/N with a decreasing flow rate of hydrogen is due to a decreasing OH band

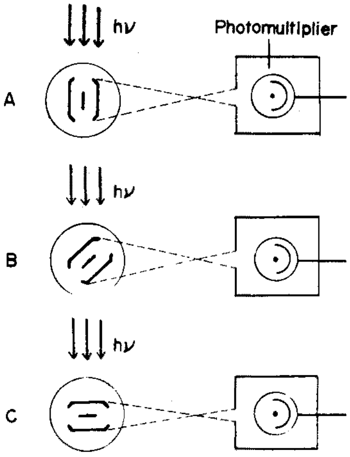


Fig. 4. Configuration of the burner head against the incident radiation. (A), Incident beam is parallel to the burner slots; (B), incident beam is 45° to the slots; (C), incident beam is perpendicular to the slots.

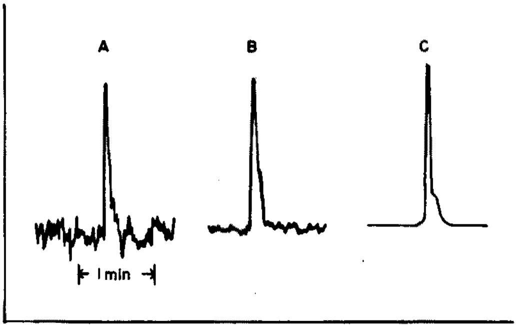


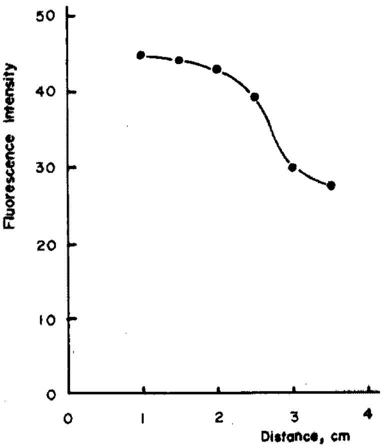
Fig. 5. Effect of the flow rate of hydrogen on fluorescence signals. Flow rate of argon, 5.7 l $\min^{-1}$. Flow rate of hydrogen, (A) 6.7, (B) 3.3, (C) 1.7 l $\min^{-1}$.

emission (280–320 nm) from the flame.

When the arsine and hydrogen gases evolved in the reaction flask were introduced into the burner, the flame occasionally blew out at hydrogen flow rates below 1.7 l $\min^{-1}$. With a decreasing flow rate of argon, the fluorescence peaks broadened. Therefore, all further measurements were made with a hydrogen flow rate of 1.7 l $\min^{-1}$ and an argon flow rate of 5.7 l $\min^{-1}$, respectively.

*Effect of burner height*

In Fig. 6, the variation of fluorescence intensity with the height of the burner is shown. The distances shown in Fig. 6 were those from the top of the burner to the position corresponding to the center of the slit cut on the detector box. It can be seen from Fig. 6 that the fluorescence intensity showed a maximum at a position 1 cm above the top of the burner. However, the optimal signal-to-noise ratio was obtained at 2.5 cm, because at this position the baffle in front



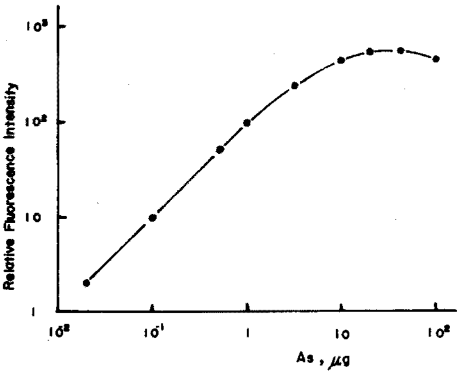


Fig. 6. Effect of the burner height on fluorescence intensity.

Fig. 7. Analytical working curve for arsenic.

of the detector box served as an eliminator of the light from the visible portion of the flame.

*Detection limit and analytical working curve*

The detection limit, defined as the quantity of arsenic for which the signal-to-noise ratio was equal to 2, was found to be 2 ng.

In Fig. 7, the analytical working curve for arsenic is shown. The working curve is linear for the plots of peak-heights from the detection limit up to 1 μg of arsenic.

In Table I, the relative standard deviation for peak heights calculated from five measurements of each quantity of arsenic is shown.

Throughout the experiments, no appreciable light scattering effects were experienced.

The reagent blank had a value of about 25 ng of arsenic; further improvements of the detection limit were not studied, but could be achieved by using

TABLE I

REPEATABILITY OF THE FLUORESCENCE INTENSITY FOR VARIOUS AMOUNTS OF ARSENIC

| *As added (μg)* | *Relative standard deviation (%)*[a] |
|---|---|
| 0.050 | 12 |
| 0.10 | 6.9 |
| 0.50 | 2.6 |
| 1.0 | 4.4 |

[a] $n=5$.

the following arrangements:

(1) a combination of the systems used in the experiment with a filter, such as a chlorine filter, suggested by Vickers *et al.*[7], to eliminate the OH band emission from the flame;

(2) the use of a two-path system of the exciting beam with a concave mirror as used by Armentrout[16];

(3) the use of an electrically heated atomizer instead of a hydrogen–argon-entrained air flame as an atom reservoir.

We would like to thank Dr. K. Yasuda, Dr. S. Murayama, and Dr. S. Iida for their valuable discussions. We are grateful to Dr. H. Yamamoto for helpful observations and a critical reading of the manuscript. Thanks are also due to Mr. I. Sugaya for assistance in the experimental work.

## SUMMARY

Non-dispersive atomic fluorescence measurements of arsenic with a gas sampling technique have been investigated. Arsenic is converted to arsine in a mixed acid medium containing iodide, tin(II) and zinc powder, and is atomized in a hydrogen–argon-entrained air flame. A microwave-excited (2450 MHz) electrodeless arsenic discharge lamp, a solar-blind photomultiplier, and a lock-in amplifier are used. The detection limit of arsenic is 2 ng and the linear working range covers nearly three decades of concentration.

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# A STUDY OF ADSORPTION CHARACTERISTICS OF TRACES OF CHROMIUM(III) AND (VI) ON SELECTED SURFACES

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In water pollution studies, samples containing heavy metals are usually collected at the point source and transferred to the laboratory for analysis. Often there is a considerable time lapse between the collection and actual analysis. This time lapse may result in a serious error in the reported data since metal ions are adsorbed on the walls of the container surfaces. Losses of metal ions from solutions due to adsorption have been known for a long time, but it has been only in the last decade or so that chemists have become more concerned. As a result, several studies dealing with the adsorption of heavy metals on the container walls have been reported in the literature[1–3]. Robertson[4] has investigated adsorption characteristics of eleven metals with polyethylene and pyrex as storing materials and found severe losses of indium, scandium, iron, silver, uranium and cobalt. Benes and Rajman[5] reported the adsorption of bivalent mercury on polyethylene surfaces and concluded that a 5 day-old neutral solution lost about 85% of the initial 6 p.p.b. of mercury(II) ions. A detailed study of materials used for storage of dilute silver solutions established the adsorption characteristics of Teflon, Vycor, polypropylene, polystyrene and coatings of paraffin, acrylic spray and Tygon paint[6].

The present study was undertaken to investigate the losses of chromium(III) and (VI) on the walls of Pyrex, flintglass and polyethylene beakers. Since these materials are very commonly used for sample storage purposes, they were selected for our work. The rate of adsorption losses on the walls of the storing materials was monitored with chromium-51 radio-tracer at different hydrogen ion concentrations. Additional experiments were attempted in an effort to stabilize chromium in solution as the ammonium pyrrolidinedithiocarbamate complex (APDC) in methyl isobutyl ketone (MIBK) with a view to suggesting a possible stable medium for this metal.

## EXPERIMENTAL

### *Apparatus and materials*

Since chromium-51 emits γ-rays, scintillation counting equipment was used. This consisted essentially of scaler (Canberra Model 870), power supply (Harrison

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6515 A) and a 5 × 5-cm sodium iodide thallium-activated well-type crystal.

Type KK Kodak double emulsion x-ray film was used for autoradiography of the tagged surfaces. Exposure times were calculated from the counts obtained from the container surfaces with a calibrated detector. The film was held in place by polyethylene bags filled with fine dry sand. The exposed film was developed by standard procedures.

The chromium tracer was obtained from New England Nuclear, Boston, Mass. Deionized water (5 ml) was added to the vial containing tracer, and carefully mixed. A known volume of tracer solution was pipeted (1 ml) into a 100-ml flask and diluted to the mark with a (1 + 19) nitric acid–water mixture. Appropriate volumes providing at least 2000 c.p.m. per ml of this stock solution were taken for the adsorption study.

Chromium carrier solution (100 p.p.m.) was prepared by diluting a 1000 p.p.m. stock solution which was made from potassium dichromate.

The chemicals used were of the highest purity commercially available.

Kimax, low form Pyrex and polyethylene (made by Bel-Art Products, New Jersey) beakers of 250-ml capacity were used. Flint glass bottles were cut to the size of 250-ml Pyrex beakers and used. Since such flint containers were of the same size and shape as the other beakers, they are referred to as flint beakers in the text. All the beakers were selected at random from new stock and treated as shown in Fig. 1.

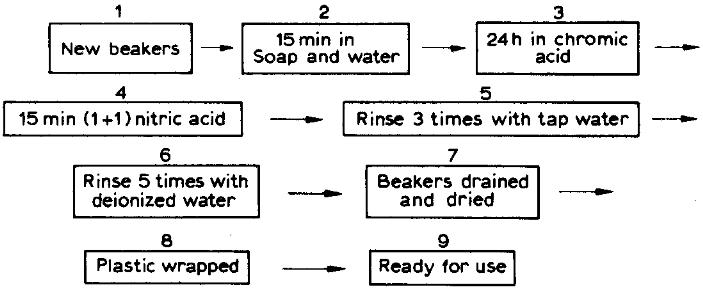

Fig. 1. Treatment of new beakers.

### *Procedure*

Chromium carrier (5 ml) was added to a 500-ml volumetric flask together with 5 ml of tracer stock solution and 2.5 ml of concentrated nitric acid[7,8]. The solution was diluted to the mark with deionized water and mixed thoroughly, and 100 ml was transferred to each of the treated Pyrex, flint and polyethylene beakers. To a second 500-ml flask, 5 ml chromium carrier and 5 ml of tracer were added. The volume was made up to about 495 ml, and the contents were transferred to a 600 ml beaker and the pH adjusted with dilute nitric acid or ammonia. The solution was then returned to the 500-ml volumetric flask and diluted to the mark, and the final pH measured. Portions (100 ml) of the adjusted solution were then added to each of the Pyrex, flint and polyethylene beakers. The above steps were repeated for adjustment and study at other pH levels. Chromium(III) in solution was oxidized and then chelated with ammonium pyrrolidinedithiocarbamate and extracted into methyl·isobutyl ketone[7] for studies of the behavior of chromium(VI).

Each of the beakers, containing 100 ml of test solution, was covered with a double layer of Saran Wrap and held at 23±2°C in the laboratory. At the end of 6, 12 and 24 h, and after 3, 5, 8, 12 and 15 day contact periods, the contents of each beaker was transferred to a holding beaker, rinsed seven times[6] with deionized water, dried and counted. The same holding beaker was used for each specific test beaker and solution throughout a time series.

The percentage of chromium adsorbed on the beakers was calculated from the total activity of 100 ml of test solution prepared at the beginning of the experiments. The counts from the standard solution were made under the same geometry and spatial orientation as those for the test beakers counted for adsorbed activity. This was achieved by evaporating 5 ml of standard solution (out of a 500-ml flask) added to filter paper cut to cover the same area as the 100-ml volume in the beaker. The filter paper strip was 25 cm long and 2.8 cm wide and the disc fitting the bottom of the beaker was 5.5 cm in diameter. The disc and filter paper strip were fixed with Duco cement or cellophane tape to the inside of the beaker, simulating the normal contact area of 100 ml of solution. The standards were prepared for each variable studied by following the above procedure. They were always counted before the test beakers.

Percentage adsorption was calculated using the formula:

$$\text{Percentage adsorption} = \frac{100B}{20A}$$

where $B$ is the total activity (c.p.m.) adsorbed on the test beaker, and $A$ is the total counts obtained by evaporating 5 ml of standard solution.

The scaler was checked by counting a standard source, and background counts were made to establish any contamination of the crystal by test beakers. The test beakers were counted by inverting the beakers on top of the crystal which was housed in the lead crystal. Halfway down the length of the crystal, a metal O-ring with an indexing notch was set. This arrangement positioned the beakers for counting with the pouring spout of the beaker in the notch of the O-ring, and provided a reproducible geometry for counting over the timed periods.

## RESULTS AND DISCUSSION

Figure 2 shows the results of the experiments with 1 p.p.m. chromium(III) solution, at pH 6.95, stored in Pyrex, flint and polyethylene beakers. In polyethylene beakers, losses reached a value of 25% of the initial metal concentration in 15 days. Flint glass retained 19% and Pyrex 17%. All three materials showed an induction period lasting about 24 h, as losses during this contact time were negligible. Once the induction period was over, chromium was found to adsorb more rapidly on the polyethylene beakers than on flint or Pyrex. Chromium(III) solutions showed a remarkable degree of stability in 0.5% nitric acid as well as at a pH of 3.1; losses of less than 0.5% were observed on the containers at the end of 15 days.

Chromium as a pollutant is present in air and water both in trivalent as well as hexavalent states[9]. Therefore, the adsorption characteristics of chromium(VI) were investigated in detail under similar conditions. The behavior of this oxidation state showed a completely different pattern from that of chromium(III). For example,

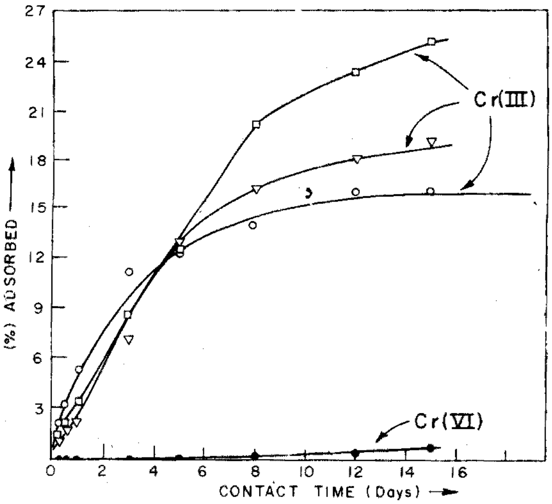

Fig. 2. Adsorption losses of chromium(III) solutions stored in Pyrex (○), flint (△), and polyethylene (□) beakers at pH 6.95. Losses of chromium(VI) (●) were negligible and the same for the three container materials.

TABLE I

STABILITY OF CHROMIUM(VI)–APDC COMPLEX IN METHYL ISOBUTYL KETONE

| *Time*[a] | *% Adsorbed* | | |
|---|---|---|---|
| | *Pyrex* | *Flint* | *Polyethylene* |
| 6 h | 0.9 | 1.9 | 1.1 |
| 12 h | 1.1 | 2.1 | 1.2 |
| 24 h | 1.5 | 3.2 | 1.4 |
| 3 days | 13.9 | 19.1 | 13.3 |
| 5 days | 75.8 | 92.9 | 84.7 |
| 8 days | 86.4 | 96.1 | 92.7 |
| 12 days | 86.9 | 96.2 | 93.2 |
| 15 days | 86.9 | 96.2 | 93.2 |

[a] Contact time.

chromium(VI) solutions exhibited good stability, even at a pH of 6.80, when stored in Pyrex, flint and polyethylene beakers for 15 days. Losses of less than 1.0% were observed on all three materials at the end of the test period (see Fig. 2).

The APDC–MIBK system was investigated to examine the stability of chromium ions in a complexed state. Chromium(III) solutions were oxidized to chromium(VI) and extracted into methyl isobutyl ketone with APDC as the organic ligand. The extract was stored in the three kinds of containers and the results obtained (see Table I) showed this system to be very unsatisfactory.

Autoradiography was performed on all three beakers holding chromium(III) solutions at a pH of 6.95. As reported earlier[6], adsorption losses were random on the surfaces, with a greater percentage being adsorbed on the bottom of the beaker.

Fig. 3. Autoradiographs showing adsorption of chromium(III) on, above, beaker bottom, and, below, beaker sides.

A typical autoradiograph of a polyethylene beaker after the contact period is shown in Fig. 3.

This work was supported in part by the National Science Foundation RANN Program, Grant No. GI-35114X1.

SUMMARY

The adsorption losses of chromium(III) or (VI) on the walls of Pyrex, flint glass and polyethylene beakers have been investigated. Chromium(III) or (VI) solutions were stored in beakers at different hydrogen ion concentrations, and losses due to adsorption were measured at various contact times by counting the $\gamma$-ray activity from chromium-51 radiotracer. At pH 6.95, chromium(III) solutions showed the greatest instability, particularly in polyethylene beakers, where losses up

to 25% were observed at the end of the 15-day contact period. Chromium(VI) showed a completely different pattern; losses less than 1% were observed at the end of 15 days on all the three types of containers.

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# IDENTIFICATION PAR SPECTROMÉTRIE RAMAN LASER DES ESPÈCES COMPLEXES INTERVENANT DANS L'EXTRACTION LIQUIDE–LIQUIDE DE FER(III) PAR L'OXYDE DE TRI-N-OCTYLPHOSPHINE

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(Reçu le 28 mars 1974)

Les composés organophosphorés, tels que le tributylphosphate (TBP), l'oxyde de tributylphosphine (TBPO) et l'oxyde de trioctylphosphine (TOPO) sont fréquemment utilisés pour l'extraction des métaux de leurs solutions aqueuses[1]. L'efficacité de l'extractant est conditionnée par la basicité du groupement P=O[2], mais elle est peu influencée par la taille des molécules[3]. C'est, par contre, de ce dernier paramètre que dépend la solubilité du composé dans l'eau[4]: le TOPO y est environ 10000 fois moins soluble que le TBPO. C'est pour cette raison que le premier agent extractant est souvent préféré au second.

L'extraction de l'eau et des acides par le TOPO pris dans différents solvants organiques a fait l'objet d'un certain nombre de publications[4–12]. En ce qui concerne l'eau, les avis concordent pour admettre l'existence d'un complexe $TOPO.H_2O$ lorsque la concentration en TOPO est inférieure à 0.1 *M*. L'extraction des acides $HNO_3$, HCl, $H_2SO_4$ a été souvent étudiée et on sait maintenant qu'il se forme des complexes différents suivant les concentrations en extractant de la phase organique et en acide de la phase aqueuse.

Pour des raisons pratiques, l'étude des processus d'extraction des métaux peut être aisément réalisée sur les ions fer(III)[13]. Des recherches ont été entreprises par Ross et White[5] sur l'extraction du fer(III) en milieu chlorhydrique acide par le TOPO en solution cyclohexanique. Ces auteurs se basent sur les rapports $[Cl^-]/[Fe]$ et $[TOPO]/[Fe]$ des phases organiques pour conclure que la composition des espèces extraites n'est pas connue de façon précise, mais qu'elle consiste probablement en un mélange de $FeCl_3.2TOPO$ et de $HFeCl_4.2TOPO$. Considerant que ces résultats ne semblent pas définitifs, nous avons cru bon refaire ce travail en nous aidant d'une méthode plus directe. Dans un article plus récent[14] en effet, nous avons montré le parti que l'on peut tirer des spectroscopies Raman qualitative et quantitative non seulement pour dénombrer les espèces complexes mises en jeu dans l'extraction liquide–liquide, mais encore pour en déterminer la stoechiométrie et la structure.

## PARTIE EXPÉRIMENTALE

### *Réactifs*

Le TOPO (Merck pur pour analyse) ne nécessite aucun traitement de purification avant l'emploi, nous avons cependant vérifié qu'il ne contenait pas d'eau. Les solutions de fer(III) sont préparées par dissolution de la quantité requise de $FeCl_3.6H_2O$ (Merck pur pour analyse) dans de l'eau tridistillée contenant la quantité voulue de HCl (Baker pur pour analyse). Les solvants—cyclohexane et benzène—sont des produits U.C.B. purs pour analyse, ils sont distillées dans le but d'éviter toute fluorescence possible lors de l'enregistrement des spectres Raman. Les réactifs utilisés pour la colorimétrie du fer, comme par exemple l'acide 5-sulfosalicylique, sont aussi purs pour analyse.

### *Méthodes d'extraction et de dosage du fer(III)*

Ces opérations sont toutes réalisées à une température de 20°C. Des volumes égaux (4 ml) de solution de TOPO et de solution aqueuse de $FeCl_3$ sont pipettés dans des tubes à bouchons rodés de 10 ml. Après agitation d'une heure dans une balancelle thermostatée à 20°C, les deux phases sont démixées par centrifugation. La phase organique est séparée de la phase aqueuse par pipetage, elles sont conservées toutes deux à 20°C. La phase organique est destinée à la prise du spectre Raman. Le fer est dosé par colorimétrie dans les deux phases. Au préalable le fer contenu dans la phase organique est réextrait par de l'acide chlorhydrique 0.5 *M*. Le rapport des concentrations en fer à l'équilibre trouvé pour les deux phases nous permet de calculer le coefficient de distribution *E*.

### *Mésures colorimétriques et enregistrements des spectres Raman*

La colorimérie du fer à l'acide 5-sulfosalicylique[15] est réalisée sur un spectrophotomètre Cary Modèle 17 en utilisant des cuves optiquement planes de 1.000 cm d'épaisseur. Les mesures d'absorbance sont faites à la longueur d'onde de 423 nm; par la méthode des moindres carrés, on obtient le coefficient d'extinction $\varepsilon = 5799$ l mole$^{-1}$ cm$^{-1}$. Les spectres Raman excités par la radiation 632.8 nm d'un laser He–Ne O.I.P. Modèle 181 E de 150 mW, sont enregistrés sur le spectromètre photoélectrique conçu par l'un de nous[16].

## RÉSULTATS EXPÉRIMENTAUX ET DISCUSSIONS

### *Travaux préliminaires*

Dans des publications récentes traitant de la spectroscopie Raman des solutions aqueuses de chlorures ferriques, il a été montré que les principales espèces présentes sont $FeCl_3.2H_2O$ de symétrie $D_{3h}$[17] et $FeCl_4^-$ de symétrie $T_d$[14,17]. Pour une solution fer(III) 1 *M*, la première espèce est la plus abondante lorsque

TABLEAU I

SPECTRES RAMAN DE $FeCl_3$ ET DE $FeCl_4^-$ EN MILIEU AQUEUX

| | | | | |
|---|---|---|---|---|
| $FeCl_3$ | $\nu_4(E')$ | $\nu_1(A'_1)$ | $\nu_3(E')$ | |
| Marston[17] | 165(*f*) | 318(*F*) | 390(*f*) | |
| | dép. | large, pol. | diffuse | |
| $FeCl_4^-$ | $\nu_2(E)$ | $\nu_4(F_2)$ | $\nu_1(A_1)$ | $\nu_3(F_2)$ |
| Michel[14] | 180(3) | 133(0.7) | 332(10) | 394 |
| | dép. | dép. | fine, pol. | diff. dép. |

la concentration en HCl se situe entre 0.5 *M* et 5 *M* environ. Pour une concentration en HCl supérieure à 6 *M*, c'est l'anion $FeCl_4^-$ qui prédomine[14].

Il est également utile de rappeler pour la suite du travail que $FeCl_3$ est surtout caractérisé par la raie $\nu_1$ de son spectre (tableau I) située vers 318 $cm^{-1}$, elle est large et totalement polarisée, et que $FeCl_4^-$ est principalement représenté par sa raie $\nu_1$ à 332 $cm^{-1}$, fine et totalement polarisée.

A notre connaissance, il n'existe aucune donnée spectrale sur l'effet Raman du TOPO et des phases organiques contenant ses complexes métalliques.

*Spectre Raman du TOPO à l'état solide*

Le spectre Raman est enregistré sur quelques milligrammes de poudre tassée dans un tube en verre mince de façon à présenter une cavité conique où le faisceau laser est focalisé. La largeur de fente spectrale *s* vers 640 nm est de 2.7 $cm^{-1}$. D'autre part l'obtention d'un bon spectre nécessite une amplification assez poussée, car la diffusion Raman du TOPO est faible. Ce fait est favorable pour l'étude des espèces minérales extraites en phase organique. Comme on le verra plus loin, on ne doit pas craindre que les bandes de l'extractant, en solution peu concentrée (0.2 *M* maximum), ne viennent se superposer au spectre de la partie inorganique des complexes. La fréquence ($\nu$ $cm^{-1}$) des raies Raman et leur intensité relative (*I*) sont présentées dans le tableau II. Les bandes faibles et très faibles s'y trouvent en majorité, seules les raies CH de valence comprises entre 2845 et 2980 $cm^{-1}$ et les raies de déformation situées vers 700 $cm^{-1}$, vers 1100 $cm^{-1}$ et comprises entre 1290 et 1460 $cm^{-1}$ sont quelque peu intenses.

TABLEAU II

SPECTRE RAMAN DU TOPO À L'ÉTAT DE POUDRE CRISTALLINE

| $\nu$ ($cm^{-1}$) | *I* | $\nu$ ($cm^{-1}$) | *I* | $\nu$ ($cm^{-1}$) | *I* |
|---|---|---|---|---|---|
| 26 | 3 | 846 | 7 | 1293 | 90 |
| 136 | 96 | 893 | 42 | 1317 | 5 |
| 197 | 23 | 926 | 3 | 1349 | 2 |
| 235 | 11 | 952 | 1 | 1367 | 5 |
| 270 | 5 | 979 | 4 | 1414 | 19 |
| 314 | 6 | 1004 | 11 | 1423 | 47 |
| 331 | 12 | 1031 | 23 | 1436 | 81 |
| 357 | 18 | 1042 | 42 | 1456 | 60 |
| 369 | 7 | 1056 | 97 | 2847 | 62 |
| 386 | 5 | 1112 | 77 | 2858 | 53 |
| 448 | 5 | 1138 | 100 | 2871 | 53 |
| 490 | 7 | 1172 | 9 | 2883 | 86 |
| 708 | 60 | 1188 | 7 | 2901 | 132 |
| 723 | 12 | 1197 | 5 | 2914 | 42 |
| 740 | 6 | 1210 | 1 | 2931 | 36 |
| 755 | 13 | 1229 | 2 | 2976 | 15 |
| 782 | 9 | 1241 | 3 | | |
| 822 | 8 | 1252 | 6 | | |

*Choix du diluant en vue de l'étude des phases organiques par spectrométrie Raman*

Notre choix doit être guidé par les nécessités suivantes:

(1) Le diluant doit être inerte tout en acceptant la mise en solution d'une quantité suffisante de TOPO ($\simeq 0.2$ *M*).

(2) La solution de TOPO ne doit pas donner lieu à la formation d'une troisième phase lors de l'extraction.

(3) Le spectre Raman du diluant doit être pauvre en raies de basses fréquences, Cette dernière exigence nous fait rejeter le tétrachlorure de carbone dès l'abord, car la région des basses fréquences est encombrée par trois raies intenses à 217, 313, et 459 $cm^{-1}$.

Deux diluants sont ainsi retenus pour effectuer les essais: le cyclohexane et le benzène. Les extractions sont réalisées selon le processus décrit plus haut et dans les conditions suivantes: une solution aqueuse de $FeCl_3$ 0.5 *M* (HCl 8 *M*) est agitée pendant 1 h à 20°C avec un égal volume de solution cyclohexanique ou benzénique de TOPO 0.2 *M*. Dans les deux cas, deux phases seulement sont obtenues. Les spectres Raman des phases organiques sont enregistrés (Fig. 1) dans les conditions suivantes: largeur de fente spectrale, $s=3.4$ $cm^{-1}$; constante de temps, $R.C.=0.2$ s; vitesse de balayage, $v=20$ $cm^{-1}$ $min^{-1}$; puissance du laser He–Ne$\simeq$170 mW à 632.8 nm.

Les valeurs des fréquences relevées sur les spectres de la fig. 1 ne varient pratiquement pas d'un diluant à l'autre. Dans le cas de la phase cyclohexanique, trois raies de l'espèce $FeCl_4^-$ reprises au tableau I sont facilement repérables, il s'agit des 108, 134 et 331 $cm^{-1}$. La raie faible et diffuse à 394 $cm^{-1}$ est masquée par les 381 et 425 $cm^{-1}$ du cyclohexane. La quatrième raie qui apparaît à 349 $cm^{-1}$ provient d'un second complexe qui sera identifié plus loin. La solution benzénique présente un effet Rayleigh plus intense qui restreint l'observation des raies de basses fréquences: les raies 108 et 134 $cm^{-1}$ de l'espèce $FeCl_4^-$ ne sont pas visibles. Avec ce diluant, les raies 332 et 350 $cm^{-1}$ sont mieux dégagées. Ceci

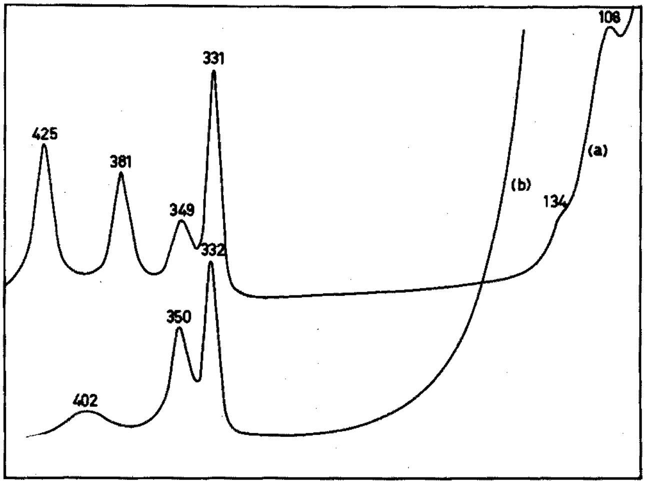


Fig. 1. Spectres Raman des phases organiques après extraction d'une solution de $FeCl_3$ 0.5 *M* (HCl 8 *M*) par une solution de TOPO 0.2 *M* dans le cyclohexane (a), et dans le benzène (b).

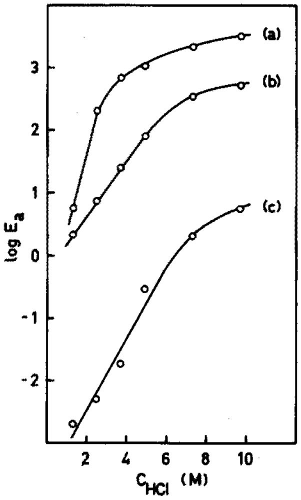


Fig. 2. Courbes d'extraction: (a) $FeCl_3$ 0.04 *M* par TOPO 0.2 *M* dans le benzène; (b) $FeCl_3$ 0.1 *M* par TOPO 0.2 *M* dans le benzène; (c) $FeCl_3$ 0.1 *M* par TBP 0.2 *M* dans le benzène.

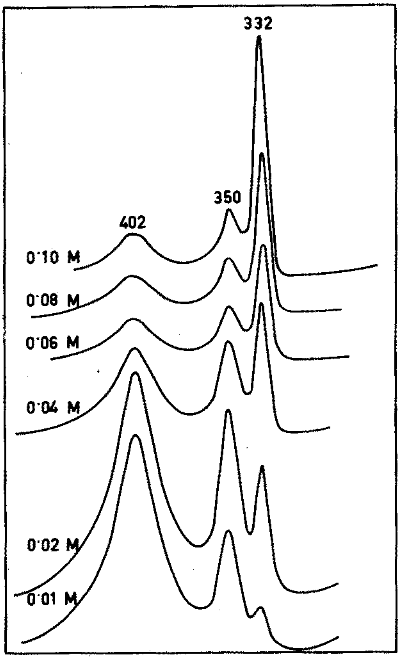
nous a incité à porter notre choix sur le benzène, d'autant plus que lors des études quantitatives des raies 332 et 350 $cm^{-1}$, c'est la méthode de l'étalon interne qui sera utilisée avec la 606 $cm^{-1}$ du benzène comme raie de référence ($I_{332}/I_{606}$, $I_{350}/I_{606}$).

*Étude de l'extraction du fer(III) par le TOPO*

Avant d'aborder l'étude spectroscopique quantitative du problème, nous avons cherché à savoir si nos résultats d'extraction confirment les données de la littérature[5].

*Extraction en fonction de la concentration en HCl.* Les résultats de nos expériences d'extraction sont portés en graphique (Fig. 2), ils sont en bon accord avec les valeurs publiées par White et Ross[5]. Comme ceux-ci nous trouvons que le coefficient de distribution $E_a$ augmente avec la concentration en l'acide chlorhydrique. Les courbes de la fig. 2 révèlent que le TOPO est un excellent agent extractant du fer(III): $E_a \simeq 500$ pour HCl 9.7 *M* lorsque $c_{Fe}/c_{TOPO} = 0.5$ (Fig. 2b). Comme on doit s'y attendre le coefficient de distribution s'accroît lorsque le rapport $c_{Fe}/c_{TOPO}$ diminue: $E_a$ monte à plus de 3000 lorsque $c_{Fe}/c_{TOPO} = 0.2$ pour HCl 9.7 *M* (Fig. 2a). La comparaison des courbes (b) et (c) pour les points correspondant à une concentration 7 *M* en l'acide chlorhydrique montre que le TOPO extrait le fer 170 fois mieux que la TBP. Ceci confirme ce que Higgins[2] a publié à propos du pouvoir extractant qui est fonction de la basicité du groupement PO.

*Étude spectroscopique semi-quantitative de l'extraction en fonction de la concentration en TOPO.* Les spectres Raman enregistrés sur les phases organiques lors des expériences préliminaires révèlent la présence de deux raies polarisées à 332 et 350 $cm^{-1}$ (Fig. 1). Ce résultat expérimental signifie que la phase organique après extraction renferme au moins deux espèces complexes de symétries différentes. Il nous reste évidemment à dénombrer exactement ces complexes, car nous avons



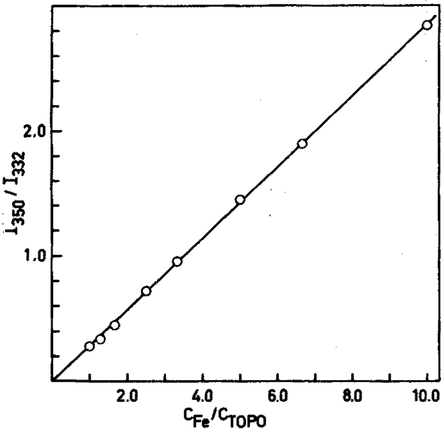


Fig. 3. Spectres Raman des phases organiques après extraction d'une solution de $FeCl_3$ 0.1 *M* (HCl 7 *M*) par des solutions de TOPO à concentrations différentes dans le benzène. Spectres enregistrés avec différentes amplifications. La raie 402 $cm^{-1}$ est due au benzène.

Fig. 4. Variation du rapport d'intensités $I_{350}/I_{332}$, relatif aux spectres de la figure 3, en fonction du rapport $c_{Fe}/c_{TOPO}$.

déjà rencontré le cas[14] où une raie Raman représentait plus d'une espèce complexe.

Nous avons repris plus en détails les expériences sur une solution 0.1 *M* en fer(III) et 7 *M* en l'acide chlorhydrique en extrayant par des volumes égaux de solutions benzéniques de TOPO de concentrations différentes (de 0.01 *M* à 0.1 *M*). Des mesures semi-quantitatives faites sur les spectres Raman des phases organiques après extraction (Fig. 3) indiquent une variation parfaitement linéaire du rapport $I_{350}/I_{332}$ en fonction du rapport $c_{Fe}/c_{TOPO}$ (Fig. 4). Cette relation simple qui existe entre les deux paramètres signifie que chaque raie Raman ne représente qu'un seul complexe, ce résultat préliminaire sera confirmé plus loin de façon directe par le contrôle de la constance du coefficient de diffusion de chacune des raies, c'est-à-dire $k_{332}$ et $k_{350}$.

### *Détermination quantitative du nombre de complexes extraits dans la phase organique*

Cette fois nous travaillons sur les intensités intégrées des raies corrigées pour leur superposition mutuelle au moyen du "310 Curve Resolver Du Pont" lorsque cela est nécessaire. Les raies Raman 332 et 350 $cm^{-1}$ ont un profil composite 65% lorentzien et 35% gaussien.

Les spectres Raman sont enregistrés avec une fente spectrale de 2.5 $cm^{-1}$ sur les phases organiques résultant de l'extraction de solutions aqueuses de

TABLEAU III

RÉSULTATS DES EXTRACTIONS RÉALISÉES EN FAISANT VARIER LA CONCENTRATION EN Fe(III) DE LA PHASE AQUEUSE ($c_{Fe}$)

($c_{TOPO}=[\mathrm{TOPO}]_0=0.200$ *M* dans le benzène, $c_{HCl}=7$ *M*)

| $c_{Fe}$ (*M*) | $[Fe]_a$ (*M*) | $[Fe_t]_0$ (*M*) | $[Fe_t]_0/c_{TOPO}$ | $I_{332}/I_{606}$ | $I_{350}/I_{606}$ | $[Fe_1]_0$ (*M*) | $[Fe_2]_0$ (*M*) |
|---|---|---|---|---|---|---|---|
| 0.0011 | — | 0.0013 | 0.0065 | 0.050 | — | 0.0013 | — |
| 0.0049 | — | 0.0046 | 0.0230 | 0.224 | — | 0.0046 | — |
| 0.0097 | — | 0.0097 | 0.0485 | 0.430 | — | 0.0097 | — |
| 0.0193 | — | 0.0195 | 0.0975 | 0.896 | — | 0.0195 | — |
| 0.0294 | — | 0.0295 | 0.1475 | 1.31 | — | 0.0295 | — |
| 0.0406 | — | 0.0401 | 0.2005 | 1.82 | — | 0.0401 | — |
| 0.0589 | — | 0.0588 | 0.2940 | 2.60 | — | 0.0588 | — |
| 0.0799 | — | 0.0793 | 0.3965 | 3.66 | — | 0.0793 | — |
| 0.0981 | 0.0002 | 0.0979 | 0.4895 | 4.22 | 0.235 | 0.0953 | 0.0026 |
| 0.1496 | 0.0279 | 0.1217 | 0.6085 | 3.69 | 1.44 | 0.0834 | 0.0383 |
| 0.1953 | 0.0711 | 0.1242 | 0.6210 | 3.45 | 2.02 | 0.0780 | 0.0462 |
| 0.2927 | 0.1582 | 0.1345 | 0.6725 | 3.04 | 2.66 | 0.0687 | 0.0658 |
| 0.5803 | 0.4410 | 0.1393 | 0.6965 | 2.49 | 3.79 | 0.0563 | 0.0830 |
| 0.8784 | 0.7318 | 0.1466 | 0.7330 | 2.21 | 4.46 | 0.0499 | 0.0967 |
| 1.183 | 1.033 | 0.1509 | 0.7545 | 1.94 | 4.82 | 0.0437 | 0.1072 |
| 1.466 | 1.306 | 0.1595 | 0.7975 | 1.89 | 5.17 | 0.0426 | 0.1169 |
| 1.857 | 1.694 | 0.1623 | 0.8115 | 1.78 | 5.54 | 0.0402 | 0.1221 |
| 2.053 | 1.883 | 0.1698 | 0.8490 | 1.73 | 5.99 | 0.0391 | 0.1307 |
| 2.985 | 2.805 | 0.1805 | 0.9025 | 1.62 | 6.24 | 0.0366 | 0.1439 |
| 3.713 | 3.511 | 0.2020 | 1.0100 | 1.47 | 6.43 | 0.0332 | 0.1688 |

concentrations variables en fer(III) (HCl 7 *M*) par des solutions benzéniques de TOPO 0.2 *M* (Tableau III). L'étude quantitative des deux raies Raman est réalisée en utilisant la méthode de l'étalon interne, en l'occurrence le benzène, dont la raie 606 cm$^{-1}$, bien dégagée, sert de raie de référence. Ainsi nous pouvons écrire que:

$$\frac{I_{332}}{I_{606}}=\frac{k_{332}}{k_{606}}\,\frac{[\mathrm{Fe}_1]_0}{[\mathrm{solvant}]_0} \qquad (1)$$

$$\frac{I_{350}}{I_{606}}=\frac{k_{350}}{k_{606}}\,\frac{[\mathrm{Fe}_2]_0}{[\mathrm{solvant}]_0} \qquad (2)$$

où $[\mathrm{Fe}_1]_0$, $[\mathrm{Fe}_2]_0$ sont respectivement les concentrations en espèces complexes 1 et 2 contenues dans la phase organique.

Dans les conditions présentes, nous pouvons considérer que la concentration en solvant est une constante, ce qui nous permet d'écrire que:

$$\frac{I_{332}}{I_{606}}=k_{332,606}[\mathrm{Fe}_1]_0 \qquad (3)$$

$$\frac{I_{350}}{I_{606}}=k_{350,606}[\mathrm{Fe}_2]_0 \qquad (4)$$

où $k_{332,606}$ et $k_{350,606}$ sont respectivement les coefficients de diffusion des raies 332 et 350 cm$^{-1}$ lorsque $k_{606}$ est pris égal à l'unité.

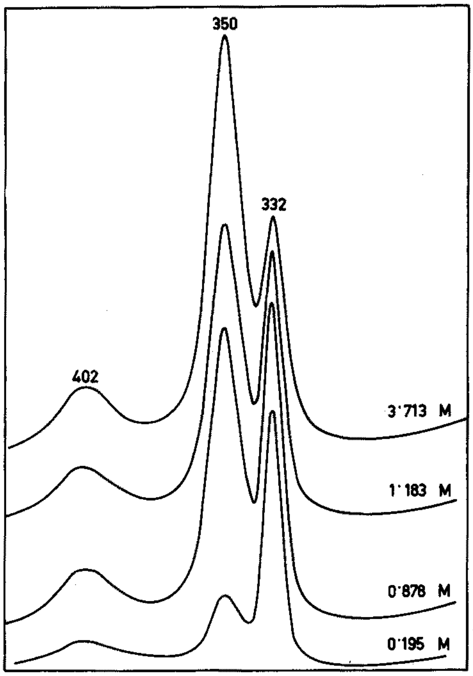


Fig. 5. Spectres Raman de phases organiques après extraction de solutions aqueuses (HCl 7 *M*) de concentrations différentes en fer(III) par une solution de TOPO 0.2 *M* dans le benzène.

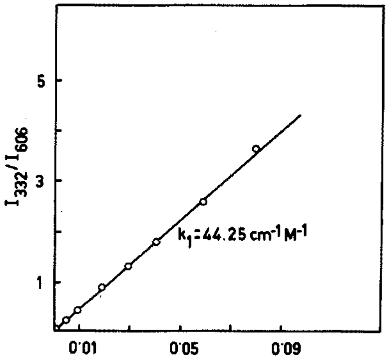


Fig. 6. Détermination du coefficient de diffusion $k_{332,606} = k_1$.

Nous avons réalisé deux séries d'expériences avec une concentration en TOPO constante (0.2 *M*), les résultats sont condensés dans le tableau III, tandis que des exemples de spectres sont présentés dans la fig. 5.

*La concentration totale en fer(III) ($c_{Fe}$) varie de $10^{-3}$ à $0.8 \cdot 10^{-1}$ M.* Dans ces conditions d'extraction, seule la raie 332 cm$^{-1}$ caractéristique de l'espèce anionique $FeCl_4^-$ apparaît. Son intensité intégrée relative, $I_{332}/I_{606} = (h_{332}/h_{606}) \cdot \Delta\nu^{\frac{1}{2}}$, augmente proportionnellement à $[Fe_1]_0 = [FeCl_4^-]_0$ (Fig. 6). $h_\nu$ représente l'intensité au maximum de la raie de fréquence $\nu$. La largeur à mi-hauteur de la raie 332 $cm^{-1}$ est bien constante, sa valeur moyenne est égale* à

$$\Delta\nu^{\frac{1}{2}}_{1} = 7.85\ cm^{-1} \pm 0.1\ cm^{-1}$$

Le graphique $I_{332}/I_{606}$ en fonction de $[FeCl_4^-]_0$ de la fig. 6 est une droite de pente égale au coefficient de diffusion $k_{332} = k_1 = 44.25$ l mole$^{-1}$ cm$^{-1}$, l'allure de cette courbe prouve que la raie 332 $cm^{-1}$ représente une seule espèce complexe.

*La concentration totale en fer(III) varie de 0.1 à 3.7 M.* Comme le montre les spectres Raman de la fig. 5, les deux raies polarisées 332 et 350 $cm^{-1}$ sont présentes dans tout le domaine de concentration. Puisqu'il y a superposition partielle de ces deux raies et puisque l'aile de la 402 $cm^{-1}$ du benzène empiète sur la 350 $cm^{-1}$, la mesure précise des intensités intégrées nécessite l'analyse de l'enveloppe du spectre sur ses composantes. Admettant que $\Delta\nu^{\frac{1}{2}}_{1} = 7.85$ $cm^{-1}$, nous trouvons, par décomposition de l'enveloppe du spectre, que la largeur à mi-hauteur $\Delta\nu^{\frac{1}{2}}_{2}$ de la 350 $cm^{-1}$ est égale à 15.6 $cm^{-1}$. L'analyse des courbes spectrales au moyen du "Curve Resolver" nous conduit à la mesure de l'intensité au maximum $h$ des différentes composantes pures qui nous permet d'écrire ce qui suit:

$$\frac{I_{332}}{I_{606}} = \frac{h_{332}}{h_{606}} \Delta\nu^{\frac{1}{2}}_{1} = k_1 [Fe_1]_0 \tag{5}$$

Connaissant $k_1$, de la relation (5), nous tirons la valeur de $[Fe_1]_0$, la concentration de la première espèce complexe, ce qui nous permet de calculer la concentration globale $[Fe_2]_0$ des complexes représentés par la raie 350 $cm^{-1}$ en partant de

$$[Fe_2]_0 = [Fe_t]_0 - [Fe_1]_0 \tag{6}$$

où $[Fe_t]_0$, la concentration totale en fer(III) extrait dans la phase organique est déterminé par colorimétrie après réextraction en phase aqueuse. En portant en graphique les valeurs de $I_{350}/I_{606} = (h_{350}/h_{606})\Delta\nu^{\frac{1}{2}}_{2}$ en fonction des valeurs calculées de $[Fe_2]_0$, nous obtenons aussi une droite de pente $k_2 = 44.59$ l mole$^{-1}$ cm$^{-1}$

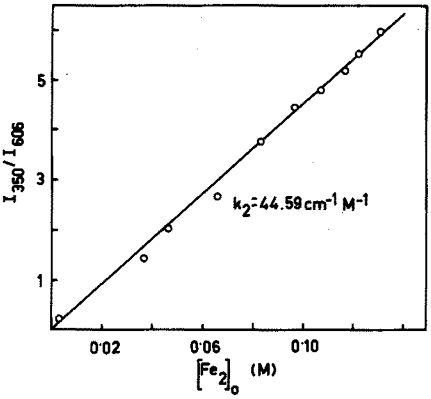


Fig. 7. Détermination du coefficient de diffusion $k_{350,606} = k_2$.

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* Marston et Bush[17] travaillant sur des solutions aqueuses de $FeCl_4^-$ avec une fente spectrale deux fois plus large trouvent une valeur $\Delta\nu^{\frac{1}{2}} = 11$ $cm^{-1}$ pour la raie 332 $cm^{-1}$.

(Fig. 7). Ceci confirme que la raie 350 $cm^{-1}$ est aussi la manifestation d'une seule espèce complexe.

*Stoechiométrie des complexes extraits en phase organique*

Comme nous venons de le constater, les intensités intégrées mesurées sur les spectres des phases organiques conduisent à l'obtention d'un seul coefficient de diffusion par raie étudiée: $k_1$ pour la raie 332 $cm^{-1}$ et $k_2$ pour la 350 $cm^{-1}$. Il est donc évident que la phase benzénique après extraction ne contient que deux espèces complexes.

Le premier complexe qui se manifeste par la raie totalement polarisée située à 332 $cm^{-1}$ représente l'entité anionique $FeCl_4^-$ de symétrie $T_d$, comme cela a déjà été prouvé dans notre article précédent[14]. Dans ce travail, nous avions montré d'autre part que $FeCl_4^-$ fait partie d'un complexe par paire d'ions où les interactions de l'anion sur le cation sont purement électrostatiques. Ceci explique que la fréquence et le profil de la raie 332 $cm^{-1}$ ne sont pas altérés lorsqu'on passe du spectre de la solution aqueuse fortement chlorhydrique au spectre de la phase organique après extraction. Pour ce premier complexe nous proposons la formule suivante

$$FeCl_4^-.n\,TOPOH^+.Cl_{n-1}^-$$

Si nous maintenons constantes les concentrations en fer(III) et en TOPO, nous constatons que l'intensité relative $I_{332}/I_{606}$ de la raie de ce complexe augmente avec la concentration en HCl employé pour l'extraction. Il est normal que la formation du complexe le plus chloré $FeCl_4^-.n\,TOPOH^+.Cl_{n-1}^-$ soit favorisée lorsque HCl est le plus fortement extrait par le TOPO, c'est-à-dire lorsque le rapport $(Fe_t]_0/c_{TOPO}$ (Tableau III) est inférieur à 0.4. Dans ces conditions, seul le complexe par paire d'ions est présent dans la phase organique. Inversément, l'intensité relative $I_{350}/I_{606}$ augmente lorsque la concentration en HCl décroît. C'est alors un complexe moins chloré qui se forme et pour lequel nous proposons la formule suivante

$$FeCl_3.m\,TOPO$$

La raie 350 $cm^{-1}$ fortement polarisée caractérise vraisemblablement la vibration $\nu_1(A')$ de l'espèce $FeCl_3$.

Pour pousser plus avant dans la résolution du problème de la stoechiométrie des deux complexes, nous considérons à nouveau la fig. 3, ainsi que les données rassemblées dans le tableau IV. Sur les spectres Raman de la fig. 3, nous constatons que la raie 350 $cm^{-1}$ du complexe $FeCl_3.m$TOPO prédomine dans le domaine des concentrations en TOPO inférieures à 0.02 *M*. De plus les chiffres du

TABLEAU IV

STOECHIOMÉTRIES DES COMPLEXES FORMÉS LORS DE L'EXTRACTION D'UNE SOLUTION DE $FeCl_3$ 0.10 *M* (HCl 7 *M*) PAR DES SOLUTIONS DE TOPO À CONCENTRATIONS DIFFÉRENTES DANS LE BENZÈNE

| $c_{TOPO}$ (*M*) | 0.01 | 0.015 | 0.02 | 0.03 | 0.04 | 0.06 | 0.08 | 0.10 |
|---|---|---|---|---|---|---|---|---|
| $[Fe]_0/[TOPO]_0$ | 0.89 | 0.87 | 0.85 | 0.79 | 0.73 | 0.70 | 0.66 | 0.64 |

tableau IV montrent que pour les basses concentrations en TOPO ($< 0.01$ *M*) le rapport $[Fe]_0/[TOPO]_0$ tend vers l'unité, ce qui nous incite à croire que nous avons un complexe 1:1 de formule $FeCl_3.TOPO$.

Examinons maintenant les spectres Raman (Fig. 3) correspondant aux concentrations en TOPO supérieures à 0.04 *M*, nous y voyons clairement que la raie 332 $cm^{-1}$ de l'espèce $FeCl_4^-$ prend le pas sur la raie 350 $cm^{-1}$. Ensuite dans le domaine des fortes concentrations en TOPO ($>0.1$ *M*), le tableau IV indique un rapport $[Fe]_0/[TOPO]_0$ tendant vers 0.5, ce qui s'accorde parfaitement avec la stoechiométrie 1:2 du complexe par paire d'ions.

### *Représentation des complexes*

*Le complexe de stoechiométrie 1:2.* Comme cela a été dit plus haut, la constance de la raie 332 $cm^{-1}$ qui se retrouve toujours à la même fréquence aussi bien en phase organique qu'en milieu chlorhydrique aqueux, signifie que la symétrie $T_d$ de $FeCl_4^-$ n'est pas du tout affectée par la complexation. Cela vient du fait que l'atome de fer de l'anion n'est pas lié par coordinence avec le TOPO. Nous admettons dès lors que les interactions sont purement électrostatiques et que nous sommes en présence d'un complexe par paire d'ions de forme quadrupôle:

$$TOPOH^+.FeCl_4^-$$
$$Cl^-.TOPOH^+$$

*Structure du complexe de formule $FeCl_3.TOPO$.* La raie située à 350 $cm^{-1}$ qui est intense et polarisée, peut correspondre à un complexe dont la partie minérale $FeCl_3$ a une structure de symétrie $C_{3v}$, comme dans $GaCl_3$ ou $D_{3h}$ comme dans $InCl_3$. Pour répondre à cette question, nous allons comparer la fréquence 350 $cm^{-1}$ du complexe extrait aux valeurs rassemblées dans le tableau V.

En ce qui concerne le gallium(III), Schug et Katzin[18] démontrent qu'il est extrait de sa solution chlorhydrique acide par l'éther isopropylique sous forme de $GaCl_4^-$ de symétrie $T_d$. La raie Raman $\nu_1$ totalement polarisée de cet anion se

TABLEAU V

COMPARAISON DES RAIES RAMAN ENVIRON DE 350 $CM^{-1}$

| | $\nu_1$ *(cm⁻¹)* | $\nu'_1$ *(cm⁻¹)* | *Symétrie* | *Remarque* |
|---|---|---|---|---|
| $GaCl_4^-$ [a] | 346[18] | | $T_d$ | $\nu'_1 > \nu_1$ |
| $GaCl_3$ [b] | | 363[18] | $C_{3v}$ | |
| $InCl_4^-$ [a] | 321[20] | | $T_d$ | $\nu'_1 < \nu_1$ |
| $InCl_3$ [c] | | 317[21] | $D_{3h}$ | |
| $FeCl_4^-$ [a] | 330[20] | | $T_d$ | |
| $FeCl_3$ [d] | | 313[17] | $D_{3h}$ | $\nu'_1 < \nu_1$ |
| $FeCl_3$ [e] | | 350[f] | $C_{3v}$ | $\nu'_1 > \nu_1$ |

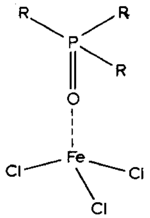
[a] $MeCl_4^-$ extrait d'une solution aqueuse chlorhydrique par l'éther.
[b] $GaCl_3$ extrait d'une solution aqueuse par l'éther.
[c] $InCl_3$ dissous dans l'éther.
[d] $FeCl_3$ ($C \geqslant 0.1$ *M*) extrait par le TOPO 0.2 *M*.
[e] $FeCl_3$ en solution aqueuse chlorhydrique ($C_{HCl} = 1$ à 3 *M*).
[f] Valeur tirée de ce travail.

situe à 346 $cm^{-1}$. Les mêmes auteurs montrent que l'extraction en l'absence d'acide chlorhydrique se fait cette fois sous la forme de $GaCl_3$ sans toutefois en préciser la symétrie. Le spectre Raman de cette espèce présente une raie intense et totalement polarisée à $\nu'_1 = 363$ $cm^{-1}$. Par contre Greenwood et coll.[19] étudiant dans l'infrarouge lointain des complexes formés à partir de $GaCl_3$ trouvent que ce trihalogénure a une structure pyramidale de symétrie $C_{3v}$. La bande $\nu'_1$ active en infrarouge a une fréquence moyenne pointée aux environs de 360 $cm^{-1}$. On constate que $\nu'_1$ est supérieur à $\nu_1$.

Après extraction par l'éther de l'indium(III) en solution chlorhydrique acide, Woodward et Taylor[20] obtiennent un spectre Raman de la phase organique qui est caractéristique de l'espèce $InCl_4^-$ de symétrie $T_d$. La raie $\nu_1$ intense et fortement polarisée se situe à 321 $cm^{-1}$. De son côté, Taylor[21] montre que $InCl_3$ dissous dans l'éther donne un complexe $InCl_3.2Et_2O$ dont la partie inorganique a une structure de symétrie $D_{3h}$. Il y correspond une raie Raman fortement polarisée de fréquence $\nu'_1 = 317$ $cm^{-1}$. On note dans ce cas que $\nu'_1$ est inférieure à $\nu_1$.

Woodward et Taylor[20] ont étudié aussi par spectroscopie Raman l'extraction dans l'éther de fer(III) en milieu chlorhydrique acide et ils ont pu prouver que c'est l'espèce $FeCl_4^-$ de symétrie $T_d$ qui est extraite. Elle est caractérisée entr'autre par une raie totalement polarisée située à $\nu_1 = 330$ $cm^{-1}$. D'autre part Marston et Bush[17] établissent que $FeCl_3$ en solution aqueuse a une symmétrie $D_{3h}$, deux molécules d'eau étant disposées symétriquement de part et d'autre du plan. En bon accord avec ce résultat, nous avons pointé la raie Raman $\nu'_1$ fortement polarisée à 313 $cm^{-1}$ [14]. Dans ce cas, la comparaison de la symétrie $T_d$ et de la symétrie $D_{3h}$ nous permet de constater que $\nu'_1$ est toujours inférieure à $\nu_1$.

Comme nous l'avons vu plus haut, le complexe $FeCl_3$.TOPO présente une raie intense et totalement polarisée à $\nu'_1 = 350$ $cm^{-1}$. En comparant celle-ci avec la raie $\nu_1$ de $FeCl_4^-$ située à 330 $cm^{-1}$, nous constatons que $\nu'_1$ est supérieure à $\nu_1$, ce qui signifie que la raie $\nu'_1$ à 350 $cm^{-1}$ appartient au spectre d'une espèce $FeCl_3$ de symétrie pyramidale $C_{3v}$.



Par la formation du complexe, $FeCl_3$ passe à une structure pyramidale parce qu'il est lié à une seule molécule de TOPO dont l'oxygène négatif repousse les 3 Cl porteurs de charges de même signe.

*Mécanisme d'extraction*

Lorsque nous considérons les spectres Raman de la fig. 3 et les résultats du tableau III, nous constatons qu'une concentration importante en TOPO entraîne l'extraction de quantités suffisantes de HCl pour former le complexe par paire d'ions dans la phase organique. Par contre, si la concentration en extractant est plus faible, le TOPO complexé préférentiellement par $FeCl_3$ n'extrait pas suffisamment de HCl, de sorte que $FeCl_3.TOPO$ prédomine largement.

Nous pouvons imaginer, comme l'ont fait avant nous Chalkley et Williams[22] au sujet de l'extraction de $FeCl_3$ en milieu HCl par l'éther, que seul le $FeCl_3$ fait les frais du partage et que $FeCl_4^-$ ne se forme dans la phase organique qu'en présence d'une quantité suffisante de HCl. Ce mécanisme est en bon accord avec les résultats des extractions réalisées avec des concentrations en $FeCl_3$ supérieures à celles de TOPO (tableau III) et pour lesquelles la prédominance du complexe $FeCl_3.TOPO$ ($[Fe_2]_0$) est nettement marquée.

Les équations suivantes peuvent être proposées:

$$\mathrm{FeCl_3} + \overline{\mathrm{TOPO}} \rightleftharpoons \overline{\mathrm{FeCl_3.TOPO}}$$

$$\overline{\mathrm{FeCl_3.TOPO}} + \overline{\mathrm{TOPO}} + \overline{\mathrm{HCl}} \rightleftharpoons \overline{\mathrm{TOPOH^+FeCl_4^-.TOPOH^+Cl^-}}$$

## RÉSUMÉ

Le partage de fer(III) entre des solutions d'acide chlorhydrique (7 *M*) et des solutions benzéniques de TOPO a été étudié en faisant varier les concentrations en fer et en TOPO. Les spectres Raman des phases organiques montrent que deux espèces complexes sont extraites. Une étude à la fois quantitative et qualitative permet de définir les domaines respectifs d'existence de ces deux complexes, leur stoechiométrie et la structure de leur partie minérale. Un mécanisme plausible est proposé pour expliquer la réaction de partage dans les différentes conditions.

## SUMMARY

The partition of iron(III) between hydrochloric acid solutions (7 *M*) and benzene solutions of TOPO has been investigated for varying concentrations of iron and TOPO. Laser Raman spectra of the organic phases indicate that two complex species are extracted. By means of both qualitative and quantitative studies, the range of conditions under which these complexes exist, has been established, and the stoichiometry of the complexes and the structure of their inorganic part has been elucidated. A mechanism is proposed to explain the partition reaction under the various conditions.

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# DOSAGE SPECTROPHOTOMÉTRIQUE DU GROUPE DES TERRES RARES DANS DIVERS TYPES DE ROCHES

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La géochimie des terres rares se développe de plus en plus car ces éléments semblent donner des indications utiles sur les processus de formation des roches. Avant de procéder à l'analyse individuelle de celles-ci, nous avons jugé nécessaire le dosage global de ce groupe d'éléments étant donné la grande diversité des roches qui sont examinées par nos géologues. Ce dosage a pour but principal de fixer une échelle des teneurs moyennes en terres rares, ceci devant nous aider dans le choix des méthodes ultérieures de séparation de ces éléments. D'autre part, comme les teneurs individuelles sont très variables d'une roche à l'autre, nous ne pourrons certainement pas obtenir tous les résultats individuels pour chacune d'elle étant donné que nous sommes limités par la sensibilité de toute méthode d'analyse chimique. Ainsi le géologue pourra disposer d'une valeur globale et de quelques valeurs individuelles pour ses propres travaux d'interprétation.

Parmi les méthodes proposées concernant le dosage de ce groupe d'éléments dans les roches, les plus utilisées sont: la gravimétrie, avec les travaux de Varshal et col.[1], Galkina et col.[2], Steele et col.[3] et Barkley[4]; et la spectrophotométrie, avec les travaux de Munshi et Dey[5], et Savvin et col.[6].

Nous avons choisi une méthode combinée gravimétrique–spectrophotométrique décrite par Jeffery[7] qui se base sur les travaux de Savvin et col.[6]. Après mise en solution acide de la roche et précipitation du groupe, les éléments sont dosés globalement spectrophotométriquement après complexation à l'arsénazo-III. Jeffery ne donne aucun résultat d'analyse et Savvin et col.[6] n'indique que quelques résultats obtenus avec des roches contenant des minéraux riches en terres rares tels que la monazite, le xénotime, la loparite, etc. Nous avons donc essayé d'appliquer cette méthode à des types de roches très différents dont les teneurs en terres rares sont relativement faibles, ce qui a nécessité quelques modifications de cette technique; les résultats obtenus nous semblent tout à fait satisfaisants.

## PARTIE EXPÉRIMENTALE

### *Principe de la méthode et préparation des solutions*

La méthode étant décrite en détail par Jeffery[7], nous n'en donnerons ici que le principe.

TABLEAU I

ROCHES EXAMINÉES

| *Roche* | *Désignation* | *Provenance* |
|---|---|---|
| T1 | Schiste à glaucophane | Socle nappe du Grand-St-Bernard, domaine pennique, Val de Bagnes, Valais, Suisse |
| T2 | Prasinite rubanée | Zone du Combin, domaine pennique, Val de Bagnes, Valais, Suisse |
| T3 | Gabbro(hypérite) | Zone de Bamble, précambrien, Norvège méridionale |
| T4 | Diabase | Zone de Kongsberg, précambrien, Norvège méridionale |
| T5(Irsac 5) | Néphélinite à leucite et mélitite (coulée intérieure – activité 1971) | Volcan du Nyiragongo, Kivu Nord, Zaïre |
| T6(Irsac 6) | Néphélinite à leucite et mélitite (coulée intérieure – activité 1971) | Volcan du Nyiragongo, Kivu Nord, Zaïre |
| T7(Irsac 2) | Néphélinite à leucite et mélitite (coulée intérieure – activité 1971) (sommet du crag) | Volcan du Nyiragongo, Kivu Nord, Zaïre |
| T8 (Irsac 3) | Enclave acide enallogène (dans laves actuelles) | Volcan du Nyiragongo, Kivu Nord, Zaïre |
| T9(Irsac 1) | Projection avec enclave ultrabasique du cratère intérieur (dans laves actuelles) | Volcan du Nyiragongo, Kivu Nord, Zaïre |
| T10(Irsac 7) | Projection vitreuse du cratère intérieur (dans laves actuelles) | Volcan du Nyiragongo, Kivu Nord, Zaïre |
| T11(NIM-G)[a] | Granite | Bushveld, Transvaal, Afrique du Sud |
| T12(NIM-D)[a] | Dunite | Bushveld, Transvaal, Afrique du Sud |
| T14(NIM-N)[a] | Norite | Bushveld, Transvaal, Afrique du Sud |
| T15(NIM-P)[a] | Pyroxénite | Bushveld, Transvaal, Afrique du Sud |
| T16(NIM-S)[a] | Syénite | Palabora, Transvaal, Afrique du Sud |
| T17(NIM-L)[a] | Lujavrite | Pilanesberg, Transvaal, Afrique du Sud |
| T20 | Serpentinite | Guatémala |
| T21 | Serpentinite | Guatémala |
| W-1[b] | Diabase | Centerville, Virginie |
| AGV-1[b] | Andésite | Guano Valley, Lake County, Orégon |
| BCR-1[b] | Basalte | Bridal Veil quadrangle (Washington–Orégon) |
| GSP-1[b] | Granodiorite | Silver Plume, Colorado |
| G-2[b] | Granite | Sullivan quarry, Bradford, Rhode Island |
| DTS-1[b] | Dunite | Hamilton, Washington |
| PCC-1[b] | Péridotite | Cazadero, Sonoma County, Californie |

[a] Série NIMROC, no. 1/177 du National Institute for Metallurgy, Johannesburg, South Africa.
[b] Standards internationaux U.S.G.S.

Après attaque de la roche par un mélange $HF–HNO_3–H_2SO_4$, le résidu est repris par l'acide chlorhydrique dilué et le groupe des terres rares séparé des autres éléments par double précipitation; tout d'abord précipitation des hydroxydes par l'ammoniaque reprise du résidu par l'acide chlorhydrique dilué, puis précipitation des terres rares sous forme d'oxalates avec adjonction d'une solution de calcium comme entraîneur. Transformation des oxalates en oxydes par calcination et reprise du résidu par l'acide chlorhydrique 0.01 *M* dans un ballon jaugé de 100 ml.

Spectrophotométrie en présence d'arsénazo-III.

Nous avons toujours procédé à l'attaque d'exactement 1 g de roche et pour les mesures spectrophotométriques nous avons travaillé dans les conditions suivantes: dans un ballon jaugé de 50 ml, introduire 2 ml de la solution de roche, correspondant exactement à 20 mg de celle-ci; y ajouter 5 ml d'une solution tampon KCl, 2 ml d'arsénazo-III et compléter au volume avec l'acide chlorhydrique 0,01 *M*. Pour la méthode d'addition, ajouter à la solution 1 à 3 ml d'une solution d'un mélange de terres rare pures à 3 $\mu$g ml$^{-1}$. Le blanc est obtenu en procédant à une attaque sans roche et en y appliquant absolument toutes les opérations ci-dessus. Ceci est indispensable étant donné que le calcium utilisé comme entraîneur réagit avec l'arsénazo-III. Par ce procédé son interférence est éliminée. Nous avons utilisé les produits Merck p.a. et pour les terres rares les produits Fluka p.a.

*Appareillage et conditions des mesures*

Les mesures spectrophotométriques ont été faites au moyen de deux appareils:

Spectrophotomètre Zeiss, type PMQ II, dans les conditions suivantes: $\lambda = 655$ nm, fente $= 0{,}03$, photorésistance, filtre $> 620$ nm, cuves de 1 cm. Comme nous le verrons dans l'étude analytique, ces mesures (sans enregistrement des spectres d'absorption) ont dû être abandonnées.

Spectrophotomètre ultraviolet Unicam, type SP8000, à enregistrement graphique, dans les conditions suivantes: $\lambda$ de 750 à 550 nm, absorbance (absorbance range) de 0 à 0,2 A.U., vitesse (scan speed) lente, c'est-à-dire 1 min pour $\Delta\lambda = 50$ nm, cuves de 1 cm.

*Roches examinées*

Nous donnons dans le Tableau I les divers types de roches dans lesquelles nous avons dosé les terres rares.

*Courbe d'étalonnage*

Dans une première série d'essais, nous avons établi des courbes d'étalonnage au moyen de quantités connues de terres rares (3 à 9 $\mu$g). Nous avons préparé des solutions de terres rares à 3 $\mu$g ml$^{-1}$ avec les mélanges suivants: (Er + Gd + Sm) et (Nd + Ho + Sm). Les deux mélanges ont donné les mêmes résultats. Ceci a d'ailleurs été confirmé par une étude de la mesure de la densité optique de chaque terre rare, à poids égal. Seul le lutétium a présenté une densité optique légèrement plus faible, mais ne gênant pas une analyse du groupe des terres rares. Nous ne donnerons pas ici les résultats obtenus par cette méthode que nous avons abandonnée, au profit de la méthode d'addition, pour les raisons décrites ci-dessous.

Tout d'abord nous avons fait les mesures de la densité optique au maximum du pic d'absorption des terres rares (spectrophotomètre Zeiss). Nous avons observé une concordance parfaite entre les résultats obtenus à plusieurs jours d'intervalle. Signalons à ce sujet que la coloration du complexe est stable au moins 24 h; nous n'avons pas contrôlé cette coloration pour une durée supérieure. Il y a également une reproductibilité parfaite entre des résultats obtenus sur deux attaques d'une même roche et ceci prouve la validité de la méthode de séparation du groupe des

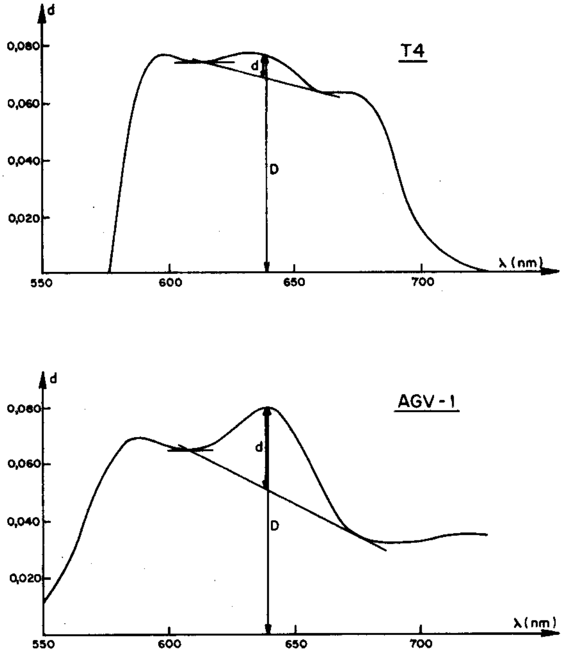

Fig. 1. Spectres de T4 et AGV-1.

terres rares par le procédé utilisé.

Comme les résultats nous paraissaient élevés, par rapport à certaines valeurs données pour les standards U.S.G.S., nous avons envisagé de tracer les spectres d'absorption (spectrophotomètre Unicam). Nous avons observé des différences d'allure des spectres en fonction des divers types de roches. Nous avons également remarqué qu'au pic d'absorption des terres rares correspondent deux minimums à des niveaux différents. Ceci nous a permis d'effectuer des mesures de l'absorbance avec plus d'exactitude et une meilleure sélectivité. En voici un exemple (Fig. 1). Pour AGV-1 on observe un pic d'absorption dû aux terres rares avec un maximum à 648 nm; par contre pour T4 la densité optique à 648 nm est élevée mais ne correspond pas à un pic net. Pour des mesures directes effectuées à cette longueur d'onde (appareil Zeiss) nous avions obtenu, pour ces deux roches, des densités optiques ($D$) presque égales correspondant à 250 p.p.m. pour T4 et 280 p.p.m. pour AGV-1. Par contre, à la vue des spectres, il est possible de corriger les résultats par rapport aux minimums du pic ($d$); nous avons alors obtenu des valeurs totalement différentes, soit 55 p.p.m. pour T4 et 220 p.p.m. pour AGV-1. Ceci étant démontré, nous avons donc poursuivi nos déterminations au moyen des spectres. Toutefois, bien que les résultats aient été améliorés, ils paraissaient toujours trop élevés. C'est pourquoi nous avons abandonné l'utilisation d'une courbe d'étalonnage et adopté la méthode d'addition (étalon interne).

*Méthode d'addition*

Etant donné que nous avons à analyser des roches de types très variés, nous sommes en présence de matrices de compositions fort diverses. Par la

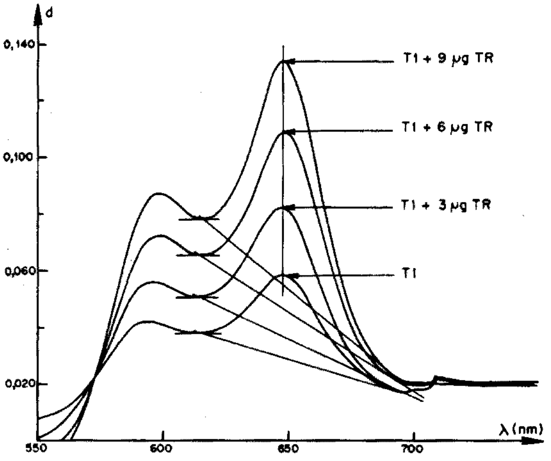

Fig. 2. Spectres de T1.

méthode d'addition qui consiste à ajouter à une quantité connue et fixe d'une roche (20 mg) des quantités croissantes d'un mélange de terres rares (3,6,9 µg) on arrive à éliminer, en grande partie du moins, les effets de matrice. En voici deux exemples.

*Roche T1 (Fig. 2).* Les mesures de *d* donnent les valeurs suivantes:

T1 $d=0{,}029$
T1 + 3 µg TR $d=0{,}045$
T1 + 6 µg TR $d=0{,}062$
T1 + 9 µg TR $d=0{,}078$

En reportant ces valeurs sur un graphique, on obtient pour Tl une teneur en terres rares de 5,2 µg, soit 260 p.p.m.

*Roche T9 (Fig. 3).* Dans ce cas on remarque l'importance de la correction de la valeur de *d*. Cette roche bien que présentant une densité optique très élevée, accuse en réalité la même teneur en terres rares que la roche T1. Les mesures de *d* corrigées par rapport aux minimums donnent les valeurs suivantes:

T9 $d=0{,}027$
T9 + 3 µg TR $d=0{,}037$
T9 + 6 µg TR $d=0{,}054$
T9 + 9 µg TR $d=0{,}066$

En reportant ces valeurs sur un graphique, on obtient une teneur en terres rares de 5,1 µg, soit 255 p.p.m.

Ces deux exemples illustrent l'effet de matrice et son élimination par la technique de l'étalon interne. Par cette méthode nous avons donc obtenu des valeurs proches de celles données pour les standards U.S.G.S., (Tableau III).

### *Étude des interférences*

Savvin et col.[6] ayant étudié les interférences de plusieurs éléments contenus dans les roches, nous n'avons examiné que celles dues à l'yttrium et au scandium.

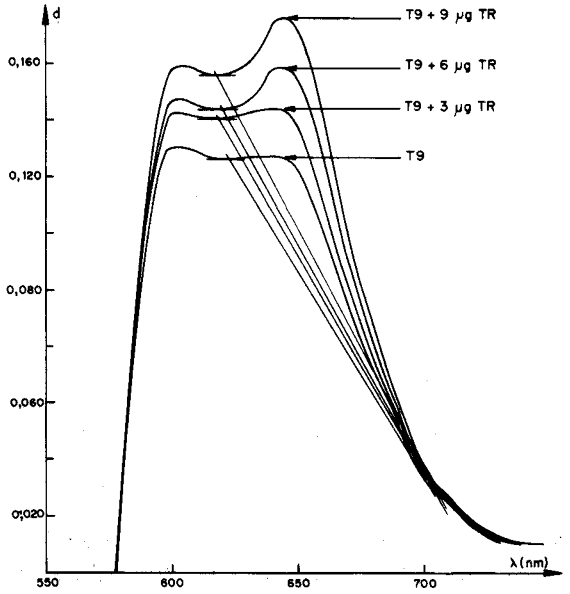

Fig. 3. Spectres de T9.

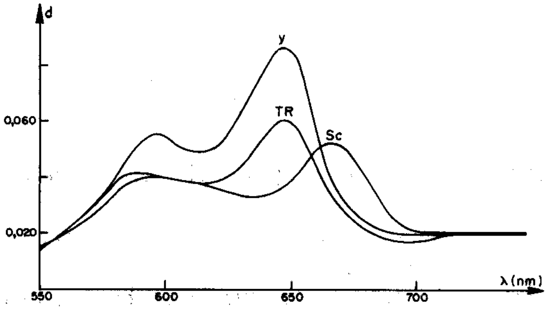

Fig. 4. Spectres de TR, Y et Sc (6 μg).

Ces deux éléments présents sous forme de traces dans la plupart des roches forment des complexes relativement stables avec l'arsénazo-III et présentent des pics d'absorption dont les maximums sont très voisins de celui des terres rares; de plus, ils sont entraînés avec celles-ci lors des séparations par précipitation. Les spectres (Fig. 4) prouvent que l'yttrium interfère à 100%, par contre le scandium semble moins gêner; de plus, à poids égal, l'yttrium présente une densité optique plus élevée que celle des terres rares (le même phénomène a été observé sur des échantillons de roches).

Nous avons donc cherché à partir de quelles proportions ces éléments gênaient le dosage. Pour cela nous avons effectué les essais consignés dans le Tableau II.

On remarque donc que l'yttrium engendre une interférence importante et on peut considérer cet élément comme gênant à partir d'un rapport Y/TR = 0,1, ce qui,

TABLEAU II

DÉTERMINATION DES INTERFÉRENCES DUES À Y ET Sc

| *Échantillon* | *d* | *Échantillon* | *d* |
|---|---|---|---|
| 6 µg TR | 0,034 | 6 µg TR | 0,036 |
| 6 µg TR+0,25 µg Y | 0,036 | 6 µg TR+0,15 µg Sc | 0,037 |
| 6 µg TR+0,50 µg Y | 0,038 | 6 µg TR+0,30 µg Sc | 0,037 |
| 6 µg TR+0,75 µg Y | 0,040 | 6 µg TR+0,60 µg Sc | 0,036 |
| 6 µg TR+1,00 µg Y | 0,042 | 6 µg TR+0,90 µg Sc | 0,039 |
| 6 µg TR+1,25 µg Y | 0,044 | 6 µg TR+1,50 µg Sc | 0,038 |
| 6 µg TR+2,50 µg Y | 0,055 | 6 µg TR+3,00 µg Sc | 0,038 |
| G-2 | 0,039 | G-2 | 0,039 |
| G-2 +0,25 µg Y | 0,041 | G-2 +0,15 µg Sc | 0,039 |
| G-2 +0,50 µg Y | 0,042 | G-2 +0,30 µg Sc | 0,039 |
| G-2 +0,75 µg Y | 0,045 | G-2 +0,60 µg Sc | 0,039 |
| G-2 +1,00 µg Y | 0,047 | G-2 +0,90 µg Sc | 0,039 |
| G-2 +1,25 µg Y | 0,049 | G-2 +1,50 µg Sc | 0,039 |
| G-2 +2,50 µg Y | 0,056 | G-2 +3,00 µg Sc | 0,039 |

dans le cas d'une roche et dans nos conditions de travail, correspondrait à une teneur en yttrium d'environ 25 p.p.m. Cette valeur est atteinte pour plusieurs roches selon les résultats publiés dans la littérature. Par contre, le scandium ne gêne pas pour des teneurs allant au moins jusqu'à 150 p.p.m.; une telle teneur n'est atteinte dans aucune roche étalon U.S.G.S.

L'étude des interférences nous permet de conclure que cette méthode globale de dosage des terres rares doit tenir compte aussi de la présence de l'yttrium. Il faut donc interpréter les résultats spectrophotométriques comme une somme "terres rares+yttrium" que nous représenterons par le symbole ΣY, La–Lu et que l'on trouve dans certains traités de géochimie[8].

## RÉSULTATS

Nous donnons dans le Tableau III les résultats obtenus pour les roches citées dans le Tableau I. Ces résultats nous permettent de faire quelques remarques. Nous avons la preuve de l'excellente reproductibilité de la méthode en considérant les roches pour lesquelles nous donnons deux résultats obtenus sur deux analyses complètes, c'est-à-dire sur deux échantillons de la même roche. Signalons que pour chaque roche, nous avons également fait plusieurs dosages spectrophotométriques à partir des 100 ml de solution obtenus après séparation du groupe des terres rares. Nous avons là aussi constaté une excellente reproductibilité d'un jour à l'autre et même sur un intervalle de plusieurs jours. La limite de dosage se situe vers 50 p.p.m., donc n.d. < 50 p.p.m.

Si l'on considère le groupe des roches provenant du volcan Nyiragongo (T5 à T10) nous pouvons faire les remarques suivantes: les laves ont une teneur relativement constante en terres rares (T5, T6, T7 et T10) et leur composition chimique en éléments majeurs est pratiquement semblable; par contre T8 et T9 ont des teneurs beaucoup plus faibles. T8 est une enclave acide, c'est-à-dire à haute teneur en $SiO_2$ (71,2%) tandis que les laves sus-mentionnées sont basiques,

TABLEAU III

DOSAGE DES TERRES RARES DANS DIVERS TYPES DE ROCHES

| *Roche* | *$\Sigma$ Y, La–Lu (p.p.m.)* | *$\Sigma$ Y, La–Lu (p.p.m.) échelle arbitraire* |
|---|---|---|
| T1 | 260 | |
| T2 | 270 | |
| T3 | 300 | |
| T4 | n.d.[a] | |
| T5 | 560 | |
| T6 | 550 | |
| T7 | 650 | |
| T8 | 260 | |
| T9 | 255 | |
| T10 | 560 | |
| T11 | 620,620 | |
| T12 | n.d.,n.d. | |
| T14 | 130,130 | |
| T15 | 50,50 | |
| T16 | 50,70 | |
| T17 | 580,580 | |
| T20 | n.d. | |
| T21 | n.d. | |
| W-1 | 210,,210 | 95 à 177 |
| AGV-1 | 220 | 170 à 210 |
| BCR-1 | 220 | 179 à 213 |
| GSP-1 | 860 | 876 à 1165 |
| G-2 | 320,320 | 279 à 369 |
| DTS-1 | n.d. | $< 10$ |
| PCC-1 | n.d. | $< 10$ |

[a] n.d. = non déterminé, $< 50$ p.p.m.

avec des teneurs en $SiO_2$ comprises entre 38,7 et 43,5%. T9 est une enclave ultrabasique qui n'a malheureusement pas pu être purifiée. Elle n'a pas pu être dégagée complètement de sa gangue de néphénilite ce qui pourrait expliquer la teneur en terres rares observée.

Pour les standards U.S.G.S. nous avons établi une échelle relative des teneurs $\Sigma$Y, La–Lu au moyen des résultats déjà publiés. Il s'agit bien entendu d'une échelle approximative étant donné la grande dispersion de certains résultats. Cette échelle nous permet tout de même de constater que nos valeurs y sont comprises, sauf pour W-1 pour lequel nous avons toujours eu des valeurs plus élevées.

## CONCLUSION

Nous avons appliqué à des types de roches très divers la méthode d'analyse du groupe des terres rares décrite par Jeffery. Nous avons dû rapidement abandonner le dosage spectrophotométrique au moyen d'une courbe d'étalonnage au profit de la méthode d'addition qui élimine les effets de matrice. De plus nous avons amélioré ce dosage en interprétant les résultats à partir des spectres et non plus à partir d'une simple mesure de la densité optique au maximum du pic des terres rares. Nous avons constaté une excellente reproductibilité des résultats entre deux analyses complètes d'une même roche. La reproductibilité est également excellente d'un jour à l'autre pour les dosages spectrophotométriques. Un écart de ±0,2 μg à ±0,4 μg conduit à un écart de ±10 p.p.m. à ±20 p.p.m. ce qui est faible et donc preuve d'une grande précision.

La durée d'une analyse est assez difficile à estimer. Il faut compter 2 à 3 jours pour l'attaque et la séparation des terres rares par double précipitation, mais on peut traiter plusieurs échantillons à la fois. Pour la spectrophotométrie elle-même il faut environ 3,5 h pour deux analyses par la méthode de l'étalon interne; soit préparation des solutions 2,5 h, mesures au spectrophotomètre Unicam 45 min, interprétation des résultats 15 à 30 min.

## RÉSUMÉ

Nous avons appliqué au dosage des terres rares dans des types de roches très divers, une méthode combinée gravimétrique–spectrophotométrique décrite par Jeffery, à laquelle nous avons apporté quelques modifications lors des dosages spectrophotométriques avec l'arsénazo-III. Etant donné la grande variété des roches qui sont étudiées, nous avons dû adopter pour ces déterminations la méthode d'addition qui élimine les effets de matrice. La limite de dosage se situe à 50 p.p.m., pour les conditions de travail. Les résultats obtenus sont satisfaisants étant donné que le but de ce travail consistait à fixer un ordre de grandeur de la teneur globale en terres rares dans divers types de roches.

## SUMMARY

The combined gravimetric–spectrophotometric method described by Jeffery has been modified with regard to the spectrophotometric determination with arsenazo-III. The modified procedure gives good precision for the rare earths in various types of rocks. A large variety of rocks was studied, hence a standard addition method was adopted to eliminate matrix effects. The lower limit of detection under the experimental conditions used was about 50 p.p.m. The results obtained were satisfactory for the purpose of obtaining an order of magnitude for the overall content of the rare earths in different types of rocks.

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# COMPUTER CALCULATION OF THE COMPOSITION OF EQUILIBRIUM MIXTURES IN SOLUTION

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The calculation of the equilibrium concentrations of species in chemical systems involving several interacting reactions is generally difficult; graphical methods[1] have been used with success, but for more complicated cases iterative methods, carried out with the aid of a digital computer, are more suitable. Computer programs have been written to perform calculations of the above sort, notably HALTAFALL[2] and COMICS[3]. Both these programs have a wide applicability extending to calculations in multi-metal–multi-ligand and (HALTAFALL) multi-phase systems. For many purposes, the chemist does not require a program of such a comprehensive nature, but one dealing with reactions between two components and their side-reactions with hydrogen or hydroxide ions. The present paper describes an ALGOL program for calculating the concentrations of species in the following systems:

(i) metal–ligand equilibria, including protonated and hydrolysed species;

(ii) metal hydrolysis equilibria involving one or two metals;

(iii) weak acid equilibria involving one or two polybasic acids and including weak acid–weak base equilibria. The program allows for the presence of a strong acid or a strong base in all the above instances.

## METHOD

$T_M$, $T_A$ and $T_H$ represent the total metal, total ligand and analytical hydrogen ion concentrations, respectively. $T_S$ and $T_B$ are total concentrations of strong acid and strong base added. The general stability constant $K_{mha}$ is defined by eqn. (1):

$$K_{mha} = \frac{[M_mH_hA_a]}{[M]^m[H]^h[A]^a} \tag{1}$$

(For hydroxy complexes see note (vi) below). The concentration, $c_{mha}$, of any species is given by eqn. (2) and the calculated total metal, ($c_M$), total ligand, ($c_A$), and analytical hydrogen, ($c_H$), by eqns. (3)–(5), respectively.

$$c_{mha} = K_{mha}[M]^m[H]^h[A]^a \tag{2}$$

$$c_M = [M] + \sum_{m=1}^{m=p} mc_{mha} \tag{3}$$

$$c_A = [A] + \sum_{a=1}^{a=r} ac_{mha} \tag{4}$$

$$c_H = [H] - [OH] + \sum_{h=1}^{h=q} hc_{mha} \tag{5}$$

where $p$, $q$ and $r$ are the maximum values of $m$, $h$ and $a$, respectively.

We can now define the following functions:

$$F_M = T_M - c_M \ ,$$

$$F_A = T_A - c_A \ ,$$

$$F_H = T_H - c_H$$

If the stability constants are known, by substituting values of [M], [H] and [A] in eqns. (2)–(5), the functions $F_M$, $F_A$ and $F_H$ can be evaluated. The correct values of the concentrations are those for which $F_M = F_A = F_H = 0$. If a set of estimates of [M], [A] and [H] leads to non-zero values $F'_M$, $F'_A$, $F'_H$, the shifts ($X_M$, $X_A$, $X_H$) in the concentrations that will simultaneously minimize the three functions can be calculated from eqns. (6)–(8) in which $F_M$, $F_A$ and $F_H$ are expanded in Taylor's series as far as the first order terms.

$$F_M = F'_M + G_M^M X_M + G_M^A X_A + G_M^H X_H = 0 \tag{6}$$

$$F_A = F'_A + G_A^M X_M + G_A^A X_A + G_A^H X_H = 0 \tag{7}$$

$$F_H = F'_H + G_H^M X_M + G_H^A X_A + G_H^H X_H = 0 \tag{8}$$

where

$$G_M^M = \frac{\partial}{\partial [M]} (F_M) \, , \quad G_M^A = \frac{\partial}{\partial [A]} (F_M) \, , \ etc.$$

The functions $G_M^M$, $G_M^A$ *etc.* can be quantified using the estimates of [M], [A] and [H], and eqns. (6)–(8) can be solved simultaneously for the shifts. The procedure is repeated with the new estimates of the concentrations and so on until the functions $F_M$, $F_A$ and $F_H$ are all satisfied within a specified convergence limit. Equations (6)–(8) are solved by means of a matrix inversion procedure used by Blackburn[4].

The above type of procedure has been used (without the proton function) in SCOGS[5] and GAUSS G[6], which are FORTRAN programs for calculating equilibrium constants from pH data. Starting from a similar mathematical basis, Ting-Po I and Nancollas[7] have written a more complicated general program which also incorporates activity coefficient corrections.

*Notes on the program*

(i) Calculations can be performed for systems involving several equilibria.

(ii) At the end of calculations with one set of equilibrium constants, any or all of these constants can be changed, or others added, and the calculations repeated with starting values of concentrations equal to the equilibrium values obtained with the first set.

(iii) The convergence parameter is normally set to $10^{-4}$, *i.e.* 0.1% error, but is adjustable.

(iv) Allowance is made for the presence of strong acid and/or strong base.

(v) Initial estimates of the free concentrations of one or both of the ligands

TABLE I

INPUT FOR THE PROGRAM

| | | |
|---|---|---|
| p | An integer indicating the type of input (=5 if both metal and ligand present, 6 for ligand only, 4 for two ligands) | |
| n | An integer equal to the number of equilibrium constants, excluding the autoprotolysis constant, to be used in a particular trial | |
| ni | An integer, used only for setting array dimensions, equal to the largest number of constants to be used in any trial of one input | |
| mt | An integer equal to the number of data points in the calculation | |
| limit | An integer equal to the maximum number of iterations allowed | |
| EX1 | Convergence parameter in the total metal concentration | |
| EX2 | Convergence parameter in the total ligand concentration | |
| EX3 | Convergence parameter in the analytical hydrogen concentration | |
| ihs | An integer, indicates presence of strong acid if ihs=2 | |
| a | An integer equal to the number of protons per ligand molecule | |
| ba | An integer equal to the number of protons on the second ligand "M" (read in only if p=4) | |
| ckwl | Autoprotolysis constant for water | |
| ivx | An integer, indicates that estimates of [M] are to be supplied if ivx=1 | |
| itx | An integer, indicates that estimates of [A] are to be supplied if itx=1 | |
| mm | An integer equal to the number of metal ions in the complex | n sets |
| mn | An integer equal to the number of protons in the complex | |
| ml | An integer equal to the number of ligands in the complex, or minus the number of hydroxide ions | |
| e | Logarithm of the overall stability constant of the complex | |
| cl | Total ligand concentration | Read only if p=4 or 5 mt sets |
| bb | Total metal concentration | |
| u | Estimate of pH | |
| ch | Concentration of strong base | |
| hcl | Concentration of strong acid (read only if ihs=2) | |
| cl | Total ligand concentration | Read only if p=6 mt sets |
| ch | Concentration of strong base | |
| u | Estimate of pH | |
| hcl | Concentration of strong acid (read only if ihs=2) | |
| vvx | Estimate of [M] (read only if ivx=1) | mt sets |
| ttx | Estimate of [A] (read only if itx=1) | |
| | If last basic symbol was a colon, read in a new value for | Up to ni sets |
| n | The number of equilibrium constants followed by an integer, the index | |
| j | the jth complex, then read in values of ml, mm, mn and e for the jth complex | |
| | If the last basic symbol was an asterisk, return to the start and await fresh batch of data | |

or metals participating in the equilibria may be supplied to the program, otherwise the free concentrations are initially set equal to the total concentrations.

(vi) Equilibrium constants, including those relating to acid dissociation reactions, are supplied to the program in the form of the logarithms of the overall stability constants. Hydroxide-containing complexes are characterized by a negative proton index, thus a complex M(OH)A with a stability constant $\beta=[\mathrm{M(OH)A}]/\{[\mathrm{M}][\mathrm{OH}][\mathrm{A}]\}$ is entered as $\mathrm{MH}_{-1}$ A with a constant $K=\{[\mathrm{M(OH)A}][\mathrm{H}]\}/\{[\mathrm{M}][\mathrm{A}]\}=\beta K_w$, where $K_w$ is the autoprotolysis constant for water.

(vii) The program calculates the sum of the squares of the deviations between the input and calculated pH values, thus providing a check on the goodness of fit when experimental pH data are processed with different sets of equilibrium constants.

(viii) No allowance is made for activity coefficient effects.

(ix) As far as possible, ALGOL identifiers in the program correspond to FORTRAN variables in the program GAUSS G.

(x) A limit to the number of iterations to be performed is supplied to the program. If this limit is reached the results are printed with the label *FALSE.

(xi) The concentrations of M, A, and H are calculated simultaneously, which should take less computing time than the consecutive calculation used in HALTAFALL and COMICS.

The full program is available on request. The input for the program is outlined in Table I. This input scheme relates to the normal modes of operation of the program, *i.e.*, metal–proton–ligand systems and weak acid–proton systems. For mixtures of two weak acids or a weak acid plus a weak base, the symbols characteristic of the metal (EX1, ivx, mm, bb, vvx) become the property of the second acid or weak base, together with the new symbol, ba. For hydrolysis reactions of one metal, the program is entered with p = 6 and the symbols characteristic of the weak acid are transferred to the metal (EX2, a, itx, ml, cl, ttx), with mm = ivx = 0. For hydrolysis equilibria in mixtures of two metals, the symbols

TABLE II

DATA FOR A SYSTEM OF DIBASIC WEAK ACID–METAL COMPLEXING IN THE PRESENCE OF DIFFERENT AMOUNTS OF SODIUM HYDROXIDE

($\log K_{011}=4.0$, $\log K_{021}=7.0$, $\log K_{101}=3.0$, $\log K_{102}=6.0$, $\log K_{111}=6.0$, $\log K_w=-14.0$)

| *Point* | $10^3\,T_M$ *(mol l⁻¹)* | $10^3\,T_A$ *(mol l⁻¹)* | $10^3$[NaOH] *(mol l⁻¹)* | $\mathrm{pH}_{in}$ | $10^3$[M] *(mol l⁻¹)* | $10^4$[A] *(mol l⁻¹)* | $\mathrm{pH}_{calc}$ | $10^3$[HA] *(mol l⁻¹)* | $10^3[\mathrm{H_2A}]$ *(mol l⁻¹)* | $10^4$[MA] *(mol l⁻¹)* | $10^4[\mathrm{MA_2}]$ *(mol l⁻¹)* | $10^4$[MHA] *(mol l⁻¹)* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5.0 | 5.0 | 0.0 | 2.5 | 4.2396 | 0.5250 | 2.6263 | 1.2411 | 2.9343 | 2.2257 | 0.1168 | 5.2619 |
| 2 | 5.0 | 5.0 | 5.0 | 3.0 | 3.2865 | 2.7514 | 3.2077 | 1.7054 | 1.0571 | 9.0424 | 2.4879 | 5.6049 |
| 3 | 5.0 | 5.0 | 9.0 | 4.0 | 2.3373 | 6.5154 | 4.0130 | 0.6324 | 0.0614 | 15.229 | 9.9220 | 1.4780 |

TABLE III

NUMBER OF ITERATIONS REQUIRED FOR DIFFERENT INITIAL ESTIMATES

| *Point* | $[M]_{in}$<br>$[A]_{in}$ | $T_M{}^a$<br>$T_A{}^a$ | $E_M{}^b$<br>$E_A{}^b$ | $T_M$<br>$E_A$ | $E_M$<br>$T_A$ | $T_M$<br>$0.1\ E_A$ | $0.1\ E_M$<br>$T_A$ | $0.1\ E_M$<br>$0.1\ E_A$ | $0.9\ E_M$<br>$0.9\ E_A$ | $1.1\ E_M$<br>$1.1\ E_A$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 8 | 4 | 4 | 8 | 5 | 7 | 6 | 4 | 4 |
| 2 | | 8 | 4 | 4 | 7 | 6 | 7 | 5 | 4 | 4 |
| 3 | | 7 | 2 | 3 | 6 | 5 | 7 | 7 | 4 | 3 |

[a] $T_M$ and $T_A$ are the total metal and ligand concentrations, respectively.

[b] $E_M$ and $E_A$ are the quilibrium free metal and free ligand concentrations.

normally associated with the ligand are attached to the second metal (EX2, a, itx, ml, cl, ttx).

## DISCUSSION

The program has been run successfully on an English Electric–Leo–Marconi KDF.9 computer in all the modes referred to above. The effect of the accuracy of the initial estimates of the concentrations on run-time was tested as follows. The equilibrium concentrations of all the species present in mixtures of a dibasic weak acid with a metal ion with which it forms complexes were calculated for different pH values. The input data and equilibrium concentrations for three points are given in Table II. The calculations were carried out with different initial estimates for the free metal and free ligand concentrations, and the number of iterations necessary in each case is shown in Table III for the three points. Regardless of the initial estimates, the equilibrium concentrations were reproduced with differences no greater than 1 in the fifth significant figure, although the convergence parameters were 0.1% of each of the total concentrations. Such accuracy should be adequate for most purposes.

It can be seen from Table III that, as expected, the more the free concentrations differ from the total concentrations, the more economical it is to use good initial estimates. Even estimates in error by a factor of ten may be better than the total concentrations. Since the same approximate input pH values were used each time, the calculations never stopped after only one cycle, even when equilibrium values of free metal and free ligand concentrations were supplied to the program.

## SUMMARY

A computer program has been written to calculate the concentrations of the species in the following systems: (1) metal–ligand equilibria; (2) metal hydrolysis equilibria involving one or two metals; (3) weak acid equilibria involving one or two polybasic acids and including weak acid–weak base equilibria. Hydrolysed and protonated species are allowed for. The necessary data are the total concentrations of the components, the equilibrium constants and an estimate of the pH.

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# SYNTHESIS OF A SULPHONATED FERROIN REAGENT FOR CHELATING IRON(II) IN STRONG ACID

## SPECTROPHOTOMETRIC DETERMINATION OF THE OXIDATION STATE OF IRON IN SILICATES

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Among the plethora of organic compounds employed for the colorimetric determination of traces of metals, the heterocyclic bases containing the α, α′-diimine structure (*i.e.* $-R-N=\overset{|}{C}-\overset{|}{C}=N-R-$, also called the methine or ferroin chromophoric group) are probably the most extensively studied class of reagents. Since the classical work of Blau[1] with the well-known 2,2′-bipyridine (Bipy) and 1,10-phenanthroline (Phen), hundreds of compounds have been prepared and characterized for analytical use. In over two decades of systematic joint work, Smith and Case and their coworkers have contributed enormously to the understanding of ferroin chemistry by synthesizing and examining a large number of compounds, several of which are outstanding for their sensitivity and selectivity as iron chromogens, *i.e.*, 4,7-diphenyl-1,10-phenanthroline (Bathophen, $\varepsilon = 22{,}400$ at 533 nm)[2,3], 2,4,6-tris-(2-pyridyl)-1,3,5-triazine (TPTZ, $\varepsilon = 24{,}100$ at 595 nm)[4–6], 2,6-bis-(4-phenyl-2-pyridyl)-4-phenyl-2-pyridine (Terrosite, $\varepsilon = 30{,}200$ at 583 nm)[7,8] and a group of pyridyl-substituted *asym*-triazines[9] represented by the most sensitive of its class the compound 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PPDT, $\varepsilon = 28{,}700$ at 561 nm)[10,11]. In further studies, it has been shown[12] that the sensitivity of a ferroin reagent towards iron(II) ions is enhanced by the replacement of the hydrogen atom by a methyl, ethyl or phenyl group *para* to the imine nitrogen in the heterocyclic ring, in that order. Thus, the most intense colour formation can be expected by compounds derived from 4-phenylpyridine or other structural analogues, *e.g.*, Terrosite, PPDT, *etc.* However, this arylpyridine is difficult to obtain in suitable quantity and is expensive.

Because of their high sensitivities and other desirable characteristics, some of these iron chromogens have found regular analytical use, but the frequently complicated nature of their synthesis has often resulted in high cost and limited accessibility. Stephen[13] showed an alternative and simple route for preparing iron reagents with comparable sensitivity and selectivity, the most important being 2,3,5,6-tetrakis-(2-pyridyl)-pyrazine (TPP, $\varepsilon = 20{,}000$ at 570 nm).

In this work, the practical accessibility of PPDT[9] is shown by an integrated total synthesis, and the preparation and some physical–chemical properties of its sulphonated derivative are described. The most probable position of entry of the sulphonic acid radical is in the phenyl groups of the benzil condensation[14]. The sulphonated derivative 3-(4-phenyl-2-pyridyl)-5,6(diphenyl-4,4′-disulphonic acid)-1,2,4-triazine di-ammonium salt (PPDT-DAS) retains the high sensitivity ($\varepsilon = 29{,}300$ at 570 nm) and selectivity of the free base PPDT in its reactions with iron(II). The formation of its water-soluble, magenta-coloured tris chelate[11] $\mathrm{Fe(PPDT\text{-}DAS)}_3^{2+}$ is possible even in molar concentrations of mineral acids.

The excellent sensitivity, stability and acid tolerance of PPDT-DAS was utilised in developing a method for the spectrophotometric microdetermination of iron(II) oxide in silicates. With the reagent incorporated in the dissolving acid mixture, iron(II) ions are complexed *in situ* as released from the silicate matrix. Under the optimal conditions established in this study, with the possibility of aerial oxidation excluded, a simple and precise method is available for geological applications, especially in experimental petrology. Interest in this type of reagent has been expressed for application to experimental petrology where generally a 10-mg synthetic silicate specimen is subjected to X-ray diffraction and electron microprobe studies in addition to the spectrophotometric determination of iron oxidation states.

## EXPERIMENTAL

### *Synthesis of reagents*

The integrated scheme for the total synthesis of PPDT and PPDT-DAS is illustrated in Fig. 1.

*4-Phenylpyridine (II).* This starting material was conveniently prepared free from other isomers by the olefin aminomethylation reaction of Schmidle and Mansfield[15]. In three batches a total of 6.47 moles (764 g) of α-methylstyrene with corresponding amounts of aqueous formaldehyde (40%) and ammonium chloride under the specified conditions yielded 552 g (54%) of an oil, 4-phenyl-1,2,3,6-tetrahydropyridine (I), which was isolated by superheated steam distillation. The residue solidified to a polymer upon cooling. The total amount of the oil was dehydrogenated in batches of 0.55 mole in nitrobenzene by using 5% palladium-on-alumina catalyst. The hydrochloric acid extract of the reaction mixture was made alkaline and distilled with superheated steam to give a yield of 413 g (77%) of 4-phenylpyridine. After two recrystallizations from hexane it melted at 74–76°C. Traces of aniline, probably derived from the catalytic reduction of some nitrobenzene, distilled over; a more inert solvent such as decahydronaphthalene may be better suited although this was not tested.

*2-Cyano-4-phenylpyridine (V).* The novel synthesis of heterocyclic nitriles by Feely and Beavers[16] was successfully applied for the preparation of 2-cyano-4-phenylpyridine via the *N*-methoxy-4-phenylpyridinium methyl sulphate quaternary salt (IV). 4-Phenylpyridine (413 g) was converted to the corresponding *N*-oxide (III) by the method of Ochiai[17] with hydrogen peroxide and glacial acetic acid, yielding 423 g (93%) of the crude product. This was used directly without purification to prepare the intermediate quaternary salt by treating with equimolar amounts of dimethyl sulphate for 2 h at water bath temperature (*ca.* 100°C). Upon the addition of the quaternary salt in aqueous solution to a 3-fold molar amount of potassium cyanide at 25–30°C, the crystalline precipitate of 2-cyano-4-phenylpyridine separated out immediately. After 3 h, the stirred suspension was suction-filtered, re-suspended

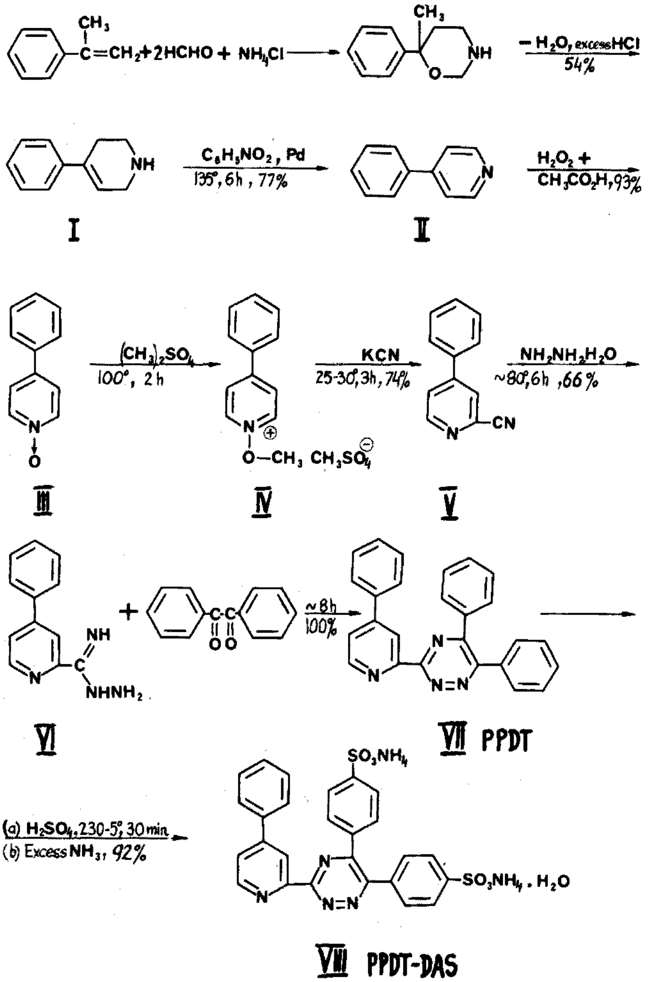

Fig. 1. Integrated scheme for the total synthesis of PPDT and PPDT-DAS.

in water, filtered and washed several times. The yield of the crude product was 328 g (74%) after drying. Small portions of this material were purified by hot Soxhlet extraction with petroleum ether (b.p. 60–80°C). More rapid purification was achieved, however, by vacuum distillation which yielded a total of 267 g (60%) of 2-cyano-4-phenylpyridine, m.p. 100°C.

*3-(4-Phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine, PPDT (VII).* This compound was prepared according to the two-step synthesis of Case[9] with some minor modifications. 2-Cyano-4-phenylpyridine (0.1 mole, 18.0 g), absolute ethanol (18 ml) and hydrazine hydrate, 99–100% (50 ml) were mixed and warmed to form a homogeneous solution. The reaction mixture was kept warm enough to prevent crystallization and magnetically stirred for 6 h to complete the reaction. After diluting the cooled reaction mixture with several volumes of water, the precipitated 4-phenylpyridyl-2-hydrazidine (VI) was filtered by suction, washed and extracted with hot benzene. Upon cooling, the separated crystals were filtered, washed with benzene–petroleum ether and dried at 60°C in a current of nitrogen. The nearly white crystals of (VI) melted, at 126°C (yield; 14.0 g, 66%). The yield obtained by Case[9] (84.4%) could not be reproduced in several batches and variations in reaction conditions. The hydrazidine (VI; 14.0 g) was mixed with an equimolar amount of benzil in 75 ml of hot absolute ethanol and the stirred mixture was allowed to cool. Rapid condensation took place by re-warming and the thick suspension was allowed to stand overnight. After diluting with petroleum ether and filtering by suction, the light yellow product was dried to give PPDT (VII) in quantitative yield. The quantitative nature of the condensation reaction was verified by repeated batches. The corresponding yield reported by Case[9] was 69.4%. The best solvent for recrystallization was boiling glacial acetic acid and water. The light yellow plates separated rapidly on cooling and were collected by filtration, washed several times with water and dried overnight at 110°C (m.p. 193–194°C). Calculated for $C_{26}H_{18}N_4$: 80.8% C, 4.7% H and 14.5% N; found: 80.8% C, 4.7% H and 14.8% N.

In several experiments, it was found that if the recrystallization of the hydrazidine (VI) from benzene was delayed, the impurities catalyzed its degradation, probably through autocondensation to form the corresponding dihydro-*sym*-tetrazine[18] derivative, and condensation with benzil was retarded as expected; in some cases, the yield of PPDT regressed to as low as 60%. However, the purification of the intermediate (VI) is simple and consistently high purity can be maintained.

*3-(4-Phenyl-2-pyridyl)-5,6-(diphenyl-4,4′-disulphonic acid)-1,2,4-triazine diammonium salt, PPDT-DAS (VIII).* The free base PPDT (10 g) was dissolved in 25 ml (46 g) of concentrated sulphuric acid in a 100-ml beaker. The mildly exothermic mixture (64°C) was stirred to complete dissolution and heated gradually to 230–235°C in 15 min. Water solubility of the product was tested at intervals by withdrawing a drop of sulphonation mixture and diluting with water. In approximately 30 min, the sample was easily soluble in cold water in contrast to the intermediate state (probably a monosulphonic acid) when boiling of the test solution was necessary. The cooled reaction mixture was then poured slowly into 400 ml of well-stirred acetone held at −30°C in a dry ice bath. The free sulphonic acid which precipitated immediately was suction-filtered and pressed down to remove as much liquid as possible. The extremely hygroscopic light yellow sulphonic acid was dissolved in water, neutralized with an excess of ammonia solution and evaporated to dryness under reduced pressure at water bath temperature. The brown gummy residue was extracted with hot dimethylformamide (DMF, 50 ml), insoluble ammonium sulphate (*ca.* 8.5 g) was filtered off, and then further extracted with 2 x 50 ml of the hot solvent until the residue was nearly colourless. The combined filtrate was evaporated under reduced pressure to a small volume (*ca.* 10 ml) and acetone (300–400 ml) was stirred into the concentrate. The precipitated ammonium salt (VIII) was collected by filtration, re-suspended in acetone and re-filtered. After air-drying, the light yellow PPDT-DAS was dissolved in a small volume of anhydrous methanol, re-precipitated with acetone, filtered and dried at 110°C for 2 h. Attempted recrystallization was less convenient. The yield was 14.2 g (91.7%); the light yellow amorphous powder does not melt below 280°C. Elemental analysis showed it to be a monohydrated salt (calculated for $C_{26}H_{24}N_6S_2O_6 \cdot H_2O$: 52.2% C, 4.4% H, 14.0% N and 10.7% S; found: 51.9% C, 4.3% H, 13.7% N and 11.1% S). The analysis gives a composition of $C_{25.9}H_{25.8}N_{5.9}S_{2.1}O_{7.1}$. The monohydrate is somewhat hygroscopic; a sample gained 6.53% of its own weight in an open vessel over one week and remained essentially stable in an open container thereafter. The weight gain is equivalent to the formation of the trihydrate.

*Sulphonation of other heterocyclic bases possessing ferroin functionality.* Symmetric tris-pyridyl- and tris-4-phenyl-2-pyridyl-triazines obtained by the trimerization of the corresponding 2-cyanopyridines[4], TPP[13] and 2,3-bis-(2-pyridyl)-5,6-dihydropyrazine[13] failed to yield water-soluble derivatives under the relatively mild reaction conditions suitable for PPDT. However, further analogues of asymmetric triazines obtained by the condensation of the corresponding 2-hydrazidines with benzil[9] (including the hitherto unreported 1-isoquinolyl derivative) sulphonated smoothly, but not the pyridil[9] and diacetyl condensation products. In some cases, chlorosulphonic acid was effective in producing water-soluble sulphonic acids of a few more resistant bases.

## SOME PROPERTIES OF PPDT-DAS

### *Solubility*

The sulphonic acid salt is highly soluble in water, mineral acids of any concentration, formamide and dimethylformamide. In aliphatic alcohols, the solubility pattern is markedly influenced by the number of carbon atoms in the solvent; methanol is the best solvent in this range, ethanol only moderately so, whereas the salt is insoluble in pentanol. PPDT-DAS is moderately soluble in pyridine but insoluble in ketones, ethers, aromatic and aliphatic hydrocarbons.

### *Stability*

The reagent shows extreme stability against oxidative and thermal degradation; the methine chromophoric group is unaffected by repeated evaporation with aqua regia or by boiling concentrated nitric acid. However, structural degradation occurs as the concentration of perchloric acid increases near its fuming temperature when PPDT-DAS is boiled with a mixture of perchloric and nitric acids. Repeated evaporation of the reagent with concentrated hydrofluoric acid has no effect on its chelating ability, nor does concentrated sulphuric acid have any effect even when heated above 240°C. Likewise, fusion with ammonium hydrogensulphate (m.p. 147°C) and sulphamic acid (m.p. 205°C) does not affect the reagent. The stability of PPDT-DAS in these acid fluxes was examined in the presence of a basaltic rock which was partially dissolved releasing some iron(II) ions which were then chelated by the reagent *in situ* in the molten acids. Moreover, during a brief period of fusion with potassium hydroxide (m.p. 380°C) the chelating ligand of PPDT-DAS remained intact, but the evolution of ammonia indicated the cationic displacement by potassium.

## SPECTROPHOTOMETRIC STUDIES

### *Reagents*

PPDT, 0.005 *M*, was prepared by dissolving 0.194 g of pure reagent in

100 ml of absolute ethanol containing a few drops of hydrochloric acid. The keeping properties are excellent in a clear bottle.

PPDT-DAS, 0.005 *M*, was prepared by dissolving 0.3 g of the monohydrate in 100 ml of water.

PPDT-DAS (2%) solutions were prepared by dissolving the salt in the following acid media: conc. HF, 20% HF, 50% HF+50% $H_2SO_4$, 10% HF+90% $H_2SO_4$, 30% HF+10% $H_2SO_4$, 20% HF+5% $H_2SO_4$, 15% HF+5% $H_2SO_4$, 10% HF+5% $H_2SO_4$, 10% HF+10% $H_2SO_4$ in DMF, 10% HF+5% $H_2SO_4$ in DMF, 25% $NH_4F$+5% $H_2SO_4$ and 20% KF+10% HF+5% $H_2SO_4$.

*Hydroxylammonium chloride, 10% aqueous.* Any iron(II) impurity was extracted in amyl alcohol as the PPDT chelate in the presence of sodium perchlorate.

*Fluoride complexing solutions.* Boric acid, saturated; aluminium sulphate, saturated; beryllium sulphate, 10% aqueous.

*Standard metal solutions.* These were prepared from "Specpure" $Fe_2O_3$, copper powder (99.997%) and cobalt sponge (99.998%), respectively.

All other reagents, chemicals and metal salts were of analytical grade.

### *Apparatus*

Absorption spectra were recorded by a Unicam SP1800 recording spectrophotometer and the analytical measurements at fixed wavelengths were obtained by a Unicam SP500 S-2 instrument equipped with an automatic sample changer and a recorder. pH measurements were made by a Metrohm–Herisau Potentiograph Type E 436. All calibration and silicate sample weighings were obtained with a Cahn G-2 Electrobalance with maximum range set at 5 mg by frequent calibration. Inexpensive plastic equipment used for the simultaneous chelate formation and sample dissolution at room temperature were size No. 1 tapered polyethylene thimbles covered by an inverted half of the same. PTFE thimbles (1.5 ml capacity) were made from cylindrical beakers by heating to the softening point of PTFE and molding to the required shape. The microdigestion assembly was constructed from heavy-walled polyethylene sample container and used in an inverted position. The PTFE thimble covered by a lid of the same plastic was fitted into the sample container lid and provisions were made for the entry and exit of nitrogen.

Microdigestion bombs (capacity 1.5 ml) with externally threaded screw tops fabricated from solid PTFE rods were used up to 200°C for the decomposition of more refractory silicates.

### *Colour reactions*

Both PPDT and PPDT-DAS form with iron(II) intensely coloured cationic chelates of the type $FeL_3^{2+}$ in acidic and slightly alkaline media. The optimal pH range for maximal colour formation is pH 3–8 for both reagents. Of all cations tested only copper(I) and cobalt(II) form coloured chelates but with significantly lower intensities. The presence of large amounts of fluoride, oxalate and malonate retards the formation of the iron(II) chelate by effectively competing with the reagents; EDTA and cyanide inhibit the colour reaction. Although both PPDT and PPDT-DAS form maximal colour with iron(II) at approximately the same pH range, the reaction velocity of the sulphonated derivative is remarkably higher in acidic medium than that of PPDT, even in molar acid concentrations where the ligand must be fully protonated. Because of the high acid tolerance of PPDT-DAS in the formation of its iron(II)-tris-chelate, the free base PPDT was examined for the purposes of comparison only.

*Extractability of iron(II) chelates*

The water solubility of the iron(II)–PPDT chelate is extremely low but turbidity problems can largely be avoided by adding ethanol. The complex can be extracted very effectively with higher alcohols as the perchlorate salt. In contrast, the iron(II)-PPDT-DAS chelate is completely water-soluble as expected, and it is not extractable from its aqueous solutions, although the coloured substance can be salted out in the presence of high concentrations of inorganic salts. On adding water this substance redissolves rapidly.

*Absorption spectral characteristics of metal chelates*

The absorption spectra of the iron(II), copper(I) and cobalt(II) chelates of the ligands PPDT-DAS and PPDT are shown in Fig. 2. The copper and cobalt complexes of PPDT-DAS and PPDT appear fairly intensely coloured. However, the absorption curves show rather broad absorption maxima for copper and the absence of a distinct peak for cobalt.

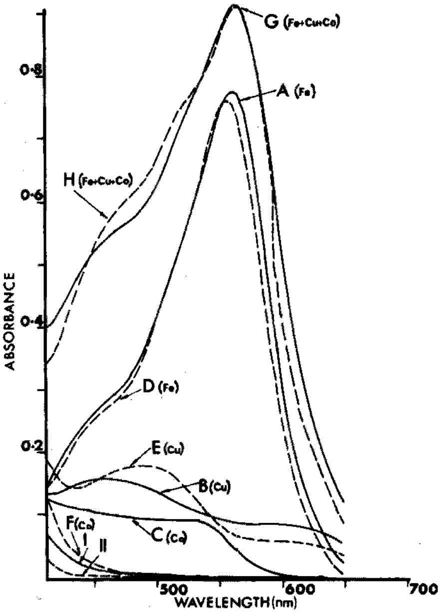

Fig. 2. Absorption spectra of PPDT-DAS and PPDT complexes at pH 4.5 measured against reagent blank in 10-mm cells. A–C and G: PPDT-DAS (aqueous medium), D–F and H: PPDT (1+1, ethanol/water medium). Metal concentrations: Fe = $2.66 \cdot 10^{-5}$ *M*, Cu = $3.09 \cdot 10^{-5}$ *M*, Co = $2.76 \cdot 10^{-5}$ *M*. Individual metal concentrations totalled to give $8.51 \cdot 10^{-5}$ *M* in curves G and H. Reagent concentrations: curves G and H, $1 \cdot 10^{-3}$ *M*; others, $5 \cdot 10^{-4}$ *M*. Curves I and II represent reagent blanks measured against water and ethanol/water (1+1), respectively.

*Molar absorptivities and reagent sensitivities*

The molar absorptivities ($\varepsilon$) and sensitivities of the iron, copper and cobalt

TABLE I

MOLAR ABSORPTIVITIES AND SENSITIVITIES

| *Reagent* | *Metal (M)* | $\lambda_{max(nm)}$ | $\varepsilon(l\,mol^{-1}\,cm^{-1})$ | $\mu g\ M\ cm^{-2}$ | *(Schilt)*[10] | |
|---|---|---|---|---|---|---|
| | | | | | $\lambda_{max(nm)}$ | $\varepsilon(l\,mol^{-1}\,cm^{-1}$ |
| PPDT | Fe | 567 | 28,700 | 0.00195 | 561 | 28,700 |
| | Cu | 490 | 5,900 | 0.0108 | 480 | 7,900 |
| | Co | —[a] | —[a] | —[a] | 516[b] | 2,200 |
| PPDT-DAS | Fe | 570 | 29,300 | 0.00191 | — | — |
| | Cu | 470 | 5,200 | 0.0123 | — | — |
| | Co | 530[b] | 3,500 | 0.017 | — | — |

[a] Absorbance is not appreciably different from that of reagent.
[b] Calculated from the shoulder value.

complexes calculated from the spectrophotometric data are shown in Table I. The molar absorptivities and $\lambda_{max}$ values found by Schilt[10] are shown for comparison.

*Cationic interferences*

As already pointed out, among all the cations tested only copper(I) and cobalt(II) formed coloured chelates but with considerably lower sensitivities than the corresponding iron(II) chelate. Because of fairly wide separation in the $\lambda_{max}$ values, spectral resolution of the ternary chelate system Fe ($2.66 \cdot 10^{-5}$ *M*)–Cu ($3.09 \cdot 10^{-5}$ *M*)–Co ($2.76 \cdot 10^{-5}$ *M*) of both reagents was attempted. The resolution was unsuccessful, but there was a significant enhancement of the iron absorption curves: the increases in absorbance were 19.1% for PPDT and 17.3% for PPDT-DAS, respectively (see Fig. 1, curves G and H).

*Colour stability of the iron complexes*

The iron(II) chelates of PPDT and PPDT-DAS showed no appreciable fading in diffuse daylight over one month of storage in stoppered flasks. However, an average of 2% bleaching occurred in 48 h in the presence of much fluoride ($>500$ p.p.m. as HF); thereafter the colour intensity remained constant.

*Calibration curves*

A standard stock solution of iron was prepared by dissolving "Specpure" $Fe_2O_3$ in 7 *M* hydrochloric acid and diluting to volume. Suitable aliquots were pipetted to prepare the working concentration by further dilution. Three calibration curves were made, one with PPDT as the chromogen and two for the aqueous medium with PPDT-DAS. Beer's Law was obeyed within the concentration ranges tested and beyond. The relative standard deviation for the calibrations was found to be as follows: (a) for PPDT, 0.005 *M* in ethanol, eight concentrations were measured within the range 13.6–122 μg Fe/50 ml (in 1+1 ethanol–water) at 570 nm with 0.28% accuracy; (b) for PPDT-DAS, 0.005 *M* (aqueous), nine concentrations were measured within the range 13.6–122 μg Fe/50 ml at 570 nm with a relative standard deviation of 0.70%; (c) for PPDT-DAS, 0.005 *M* (aqueous), ten concentrations were measured within the range 49–246 μg Fe/100 ml at 570 nm with a relative standard deviation of 0.51%.

In addition, a separate calibration graph was prepared for subsequent use in silicate analysis based on the most probable FeO values of 12 international standard rocks. It was found necessary to duplicate calibration conditions as close as possible to actual analytical use. A total of 41 analyses were made and the ratio of absorbance to concentration had a linear relationship with a relative standard deviation of 1.19%. The "silicate" calibration differed by 1.11% from the value of the "chemical" calibration. The effective molar absorptivity for the colour system calculated from the data of standard rock analysis was found to be $\varepsilon = 29{,}400$.

## APPLICATION TO SILICATE ANALYSIS

Although the determination of total iron (*i.e.*, in the presence of an added excess of a reducing agent) in silicates by chemical means is a relatively simple matter, well-documented special problems[19,20] are frequently encountered in the determination of iron(II). One of these is aerial oxidation during or after the decomposition step which often necessitates the use of special techniques such as decomposition by acid or fusion under inert atmospheres. Wilson[21] minimized the risk of oxidation by acid attack of the finely ground sample at room temperature in the presence of ammonium vanadate, the unreduced oxidizing agent being determined titrimetrically with standard iron(II) solution. Schafer[19] and Kiss[22] determined FeO in silicates by hydrofluoric–sulphuric acid decomposition under constant nitrogen flow; the liberated iron(II) was titrated with standard dichromate solution by visual and potentiometric end-point detection, respectively. For the spectrophotometric determination of iron on the microanalytical scale the most important reagents are Bipy, Phen and less frequently TPTZ. As part of a comprehensive scheme for minerals and rocks, Riley and Williams[23] determined FeO by dissolving a 5-mg sample in a hydrofluoric–sulphuric acid mixture in a PTFE tube, and measuring the absorbance of the iron(II)–Bipy complex formed subsequently. These authors pointed out not only the absolute necessity of excluding air in the decomposition process but also the interference caused by the presence of fluoride; both gave low recoveries of iron(II) oxide. Nevertheless, satisfactory precision and accuracy were obtained. Langmyhr and Graff[24] attempted to determine FeO from the solution prepared by hydrofluoric acid decomposition of silicates in a PTFE bomb, and although the results were acceptable for samples with low iron content, there was a predictable decrease in recovery for all silicates high in FeO. Subsequently they identified the compound $Fe(II)Al(Fe(III))F_5 \cdot x\ H_2O$ among several insoluble or sparingly soluble precipitates which were formed on hydrofluoric acid attack of silicates. In an effort to eliminate oxidation problems, Shapiro[25] dissolved 10-mg samples in the presence of an excess of Phen. However, colour instability was noted as the chromogen slightly decomposed on heating, and acceptable results could be obtained only by adhering to identical heat treatment of both the standards and the samples.

### *Preliminary studies*

In order to ascertain the feasibility of using PPDT-DAS directly in the dissolution process, qualitative experiments were carried out by mixing a finely ground silicate with PPDT-DAS solutions prepared in various acid combinations

TABLE II

RECOVERIES OF IRON(II) OXIDE IN SILICATE DISSOLUTION

| *Acid mixture + 2% PPDT–DAS* | *Recovery (%)* | | *Conditions* |
|---|---|---|---|
| | *Diabase W-1* | *Basalt BCR-1* | |
| Conc. HF | 77.7 | 62.2 | 20 min heating under |
| 20% HF | 83.4 | — | Overnight standing in under $CO_2$ |
| | 78.5 | — | Overnight standing in under $CO_2$ + 20 min heating |
| | 86.8 | — | 20 min heating under |
| 20% HF + 10% $H_2SO_4$ | — | 78.3 | 20 min heating in air |
| | — | 79.0 | 20 min heating in air followed by 90 min standing[a] |
| | — | 77.1 | 20 min heating in air followed by 48 h stan |
| 10% HF + 5% $H_2SO_4$ | — | 90.3 | 20 min heating in air |
| | — | 91.5 | 20 min heating in air followed by 90 min standing[a] |
| | — | 91.5 | 20 min heating in air followed by 48 h stan |
| | — | 77.5 | 90 min standing in ai |
| | — | 80.3 | 90 min standing und $CO_2$ |
| | — | 97.7 | 48 h standing in air in |
| | — | 96.5 | 48 h standing in air i dark + 20 min heatin |
| | — | 95.0 | 48 h standing in C dark |
| | — | 96.5 | 48 h standing in C dark + 20 min heatin |
| | — | 99.0 | 72 h standing in air in |
| 10% HF + 90% $H_2SO_4$ | — | ~100 | 10 min heating in C 100°C |
| | — | ~100[b] | 10 min heating in C 100°C |
| | — | ~100[c] | 10 min heating in C 100°C |
| | — | 25 | 10 min standing in in cold |
| 10% HF + 10% $H_2SO_4$ in DMF | — | 66.8 | 15 min heating in air |
| 10% HF + 5% $H_2SO_4$ in DMF | — | 78.7 | 4 min heating at b. DMF |

[a] Denotes the re-measurement of absorbance of diluted solutions.

[b] USGS Dunite DTS-1.

[c] JGS Basalt JB-1.

($HF + H_2SO_4$), including solutions of ammonium and potassium fluorides in weak sulphuric acid (buffering effect) and fluoboric–sulphuric acid mixtures, and observing the rate of colour formation in the cold or on heating. The colour formation was practically unaffected by any concentrations of hydrofluoric acid but became markedly sluggish when more than 15% sulphuric acid was present. Ammonium or potassium fluoride attacked silicates only slightly in boiling solutions as evidenced by the formation of the magenta colour, but the attack increased significantly when sulphuric acid (5–10%) was added. Likewise, fluoroboric acid released more iron in the presence of sulphuric acid than alone. The highest rate of colour formation was observed with 10% $HF + 5\%\ H_2SO_4 + 2\%$ PPDT-DAS mixture when the suspended silicate powder was allowed to stand in the cold or heated. Hot phosphoric acid dissolved a fairly wide range of silicates, but it retarded colour formation by competing complexation.

In the second phase of experiments concerned with the quantitative measurements of FeO in four international standard rocks, the finely ground sample (1–3 mg) was dissolved in a variety of acid compositions containing hydrofluoric and sulphuric acids and the reagent PPDT-DAS, and after buffering, the intensities were measured at 570 nm. The most probable values of FeO were taken as 100% recovery; the results (an average of 2 separate weights) are shown in Table II.

The main conclusions are as follows.

(1) The use of concentrated or diluted hydrofluoric acid is undesirable even if the iron(II) chelate formation is possible under the variety of conditions tested.

(2) The fastest colour formation takes place with 10% $HF + 5\%\ H_2SO_4 + 2\%$ PPDT-DAS; this also coincides with the highest recovery, but a 100% recovery of FeO for the basalt BCR-1 could not be achieved.

(3) Neither the immediate heating of the rock powder in contact with any strengths of acid mixtures, nor heating after prolonged standing improved the yield. Possibly, a slow rate of competing fluoro-complex formation is accelerated by heat.

(4) A suppression of fluoro-complex formation was expected in anhydrous DMF medium, but this was unsuccessful, even though the colour formation was almost instantaneous on heating.

(5) The most successful (*i.e.*, almost always quantitative) recovery experiments were obtained with a 2% solution of PPDT-DAS dissolved in 10% hydrofluoric acid and 90% sulphuric acid under $CO_2$ at 100°C. Since hydrofluoric acid behaves as an anhydrous acid in this mixture, dissolution is rapid even for refractory silicates such as corundum eclogite and garnet. Probably, under anhydrous acidic conditions, the silicon liberated from the silicate matrix by-passes the fluorosilicic acid[24] stage, and forms silicon tetrafluoride. At the same time, the strong sulphuric acid medium enhances the displacement of fluoride from the salts to yield sulphates. The coloured iron(II) chelate forms instantly on dilution and buffering.

The potential of the colour formation with PPDT-DAS dissolved in 10% $HF + 5\%\ H_2SO_4$ was also investigated. The rate of iron(II) release from standard rocks (1–3 mg samples) was measured spectrophotometrically after 5,15,30 and 60 min contact with the acidic PPDT-DAS solutions. The rate of iron(II) release by acid attack on various silicates is shown in Fig. 3.

The remarkable difference in dissolution velocity of several rock types is a clear indication of their relative resistance towards acidic leach. Not surprisingly, the velocity is also influenced by the particle size as shown clearly by the curves A and B for BCR-1 basalt. The fastest dissolution rates were observed for acidic rocks such as granite, granodiorite, andesite and tonalite in 10% HF + 5% $H_2SO_4$ + 2% PPDT-DAS, whereas the intermediate and basic rocks (*e.g.*, basalt, basanite and syenite), after an initially rapid colour reaction, produced extremely low gradient curves which required up to 48 h of standing to approach 100% recovery. Ultramafic rocks (*e.g.*, peridotite and dunite) occupy an intermediate position for dissolution rates, but attack on refractory chromite (frequently present) is questionable. In an effort to accelerate the dissolution rates for basaltic rocks, various other acid-mixture concentrations were unsuccessfully tested. Even when the initial rates of acid attack was increased, the flat plateau equilibration as well as the effect of atmospheric oxidation became more pronounced. The extreme case of silicate dissolution within these experiments is shown by decomposing the basalt BCR-1 in a (1 + 1) hydrofluoric–sulphuric acid mixture containing the reagent (see curve no. 3). Since no complex formation takes place under these conditions, the decrease in FeO recovery within 2 h of standing at room temperature is a clear indication of aerial oxidation. The behaviour of the chemically reactive synthetic glasses used in experimental petrology (*i.e.*, lunar basalt no. 14310, curve G and olivine-melilitite, curve F) in 10% HF + 5% $H_2SO_4$ + 2% PPDT-DAS is interesting: since there is no complication arising from the presence of minerals as in natural rocks, the sample decomposition is extremely fast; the failure to reach 100% recovery seems to be due to fluoride interference, and the slow decrease of the plateau value initially reached in the course of 60 min standing reflects aerial oxidation.

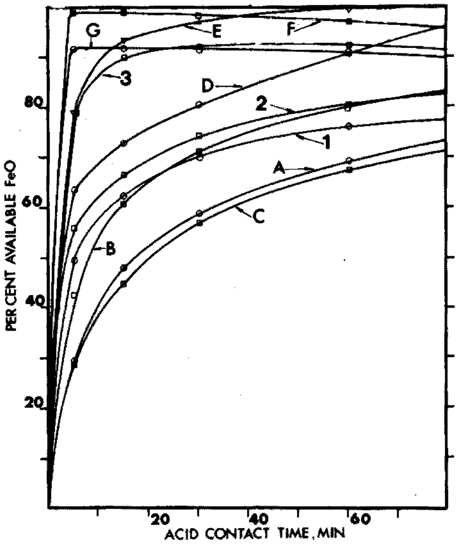

Fig. 3. Rate of iron(II) release from silicate matrix by acid attack at room temperature. The acid mixture used was 10% HF + 5% $H_2SO_4$ + 2% PPDT-DAS for curves A (basalt BCR-1, coarse), B (basalt BCR-1, fine), C (basalt JB-1), D (granite G-2), E (granodiorite JG-1), F (olivine melilitite glass) and G (lunar basalt glass No. 14310). Curves 1–3 represent variations in acid composition for basalt BCR-1: No 1, 20% HF + 10% $H_2SO_4$ + 2% PPDT-DAS; No. 2, 30% HF + 15% $H_2SO_4$ + 2% PPDT-DAS; and No. 3, 50% HF + 50% $H_2SO_4$ + 2% PPDT-DAS.

### *Attempted elimination of fluoride interference*

As already pointed out, the presence of free hydrofluoric acid in the silicate dissolution causes low results for high FeO-bearing samples[23, 24] through the formation of fluoro-complexes containing ferrous iron. Usually, boric acid, aluminium(III) or beryllium(II) has been used to render free hydrofluoric acid harmless after the sample decomposition is complete. In the present study, aluminium(III) was found to be only marginally more effective in complexing free fluoride than boric acid, but the somewhat lower recoveries could not be increased for basaltic rocks. This problem is demonstrated by the analysis of the basalt BCR-1: eight sample dissolutions were allowed to stand for two days, and the intensely coloured solutions were diluted to volume, with aluminium(III) added, and measured at 570 nm. After 21 days of equilibration, the original values increased by 5% approximating total recovery, but after this period of standing the absorbances remained essentially constant.

### *Performance of other ferroins in the acidic system*

Sulphonated ferroins having lower sensitivities for iron(II) than PPDT-DAS could be advantageously employed for the analysis of a wider range of silicates (*e.g.*, permitting larger samples to be taken). In addition to PPDT-DAS, several other sulphonated ferroins were examined for comparison of their chelating performance under acidic conditions. Solutions of the following reagents were prepared in a 10% HF + 5% $H_2SO_4$ mixture: phen-5-sulphonic acid (1), bathophen-disulphonic acid (2), the sulphonated derivatives of 3-(-pyridyl)-5,6-diphenyl-1,2,4-triazine (3), 3-(4-ethyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (4) and 3-(1-isoquinolyl)-5,6-diphenyl-1,2,4-triazine (5). A few milligrams of silicate were suspended in the acidic reagent solutions and set aside briefly. The relative velocity of colour formation was then compared on a qualitative basis. Reagents (1) and (2) were most sensitive to acid and the iron(II) chelates formed too slowly to inhibit aerial oxidation. Reagent (5) occupied an intermediate position with its blue chelate formation. Reagents (3) and (4), being closely related to PPDT-DAS, reacted much faster than the others as expected, but had noticably slower rates than PPDT-DAS.

## RECOMMENDED PROCEDURES

### *Sample preparation*

Prepare the sample by thoroughly grinding in a small agate or tungsten carbide mortar (depending on the hardness) under acetone to avoid oxidation. The silicate should be as homogeneous as possible and the extremely fine state of subdivision necessary can be attained by repeatedly grinding under a layer of acetone until no grittiness is felt. When the powder is air-dry, further drying at 110°C for 2 h will ensure stable readings on the microbalance. If the silicate is known to be hygroscopic, the best compromise is to equilibrate the sample to ambient air humidity.

### *Method A. Simultaneous decomposition and chelation*

Because of the mild reaction conditions this procedure should be used only for silicates known to decompose easily. Quantitative and qualitative experiments have shown that among rocks granite, granodiorite, dacite, andesite, tonalite, peridotite and dunite decompose with ease at room temperature. Also among minerals biotite, muscovite, lepidolite, phlogopite, feldspar, talc, amphibole and wollastonite can be subjected to this method of decomposition. Depending on the magnitude of iron(II) oxide or the amount of material available, weigh 1–5 mg of sample (CAHN G-2 Electrobalance) into Size No. 1 polyethylene thimbles. By a capillary pipette add a few drops of aqueous 20% acetone solution and carefully rock the contents to yield an even suspension. Add 1.0 ml of acid/reagent solution (10% HF + 5% $H_2SO_4$ + 2% PPDT-DAS) to the suspension and further homogenize with the aid of an electric vibrator. The addition of the acid/reagent solution sometimes encourages coagulation of the suspended particles, but rapid dispersion can be secured if the vibration is continued. Colour formation takes place rapidly by the time the last agglomerate has been homogenized. Cover the thimble with another cut in half and leave it in the dark at room temperature. For granites and granodiorites, overnight standing is sufficient; for all other types of silicates a maximum of 24 h of standing should be allowed. Wash the intensely coloured solutions carefully into 100-ml volumetric flasks containing 10 ml of saturated boric acid, mix well, add 10 ml of 2 *M* sodium acetate buffer, mix again, and dilute to volume by rinsing the thimble and its cover. Measure the absorbance at 570 nm in 10-mm quartz cells against a reagent blank prepared in the same manner. Calculate the FeO concentration using the calibration data based on international standard rocks.

*Method B. Acid decomposition by heating*

The main advantage of this method is that a considerably wider range of silicates can be decomposed successfully, because there is no need to limit the acid concentrations and the sample may be heated for as long as necessary at up to 200°C. The majority of silicate rocks not listed in Method A (*e.g.*, basalt, basanite, pyroxenite and syenite) are decomposed readily by a mixture of 20% HF + 40% $H_2SO_4$ at 100°C in a nitrogen atmosphere. More resistant silicates (*e.g.*, eclogite, garnet and pyroxene) can be brought into solution by a mixture of 10% HF + 90% $H_2SO_4$ at a maximum of 200°C in a PTFE microbomb under nitrogen.

Weigh 1–5 mg of finely powdered sample in a 1.5-ml PTFE thimble, moisten with 3–4 drops of aqueous 20% acetone solution and homogenize carefully by rocking the thimble. Add 6 drops (*ca.* 0.3 ml) of 20% HF + 40% $H_2SO_4$ (saturated with nitrogen), mix briefly, then cover with a PTFE lid, and attach the sample holder to the digestion apparatus without delay. Allow a steady flow of nitrogen to flush the apparatus for 10 min, and then lower it into a steam bath for 20 min. Withdraw the apparatus and allow to cool under nitrogen. After disassembling the sample holder, transfer the contents of the PTFE thimble to a 100-ml volumetric flask containing 10 ml of saturated boric acid and 10 ml of 0.005 *M* PPDT-DAS. Add 10 ml of 2 *M* sodium acetate buffer, mix and dilute to volume by repeatedly washing the thimble. Measure the absorbance at 570 nm in 10-mm quartz cells against a reagent blank prepared in the same manner. Calculate the FeO concentration from the calibration data based on international standard rocks.

Garnet, corundum and eclogite are best decomposed by using a PTFE microbomb as follows. Weigh 1–3 mg of finely powdered sample in a PTFE microbomb (1.5-ml capacity), homogenize with 2–3 drops of concentrated sulphuric acid and add *ca.* 0.3–0.4 ml of 10% HF + 90% $H_2SO_4$ mixture (saturated with nitrogen). Flush the bomb with a current of nitrogen, screw the top securely and mix thoroughly using an electric vibrator. Heat the sample at 100–200°C for 10–30 min. After cooling to room temperature, open the bomb carefully and drive off as much volatile acid fumes as possible in a current of nitrogen. Transfer the contents to a 100-ml volumetric flask containing 10 ml of saturated boric acid, 10 ml of 0.005 *M* PPDT-DAS and 10 ml of 2 *M* sodium acetate buffer. Dilute to volume by rinsing the bomb repeatedly. Mix and measure the absorbance at 570 nm in 10-mm quartz cells against a reagent blank prepared in the same manner. Calculate the FeO concentration using the calibration data based on international standard rocks.

Replacement of the PTFE equipment with inexpensive polyethylene and polypropylene is inadvisable; both plastics are attacked slightly by the concentrated acid mixture at *ca.* 100°C as evidenced by some degree of discolouration. Also the incidence of somewhat high FeO values showed the presence of active carbonaceous material which acted as a reducing agent.

*Method C. Determination of total iron (as* $Fe_2O_3$*)*

Since the use of a protective atmosphere for the silicate dissolution in the measurement of total iron is unnecessary, either method A or B could be expected to function adequately. However, the presence of free hydrofluoric acid causes low results if the fluoride is not expelled by preliminary heating to the stage of sulphuric acid fumes.

Direct measurement of total iron may be carried out as for Method B. If there is adequate amount of sample available the processing of a larger sample weight is preferable to ensure a reasonable degree of homogeneity.

Weigh 10–30 mg of finely powdered silicate into a 10-ml platinum evaporating dish, moisten with a few drops of water and add 1 ml of sulphuric acid (1 + 1). Swirl the contents carefully and add 4 ml of concentrated hydrofluoric acid. Evaporate on a water bath to near dryness, add a further 2 ml of hydrofluoric acid and evaporate again to incipient crystallization. Transfer the dish to a hot plate set on low heat and gradually increase heating until copious fumes of sulphur trioxide are evolved. Dissolve the cooled salts in *ca.* 5 ml of water by warming if necessary and transfer the contents to a 100-ml volumetric flask. Dilute to volume by rinsing the dish thoroughly. Pipette 5–10-ml aliquots into 100-ml volumetric flasks, add 10 ml of 10% (w/v) hydroxylammonium chloride solution, mix and set aside for 15 min. Add 10 ml of 0.005 *M* PPDT-DAS solution followed by 10 ml of 2 *M* sodium acetate buffer, and dilute to volume. Measure the absorbance at 570 nm in 10-mm quartz cells against a blank as reference prepared in the same manner. Calculate the total iron as $Fe_2O_3$ from the calibration data based on international standard rocks.

The results obtained on standard rocks and other materials by methods A, B and C are presented in Table III.

TABLE III

MICRO-ANALYSIS OF IRON OXIDATION STATE IN SILICATES BY PPDT-DAS

| *Sample* | *% FeO* | $S_r$ | *No. of detns.* | *Other values* |
|---|---|---|---|---|
| *Method A* | | | | |
| Granite GH | 0.86 | 2.83 | 4 | 0.84 |
| Granite GA | 1.32 | 2.47 | 4 | 1.32 |
| Granite G-2 | 1.49 | 3.57 | 3 | 1.45 |
| Granodiorite GSP-1 | 2.27 | 1.51 | 7 | 2.31 |
| Granodiorite JG-1 | 1.63 | 2.33 | 4 | 1.63 |
| Andesite AGV-1 | 2.15 | 1.33 | 7 | 2,02, 2.20[a] |
| Tonalite T-1 | 2.96 | 0.97 | 4 | 2.91 |
| Peridotite PCC-1 | 5.34 | 1.12 | 4 | 5.14, 5.24 |
| Dunite DTS-1 | 7.02 | 1.06 | 4 | 6.98, 7.23 |
| Basalt BCR-1 | 8.78 | 0.97 | 10 | 8.80, 8.97 |
| Basalt JB-1 | 5.88 | 1.11 | 4 | 5.98[b] |
| Basalt BR | 6.42 | 0.46 | 6 | 6.57 |
| Corundum eclogite R 372 | 2.08 | 0.34 | 4 | 2.18[c] |
| Biotite | 24.05 | 0.34 | 2 | 23.92[c] |
| Olivine Melilitite glass 2929B + $CO_2$ | 11.39 | 0.36 | 4 | 11.39[c], 11.43[c] |
| Tholeiite Glass B | 1.84 | — | 2 | 1.69[c], 1.74[c] |
| *Method B* | | | | |
| Basalt BCR-1 | 8.91 ± 0.03 | — | 2 | 8.80, 8.97 |
| Basalt JB-1 | 5.96 ± 0.03 | — | 4 | 5.98[b] |
| Basalt BR | 6.64 ± 0.03 | — | 4 | 6.57 |
| *Method C (total iron as $Fe_2O_3$)* | | | | |
| Basalt BCR-1 | 13.46 ± 0.04% $Fe_2O_3$ | | 7 | 13.40 |
| Basalt JB-1 | 8.80 ± 0.03% $Fe_2O_3$ | | 8 | 8.89, 9.04 |
| Olivine Melilitite glass 2929B + $CO_2$ | 13.42 ± 0.05% $Fe_2O_3$ | | 8 | 13.60[c] |

[a] Mean value of 16 microanalyses with TPTZ as chromogen.

[b] Voltametric titration with potassium dichromate.

[c] Other micro-analytical results with Phen as chromogen.

## CONCLUSIONS

PPDT-DAS very nearly fulfills the requirements of an ideal iron chromogen. Its extreme sensitivity and good selectivity are comparable to Terrosite, but unlike Terrosite, its water solubility, broad pH range for maximal colour formation and tolerance of molar acid concentrations in its chelation with iron(II) make it a most useful reagent. The integrated synthetic route leading to PPDT-DAS is relatively simple, which should make the reagent readily accessible for routine analytical applications. In another aspect of this study PPDT-DAS was successfully applied to the spectrophotometric microdetermination of iron(II) oxide in milligram quantities of silicate samples. The novel feature of this application is the simultaneous chelate formation with the release of iron(II) from the silicate matrix in the cold by a solution of PPDT-DAS in hydrofluoric and sulphuric acids. While air oxidation problems were completely eliminated, the necessarily limiting parameters in the optimized procedure left some resistant minerals (*e.g.*, garnet, zircon, tourmaline, chromite and pyrite) largely undecomposed. Consistently good precision and accuracy were obtained for all acidic and ultramafic rocks, but somewhat low results were obtained for basalts or other rock types of intermediate basicity. A fairly wide range of refractories was successfully decomposed in hot concentrated hydrofluoric and sulphuric acid mixtures under an inert atmosphere in a microdigestion bomb, whereby FeO values could be secured with good reliability.

For the simultaneous decomposition and chelation, the most serious problem is the need to use hydrofluoric acid. There is evidence for a slow rate of iron fluoride complex formation which competes with the initially rapid colour reaction often resulting in incomplete recovery of iron(II) oxide. Although various fluoride complexing agents are effective in rendering free hydrofluoric acid harmless, the release of iron from its fluorocomplex by using boric acid, aluminium(III) or beryllium(II) ions was unsuccessful. The fluoride tolerance is improved remarkably by limiting the amount of hydrofluoric acid used in the decomposition methods under heating conditions. Protection from aerial oxidation is imperative in these procedures, otherwise no iron(II)–PPDT-DAS chelation takes place. Application of a high-temperature flux such as lithium tetraborate to the microfusion of a few milligrams of silicate under inert atmospheric conditions and subsequent leaching of the fusion cake in PPDT-DAS solution acidified with sulphuric acid would pose a difficult technical challenge.

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## SUMMARY

The relatively easy accessibility of the ferroin chromogen 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PPDT) and its diammonium disulphonate derivative (PPDT-DAS), is described via an eight-step total synthesis. PPDT-DAS shows extreme resistance to thermal and oxidative degradation and also forms the tris-chelate with iron(II) ions in molar acid concentrations. Maximal colour is formed at pH 3–8 with a molar absorptivity of 29,300 at 570 nm. Only fluoride ($>500$ p.p.m.), EDTA, cyanide and comparable amounts of copper(I) and cobalt(II) interfere. The reagent PPDT-DAS was used for the spectrophotometric microdetermination of FeO in silicates. Any possibility of aerial oxidation was excluded by the simultaneous chelation of iron(II) in the acid decomposition step. More refractory materials were decomposed in PTFE bombs. Good precision and accuracy were obtained for the analysis of 1–5 mg samples with an average relative standard deviation of 1.33%.

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# A ROUTINE METHOD FOR THE DETERMINATION OF ARSENIC IN PLANTS, SEDIMENTS AND NATURAL WATERS

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Arsenic has frequently been separated as its volatile hydride, arsine, before its determination, either directly as the arsine-complex of diethyldithiocarbamate in pyridine or, after oxidation to arsenic(V), by the molybdenum blue procedure. However, the reduction of arsenic(V) to arsine and the evolution of arsine have been reported to suffer from interferences[3,4] and from high blank values[5].

Other methods of separation that have been used are distillation as arsenic trichloride[6], solvent extraction of arsenic trichloride[7] or of the diethylammonium diethyldithiocarbamate complex[8], and coprecipitation with thionalide or of the carbamate complex with copper carbamate[9]. Arsenic(III) has also been determined directly by single-sweep polarography[10]. All of these separation methods require the arsenic to be in the trivalent state which must usually be formed by reduction, and some of the methods require the addition of large amounts of acid which increases the blank value.

Atomic absorption spectrometry has been used for the direct determination of arsenic in aqueous solutions[11]. However, interferences from light scattering are severe, because the absorption band is in the u.v. region, while aspiration of arsine into the flame, although avoiding many potential interferences, suffers from the inherent limitations of arsine evolution.

Arsenic(V) has been separated in the milligram range by homogeneous precipitation as arsenic sulphide[12], and in the microgram range by coprecipitation with molybdenum sulphide[13]; in the latter case, X-ray fluorescence spectrometry was applied. The coprecipitation of arsenic with molybdenum appeared to offer a simple, sensitive and rapid means of separating both arsenic(III) and (V), as well as a low reagent blank value.

In the present work, the coprecipitation procedure was modified so that the precipitate could be collected by centrifugation to allow several samples to be handled simultaneously; the arsenic was then determined by the molybdenum blue procedure as it is sensitive and relatively free from interferences[5]. It was found possible to determine the arsenic content of twenty-two samples (in duplicate with two blanks and two standards) in eight hours over two working days.

## EXPERIMENTAL

### *Apparatus*

Arsenic and molybdenum sulphides were sedimented in pyrex test tubes

(18 × 125 mm, medium wall) by centrifuging at 2,560 g in a MSE mistral refrigerated centrifuge at 15°C.

Pyrex test tubes (22 × 150 mm) were used for the dry and wet ashing of up to 0.2 g of plant material and sediment. Tubes were heated in a 4-cm deep aluminium block resting on a thermostated aluminium frypan.

### *Reagents*

All solutions were prepared with deionized water. All the acids used were of AnalaR grade.

*Sodium hydrogen carbonate–silver oxide reagent.* Mix 25 g of sodium hydrogen carbonate (AnalaR) with 1 g of silver oxide.

*Sodium molybdate–sodium nitrate solution.* Prepare an aqueous solution containing 1.0% (w/v) sodium molybdate and 4.8% (w/v) sodium nitrate.

*Hydrochloric acid wash solution.* Prepare a 1 *M* hydrochloric acid solution and add 0.25 ml of aqueous 2% (w/v) thioacetamide solution and 10 drops of 1.0% (v/v) triton-X100 for each 500 ml of acid.

*Mixed molybdate reagent.* Mix 3.3 ml of 7.5 *M* sulphuric acid, 3.0 ml of 4.8% (w/v) ammonium molybdate solution and 1.0 ml of 0.274% (w/v) potassium antimony tartrate solution (1 mg Sb $ml^{-1}$), and dilute to 31 ml. Dilute 13 ml of freshly prepared 0.88% (w/v) ascorbic acid solution (0.05 *M*) to 31 ml, and mix with the previous solution.

*Reducing solution.* Dissolve 0.56 g of sodium metabisulphite in 29 ml of deionized water. Add 4 ml of 1.4% sodium thiosulphate solution, mix, and add 0.5 ml of 7.5 *M* sulphuric acid solution.

### *Standard arsenic solution*

Prepare a stock solution of arsenic(V) containing 2 mg As $ml^{-1}$ using AnalaR sodium dihydrogenarsenate, after it has been standardized colorimetrically against AnalaR arsenic(III) oxide. Working solutions containing 2 $\mu g$ As $ml^{-1}$ were prepared with deionized water in pyrex glass containers and were found to be stable for at least four months.

### *Treatment of glassware*

All glassware was soaked in detergent, and rinsed with tap water, 0.5 *M* sulphuric acid and finally with distilled water.

### *Preparation of samples for analysis*

Freeze-dried plant material was ground in a small coffee grinder and dried over Linde molecular sieve type 4A.

Sediment samples, obtained from the Waikato river[4], were freeze-dried, ground in an agate mortar and pestle to pass a 120-mesh nylon sieve, and dried as for the plant material.

Water samples, from the Waikato river[4], were filtered within 6 h of collection through a Whatman glass fibre filter GF/C and acidified with 5 ml of 7 *M* hydrochloric acid before storage at 4°C.

### *Determination of arsenic in plants*

*Dry oxidation with sodium hydrogen carbonate–silver oxide reagent.* Mix 0.2 g of plant material and 0.2 g of sodium hydrogen carbonate–silver oxide reagent with a Vortex mixer and ash at 450°C for 6 h in a pyrex test tube. Add 0.8 ml of concentrated hydrochloric acid, warm at 70°C for 15 min, add deionized water, warm at 70°C for 20 min and dilute to 10 ml.

*Wet oxidation with nitric acid.* To 1.0 g of dry ground plant material in a 100-ml conical flask with a B24 joint, add 10 ml of concentrated nitric acid, and place a B24 cone in the flask. Warm gently until the initial reaction subsides. Heat at 115–120°C until the solution clears (about 24 h) and take to dryness at less than 160°C, after removing the B24 cone. Add a little water and take to dryness again. Add 1.0 ml of concentrated hydrochloric acid and heat at 80°C until evolution of gas ceases (about 15 min). Add 9.0 ml of deionized water and heat at 70°C for 15 min. Cool and allow the sediment to settle.

*Precipitation of arsenic sulphide (recommended method).* Take an aliquot of the acidic solution of plant ash, up to 5.5 ml, dilute to 5.5 ml with water if necessary, add 2.0 ml of 10 *M* hydrochloric acid and 0.2 ml of sodium molybdate–sodium nitrate solution and mix with a Vortex mixer. Then add one drop (0.03 ml) of aqueous 0.25% (w/v) sodium dodecylsulphate solution and 0.5 ml of aqueous 2.0% (w/v) thioacetamide solution. Mix each tube, after the final addition, with a Vortex mixer and stand for 10 min. Heat the solution at 60–65°C for 15 min, cool in a stream of air for 0.5 h and centrifuge at 2,500 g for 15 min. Suck off the supernate, wash the precipitate by adding 5 ml of the 1 *M* hydrochloric acid wash solution and mix for 4 s with the Vortex mixer so that the solution spins up the wall of the tube. Centrifuge the precipitate down again at 2,500 g for 10 min. Repeat this washing procedure twice more for extracts of plant material.

*Dissolution of sulphides (recommended method).* Redissolve the sulphide precipitates by adding 0.05 ml of concentrated nitric acid, letting them stand until the elemental sulphur alone has not dissolved (usually the digests were left overnight) and by heating at 120°C for 30 min and for 1.5 h at 150–160°C, so that the nitric acid refluxes on the walls and most is finally driven off. Allow the samples to cool and add a further 0.005 ml of nitric acid to oxidize any reduced molybdenum. After adding 1.00 ml of deionized water to each sample, mix each one and stand for 1–2 h before adding 1.00 ml of the mixed molybdate reagent. Wait for 1–4 h and determine the absorbance at 850 nm in a 1-cm cell, against a reagent blank.

When it is necessary to prevent any arsenate present in the digested precipitate from reacting with the mixed molybdate reagent[15], add 0.5 ml of reducing agent after addition of the water and leave the solution for 30–60 min before adding 0.5 ml of a double-strength mixed molybdate reagent.

### *Determination of arsenic in sediments*

*Digestion with nitric acid.* Heat 0.2 g of ground sediment with 2 ml of concentrated nitric acid in a pyrex test tube at 120°C until the solution clears, and evaporate to dryness at the same temperature with the aid of a heat lamp to avoid bumping. Dissolve the residue in 0.8 ml of concentrated hydrochloric acid, as described for plant material, and dilute to 10 ml.

*Fusion with sodium hydroxide.* Weigh 0.2 g of ground sediment into a nickel crucible and mix with 0.2 g of sodium hydrogen carbonate–silver oxide reagent. Ash at 450°C for 6 h. Fuse the residue with 2 g of AnalaR sodium hydroxide at 370°C for 1.5 h on a hot plate. Cool, add 20 ml of water, heat at 70°C for

1 h, and rinse into a 100-ml conical flask. Add 12 ml of concentrated hydrochloric acid and heat at 70°C until the solution is clear. Evaporate at 100°C until almost dry. Add 8 ml of concentrated hydrochloric acid and about 10 ml of water. Heat at 70°C until the bulk of the material has dissolved. Filter off the precipitated silica under vacuum and wash the precipitate well. Transfer the filtrate to a 100-ml volumetric flask and make up to volume.

*Precipitation of arsenic sulphide.* Carry out as described for plant material.

### *Determination of arsenic in natural waters*

*Evaporation.* Evaporate about 300 ml of filtered water (in aliquots), in a 150-ml round-bottomed flask, to a small volume, and transfer along with washings to a polystyrene test tube (final volume about 10 ml). Precipitate and determine the arsenic in a suitable portion as described for plant material.

## DISCUSSION AND RESULTS

### *Coprecipitation of arsenic sulphide*

The coprecipitation procedure described by Reymont and Dubois[13] failed to yield a precipitate which could be recovered by centrifuging at 2,500 g. However, it was found that by increasing the molybdenum added from 0.2 mg to 2 mg, using 2 *M* hydrochloric acid in place of perchloric acid, and adding the neutral detergent, triton-X100, resulted in coagulation of the sulphide precipitate. The neutral detergent, triton-X100, did not precipitate arsenic completely in the presence of silica, however, (see below) and while the anionic detergent, sodium dodecyl sulphate, almost overcame this interference, the recovery of standards alone tended to fluctuate. This was overcome by the addition of nitrate, which appeared to increase the number of sulphide particles and coagulated the precipitate so that it was not readily dislodged by sucking out the supernatant liquid. The coagulant, toluene-3,4-dithiol[14], did induce a voluminous precipitate but the recovery of arsenic standards was reduced.

As well as reducing the variability of recovery for standards alone, the addition of nitrate increased the recovery slightly for both standards and samples, so that values found for samples of sediment, river water and an aquatic weed remained the same within experimental error.

### *Digestion of the precipitate*

This precipitate was dissolved in nitric acid by heating at 120°C and then at 150–160°C to reflux the acid on the walls. The latter step was found to be essential to avoid a reduced colour yield with less than 1 μg of arsenic in the molybdenum blue reaction. It appeared that colour development alone was inhibited since that from sodium arsenate added to a blank sample was equally affected. Such neutral and cationic detergents have been reported to reduce the colour development in phosphorus determinations[16].

### *Recovery of arsenic(V)*

The recovery of arsenic(V) carried through the procedure was 99% for 2 μg of arsenic. Linear calibrations graphs were obtained over the range 0.02–8 μg arsenic (absorbance 0.002–0.876).

*Method of oxidation for plant tissue*

Although many investigators have reported losses of arsenic on wet ashing with sulphuric acid–nitric acid mixtures, Gorsuch[17] considered that such losses in fact occurred after the digestion. Down and Gorsuch[18] found that radioactive arsenic was retained on digestion of cocoa and sodium chloride with sulphuric acid–nitric acid mixtures, whereas sulphuric acid–hydrogen peroxide digestion in the presence of sodium chloride caused large losses. Probably the nitric acid prevents the formation of arsenic(III) which would voltatilize as arsenic trichloride (b.p. 130°C). Nitric acid digestion alone was found by Portman and Riley[5] to retain added arsenate completely.

Dry ashing at 450°C resulted in the loss of 21% of the arsenic compared with nitric acid digestion (Table I), as has been reported by other investigators[19]. The addition of magnesium oxide to the plant material, as recommended by Albernethy and Gibson[20] for coal, retained only slightly more arsenic. The equally volatile element, sulphur, can be retained on dry ashing plant material and soil with sodium hydrogen carbonate and silver oxide[21]. The dry ashing of *Ceratophyllum* with these two reagents retained the arsenic within the limits of experimental error. Ratios of reagents to plant material from 4:1 to 1:1 had no apparent effect on the amount of arsenic found (Table I). The blank value for the reagent alone was less than 0.01 μg As $g^{-1}$ of reagent.

TABLE I

THE EFFECT OF THE METHOD OF OXIDATION

*Dry ashing at 450°C*

| *Plant material[a] (mg)* | *Addition* | *As found[c] (μg $g^{-1}$)* |
|---|---|---|
| 100 | — | 662 |
| 100 | MgO (50 mg) | 680 |
| 100 | MgO (100 mg) | 718 |
| 100 | $NaHCO_3/Ag_2O$(100 mg) | 842 |
| 100 | $NaHCO_3/Ag_2O$(200 mg) | 850 |
| 50 | $NaHCO_3/Ag_2O$(200 mg) | 845 |
| 25 | $NaHCO_3/Ag_2O$(200 mg) | 852 |
| 100 | $NaHCO_3/Ag_2O$(100 mg)<br>Then fused with NaOH (2 g) | 843 |

*Wet ashing*

| *Plant material* | *Addition* | *As found (μg $g^{-1}$)* |
|---|---|---|
| 100 | Nitric (2 ml)[b] | 846 |
| 100 | Nitric (2 ml)+perchloric (1 ml) | 852 |

[a] Dried ground *Ceratophyllum demersum.*

[b] Digested with acid in a 22 × 150 mm test tube at 120°C and dried at 160°C.

[c] The sulphides were precipitated with 0.5 ml of sodium molybdate solution and triton-X100 (1 drop. 0.5%).

Wet ashing of the plant material with nitric acid alone appeared to oxidize all of the organic matter. The addition of perchloric acid and subsequent drying of the residue at 160°C made little change to the arsenic content found (Table I).

Fusion with sodium hydroxide of the residue from dry oxidation of the plant material also gave a similar value for the arsenic content.

Wet ashing with nitric acid or nitric acid–perchloric acid, dry ashing in the presence of sodium hydrogen carbonate together with silver oxide as an oxidant, and fusion with sodium hydroxide, were all equally effective in retaining and oxidizing arsenic in small samples of *Ceratophyllum*. Later, it was found that in larger samples (2 g) of tomato shoots, complete destruction of carbon by dry ashing was difficult, with the result that recovery of added arsenic was incomplete and wet ashing with nitric acid was necessary.

### *Interferences*

*Sulphides precipitated in acidic solution.* Sb(III), Hg(II), Ag, Sn(IV) and Bi(III) (0.5 g of each together) were found by Reymont and Dubois[13] to coprecipitate with arsenic and molybdenum but to have no effect on the recovery of arsenic over a range of acid concentrations from 0.7 to 4.9 *M* perchloric acid. Of these elements, Bi(III), Hg(II) and Ag (1 mg separately) were found by Portman and Riley[5] to reduce the colour yields of the reaction by less than 4%. Tin(IV) (10 μg) interfered more seriously while antimony(III) (10 μg) had no effect. Copper(II) interfered because of its own absorbance at 850 nm.

Table II shows that, in the present method, copper(II) both absorbed at 850 nm and reduced the recovery of arsenic. The latter may be related to the formation of a bulky precipitate of copper(I) chloride formed after reduction of the copper by the reagent. However, these elements are not likely to occur in quantities that would cause such significant interference in biological materials.

*Removal of silica and phosphorus interference.* River water samples which appeared to contain much silica, reduced the amount of precipitate and the recovery of added arsenic when triton-X100 was used. Silicic acid solutions prepared from sodium metasilicate and allowed to stand for four days interfered strongly with the precipitation of arsenic sulphide (Table III). Since freshly prepared silicic acid had little effect on the recovery of arsenic, it is likely that polymerized silicic

TABLE II

THE EFFECT OF COPPER(II) ON THE RECOVERY OF ARSENIC

(Precipitation was carried out with 0.2 ml of $NaMoO_4$ solution and SDS. The colour was developed on a total volume of 2.0 ml. The net absorbance at 850 nm was determined by subtracting the reagent blank.)

| *mg Cu(II) present* | *μg As present* | *Net absorbance* |
|---|---|---|
| 1 | 0 | 0.033 |
| 1 | 2 | 0.239 |
| 0 | 2 | 0.218 |

TABLE III

THE EFFECT OF SILICA ON THE RECOVERY OF ARSENIC

| *Si (mg)*[a] | *As (μg)*[b] | *Net absorbance*[c] *(+triton-X100)* | *% Recovery*[d] | *Net absorbance*[c] *(+SDS)* | *% Recovery*[d] |
|---|---|---|---|---|---|
| 0 | 2 | 0.215 | 100 | 0.215 | 100 |
| 15 | 0 | 0.000 | | 0.006 | |
| 15 | 0 | | | 0.000[e] | |
| 1 | 2 | 0.214 | 100 | 0.215 | 100 |
| 5 | 2 | 0.214 | 98 | 0.217 | 100 |
| 15 | 2 | 0.215 | 97 | 0.218 | 98 |
| 5[f] | 2 | 0.008 | 4 | 0.213 | 97 |
| 15[f] | 2 | 0.005 | 2 | 0.213 | 95 |

[a] Added as sodium metasilicate.
[b] Added as sodium arsenate.
[c] Colour developed in a total volume of 2.0 ml.
[d] Corrected for the arsenic contamination of the silica solution.
[e] Reducing agent added before colour development.
[f] Stood acidified for 4 days.

TABLE IV

THE RECOVERY OF ARSENIC FROM CONCENTRATED WAIKATO RIVER WATER

| | | |
|---|---|---|
| *μg As added* | 0 | 2 |
| *μg As found + triton-X100*[a] | 0.41 | — |
| *μg As found + SDS* | 1.91[b] | 3.88 |

[a] One drop 0.5% added to solution.
[b] This amount was found in 150 ml of water.

acid prevents the precipitation of sulphides.

This interference of silica was almost overcome by the use of the anionic detergent sodium dodecyl sulphate, in place of triton-X100 (Table III). With river water samples, however, there remained some slight interference (Table IV), the recovery of added arsenic(V) being reduced to 85–95%. It is therefore necessary to add standard arsenic(V) to a duplicate sample to correct for this.

Phosphate could seriously interfere since it is usually present in plant material in the range 0.1–1.0%. After the precipitate had been washed three times with 1 *M* hydrochloric acid, the absorbance caused by phosphate (8 mg P added) was 0.005. The residual contamination appeared to be within the precipitate since washing it 4 times reduced the absorbance by 0.001. The absorbance caused by phosphate was reduced to 0.001 when sodium dodecyl sulphate was used to coagulate the sulphides in a solution of ashed maize shoot (0.5 g) containing 3.4 mg of phosphate, whereas that in triton-coagulated precipitates ranged from 0.008 to 0.034.

While sodium dodecyl sulphate almost eliminated the interference of silica and phosphate in the procedure, the recovery of standard arsenic samples fluctuated slightly. This was overcome by the addition of 9 mg of nitrate to each tube before the thioacetamide; the precipitate coagulated and was much harder to dislodge when the supernate was sucked out.

Although the sulphides were then precipitated in the presence of sodium dodecyl sulphate, the precipitate was washed with 1 *M* hydrochloric acid containing triton-X100, since it seemed to wet the precipitate better than SDS.

### *Molybdenum*

The molybdenum used to carry down the arsenic sulphide can increase the blank value on development of the colour[5]. Increased blank values were found after sodium dodecyl sulphate had been used and it appeared that a greater quantity of molybdenum sulphide precipitated, leading to a white insoluble solid after nitric acid digestion. This blank was reduced by using 0.2 ml of sodium molybdate solution, a step which had no effect on the recovery of arsenate (Table V). For the solutions of digested plant material equivalent to 0.5 g of plant material, the volume was further reduced to 0.04 ml because the sulphide precipitates were readily formed.

### *Precision and accuracy*

Some sediment samples analysed by the modified Gutzeit procedure[1] were found[4] to prevent complete recovery of added arsenate. The arsenic contents of a sediment and of *Ceratophyllum* determined by both the present method and the modified Gutzeit methods are shown in Table VI. The two methods agree within

TABLE V

THE RECOVERY OF ARSENATE WITH DIFFERENT QUANTITIES OF MOLYBDENUM[a]

| *Sodium molybdate solution (ml)* | *As(V) (μg)* | *Net absorbance* |
|---|---|---|
| 0.1 | 0.1 | 0.012 |
| 0.1 | 2.0 | 0.210 |
| 0.5 | 0.1 | 0.012 |
| 0.5 | 2.0 | 0.214 |

[a] Determined in the presence of sodium dodecyl sulphate without nitrate.

TABLE VI

COMPARISON OF THE MODIFIED GUTZEIT PROCEDURE WITH THE PRESENT METHOD

| *Sample analysed* | *Method* | *μg As g⁻¹* |
|---|---|---|
| Waikato river sediment[a] | Gutzeit, result uncorrected | 690 |
| Waikato river sediment[a] | Gutzeit, result corrected for reduced recovery of added standard | 900 |
| Waikato river sediment[a] | Present method | 910 |
| *Ceratophyllum demersum* | Gutzeit method | 1050 |
| *Ceratophyllum demersum* | Present method | 1020 |
| *Ceratophyllum demersum* | Present method | < 5[b] |

[a] Wet ashed.

[b] Reducing agent added before developing the colour

TABLE VII

RECOVERY OF ARSENATE ADDED TO DIGESTS[a]

| *Solution* | *As added (μg)* | *As found (μg)* | *% Recovery* |
|---|---|---|---|
| Plant ash | 0 | 7.14[a] | — |
| | 2 | 9.18[a] | 102 |
| Sediment, wet-ashed | 0 | 0.26 | — |
| | 5 | 5.22 | 99 |
| Sediment, fused with NaOH | 0 | 0.09 | — |
| | 2 | 2.10 | 101 |

[a] Determined in the presence of sodium dodecyl sulphate without nitrate.
[b] Colour developed in a total volume of 4 ml.

experimental error, after the reduced recovery of arsenic in the sediment by the Gutzeit method has been corrected for. The selectivity of the present method was demonstrated by the lack of colour development when the reducing reagent was added before the mixed molybdate reagent. Arsenic(V) added to solutions of plant ash, digested sediment and fused sediment was also recovered within experimental error (Table VII). These results suggest that the interference found in the evolution of arsine from digested sediment samples did not apply to the precipitation of arsenic as the sulphide.

The mean and standard deviation of ten determinations on aliquots of a sample of dissolved *Ceratophyllum* ash was 2.72 ± 0.016 μg As (coefficient of variation, 0.6%) while those on aliquots of a fused sediment were 0.078 ± 0.014 μg As (coefficient of variation, 18%). The absorbance of a blank carried through the procedure was usually 0.001 (volume, 2 ml), which was greater than that of the mixed molybdate reagent alone (0.001–0.002).

A sample of maize shoot, grown in the glasshouse with nutrient solutions in peat, perlite and sand media, contained 0.08 μg As $g^{-1}$ (dry weight). This compares with the arsenic content of 0.13 μg $g^{-1}$ reported for kale powder by Bowen[22]. The addition of 0.5 μg As $g^{-1}$ of maize shoot resulted in the recovery of 0.54 μg As $g^{-1}$, an increase of 8% (determined without the addition of nitrate). Although it appears that not all of the arsenic in the solution of plant ash was precipitated, levels of arsenic in plant tissue of about 1 μg $g^{-1}$ can be determined with an accuracy of better than 5%.

## SUMMARY

Coprecipitation with molybdenum sulphide in 2 *M* hydrochloric acid solution is proposed for the recovery of microgram amounts of arsenic from solutions prepared by ashing plants and sediments, and from natural waters. After dissolution of the sulphide precipitate, arsenic is determined photometrically by a molybdenum blue method. The overall recovery for the procedure is 99%. Arsenic was determined in solutions of plant ash at the 2-μg As level with a coefficient of variation of 0.6%.

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# THE APPLICATION OF COLUMN REDOX–EXTRACTION CHROMATOGRAPHY TO THE SEPARATION OF SOME ACTINIDE ELEMENTS

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The application of extraction chromatography to the determination of several radionuclides in various materials has recently been reported[1–3]. Furthermore, it has been demonstrated that a redox reagent such as tetrachloroquinone or tetrachlorohydroquinone can be supported on a polymeric material, and that some ions can be quantitatively reduced or oxidized on these electron-exchange columns[4–6]. Scibona *et al.*[7] have evaluated the efficiency of the electron exchange at the interface between tetrachlorohydroquinone in an organic solvent and a metal ion in an aqueous solution. Coleman and Weaver[8] have used 2,5-di-tert-butylhydroquinone dissolved in an organic phase for the selective stripping of plutonium by reduction to plutonium (III). The possibilities of redox chromatography have been emphasized in a recent Russian review[9], which reports the results obtained with columns consisting of a solid material (adsorbing substances and ion-exchange resins) supporting a redox compound.

The present paper describes a new technique in which both the extractant and the reducing agent are supported on an inert polymeric material; some chromatographic separations pertaining to neptunium and plutonium at trace level have been performed on these redox–extraction columns.

## EXPERIMENTAL

### *Equipment and reagents*

A scaler ASPN (Italy) connected to a 2-in. ZnS(Ag) detector was used for the α-counting.

α-Spectrometry was performed with a solid-state detector connected to an Ortec (U.S.A.) chain and to a Laben 400-channel analyzer (Italy).

The chromatographic columns made of Perspex had an internal diameter of 1 cm.

Tetrachlorohydroquinone (Fluka, Switzerland), 2,3-dichloro-1,4-naphthaquinone and 1,5-dichloroanthraquinone (BDH, England), 2,5-di-tert-butylhydroquinone (Koch–Light, England), and 2,5-di-tert-pentylhydroquinone (Eastman–Kodak, U.S.A.) were used as the redox reagents.

2,3-Dichloro-1,4-naphthahydroquinone was obtained by reducing the quinone form on the column with a tin(II) chloride solution. 1,5-Dichloroanthrahydroquinone was prepared by means of catalytic reduction with hydrogen.

Tri-*n*-octylphosphine oxide (TOPO; Eastman–Kodak, U.S.A.), was employed as the extractant.

Microthene-710 (microporous polyethylene; 100-170 mesh; Columbia Organic Chem., U.S.A.) was used as the inert support for the redox-extracting system.

All the other reagents were analytical grade (C. Erba, Italy).

The actinide elements ($^{233}$U, $^{237}$Np, $^{238}$Pu, $^{241}$Am) were supplied by the Amersham Centre (England) and their purity was checked by α-spectrometry.

### *Procedure*

Amounts corresponding to about 10,000 d.p.m. of each radionuclide were used for the separation tests. The elution diagrams were obtained by collecting 2-ml portions of the eluate; the activities of these fractions were measured after the aqueous solution had been evaporated. α-Spectrometry was performed when any overlapping of two α-emitters in the elution diagram occurred. When hydrofluoric acid solutions were used, the hydrofluoric acid was eliminated by previous evaporation in Teflon beakers.

### *Preparation of redox extraction columns*

*TCHQ–TOPO column.* 100 mg of tetrachlorohydroquinone (TCHQ) dissolved in 0.5 ml of diethyl ether were added to 3.5 ml of 0.1 *M* TOPO in cyclohexane; the final solution was taken up on 5 g of Microthene-710 and the slurry was transferred to the chromatographic column with 6 *M* hydrochloric acid.

*DCNHQ–TOPO column.* 100 mg of 2,3-dichloro-1,4-naphthaquinone were dissolved in 5 ml of acetone and the solution was added gradually to 2.5 g of Microthene-710. After each addition, the solvent was evaporated by stirring at room temperature under a gentle flow of warm air. This mixture was transferred to a chromatographic column and the compound was reduced by percolating a warm solution of tin(II) chloride in concentrated hydrochloric acid through the column. Complete reduction occurred in a few minutes and the colour changed from yellow to pale violet. The Microthene–DCNHQ mixture was first washed batchwise with concentrated hydrochloric acid and then with distilled water until the washings were neutral. The wet powder was collected on a sintered glass filter of high porosity, dried at 100°C and mixed with 2 ml of 0.1 *M* TOPO in cyclohexane; this mixture was finally transferred to a chromatographic column.

*DBHQ–TOPO column.* A single cyclohexane solution containing 2,5-di-tert-butylhydroquinone (DBHQ; 0.1 *M*) and TOPO (0.1 *M*) was prepared; 2 ml of this solution were mixed with 2.5 g of Microthene-710 and the slurry was transferred to the column with 6 *M* hydrochloric acid.

*DPHQ–TOPO column.* The column with 2,5-di-tert-pentylhydroquinone (DPHQ) was prepared as described for the DBHQ–TOPO column.

It was not possible to prepare a column of 1,5-dichloroanthrahydroquinone, as this compound was rapidly oxidized to the quinone form.

All the columns had an internal diameter of 1 cm and a height of about 10 cm.

## RESULTS

Preliminary tests were carried out to study the retention of the above four stable hydroquinones supported with TOPO on Microthene-710 when washed with 6 *M* hydrochloric acid. The TCHQ–TOPO column showed a substantial loss of the reductant; DCNHQ was better retained on the column, and this reductant was employed[10] for the reduction of plutonium to Pu(III), and neptunium to Np(IV). However, this reductant became progressively superseded, because DBHQ and especially DPHQ, which also gave the same reductions, showed better features as far as retention on the Microthene-710 and the preparation of the column were concerned.

In effect, a DPHQ–TOPO column did not show any appreciable loss of the reductant or the extractant after washing with 3 l of 6 *M* hydrochloric acid; in addition, DPHQ is sufficiently soluble in cyclohexane. On account of these factors, DPHQ was selected for further experiments.

First of all, the behaviour of a TOPO column with respect to the different valence states of plutonium and neptunium, prepared as suggested by Foti and Freiling[11], was studied. Pu(III) and Np(V) were not retained, while Pu(IV), Pu(VI), Np(IV), and Np(VI) remained on the column and could be eluted with 1 *M* hydrofluoric acid; these results are consistent with the liquid–liquid extraction curves of the various valence states of plutonium[12].

Four different columns were prepared to demonstrate the reducing capacity of a DPHQ–TOPO column with respect to plutonium and neptunium in 6 *M* hydrochloric acid: the results, reported in Table I, show that a complete reduction of Pu(VI) and Pu(IV) to Pu(III), and of Np(VI) and Np(V) to Np(IV), can be obtained when a TOPO–DPHQ column is used.

The reducing effect of this column was also studied as a function of the flow rate. As expected, the reduction of plutonium to Pu(III) and of neptunium to Np(IV) in 6 *M* hydrochloric acid was inversely proportional to the flow rate of the solution (Fig. 1); it appeared also that a reduction greater than 99% was obtained when a flow rate of 0.5 ml min$^{-1}$ was used; therefore this value was chosen for the subsequent separations.

On the basis of the preliminary results described, three separations of actinide elements were carried out, *i.e.* Pu–Np, Pu–U and Am–Np.

As Fig. 2 shows, it was not possible to separate plutonium from neptunium

LE I

UCTION OF PLUTONIUM AND NEPTUNIUM BY A MICROTHENE–TOPO–DPHQ COLUMN

| *of column* | *Pu(III) (%) in 20 ml 6 M HCl* | *Pu(IV)+Pu(VI) (%) in 20 ml 1 M HF* | *Np(V) (%) in 30 ml 6 M HCl* | *Np(IV)+Np(VI)(%) in 20 ml 1 M HF* |
|---|---|---|---|---|
| othene PO | 54 | 46 | 30 | 70 |
| othene PO–DPHQ | >99 | <1 | <1 | >99[a] |

bably only Np(IV).

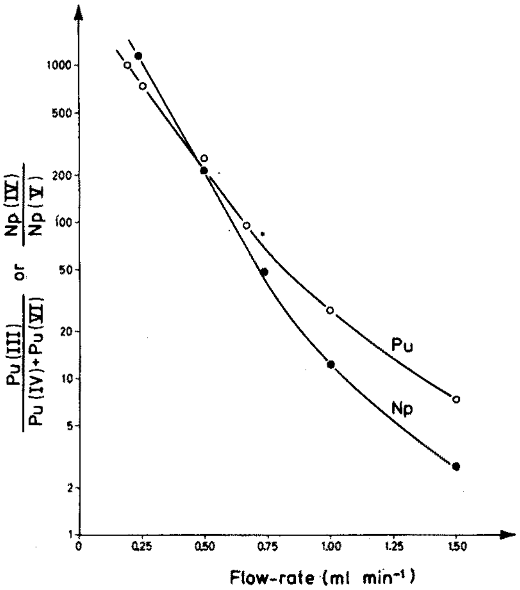

Fig. 1. Reducing effect of supported DPHQ on Pu(IV) and Pu(VI), and on Np(V) and Np(VI), as a function of the flow rate.

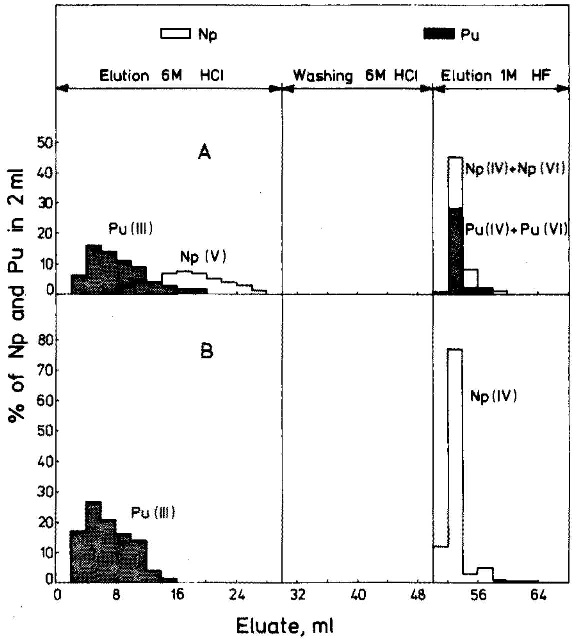

Fig. 2. Separation of neptunium and plutonium in 6 $M$ HCl. (A) Microthene–TOPO column; (B) Microthene–TOPO–DPHQ column.

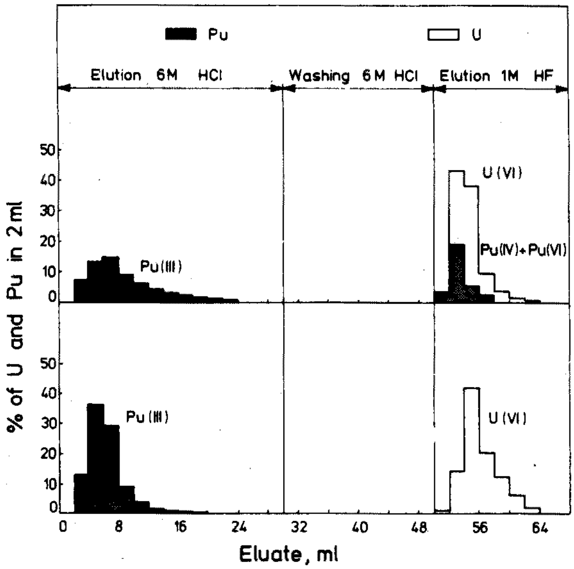

Fig. 3. Separation of uranium and plutonium in 6 *M* HCl. (A) Microthene–TOPO column; (B) Microthene–TOPO–DPHQ column.

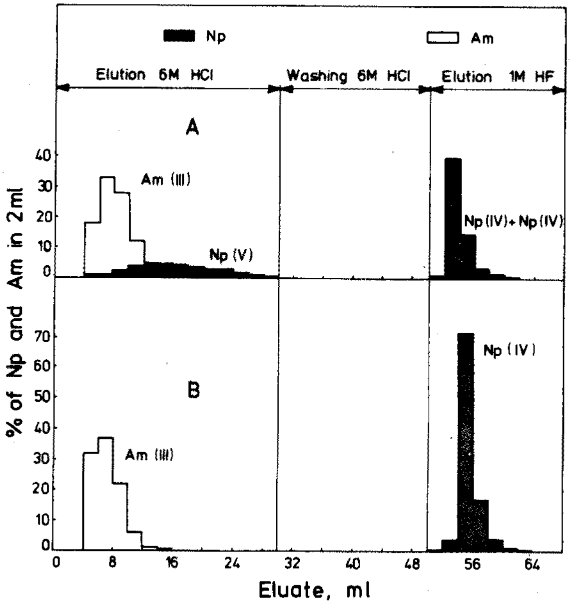

Fig. 4. Separation of americium and neptunium in 6 *M* HCl. (A) Microthene–TOPO column; (B) Microthene–TOPO–DPHQ column.

quantitatively with a TOPO column (elution diagram A) because of the simultaneous presence of different valence states of both elements in 6 *M* hydrochloric acid. However, a complete separation was obtained with a TOPO–DPHQ column which reduces plutonium to Pu(III) and neptunium to Np(IV) (elution diagram B).

Figure 3 shows the separation of plutonium from uranium with a TOPO column (elution diagram A) and with a TOPO–DPHQ column (elution diagram B); in the second case, plutonium is reduced to Pu(III), while uranium is extracted as U(VI) by TOPO[13].

The separation of americium from neptunium is shown in Fig. 4; when a TOPO–DPHQ column is used, all neptunium is reduced to Np(IV) which remains on the column.

## DISCUSSION

The redox–extraction chromatography method is a new technique which can be very usefully applied to separate trace amounts of actinide elements. The technique is based on the reducing properties of some hydroquinones and on the extracting properties of an organic extractant. The choice of the two supported compounds was made on the basis of their physicochemical behaviour. In a first approach to this problem, the redox potentials of transuranic elements and of some quinone–hydroquinone systems were taken into account. Particularly, the compounds having standard redox potentials[14–16] lower than 0.74 V—the value for the Np(V)/Np(IV) couple—were selected; in fact, the reduction of all the oxidation states of plutonium and neptunium to Pu(III) and Np(IV)[17] is possible below this value.

The possibility of transforming the reduced form of the redox compound to the oxidized form and *vice versa* has been demonstrated by using alternately cerium(IV) and tin(II) solutions[4]; the electron exchange capacity did not decrease appreciably after ten cycles.

The described method has the advantage that it is not necessary to add any reducing agent ($NaNO_2$, Fe(II), $NH_2OH$, *etc.*) to the feed solution; furthermore, DPHQ is homogeneously distributed all along the column, thus preventing any reoxidation of the reduced state of the element.

The technique is suitable for the reduction of plutonium and neptunium at trace level, but it could not work for weighable quantities of these elements. In fact, Pu(IV) and Pu(VI) oxidize the hydroquinone form present in the upper section of the column to the quinone form, and the following Pu(IV) and Pu(VI) are extracted by TOPO before being reduced; however, this drawback can be overcome by placing on the extracting column a quantity of Microthene–DPHQ sufficient to reduce plutonium previously.

A disadvantage of the described technique is the relatively low flow rate which is necessary for quantitative reduction; however, it is likely that a temperature increase would improve the kinetics[6].

Nitric acid solutions at concentrations higher than 1 *M* rapidly oxidize the DPHQ to DPQ; nevertheless, a quantitative reduction of plutonium to Pu(III) was obtained in 0.5 *M* nitric acid. The supported DPHQ was found to be stable with sulphuric acid at concentrations up to 3 *M*.

Research is now in progress to study the application of this separative technique in nitric and sulphuric acid media.

The authors are indebted to Mr. E. Casciola for his assistance in the experimental work.

## SUMMARY

The application of a new technique to the separation of some actinide elements by means of a single reducing and extracting column is described. Tri-*n*-octylphosphine oxide (TOPO) was used as the extractant. The following reducing agents were supported on microporous polyethylene together with TOPO: tetrachlorohydroquinone, 2,3-dichloro-1,4-naphthahydroquinone, 2,5-di-tert-butylhydroquinone and 2,5-di-tert-pentylhydroquinone. The last compound was chosen for the separation experiments; it allowed quantitative reduction of plutonium to Pu(III) and of neptunium to Np(IV). The separations Pu(III)–Np(IV), Pu(III)–U(VI) and Am(III)–Np(IV) in 6 *M* hydrochloric acid were obtained.

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# 2-NITRODIPHENYLAMINE AS A VERSATILE HIGH-POTENTIAL REVERSIBLE OXIDATION–REDUCTION INDICATOR

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The tris(1,10-phenanthroline)iron(II) complex is the most favoured high-potential indicator for titrations with cerium(IV) sulphate. Although this indicator is often regarded as a near approach to an ideal oxidation–reduction indicator, it is not without its limitations. It is not satisfactory for the titration of antimony(III)[1], arsenic(III)[2,3], oxalic acid[4–6], uranium(IV)[7,8], molybdenum(V)[9] and vanadium(IV)[10], which require special titration conditions and the use of catalysts. The main difficulty in these cases is the slow rate of reduction of the oxidized form of the indicator, ferriin, by the reductant. It is usually believed that the use of ferroin does not involve any induced reactions, unlike the diphenylamine indicators, but this is not so. The conditions described for the titration of arsenic(III)[3], uranium(IV)[7,8] and oxalic acid[5,6], undoubtedly involve induced reactions. Bishop[11] states that the indicator is unsatisfactory in titrations of hexacyanoferrate(II) with cerium(IV) in various acidic media. Sometimes, the dissociation of the indicator and its oxidized form must be considered[11]. A significant drawback of ferroin is its unsuitability for titrations in media containing perchloric acid, where it precipitates out as the perchlorate salt.

Diphenylamine derivatives give more vivid colour changes than ferroin with cerium(IV) sulphate and other oxidants. 2-Carboxydiphenylamine (*N*-phenylanthranilic acid) was long thought to have a potential of 1.08 V[12], but Belcher *et al.*[13] showed that its transition potential is 0.89 V in 0.5 *M* sulphuric acid, 0.87 V in 1.0 *M* acid and 0.88 V in 2.0 *M* acid; and that phosphoric acid was necessary for this indicator in the titration of dichromate in media 2–4 *M* in sulphuric acid. Frumina *et al.*[14] examined, as colorimetric reagents for vanadium(V), *N*,*N*-di(2-carboxyphenyl)-benzidine, 2-carboxy-2′-methoxydiphenylamine, and 2-carboxydiphenylamine-4′-sulphonic acid, but not as redox indicators. 4-Nitrodiphenylamine was reported to have a transition potential of 0.99 V by Hammett *et al.*[15], but no detailed examination of its indicator properties has been made, perhaps because of its commercial unavailability. However, the 2-nitro compound is readily available at a price much cheaper than that of ferroin or *N*-phenylanthranilic acid.

2-Nitrodiphenylamine, in the iron(II)–cerium(IV) sulphate titration in 0.5–2.0 *M* sulphuric acid media, shows an essentially constant transition potential of 1.09 V, whereas ferroin shows a decrease from 1.09 V to 1.04 V as the concentration of sulphuric acid is increased from 0.5 *M* to 2.0 *M*. 2-Nitrodiphenylamine has a pale yellow colour at the concentrations employed as indicator, and is oxidized by cerium(IV) to an intense reddish violet compound. Details of investigations that led to the establishment of conditions for the satisfactory reversible functioning of the new indicator for the titration of iron(II) with cerium(IV) sulphate, potassium dichromate and sodium vanadate are described below. The indicator has the advantage over ferroin that it is also satisfactory in perchloric acid media. Tungstic acid does not interfere in the titration of iron(II) with cerium(IV) sulphate, potassium dichromate or sodium vanadate in sulphuric acid media.

## EXPERIMENTAL

### *Indicator solution*

A 0.05 *M* solution of 2-nitrodiphenylamine (Fluka, Puriss) was prepared in concentrated (AnalaR) sulphuric acid, and a 0.005 *M* solution was prepared by dilution with concentrated sulphuric acid. As indicator, 0.1–0.2 ml of the 0.005 *M* solution was used for 50 ml of titration mixture. The indicator solutions are stable for over eight months. The Fluka pract. grade is also quite satisfactory.

### *Reagents*

A 0.1 *N* solution of cerium(IV) sulphate in 0.5 *M* sulphuric acid was prepared and standardized by the method of Willard and Young[16]. A 0.1 *N* iron(II) solution in 0.5 *M* sulphuric acid was prepared from AnalaR ferrous ammonium sulphate and standardized with cerium(IV) sulphate. A 0.1 *N* sodium metavanadate solution was pepared from ammonium metavanadate and standardised by the method of Rao *et al.*[17]. A 0.1 *N* solution of potassium dichromate was prepared from an AnalaR sample.

All other chemicals used were of analytical-reagent grade.

### *Titration of iron(II) with cerium(IV) sulphate*

In titrations of iron(II) with 0.1 *N* cerium(IV) sulphate in sulphuric acid, the indicator functions reversibly. The colour change at the end-point is sharp

TABLE I

TITRATION OF IRON(II) WITH CERIUM(IV) SULPHATE WITH 2-NITRODIPHENYLAMINE AS REVERSIBLE INDICATOR

| *Iron(II) taken (meq)* | *Iron(II) found (meq)* | | | | |
|---|---|---|---|---|---|
| | *0.5 M $H_2SO_4$* | *1.0 M $H_2SO_4$* | *3.0 M $H_2SO_4$* | *4.0 M $H_2SO_4$* | *6:0 M $H_2$* |
| 0.4198 | 0.4198 | — | 0.4198 | — | 0.4198 |
| 0.5000 | 0.5000 | 0.5000 | — | 0.5000 | 0.5000 |
| 0.5099 | 0.5107 | — | 0.5107 | — | 0.5107 |
| 0.5396 | — | 0.5406 | — | 0.5406 | — |
| 0.6098 | — | 0.6088 | 0.6088 | 0.6088 | — |
| 0.6396 | 0.6406 | — | 0.6406 | — | — |
| 0.7298 | — | 0.7308 | — | 0.7308 | 0.7308 |
| 0.7997 | 0.7979 | — | 0.7979 | — | 0.7979 |
| 0.9196 | 0.9217 | 0.9217 | — | 0.9217 | — |
| 0.9396 | 0.9376 | — | 0.9376 | — | — |

to a vivid reddish violet. With 0.1 ml and 0.2 ml of the indicator solution per 50 ml of the titration mixture, the indicator correction is negligible for 0.1 *N* cerium(IV) solution; the addition of an extra 0.02 ml of oxidant over that corresponding to the true equivalence point gives a very bright colour. When 0.3–0.4 ml of indicator solution is used, the indicator correction is only 0.02 ml of the titrant solution. The colour changes are easily discernible even under fluorescent tube lighting. The colour change can be reversed quite a number of times. In 0.5–1.0 *M* sulphuric acid media, the pink colour of the oxidized indicator is stable for 3 min, in 2.0 *M* sulphuric acid for 6 min, in 3.0 *M* sulphuric acid for 10 min, and in 5.0 *M* sulphuric acid for 40 min; in a 5.0 *M* sulphuric acid medium, the oxidized indicator is much brighter in colour. Iron(II) cannot be titrated with cerium(IV) at acidities above 7.0 *M* because of the slow rate of reaction of the oxidized indicator with iron(II). Some representative results are presented in Table I. The average error of determination is less than ±0.2%.

*Interferences.* During titrations of iron(II) in 0.5–2.0 *M* sulphuric acid, acetic acid up to 5.0 *M*, phosphoric acid up to 0.6 *M*, perchloric acid up to 3.0 *M*, tungstic acid up to 0.002 *M*, manganese(II) up to 0.06 *M* and arsenic(III) up to 0.0025 *M* do not interfere. It is significant that perchloric acid (1–3 *M*) markedly increases the brightness and stability of the colour in solutions containing 0.5 *M* sulphuric acid. In 0.5 *M* sulphuric acid–3 *M* perchloric acid, the colour is stable for 1 h.

### *Titrations of iron(II) with 0.01 M cerium(IV) solutions*

Titrations of 0.01 *M* iron(II) solutions with 0.01 *M* cerium(IV) sulphate solutions in sulphuric acid media, 0.1 ml of 0.005 *M* indicator solution being used, give accurate results, if an indicator correction of 0.1 ml of 0.01 *M* cerium(IV) sulphate is deducted. It will be noted that this is the theoretical quantity of cerium(IV) required for the oxidation of the indicator, assuming a two-electron withdrawal in the oxidation.

### *Titrations of iron(II) in hydrochloric acid media*

These titrations are rather unsatisfactory, owing to the instability of the oxidized indicator. However, satisfactory titrations can be made in 0.5–2.0 *M* hydrochloric acid medium with the addition of 10–15 ml of syrupy phosphoric acid.

### *Titrations of hexacyanoferrate(II) with cerium(IV) sulphate*

2-Nitrodiphenylamine is not satisfactory in these titrations, as is the case with ferroin[11].

### *Titrations of iron(II) with potassium dichromate*

2-Nitrodiphenylamine functions satisfactorily in titrations with 0.1 *N* or 0.01 *N* potassium dichromate when the sulphuric acid concentration lies in the range 5.0–7.0 *M*. When the acid concentration is below 5.0 *M*, oxidation of the indicator is sluggish; above 7.0 *M*, the reduction of the oxidized indicator by iron(II) becomes slow. Titrations with 0.1 *N* potassium dichromate are accurate and an indicator correction is not required. In titrations with 0.01 *N* potassium dichromate, an indicator correction of 0.1 ml must be deducted. The pink colour of the oxidized indicator at the equivalence point is very bright and remains stable for more than 1 h.

Comparative studies have shown that the colour change at the equivalence point in the iron(II)–dichromate titration is much more distinct with 2-nitrodiphenylamine than with ferroin. This is undoubtedly due to the intense pink colour of the oxidized 2-nitrodiphenylamine masking the light green colour of chromium(III). Representative results of titrations conducted in 6.0 *M* sulphuric acid, given in Table II, show that the average error of determination is less than ±0.2%.

TABLE II

TITRATION OF IRON(II) WITH POTASSIUM DICHROMATE OR SODIUM VANADATE IN 6.0 *M* SULPHURIC ACID WITH 2-NITRODIPHENYLAMINE AS REVERSIBLE INDICATOR

| *Titrations with 0.1 N solutions* | | *Titrations with 0.01 N solutions* | |
|---|---|---|---|
| *Iron(II) taken (meq)* | *Iron(II) found (meq)* | *Iron(II) taken (meq)* | *Iron(II) found (meq)* |
| *Titrations with dichromate* | | | |
| 0.4297 | 0.4297 | 0.3998 | 0.3998 |
| 0.5198 | 0.5198 | 0.5298 | 0.5308 |
| 0.6197 | 0.6207 | 0.6098 | 0.6088 |
| 0.7196 | 0.7176 | 0.7396 | 0.7406 |
| 0.8997 | 0.9016 | 0.9217 | 0.9196 |
| *Titrations with vanadate* | | | |
| 0.4098 | 0.4098 | 0.5000 | 0.5000 |
| 0.5337 | 0.5337 | 0.6238 | 0.6238 |
| 0.6396 | 0.6386 | 0.7098 | 0.7108 |
| 0.7308 | 0.7298 | 0.8254 | 0.8237 |
| 0.8098 | 0.8117 | 0.9198 | 0.9197 |
| 0.9296 | 0.9317 | 0.9497 | 0.9515 |

TABLE III

TRANSITION POTENTIALS OF 2-NITRODIPHENYLAMINE AND THE CALCULATED FORMAL POTENTIALS

(In all cases iron(II) was titrated).

| *Titrant* | $H_2SO_4$ *(M)* | *Transition potential* ($E_t$) *(V vs. N.H.E.)* | *Estimated formal potential* ($E_0$) *(V)* |
|---|---|---|---|
| Cerium(IV) sulphate | 0.5 | 1.09 | 1.12 |
| Cerium(IV) sulphate | 1.0 | 1.09 | 1.12 |
| Cerium(IV) sulphate | 2.0 | 1.09 | 1.12 |
| Cerium(IV) sulphate | 4.0 | 0.97 | 1.00 |
| Cerium(IV) sulphate | 5.0 | 0.95 | 0.97 |
| Cerium(IV) sulphate | 6.0 | 0.91 | 0.94 |
| Potassium dichromate | 5.0 | 1.07 | 1.10 |
| Potassium dichromate | 6.0 | 1.03 | 1.06 |
| Potassium dichromate | 7.0 | 0.98 | 1.01 |
| Sodium vanadate | 5.0 | 1.01 | 1.04 |
| Sodium vanadate | 6.0 | 1.01 | 1.04 |
| Sodium vanadate | 7.0 | 0.93 | 0.96 |

*Titrations of iron(II) with sodium vanadate*

Titrations of iron(II) with sodium vanadate can readily be made with 2-nitrodiphenylamine as indicator, when the sulphuric acid concentration is 5.0–7.5 *M*. Oxidation of the indicator is slow below 5.0 *M* acid concentrations, and above 7.5 *M* the reduction of oxidized indicator by iron(II) is slow. The colour change at the equivalence point is from light green to bluish pink, and is more vivid than with ferroin; the oxidized indicator is stable for more than 1 h. In titrations with 0.1 *N* solutions, the indicator correction is negligible, but with 0.01 *N* solutions, the correction value of 0.1 ml must be deducted. Representative results are presented in Table II.

*Transition potentials of 2-nitrodiphenylamine*

These were determined by the method of Knop[18] in the various systems and are listed in Table III. The values are subject to a variation of ±0.01 V.

## DISCUSSIOn

In the case of ferroin, the reduced form of the indicator has an intense red colour (molar absorptivity, ca. 11,000 $1\ \text{mol}^{-1}\ \text{cm}^{-1}$) while the oxidized form has a light blue colour, which may not become visible until a large percentage of the indicator has been oxidized. Although visibility is subject to a personal factor, it is reasonable to assume that the blue colour would be visible only after 90% of the indicator has been oxidized. In the case of 2-nitrodiphenylamine, the unoxidized indicator has a very light yellow colour, while the oxidized indicator has a very intense reddish violet colour. In view of its very high molar absorptivity *ca.* 37,000 $1\ \text{mol}^{-1}\ \text{cm}^{-1}$), it may be assumed that the end-point of the titration will be indicated when only 10% of the indicator has been oxidized. Assuming that the oxidation of 2-nitrodiphenylamine is a case of 2-electron change, like that of diphenylamine, we can calculate from the equation:

$$E_t = E'_0 + \frac{0.059}{2}\log\left(\frac{[\text{Ind}_{\text{ox}}]}{[\text{Ind}_{\text{red}}]}\right) = E'_0 + \frac{0.059}{2}\log\left(\frac{0.1}{0.9}\right)$$

that the formal potential of the indicator will be about 0.03 V more than the transition potential. In the case of ferroin, the formal potential will be about 0.05–0.06 V less than the transition potential. The formal potentials of 2-nitrodiphenylamine calculated in this manner under various conditions are listed in Table III.

A very interesting point emerges from an examination of these transition potentials; the transition potentials of the indicator in 5.0 *M* sulphuric acid vary with the oxidant, being 0.95 V with cerium(IV) sulphate, 1.07 V with dichromate and 1.01 V with vanadate, iron(II) being titrated in all cases. This type of detailed study does not appear to have been made with other indicators. Varying the titrand system may also cause variation in the transition potential; studies in this direction are in progress. The formal potential of ferroin in 1.0 *M* sulphuric acid is 1.06 V[19], while that of nitroferroin is 1.25 V. The present data show that the introduction of a nitro group in the 2-position raises the formal potential of diphenylamine from 0.79 V to 1.11 V.

2-Nitrodiphenylamine has the further advantage that it can be used in perchloric acid media, and is very much cheaper than nitroferroin.

## SUMMARY

The use of 2-nitrodiphenylamine as a reversible indicator has been investigated in the titration of iron(II) with cerium(IV) sulphate, potassium dichromate and sodium vanadate in sulphuric acid media. Accurate results can be obtained with cerium(IV) sulphate in 0.5–5.0 *M* acid, with potassium dichromate in 5.0–7.0 *M* acid, and with sodium vanadate in 5.0–7.5 *M* acid. With cerium(IV) sulphate the titrations are preferably conducted in 2.0 *M* sulphuric acid or in a 1.0 *M* sulphuric acid–1.0 *M* pechloric acid medium. Tungstic acid, acetic acid, arsenic(III) and manganese(II) do not interfere. In titrations of iron(II) with dichromate and vanadate, the colour changes at the end-point are much more vivid with 2-nitrodiphenylamine than with ferroin.

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# THE ANODIC OXIDATION OF BASES IN THE SOLVENT *m*-CRESOL

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Acid–base titrations can be carried out successfully in the solvent *m*-cresol[1]. This is important for the determination of the acid or base content of some polymers for which *m*-cresol is a good solvent. The study of acid–base coulometry in *m*-cresol was started because of the several advantages offered by coulometry: greater sensitivity, no problems with unstable titrants, and no need for standardization of titrants.

Preliminary experiments in which constant-current coulometric titrations were carried out in solutions of tetraethylammonium perchlorate in *m*-cresol showed that the electrochemical generation of base (*m*-cresolate) at platinum electrodes does occur with 100% current efficiency. However, in these experiments, generation of acid did not occur with 100% current efficiency.

The present study of the anodic oxidation of bases in *m*-cresol was undertaken to establish conditions for 100% current efficiency in the generation of acid in *m*-cresol.

## EXPERIMENTAL

### *Chemicals*

*m*-Cresol (Merck "Zur Synthese") was purified by distilling (b.p. 201–202°C), drying for 24 h on molecular sieve (3Å, Union Carbide) and distilling again (b.p. 201–202°C). The second distillate was used within a day. Some batches purified by this method still had a detectable acid or base content. Only those batches were used that showed no detectable amount of acid or base in acid–base titration and had a range from $-1.55$ to $+0.7$ V in polarography with tetraethylammonium perchlorate as supporting electrolyte.

Sodium cresolate solutions were prepared by dissolving the appropriate amount of sodium in *m*-cresol.

Tetraethylammonium perchlorate (TEAP; Eastman, reagent grade) was recrystallized from ethanol.

1,3-Diphenylguanidine (Eastman, reagent grade), tetramethylammonium chloride (Eastman, reagent grade), tetramethylguanidine (Eastman, pract. grade), morpholine (Merck, "Zur Synthese"), strychnine (Merck, purum), triethylamine (Koch-Light, puriss.), n-butylamine (Fluka, puriss.) and mercury (Drijfhout, polarographic grade) were used as received.

*Apparatus*

A Radiometer polarograph type PO4, equipped with a Sargent IR compensator model A, was used. The polarographic cell was thermostatted at 20±0.01°C, and a three electrode system was used. The reference electrode (Ag/AgCl) in 0.1 *M* tetramethylammonium chloride in *m*-cresol was connected *via* a salt bridge with 0.1 *M* tetraethylammonium perchlorate in *m*-cresol to the test solution. The auxiliary electrode was a mercury pool. The characteristics of the DME were: *h*, 56 cm; *m*, 2.87 mg $s^{-1}$; *t*, 2.70 s (open circuit in 0.1 *M* TEAP in *m*-cresol).

For the rotating disc electrode equipment, the indicator electrode was a Tacussel platinum ring/disc electrode with a driving mechanism (type Asservitex) of which the ring section was not used. The area of the disc was 8.04 $mm^2$. The potentiostat was a Bipad type from Tacussel. The reference electrode, salt bridge

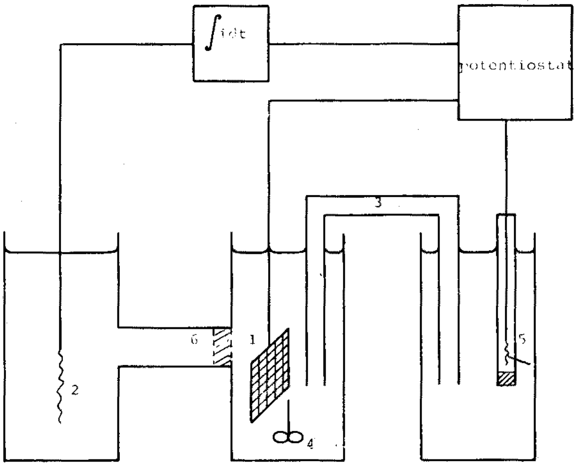


Fig. 1. Apparatus for constant-potential coulometry.

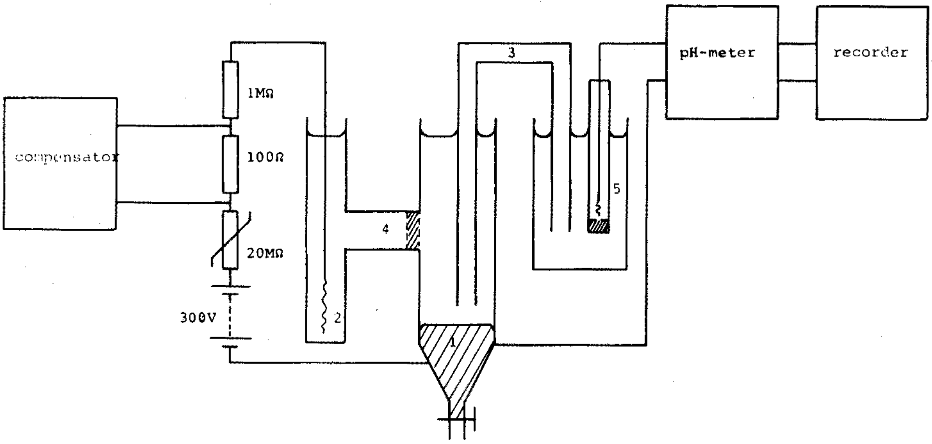


Fig. 2. Apparatus for chronopotentiometry.

and auxiliary electrode were as described above. Measurements were carried out at room temperature.

For the constant-potential coulometric equipment, an H-type cell was operated at room temperature; the compartments of the cell were separated by a G-4 glass frit. A Tacussel Bipad potentiostat and an electronic integrator constructed from a Keithley operational amplifier, type K301, were used. The platinum gauze working electrode had an area of 4 cm$^2$, and the auxiliary electrode was a platinum wire. The reference electrode was Ag/AgCl in 0.1 *M* tetramethylammonium chloride in *m*-cresol, and was connected to the test solution *via* a 0.1 *M* TEAP in *m*-cresol salt bridge. The arrangement is shown in Fig. 1.

For the chronopotentiometry equipment, the H-type cell was again operated at room temperature, and a G-4 glass frit separated the compartments. The working electrode was a mercury pool (area, 3.87 cm$^2$) at the bottom of one compartment. The auxiliary electrode was a platinum wire in the other compartment. The reference electrode was an Ag/AgCl electrode in 0.1 *M* tetramethylammonium chloride in *m*-cresol; this electrode was connected to the test solution *via* a salt bridge of 0.1 *M* TEAP in *m*-cresol. The outlet of this salt bridge was brought close to the surface of the mercury pool. The circuit consisted of a 300-V stabilized power supply (v.d. Heem, type 8619), a large resistor, a Knick pH meter type PH23, and a Philips recorder type PM8100. The exact current was measured across a 100-ohm precision resistor in the circuit with a compensator galvanometer (Bleeker, type 2164). A schematic diagram is given in Fig. 2.

### *Procedures*

*Polarography.* As supporting electrolyte 0.1 *M* TEAP was used. Stock 0.01 *M* solutions (accurately standardized by titration) of the bases were used to prepare dilution series in the concentration range $5 \cdot 10^{-4}$ *M* to $1.5 \cdot 10^{-3}$ *M* (in 0.1 *M* TEAP in *m*-cresol).

These solutions were placed in the polarographic cell and deoxygenated by bubbling nitrogen (purified over copper at 400°C) through the solution for 20 min. The polarographic curves were recorded without damping at a speed of 0.2 V min$^{-1}$, with the sensitivity at 5 $\mu$A full scale.

*Constant potential coulometry.* Into the compartment of the working electrode was placed 25 ml of a solution of 0.1039 *M* n-butylamine in 1 *M* TEAP, and the other compartment was filled with 1 *M* TEAP. With the potentiostat the working electrode was maintained at +0.650 V. The solution in the working electrode compartment was stirred. After 10 h, the electrolysis was stopped, the integrator was read and a sample was taken, which was titrated for n-butylamine content.

*Voltammetry at the rotating platinum disc electrode.* Voltammetric curves were recorded by measuring the disc current *versus* the disc voltage, for different rotating speeds of the electrode in a solution of $10^{-3}$ *M* n-butylamine in 0.1 *M* TEAP. Oxygen was removed by bubbling nitrogen through the solution for 20 min.

*Chronopotentiometry.* As supporting electrolyte 0.1 *M* TEAP was used. From a stock solution of 0.01 *M* n-butylamine in 0.1 *M* TEAP in *m*-cresol, dilutions were made with 0.1 *M* TEAP to give concentrations in the range $5 \cdot 10^{-4}$ *M* to $2 \cdot 10^{-3}$ *M*. These solutions were placed in the cell. The chronopotentiogram was recorded after the solutions had been deoxygenated by bubbling nitrogen for 20 min.

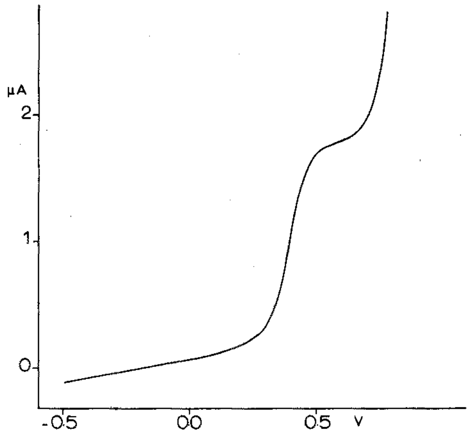
When current reversal chronopotentiograms were recorded, the current was reversed before the occurrence of the transition.

## RESULTS

### *Polarography*

The polarographic oxidation waves of all the nitrogen bases investigated and of sodium cresolate all show the same characteristics. A typical example is the oxidation wave of sodium *m*-cresolate (Fig. 3). The slope of the graph of $E_{\mathrm{DME}}$ *versus* $\log(i/(i_d - i))$ is 82 mV in this case, showing that the oxidation is irreversible. For morpholine, the influence of the height of the mercury column on the diffusion current was determined. The diffusion current *versus* the square root of the mercury height was linear (Fig. 4), indicating that the oxidation of morpholine is diffusion-controlled.

The compounds tetramethylguanidine,strychnine and n-butylamine gave a so-called "prewave" preceding the normal oxidation wave. The height of this prewave was independent of concentration, while the total height of the prewave and normal



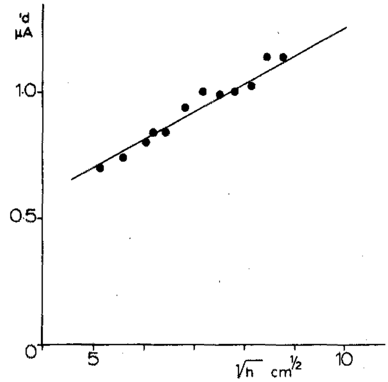


Fig. 3. Polarographic curve for $1.5 \cdot 10^{-3}$ *M* sodium *m*-cresolate in 0.1 *M* TEAP in *m*-cresol.

Fig. 4. Diffusion current for the anodic oxidation wave of $10^{-3}$ *M* morpholine in 0.1 *M* TEAP in *m*-cresol *versus* (mercury height)$^{\frac{1}{2}}$.

TABLE I

TOTAL WAVE HEIGHT AND HEIGHT OF PREWAVE FOR THE POLAROGRAPHIC OXIDATION OF STRYCHNINE

| *Concn. (M)* | $i_d$ *total wave (μA)* | $i_d$ *prewave (μA)* |
|---|---|---|
| $5 \cdot 10^{-4}$ | 0.48 | 0.19 |
| $7.5 \cdot 10^{-4}$ | 0.68 | 0.18 |
| $10^{-3}$ | 0.90 | 0.17 |
| $1.5 \cdot 10^{-3}$ | 1.40 | 0.17 |

TABLE II

POLAROGRAPHY OF BASES IN *m*-CRESOL

(Supporting electrolyte 0.1 *M* TEAP)

| *Compound* | $E_{\frac{1}{2}}$ *(V vs. Ag/AgCl)* | $I_d$ *(μA mM$^{-1}$ mg$^{-\frac{2}{3}}$ s$^{\frac{1}{2}}$)* | p$K_a$ |
|---|---|---|---|
| Dimethylaminoazobenzene | 0.52 | 0.398 | 11 |
| Strychnine | 0.43 | 0.388 | 13 |
| n-Butylamine | 0.41 | 0.419 | 13.9 |
| Morpholine | 0.40 | 0.408 | 12.1 |
| Triethylamine | 0.39 | 0.395 | 14.2 |
| Sodium *m*-cresolate | 0.38[5] | 0.398 | — |
| 1,3-Diphenylguanidine | 0.38 | 0.376 | — |
| Tetramethylguanidine | 0.38 | 0.389 | 14.5 |

wave was related to the concentration (see Table I). Most likely this prewave is due to adsorption[2].

The polarographic results are summarized in Table II. A comparison of the $E_{\frac{1}{2}}$ values for the oxidation of the bases with their p$K_a$ values in *m*-cresol (Table II) shows that a strong base is oxidized more easily than a weak base. This can be explained if it is assumed that in fact the *m*-cresolate ion is oxidized, because the concentration of free cresolate ions is determined by the equilibrium constants of the reaction

$$\mathrm{B + HCres \leftrightharpoons BH^+ Cres^- \leftrightharpoons BH^+ + Cres^-}$$

From Table II it can be seen that the diffusion current constants ($I_d$) are about the same for all bases. The mean value is 0.396 μA mM$^{-1}$ mg$^{-\frac{2}{3}}$ s$^{\frac{1}{2}}$.

The diffusion constant can be calculated from the DME characteristics $m^{\frac{2}{3}}\,t^{\frac{1}{6}} = 2.383$ mg$^{\frac{2}{3}}$ s$^{-\frac{1}{2}}$, and the Ilkovic equation $i = 607nD^{\frac{1}{2}}\,cm^{\frac{2}{3}}\,t^{\frac{1}{6}}_{\mathrm{max}}$. The value was found to be $4.2 \cdot 10^{-7}$ cm$^2$ s$^{-1}$, if a one-electron transfer is assumed.

*Oxidation of n-butylamine in m-cresol at the rotating platinum disc electrode*

The current–voltage curves for the oxidation of a solution of $10^{-3}$ *M*

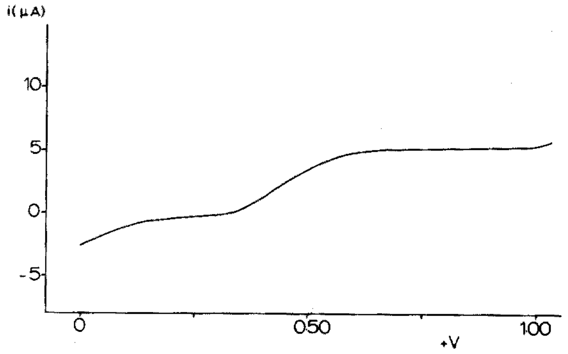
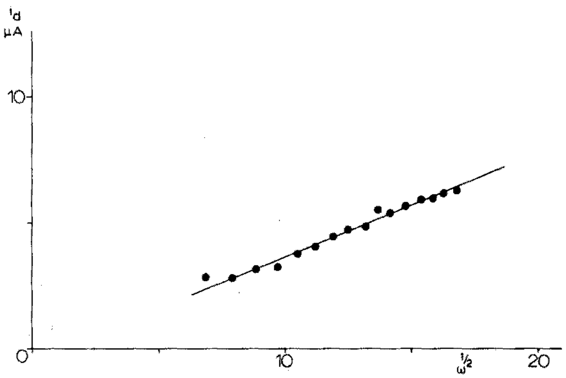


Fig. 5. Oxidation of $10^{-3}$ *M* n-butylamine in 0.1 *M* TEAP in *m*-cresol at the rotating platinum disc at 1800 r.p.m.



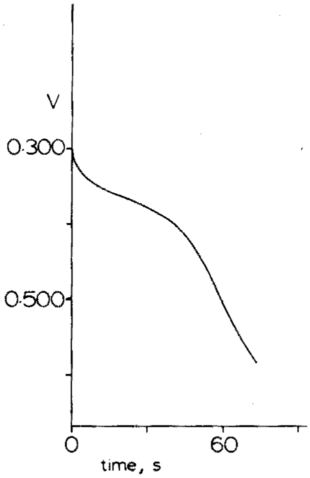


Fig. 6. Diffusion current *versus* (rotation speed)$^{\frac{1}{2}}$ for the oxidation of $10^{-3}$ *M* n-butylamine in 0.1 *M* TEAP in *m*-cresol at the rotating platinum disc.

Fig. 7. Chronopotentiogram of $10^{-3}$ *M* n-butylamine in 0.1 *M* TEAP in *m*-cresol. Current, 34.8 µA.

n-butylamine in 0.1 *M* TEAP in *m*-cresol were recorded at different rotating speeds of the disc. A typical voltammetric curve is shown in Fig. 5. It can be seen that oxidation of either the solvent or the supporting electrolyte starts at about +0.95 V. From the curves, the limiting current at different rotating speeds was determined; Fig. 6 shows the graph of the limiting currents *versus* the square root of the rotating speed. With the Levich equation, $i=0.62\ nF\ AD^{\frac{2}{3}}\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}}c$, the diffusion coefficient can be calculated from the slope of this graph. With the kinematic viscosity $\nu=0.2013$, the value $4.4\cdot10^{-7}$ cm$^2$ s$^{-1}$ was found for the diffusion coefficient. This is in good agreement with the value $4.2\cdot10^{-7}$ found from the Ilkovic equation in the polarographic determination.

*Coulometry at constant potential*

After 10 h of electrolysis of 25 ml of a solution containing 0.1039 *M* n-butylamine in 1 *M* TEAP, 212.9 µeq of electrical charge had passed through the cell. In this time, the titer of the n-butylamine solution decreased to 0.0950 *M*, corresponding to a conversion of 222.5 µmole of n-butylamine. This confirms the one-electron transfer already found in polarography and voltammetry at the rotating disc electrode.

*Chronopotentiometry*

Chronopotentiograms were recorded for solutions of n-butylamine in 0.1 *M* TEAP in *m*-cresol in the concentration range $5\cdot10^{-4}$ *M* to $2\cdot10^{-3}$ *M*. The current was between 56.8 and 26.9 µA. A typical chronopotentiogram is given in Fig. 7. The results of the experiments are given in Table III, which shows that the product $i\tau^{\frac{1}{2}}$ is constant, indicating that the oxidation of n-butylamine in *m*-cresol is diffusion-controlled.

BLE III

IRONOPOTENTIOMETRY OF n-BUTYLAMINE IN 0.1 *M* TEAP IN *m*-CRESOL[a]

| | *Current (μA)* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *43.3* | | | *34.8* | | | *31.4* | | |
| *nc. (M)* | $\tau$ | $E_{\frac{1}{2}}$ | $\tau_r/\tau_f$ | $\tau$ | $E_{\frac{1}{2}}$ | $\tau_r/\tau_f$ | $\tau$ | $E_{\frac{1}{2}}$ | $\tau_r/\tau_f$ |
| $10^{-4}$ | 8.8 | 0.350 | 0.32 | 12.5 | 0.350 | 0.32 | 16.0 | 0.349 | 0.32 |
| $\cdot 10^{-4}$ | 14.7 | 0.344 | 0.23 | 23.0 | 0.344 | 0.20 | 28.3 | 0.346 | 0.20 |
| $^{-3}$ | 25.4 | 0.349 | 0.12 | 44.0 | 0.349 | 0.11 | 57.0 | 0.349 | 0.10 |
| $\cdot 10^{-3}$ | 54.9 | 0.337 | 0.11 | 80.4 | 0.337 | 0.09 | 97.8 | 0.336 | 0.08 |
| $10^{-3}$ | 95.0 | 0.336 | 0.05 | 144 | 0.338 | 0.04 | | | |
| | *26.4* | | | *20.0* | | | *16.8* | | |
| $10^{-4}$ | 20.0 | 0.352 | 0.26 | 41.0 | 0.350 | 0.13 | 70.0 | 0.352 | 0.10 |
| $\cdot 10^{-4}$ | 38.5 | 0.348 | 0.16 | 62.4 | 0.340 | 0.12 | 80.9 | 0.345 | 0.10 |
| $^{-4}$ | 79.0 | 0.348 | 0.08 | 120 | 0.348 | 0.09 | 170 | 0.348 | 0.07 |
| $\cdot 10^{-3}$ | 139 | 0.337 | 0.06 | 220 | 0.337 | 0.05 | 313 | 0.338 | 0.04 |

in s; $E_{\frac{1}{2}}$ in V *versus* Ag/AgCl; $\tau_r$, transition time reduction; $\tau_f$ transition time oxidation.

The value $\partial E_{\frac{1}{2}}/\partial \ln i_0$ at constant concentration is approximately zero, whereas $\partial E_{\frac{1}{2}}/\partial \ln c$ at constant current is negative. The ratio of the transition time for the reduction to the transition time for the oxidation when current reversal is applied, is dependent on bulk concentration and becomes less when the bulk concentration is increased.

Comparison of these facts with the diagnostic criteria for various kinetic schemes in chronopotentiometry given by Reinmuth[3], indicates that the electron transfer is followed by a chemical reaction of higher than first order.

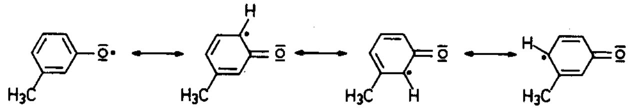
## DISCUSSION

When a base B is dissolved in *m*-cresol the following equilibria are established:

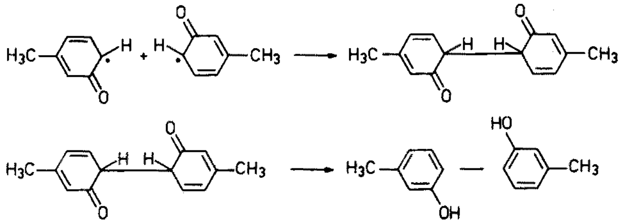
$$B + HCres \rightleftharpoons BH^+Cres^- \rightleftharpoons BH^+ + Cres^-$$

From the fact that the oxidation of bases in *m*-cresol is diffusion-controlled and that the $E_{\frac{1}{2}}$ values decrease with increasing p$K_a$ values for different bases, it can be concluded that the *m*-cresolate ion is the electroactive species and that the equilibria between free base, ion pair and *m*-cresolate ion are rapid. As the experiments show that the oxidation is a one-electron process, its initial product must be the phenoxy radical.

Chronopotentiometry indicated that this phenoxy radical is subject to a further chemical reaction of higher than first order. For the phenoxy radical, different resonance structures are given[4]:



These radicals can react to give dimers:



It is most likely that the electrochemical step is followed by a dimerization.

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## SUMMARY

The oxidation of bases in the solvent *m*-cresol was investigated by polarography, voltammetry at the rotating platinum disc electrode and by chronopotentiometry. It was shown that the *m*-cresolate ion is the electroactive species in this reaction. The oxidation is a one-electron process giving a phenoxy radical. This phenoxy radical is converted in a chemical reaction of higher than first order, most likely to the dimer.

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# KINETIC–COULOMETRIC DETERMINATION OF MERCURY IN BIOLOGICAL SAMPLES*

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The problems of mercury in the environment and the detrimental effect of mercury compounds on biological systems have received much publicity in the past few years. Presently, some investigators feel that the problem of mercury pollution is not one of recent origin, but one of recent discovery[1,2]. Whether the amount of mercury in the environment is increasing or decreasing, the toxicity of mercury and its compounds is certain[3]. In order to study the absorption and excretion of mercury by organisms, accurate and sensitive methods for the assay of the element are necessary. The most widely accepted method for the determination of trace quantities of mercury is flameless atomic absorption spectrometry[4,5].

An alternative method for the determination has been developed, which is based on the catalysis of the reaction

$$\mathrm{Fe(CN)_6^{4-}} + 3(\text{1,10-phenanthroline}) \rightleftharpoons \text{ferroin}^{2+} + 6\,\mathrm{CN^-} \qquad (1)$$

by mercury(II) ion. The cyanide ion that is released in the reaction is titrated with electrogenerated iodine.

$$\mathrm{I_2 + CN^- \rightleftharpoons ICN + I^-} \qquad (2)$$

The optimal conditions for the replacement reaction and the subsequent measurement of the cyanide ion have been reported[6]. The coulometric procedure is analogous to the Cotlove method for the determination of chloride[7]. Coulometry has also been used for the determination of the activity of acid or alkaline phosphatases in serum[8] and for the determination of blood glutathione[9].

In the preparation of samples for mercury assay, care must be taken to avoid loss of mercury through volatilization[10,11]. The digestion procedure of Rolfe *et al.*[12] overcomes the problem of volatilization and is entirely satisfactory for samples which contain relatively small amounts of organic matter. In this procedure, the sample is destroyed in a sealed pressure bottle by strong oxidizing agents. For solid samples, the digestion procedure of Gorsuch[13], in which the sample is digested in a closed system by strong acids, is effective.

After most of the organic matter in the sample has been destroyed, the mercury present in the sample is extracted with dithizone in toluene. The addition

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of chloride and EDTA before the extraction will prevent silver, which interferes in the kinetic–coulometric procedure, from being extracted[14]. The mercury is then back-extracted into 5 $M$ hydrochloric acid for assay by the kinetic–coulometric procedure. Catalysis of the kinetic reaction is dependent on the activity of the mercury in the sample. The activity of the mercury is influenced by the chloride content of the test solution. In order to avoid errors in the assay procedure, the method of standard additions is employed to compensate for small changes in mercury activity due to changes in chloride concentration.

## EXPERIMENTAL

### *Materials*

All glassware was washed with 10% nitric acid and rinsed with deionized water. All reagents used were tested for mercury contamination before use and were used without further purification except as noted.

*Mercury solutions.* Dissolve mercury(II) chloride (0.1354 g) in 1.0 $M$ sulfuric acid and dilute to 100 ml with 1.0 $M$ sulfuric acid. This stock solution (1 mg Hg $ml^{-1}$) is diluted by a factor of fifty with 0.1 $M$ nitric acid to yield a solution that contains 0.1 $\mu$g Hg/5 $\mu$l. For dimethylmercury solution, dissolve 1.00 ml of a solution containing 3.069 g $ml^{-1}$ in 95% ethanol and dilute to 100 ml with 95% ethanol; dilute 4 ml of this solution to 100 ml with 95% ethanol to give a solution that contains 0.534 $\mu$g/5 $\mu$l.

*Hydroxylammonium chloride, 10%.* Dissolve 25 g of the reagent in approximately 60 ml of water, add 4 drops of phenol red indicator, and make alkaline with ammonia solution to the full red color of the indicator. Cool and extract with a 0.01% (w/v) solution of dithizone in chloroform, using 5-ml portions until the last extract remains green. Then, wash the solution free of excess of dithizone by repeated extraction with 10-ml portions of chloroform. Warm the solution to expel the dissolved chloroform. After cooling, dilute to 250 ml with water.

*Dithizone in toluene.* Dissolve 10 mg of the purified reagent in 500 ml of toluene and store in dark glass.

*Clark and Lubs buffer pH 3.0.* Dissolve 10.212 g of potassium hydrogen phthalate in water, add 223 ml of 0.1 $M$ hydrochloric acid and dilute to 1 l with water.

*1,10-Phenanthroline solution.* Dissolve 0.615 g of the reagent in water and dilute to 1 l with water.

*0.001 M Hexacyanoferrate(II).* Dissolve 0.4224 g of $K_4Fe(CN)_6 \cdot 3H_2O$ in water and dilute to 1 l with water.

*Borate buffer, pH 9.2, containing 0.1 M potassium iodide.* Dissolve 3.8 g of sodium borate decahydrate and 16.6 g of potassium iodide in water and dilute to 1 l with water.

### *Procedure*

*Digestion of samples.* For urine and serum, place the sample (50 ml of urine or 2 ml of serum) in a 250-ml pressure bottle. Add mercury to some of the samples at this time to study recoveries. Add 10 ml of (1+3) sulfuric acid–nitric acid and 20 ml of 6% (w/v) potassium permanganate solution. Seal the bottle and place it in a beaker of boiling water. After 2 h of heating, remove the bottle from the boiling water, allow to cool, and open carefully. Destroy the excess of permanganate by the addition of hydroxylamine; add 5 ml of hydroxlamine solution in excess, followed by 10 ml of ammonia liquor (*d* 0.88).

For fish and fish protein concentrate, add weighed samples to the flask of the apparatus described by Gorsuch[13]. Add 20 ml of water and 20 ml of (1+3) sulfuric acid–nitric acid to the flask, and digest the sample as recommended by Gorsuch. Add mercury compounds to some of the samples before the addition of the acids in order to study recoveries. When the digestion is complete, add 30 ml of ammonia liquor and 20 ml of hydroxylamine solution to the digest.

*Extraction.* For extraction, transfer the digested sample to a 500-ml separatory funnel and add 8 ml of the dithizone solution. Stopper and shake for 1 min; then allow to stand until the layers separate. Discard the aqueous layer and transfer the organic layer to a 60-ml separatory funnel. Wash three times, without mixing, with 10-ml portions of water. Finally, add 3 ml of 5 *M* hydrochloric acid to the funnel and mix by shaking the funnel vigorously for 1 min. Transfer the aqueous layer to a 100-ml volumetric flask and wash the organic layer three times, without mixing, with 10-ml portions of pH 3.0 buffer. Add the washings to the volumetric flask. Add 3 ml of 5 *M* sodium hydroxide solution to the flask and fill the flask to the mark with pH 3.0 buffer.

*Titration.* Add four 10-ml aliquots of this solution to 25-ml glass-stoppered Erlenmyer flasks, and to three of the flasks add 0.1, 0.2 and 0.3 μg of mercury(II), as the chloride. Add 1.5 ml of 1,10-phenanthroline solution to each of the flasks. Place the flasks in a 60°C constant-temperature bath for 10 min. Then add 3.0 ml of 0.001 *M* hexacyanoferrate(II) solution to each of the flasks, stopper the flasks and replace in the bath. At the end of 5 min of reaction, remove the flasks from the bath, and stop the reaction by the addition of 0.9 ml of 1.0 *M* sodium hydroxide solution. Titrate a 4-ml aliquot of each of these solutions with electrogenerated iodine, using a generating current of 1 mA and a biamperometric end-point detection system. The buffer used in the titrations is borate pH 9.2 containing 0.1 *M* iodide.

## RESULTS

The amounts of cyanide titrated in each determination can be calculated from Faraday's law. However, when the method of standard additions is employed, this operation is unnecessary if the same current is used in all of the titrations. In this case, the generation time in seconds can be plotted directly against the mercury present in the test solutions, for say, three additions of standard, and the unknown concentration can be determined by extrapolation in the conventional manner. The mercury content of 24-hour specimens can then be calculated by taking into account the various aliquot sizes.

Results of tests with urine samples are given in Table I. Assays of 24-h urine samples are listed in Table II. The results of the analysis of serum samples are shown in Table III. The recoveries of mercury added to samples before analysis are reported in Tables I and III. The form of mercury used in the recovery studies was the chloride. Table IV shows the results of assays of fish and fish protein concentrate with the recoveries of mercury added to the samples as the chloride and as dimethylmercury. The concentrations of mercury in the samples determined by

## TABLE I

## MERCURY IN URINE SAMPLES

(A 50-ml aliquot of the sample was taken in all cases)

| *Sample* | *Mercury added (µg)* | *Average mercury found (µg)* | *Average deviation (µg)* | *Recovery (%)* |
|---|---|---|---|---|
| TR 5/2 6PM | — | 0.9[a] | 0.02 | — |
| VO/5/23 3PM | — | 0.4[a] | 0.01 | — |
| TR 5/2 10PM | — | 0.6[a] | 0.02 | — |
| TR 5/8 11AM | — | 0.7[a] | 0.02 | — |
| TR 5/2 10PM | 5.0 | 5.5[b] | — | 98.0 |
| TR 5/8 11AM | 5.0 | 5.8[b] | — | 102.0 |
| TR 5/8 11AM | 10.0 | 11.3[b] | — | 106.0 |

[a] Average of 3 determinations

[b] Average of 2 determinations; average deviation not calculated.

## TABLE II

## MERCURY IN 24-HOUR URINE SAMPLES

(A 50-ml aliquot was taken in all cases)

| *Sample* | *Total sample (ml)* | *Average mercury found[a] (µg)* | *Total mercury present (µg)* |
|---|---|---|---|
| SL 4/24 | 620 | 1.7 | 21.1 |
| DK 5/3 | 620 | 0.9 | 11.2 |
| BS 5/1 | 1800 | 0.2 | 7.2 |
| JL 5/1 | 2900 | 0.3 | 17.4 |
| SB 5/2 | 1420 | 0.6 | 17.0 |
| FM 4/29 | 2600 | 0.5 | 26.0 |

[a] Average of 2 determinations.

## TABLE III

## MERCURY IN SERUM SAMPLES

| *Sample, 2 ml* | *Mercury added (µg)* | *Average mercury found[a] (µg)* | *Average deviation (µg)* |
|---|---|---|---|
| Versatol Lot 0002018 | — | 0.40 | 0.01 |
| Versatol Lot 0002018 | — | 0.40 | 0.01 |
| Versatol Lot 0002018 | — | 0.40 | 0.02 |
| Univ. Hosp. Serum Pool 1 | — | 0.72 | 0.05 |
| Univ. Hosp. Serum Pool 1 | — | 0.63 | .03 |
| Univ. Hosp. Serum Pool 2 | — | 0.50 | 0.03 |
| | | | *Recovery (%)* |
| Versatol Lot 0002018 | 0.5 | 0.93[b] | 106.0 |
| Versatol Lot 0002018 | 0.5 | 0.90[b] | 100.0 |
| Univ. Hosp. Serum Pool 2 | 0.5 | 0.97[b] | 94.0 |

[a] Average of 3 determinations.

[b] Average of 2 determinations.

TABLE IV

MERCURY IN FISH AND FISH PROTEIN CONCENTRATE

| *Sample* | *Concentration found, this method*[a] *(p.p.m.)* | *Average deviation, (p.p.m.)* | *Concentration, Bureau of Fisheries (p.p.m.)* |
|---|---|---|---|
| 21-901 | 1.28 | 0.03 | 1.50 |
| FPC | 0.60 | 0.02 | 0.55 |
| 12-113 | 0.77 | 0.02 | — |

| | *Weight (g)* | *Mercury added (μg)* | *Mercury found (μg)* | *Recovery (%)* |
|---|---|---|---|---|
| 12-113 | 0.7582 | 0.50 as $HgCl_2$ | 1.05 | 94.0 |
| 12-113 | 1.0964 | 0.50 as $Hg(CH_3)_2Hg$ | 1.40 | 107.5 |
| 12-113 | 1.3865 | 0.50 as $Hg(CH_3)_2Hg$ | 1.55 | 94.3 |

[a] Average of 3 determinations.

the Department of Commerce, Bureau of Fisheries are included in Table IV. The Bureau of Fisheries uses a flameless atomic absorption technique to assay samples for mercury. Fish sample 12–113 had dried before weighing and could not be compared with the results of the flameless a.a.s. method. This dried sample was used to study recoveries of added mercury.

## DISCUSSION

The procedure given above provides an alternative method for the determination of mercury in biological samples. The amounts of mercury found in 24-h urine samples are similar to the 7.6 μg/day reported by Gibbs[15]. The amounts of mercury found in the fish samples that were analyzed by this method are in agreement with the values determined by the Bureau of Fisheries. Satisfactory recoveries (94.0–107.5%) of mercury added to the samples were obtained, indicating that little or no mercury is lost during the procedure.

Kinetic methods of analysis offer greater sensitivity than many other methods of analyis. Elements for which kinetic methods may be employed can be found in the monograph by Yatsimirskii[16] or the article by West[17]. When the sensitivity of these methods is coupled with a precise and accurate method of determination, such as coulometry, a highly reliable method of trace analysis is obtained.

The digestion procedures used here are designed for mercury assays, but should find applications in the analysis of samples which contain other volatile components. Dithizone was the reagent of choice for the separation of mercury from the digested samples, since it has a large affinity for mercury(II) ($\log E_{MR_n} = 43.8$ for dithizone in chloroform)[18], and silver, which interferes in the kinetic reaction, can be excluded from the extraction by adding suitable masking agents.

## SUMMARY

A method for the determination of the mercury in biological samples has

been developed. Procedures for the destruction of the samples ensure that no mercury is lost by volatilization. The mercury present in the samples is assayed by a kinetic–coulometric method that is sensitive to 10 p.p.b. of mercury. Recoveries of mercury added to samples before analysis range from 94.0 to 107.5% of the added mercury. The amounts of mercury found in the urine and fish samples analysed by this method are in agreement with those levels determined by other procedures.

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## SHORT COMMUNICATION

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# Molecular emission cavity analysis (MECA) — A new flame analytical technique

## Part IV. The determination of arsenic and antimony

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The determination of arsenic by flame atomic spectrometry presents some difficulties because its resonance lines occur in the far ultra-violet region of the spectrum; also, the ground-state atoms of antimony are difficult to excite by thermal means. Studies[1,2] of the atomic emission of arsenic and antimony have been made, however, by measuring their chemiluminescent emission in the reaction zone of an oxyacetylene flame, whilst an organic solvent was aspirated. Under these conditions a limit of detection for arsenic of 2.2 p.p.m. was obtained. West *et al.*[3] claimed detection limits of 1 p.p.m. of arsenic by atomic fluorescence at 189 nm in an air–acetylene flame and 0.2 p.p.m. in the nitrogen–hydrogen flame. The detection limit for antimony at 217 nm obtained by a similar method[4] was 0.05 p.p.m.

Several publications have reported the use of arsine and stibine for the determination of arsenic and antimony by atomic spectrometry as a means of obtaining more sensitivity. Chu *et al.*[5] described a method for the flameless determination of sub-$\mu$g amounts of arsenic at 193.7 nm, based on arsine evolution in an electrically heated absorption tube; their procedure involved a pre-reduction of arsenic from the pentavalent to the trivalent state before arsine was generated from an acidic solution containing zinc granules. Braman *et al.*[6] described an atomic emission method for the determination of arsenic and antimony at 228.8 and 252.5 nm, respectively, in a d.c. discharge, based on arsine and stibine evolution from an aqueous 1% sodium borohydride solution; no prior reduction for arsenic or antimony was needed, and the limits of detection were 0.5 and 1.0 ng for arsenic and antimony, respectively. Yamamoto *et al.*[7] described an atomic absorption method for the determination of antimony at 231 nm in an argon–hydrogen flame; antimony(III) in acidic solution was converted to stibine by zinc tablets made from zinc powder (200 mesh) and water, and the sensitivity was about 0.004 p.p.m. of antimony.

### *Determination of arsenic and antimony by MECA*

In molecular emission cavity analysis, the sample is placed within a small cavity at the end of a rod, which is then positioned in a hydrogen–nitrogen flame, so that the flame-gases flow almost vertically past the entrance of the cavity. The sample in the cavity is vaporized, and emits band emissions characteristic of the elements in the sample. Previous papers have described the application of this technique to the determination of sulphur[8], selenium and tellurium[9], and boron[10].

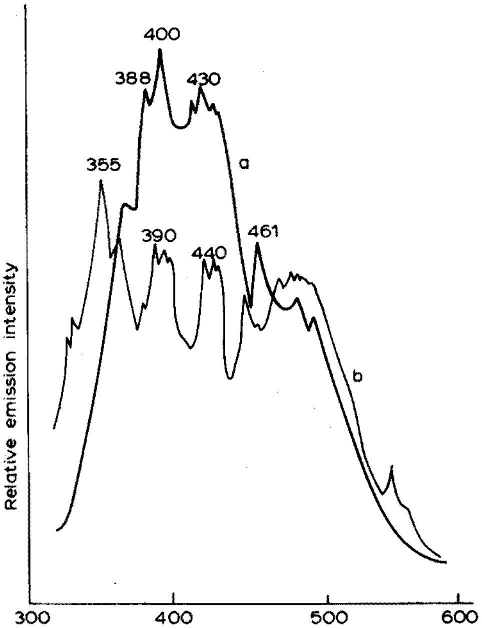
If arsenic or antimony is aspirated as the chloride into a hydrogen diffusion flame, a faint bluish-white emission is obtained. When placed in the cavity, these samples give similar emissions in the flame outside the cavity. Introduction of oxygen into the cavity, however, gives an intense emission restricted within the cavity. As with boron[10], in order to decrease the number of interferences, especially those of metal ions causing the formation of involatile metal salts, and to extend the applications of the method to millilitre samples[10], a volatilization system has been applied. Arsenic and antimony are reduced by sodium borohydride to arsine and stibine, respectively, and the gases are swept into the MECA cavity, placed in a hydrogen–nitrogen diffusion flame, by a slow stream of nitrogen. The intensity of the resulting band emission within the cavity is recorded as a function of time, and the maximal emission intensity is measured at the appropriate wavelengths. Under such conditions, the emission of arsenic and antimony occurs in the flame above the cavity. However, by mixing oxygen with the nitrogen carrier-gas just before it enters the cavity, the emission can be restricted within the cavity[10].

Sodium borohydride was chosen as a reductant, as it is powerful enough to reduce trivalent and pentavalent arsenic or antimony to the hydrides[6]. The generation of arsine and stibine by zinc granules was also studied. Because the use of zinc needs a pre-reduction step[5-7] and because of the small size of the reaction tube in the volatilization system, the use of sodium borohydride was preferred.

With this system, the molecular emission spectra of arsenic and antimony were recorded by injecting a 1-ml sample, containing a relatively large amount (1 mg) of arsenic or antimony, into the reaction tube and passing a slow stream of nitrogen through the tube to carry the gases evolved to the cavity. This gave a constant emission intensity for about 2 min. The spectra obtained are shown in Fig. 1. Arsenic and antimony were found to give broad spectra covering the range 330–550 nm, with the most intense peaks at 400 and 355 nm, respectively. The only antimony continuum reported in a flame was obtained by Dagnall *et al.*[11], and this was mostly in the visible region with a maximum at 578 nm. The emission has also been studied in arcs and a discharge tube and was attributed to SbO species[12-13]. The species responsible for the emission band of arsenic is not known unequivocally.

The effect of time of generation of arsine from 10 μg of arsenic was investigated. It was found that 1 min was sufficient to give maximal production of arsine. The sensitivity for arsenic obtained by peak height measurement was increased about five times compared to that obtained by measuring the emission intensity directly after the injection of the sample, because the maximal production of arsine is achieved before sweeping into the cavity.

The effect of flame composition on the emission intensity from 50 μg of arsenic was studied at two different nitrogen flow rates. Figure 2 shows that the optimal flow rates for hydrogen and nitrogen in the flame are 1.7 and 3.5 l min$^{-1}$, respectively. The effect of nitrogen carrier-gas flow rate on the emission response was also studied. A higher carrier-gas flow rate reduced the time required to sweep



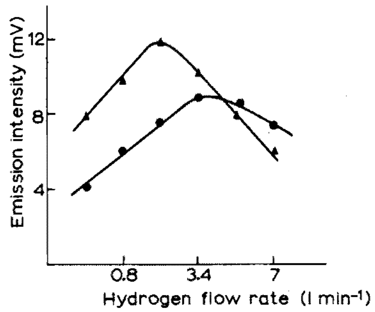


Fig. 1. Spectra of (a) arsenic; (b) antimony. $H_2=3.4$ l $min^{-1}$, $N_2=5.5$ l $min^{-1}$, $O_2$ in cavity=110 ml $min^{-1}$.

Fig. 2. Effect of hydrogen flow rate on arsenic emission intensity at 400 nm. (▲) 3.5 l $N_2$ $min^{-1}$; (●) 5.5 l $N_2$ $min^{-1}$.

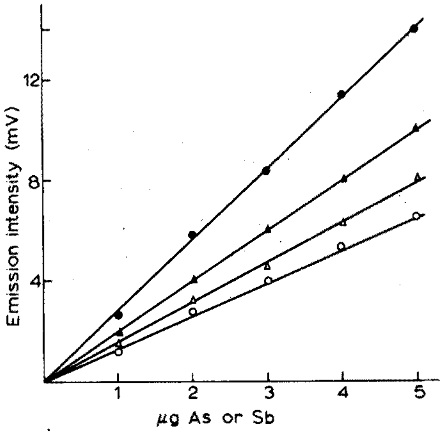


Fig. 3. Calibration plots for: (▲) Sb, with He–$H_2$ flame; (●) As with He–$H_2$ flame; (△) Sb with $N_2$–$H_2$ flame; (○) As with $N_2$–$H_2$ flame.

out the hydride and thus increased the peak emission intensity. The maximal emission intensity for 1-ml samples occurred at 160–200 ml $min^{-1}$ of nitrogen.

The optimal conditions for arsenic were also found to be optimal for antimony. On the basis of these results, a procedure was devised for the determination of arsenic or antimony in aqueous solutions. Linear calibration graphs (Fig. 3) were obtained in the range 0.5–5 p.p.m. of arsenic and antimony, by the recommended procedure, with a standard deviation of 0.14 p.p.m. Also, as shown in Fig. 3, the sensitivity for arsenic and antimony was enhanced by using helium instead of nitrogen in the flame and as a carrier-gas. This probably arises from the decreased collisional deactivation in the presence of the monoatomic helium.

### *Interferences*

Large amounts of certain metal ions will react with the sodium borohydride to produce metal borides or the free metal suspension. Several cations and anions were tested for interference: 20 μg of $Al^{3E}$, $Ge^{4E}$, $Ga^{3E}$, $Cd^{2E}$, $Mn^{2E}$, $Co^{2E}$, $Ni^{2E}$, $Zn^{2E}$, $Cl^{G}$, $NO_3^{G}$, $SO_4^{2G}$ and $PO_4^{3G}$ did not interfere in the determination of 4 μg of arsenic or antimony; 10 μg of $Cu^{2E}$ and $Ag^{E}$ decreased the emission response of arsenic and antimony by about 25%, but 4 μg of copper and silver did not interfere. The interference could arise from the formation of copper or silver arsenide or antimonide. Because of the almost complete spectral overlap, arsenic and antimony interfered in the determination of each other.

### *Experimental*

The spectroscopic equipment and the experimental techniques used were as described previously[8‡10] unless otherwise stated.

*The volatilization system.* The apparatus for the generation of arsine and stibine was similar to that described previously[10] for generation of methyl borate, and was connected to the cavity *via* an injection head supplied with oxygen[10]. The volatilization chamber was a test tube with a side arm covered with a septum to serve as an injection port. A two-way tap was connected to the system, as shown in Fig. 4, to allow the nitrogen carrier-gas to pass to the cavity without passing through the reaction tube, so as to give a constant background before and after sweeping through the evolved gases. The sample to be analysed was injected into the reaction tube at room temperature. When reaction was complete, the two-way tap was turned, to allow the nitrogen to pass through the reaction tube and carry the accumulated gases into the cavity. A cotton wool plug was inserted in the tube between the reaction vessel and the cavity to prevent carry-over of sodium-containing mist.

*Reagents.* Standard arsenic and antimony solutions (1000 p.p.m.), were prepared by dissolving, respectively, 0.68 g of A.R. arsenic(III) oxide in 500 ml of distilled water containing 2 g of sodium hydroxide, and 1.53 g of antimony

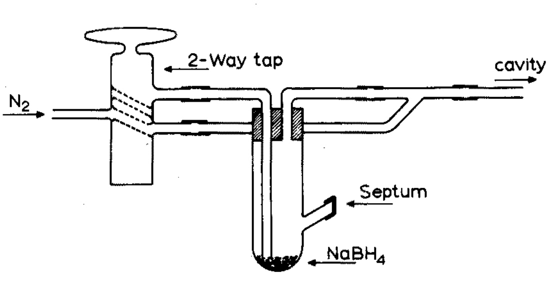


Fig. 4. Volatilization system for generation of arsine and stibine.

potassium tartrate in 500 ml of distilled water.

*Optimal gas flow rates.* Nitrogen: 3.5 l min$^{G1}$ (or helium at the same flow rate). Hydrogen: 1.7 l min$^{G1}$. Nitrogen carrier gas: 160 ml min$^{G1}$ (or helium at the same flow rate). Oxygen into cavity: 110 ml min$^{G1}$).

*Procedure.* The two-way tap was set to allow the nitrogen to pass to the cavity without passing through the reaction tube. The test solution (1 ml, containing 0.1–5 μg of arsenic or antimony) was injected through the septum into the reaction tube containing 0.3–0.5 g of sodium borohydride. Reduction was allowed to continue for 1 min. The two-way tap was turned to allow the carrier gas to pass through the tube and carry the evolved gas to the cavity. The peak emission intensity was measured at 400 nm for arsenic, or 355 nm for antimony. Calibration graphs were prepared by taking standard arsenic or antimony solutions (1 ml) through this procedure. After 3 ml of sample had been injected, the tube was replaced with a clean one containing fresh sodium borohydride.

The emission response began almost immediately after turning the two-way tap, reached a maximum within 1–2 s, and decreased to the background value over 40 s..

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*Analytica Chimica Acta*, 72 (1974) 188–193

## SHORT COMMUNICATION

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# Observations on the atomic absorption behaviour of some of the rare earth elements

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The rare earth elements (or lanthanides) all exhibit very similar chemical and physical properties. Their oxides occur together in mixed ores such as monazite and bastnaesite. The recent increased availability of these metals in pure form has resulted in a rapid growth in the number of industrial applications of the metals and their compounds, and considerable interest now exists in their determination by spectroscopic methods, which alone can provide the necessary selectivity. Scandium and yttrium are usually included with the rare earths in any published work.

Fassel and Mossotti[1] in 1963, using a fuel-rich oxyacetylene flame and photographic detection, found that the four scandium wavelengths of 390.7, 391.2, 402.0 and 402.4 nm all gave sensitivities of 5 $\mu$g ml$^{-1}$. The spectral line at 410.2 nm returned a sensitivity of only 100 $\mu$g ml$^{-1}$, though other literature reports show this to be the most sensitive. In 1966, Amos and Willis[2], describing the introduction of the nitrous oxide–acetylene flame, reported a sensitivity of 0.8 $\mu$g ml$^{-1}$ for scandium at 391.2 nm and 5.0 $\mu$g ml$^{-1}$ for yttrium at 410.2 nm, and determined the sensitivity for most other rare earth elements, each at several resonance lines. Jaworowski *et al.*[3], evaluating the total consumption oxyacetylene burner of Kniseley *et al.*[4], and the laminar-flow nitrous oxide–acetylene burner of Amos and Willis[2], concluded that the nitrous oxide–acetylene flame "outperforms" the oxyacetylene flame in analysis for rare earths, though this may be a result of flame length rather than flame reaction. Kinnunen and Lindsjo[5] reported on the interferences encountered between twelve rare earth elements in a phosphate rock matrix. Europium was determined in yttrium phosphors by Scott[6] who claimed coefficients of variation of 1.4% within the europium range 2.30–5.45%, with no interference from yttrium or vanadium. Van Loon *et al.*[7] described a procedure for determining nine rare elements in zirconium and calcium rare-earth silicates. The addition of lanthanum chloride was said to overcome most interference problems. The emission technique was shown by Fassel *et al.*[8] to be superior to absorption for the determination of rare earth elements. Other workers[9–13] have reported serious chemical interferences by mineral acids and metal ions.

However, mention is rarely made of the general difficulties in the deter-

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mination of these elements, in particular, the effects of variations of fuel flow rate and observation height on their absorption characteristics. The following observations, carried out on two different atomic absorption spectrophotometers, show that, in general, the parameters are element-dependent rather than instrument-dependent. They should therefore assist the analyst in deciding upon the conditions to be used in routine analysis.

### *Experimental*

*Apparatus.* Two atomic absorption spectrophotometer models were used to determine whether the effects of variations in instrumental parameters were common to both. The instruments were a single-beam Unicam SP90 Series 2, with an AR25 recorder readout, and a Unicam SP1900 double beam spectrophotometer reading out into a DR10 digital printer. Hollow-cathode lamps were also Pye Unicam, and rare earth metals were Specpure quality (Johnson Matthey).

*Sample preparation.* All of the rare earths considered tend to form an oxide film on their surfaces where exposed to moist air. Therefore precautions, such as storing in sealed containers, must be taken. Portions (1.000 g) of the pure metal were dissolved in 20 ml of 20% hydrochloric acid and diluted to 100 ml with water, to give working stock solutions of 10,000 mg $l^{-1}$.

*Ionization.* Amos and Willis[2] discussed the ionization of the rare earth metals in the nitrous oxide–acetylene flame and overcame the effect by addition of either $K^+$ or $Cs^+$ as an ionization buffer. All of the results given here were obtained with the addition of 1,000 mg $l^{-1}$ K as KCl to the solution.

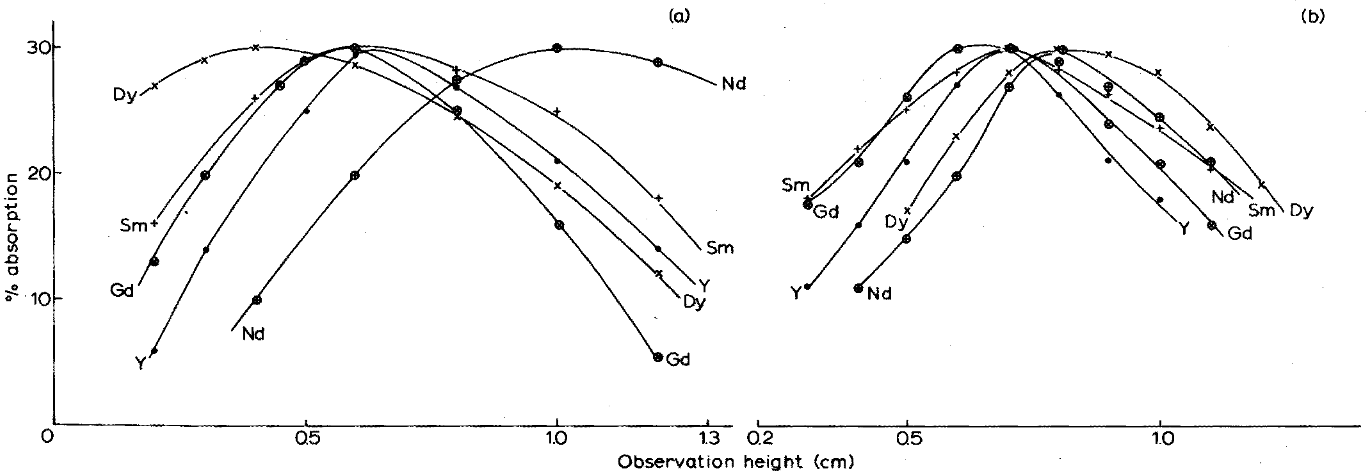
*Instrumental parameters.* Most of the elements described here have several suitable wavelengths for absorption and these are dealt with elsewhere[1,2,8].

### *Results*

Figures 1 and 2 show the effects of varying observation height at optimal fuel flow, and of varying the fuel flow at optimal observation height, on the absorption characteristics of the rare earths. All parameters are listed in Table I. Unlike the majority of elements determined by atomic absorption, the optimal conditions for rare earths appear to be obtained only by critical adjustment of these parameters.

From the SP90 results for each of the two parameters, it appears that only one element out of the five in each case behaves differently from the majority. For example, if the acetylene flow were set at about 4.3 l $min^{-1}$, this would suit all of the elements except samarium whose sensitivity would be reduced by about 25%. Similarly, the sensitivity of neodymium would be reduced by about 35% if the optimal observation height of 0.6 cm for the remaining elements were used.

In the case of the other instrument used, the SP1900, although most of the graph shapes are very similar to those for the SP90, the common setting used on the SP90 for all but one element does not hold for the SP1900. For example, the optimal acetylene flow settings are samarium 4.1, neodymium 4.2, gadolinium 4.3, yttrium and dysprosium 4.4 l $min^{-1}$, and if an average setting of 4.3 were used the losses in sensitivity would be 13% for yttrium, and 10% for samarium. These losses, however, are not serious and, provided that sensitivity is not the limiting factor in a particular determination, the single fuel flow setting of 4.3 l



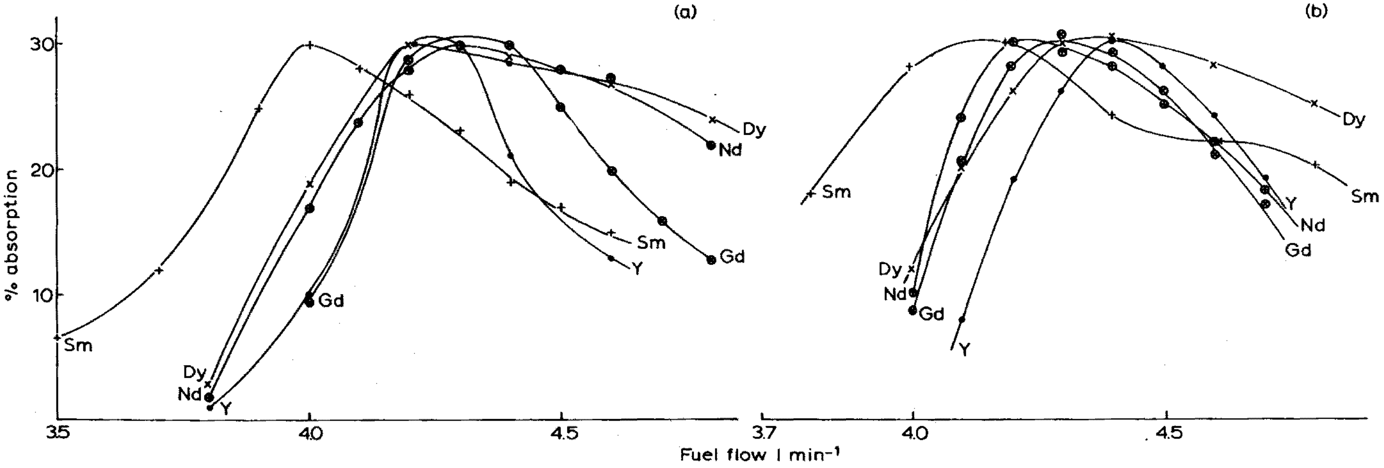


Fig. 1. Effect of observation height on absorbance of rare earth elements. (a) SP90, (b) SP1900.

Fig. 2. Effect of fuel flow rate on absorbance of rare earth elements. (a) SP90, (b) SP1900.

TABLE I

INSTRUMENTAL CONDITIONS

(In all cases, the slitwidth was 0.05 mm for the SP90 and 0.20 mm for the SP1900. A nitrous oxide burner was used, and the nitrous oxide flow rate was 5.0 l min$^{-1}$)

| | | *Dy* | *Gd* | *Nd* | *Sm* | *Y* |
|---|---|---|---|---|---|---|
| *Wavelength (nm)* | | 421.2 | 368.4 | 492.5 | 429.7 | 410.2 |
| *Observation height (cm)* | SP90 | 0.4 | 0.6 | 1.0 | 0.6 | 0.6 |
| | SP1900 | 0.8 | 0.7 | 0.8 | 0.7 | 0.7 |
| *Acetylene (l min$^{-1}$)* | SP90 | 4.2 | 4.3 | 4.3 | 4.0 | 4.3 |
| | SP1900 | 4.4 | 4.3 | 4.2 | 4.1 | 4.4 |

TABLE II

SENSITIVITIES, DETECTION LIMITS AND PRECISIONS (REPRODUCIBILITIES) OBTAINED

| *Element* | *SP90* | | | *SP1900* | | |
|---|---|---|---|---|---|---|
| | *Sensitivity for 1% abs. (μg ml$^{-1}$)* | *Detection limit (μg ml$^{-1}$)* | *Precision (%)* | *Sensitivity for 1% abs. (μg ml$^{-1}$)* | *Detection limit (μg ml$^{-1}$)* | *Precision (%)* |
| Gd | 40 | 15 | 1.8 | 14.5 | 3.0 | 1.0 |
| Dy | 1.0 | 0.4 | 0.90 | 0.20 | 0.06 | 0.40 |
| Nd | 11 | 2.0 | 4.9 | 4.5 | 0.6 | 0.70 |
| Sm | 2.7 | 1.0 | 2.8 | 2.0 | 0.06 | 0.39 |

min$^{-1}$ could be used. As far as observation height on the SP1900 is concerned, the elements tend to form two groups; samarium, gadolinium and yttrium all have optimal observation heights of 0.7 cm, whilst dysprosium and neodymium are best at 0.8 cm. However, if an average height of 0.75 cm were used, the worst reduction in sensitivity would only be about 5%. Therefore, for general routine analysis, a fuel flow of 4.3 l min$^{-1}$ with an observation height of 0.75 cm on the SP1900 would be satisfactory for most work. On the SP90, conditions of 4.3 l min$^{-1}$ and 0.6 cm would suffice for yttrium, gadolinium and dysprosium, but for samarium and neodymium one of the parameters would need changing. Table I lists those parameters in more detail and for individual elements these are the recommended ones; but where several elements are to be determined sequentially, the above compromise conditions will normally suffice.

The sensitivities and detection limits (Table II) were all obtained with the individually listed parameters for each element; where the compromise conditions are used, obviously the performance figures will be somewhat worse.

*Precision analysis*. The initial object of this work was to determine the precision with which major levels of these rare earth metals could be determined. With analogue readout instruments, *e.g.* the SP90, precision is poor at major levels, but the application of "difference atomic absorption" improves the precision[14,15]. Table II shows the precision obtained on aqueous solutions giving rise to an absorbance signal of about 0.5 under the conditions in Table I. Precision, defined as the coefficient of variation of 10 readings and expressed as a percentage, is a measure of the repeatability of a signal, and is measured on a solution giving a signal of about 0.5 absorbance. The results show how the double-beam SP1900 gives precisions which are superior to those which can be obtained when the single-beam instrument is used.

The literature clearly shows that many chemical interferences occur in the determination of these elements. This was confirmed by measuring the absorbance of the elements gadolinium, dysprosium, neodymium, samarium and yttrium in a mixed solution on the SP1900, and comparing the results with the absorbance of their individual solutions. Table III shows that even when all five elements are determined under optimal conditions, interelement interferences remain. Further investigation was outside the scope of this work.

TABLE III

INTERFERENCES OF THE RARE EARTHS IN A MIXED SOLUTION

| *Element* | *Solution strength ($\mu g\ ml^{-1}$)* | *Absorbance* | |
|---|---|---|---|
| | | *Individual solution* | *Mixed solution* |
| Gd | 1000 | 0.310 | 0.350 |
| Dy | 20 | 0.270 | 0.440 |
| Nd | 500 | 0.450 | 0.600 |
| Sm | 500 | 0.500 | 0.378 |
| Y | 200 | 0.815 | 0.805 |

## *Conclusion*

The inherently poor sensitivities and detection limits for most of the rare earths, when compared with some of the more common elements, makes difficult the application of atomic absorption to the determination of trace concentrations. It appears, however, that the majority of interest lies in the determination of minor and major components of these elements. The technique of atomic absorption spectrophotometry is then more suitable, provided that careful attention is given to the problem of interferences, arising from mineral acids and other rare-earth elements, and also that the critical nature of the basic instrumental parameters is realized.

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## SHORT COMMUNICATION

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# Selective determination of iron in alloys by reaction with 2,3-pyridinediol and ring colorimetry

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*o*-Dihydroxy compounds of pyridine are known to form complexes with iron[1]. The stepwise formation of blue and red complexes of iron(III) with 2,3-pyridinediol has been elucidated spectrophotometrically[1]. This reagent can be more usefully and conveniently employed for the selective determination of iron, especially when present in trace concentrations, if it is used in conjunction with ring-oven colorimetry[2]. The ring colorimetric procedure is shown here to be excellent for the evaluation of traces of iron in alloys.

### *Experimental*

*Reagents.* An ethanolic 0.5% solution (brown coloured) of 2,3-pyridinediol (Aldrich) was used. All other reagents were of analytical grade. Anions were tested as their sodium or potassium salts, while cations were taken as their chlorides or nitrates; solutions were standardized by the usual methods, where necessary.

Iron(III) perchlorate (0.1 mg $ml^{-1}$) solution was used as the standard.

*Apparatus.* A Weisz ring oven (National Appliances Co., Portland, Oregon) was used, with an Agla micrometer syringe for the application of test solution to the filter paper on the ring oven.

*Procedure.* Place a filter paper (Whatman No. 41, 55 mm diameter) on the ring oven maintained at 100–110°C and fix in position with the retainer ring. Spot the central area of the filter with the reagent (2 drops) and dry. Next, apply a known volume of the test solution with an Agla micro syringe, dry, and then wash the complex to the ring zone with five 15-μl portions of water. A bluish-violet ring indicates the presence of iron(III). Spray the ring wih aqueous 6% (w/v) sodium hydroxide so that the blue colour changes to red. Compare the intensity of the ring with a standard scale prepared by taking 1, 2, 4, 6, 8, 10 and 12 μl of the standard iron(III) solution through the procedure.

### *Results*

Tests carried out in the range 0.18–0.72 μg of iron(III) gave results which showed errors ranging from 0% to −3%.

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The range for the determination of iron was found to be 0.15 – 0.7 μg in the total ring; outside this range, visual comparison was not feasible.

The validity of the procedure was tested for two different alloys after dissolution in hydrochloric acid. The results are shown in Table I.

TABLE I

ANALYSIS OF ALLOYS

| *Alloy taken* | *Iron present (%)* | *Iron found*[a] *(%)* | *Error (%)* |
|---|---|---|---|
| BCS 181/1; 4% Cu–Al alloy; other constituents present were Cd, Zn, Mg, Ni, Si and Fe | 0.36 | 0.34 | –5.5 |
| BCS 178/1; tin base white metal; other constituents present were Zr, Al, Cd, Sb, Sn, Bi, As and Fe | 0.072 | 0.070 | –2.8 |

[a] Average of three results.

The interferences of various ions were studied by developing rings for 0.6 μg of iron(III) in the presence of varying amounts of foreign ion up to 15 μg. Ions found not to interfere are:

$NH_4$, Li, Na, K, Rb, Cs, Ag, Cu(I), Cu(II), Hg(I), Hg(II), Cd, Be, Mg, Ba, Sr, Ca, Pb(II), Sn(II), Sn(IV), Ni, Co(II), Zn, Mn(II), Cu(III), Al, Ga, In, Tl(I), Tl(III), Bi, Sb(III), Sb(V), As(III), As(V), Se(IV), Se(VI), Te(IV), Te(VI), Nb, Ta, V(IV), V(V), Pt(IV), Au(III), Os(VIII), Ir(III), Ir(IV), Ru(III), Rh(III), Pd(II), Ge, Ti(IV), Th(IV), U(VI), La(III), Zr(IV), $Cr_2O_7^{2-}$, $Cl^-$, $Br^-$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $CN^-$ and $SCN^-$. However, W(VI), Mo(VI), $S_2O_3^{2-}$, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$, $C_6H_5O_7^{3-}$, $Ce^{4+}$, $F^-$, $I^-$ and $IO_3^-$ interfered.

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## SHORT COMMUNICATION

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### Determination of carbohydrates by thermometric titrimetry

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In the field of carbohydrate chemistry, one of the most widely applied reactions is that in which the carbohydrates are oxidized by periodate. The analysis of the reaction products has been used for various purposes, including structural analysis as well as a method of assay for the 1,2-diol systems. In a recent review of the periodate oxidation of diols, Dryhurst[1] indicated that the correct choice of pH for the oxidation is of significance in determining the rate of the oxidation and the relative amounts of the reaction products obtained. In the classical Malaprade reaction[2] the use of an acidic medium (1.5 *N* with respect to sulphuric acid) is advocated, and the time required for completion of the reaction may be up to 12 h. In a less acidic medium (pH 1.6) the reactions are faster[3]. Price *et al.*[4,5], in a study of the effects of variation of pH on the reaction rate, showed that in the neutral and basic pH range the reaction rate decreased with increasing pH. If phosphate buffers are used to control the pH, over-oxidation and other undesirable reactions occur[6], and hence the use of such buffers is to be avoided in quantitative work. A solution of sodium metaperiodate has a pH of about 4 and thus must be acidified before use.

The usual method of assay is to add an excess of the acidified periodate reagent and, after the oxidation of the carbohydrate is complete, to determine the excess of the periodate by addition of potassium iodide and titration of the liberated iodine. This method is subject to error for various reasons, including a slow reaction between periodate–glycol complexes and iodide ion[3] in neutral solution, and consumption of iodine by some of the intermediates produced during the reaction[7]. These errors may be significant when arsenite is used as the titrant. In the presence of acid these intermediates do not consume iodine and thus, as an excess of acid is present in the thiosulphate method of Malaprade, the latter method is preferred by some workers.

Many industrial samples containing carbohydrates are coloured (often as a result of partial caramelization of the carbohydrate or as a result of the addition of permitted food colours), hence methods of assay involving visual methods for detection of the equivalence point may be subject to error. Instrumental methods involving potential measurements often fail because of the surface-active materials

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present and also because of the relatively low conductivity of the sample solutions.

The use of thermometric methods in such solutions has been previously described[8], and the use of thermometric titrimetry for redox reactions with relatively high enthalpy changes has been reported[9].

Preliminary investigations of various methods for the determination of periodate in the presence of iodate indicated that the reaction between hydrazine sulphate and periodate has a very high enthalpy change both in acidic medium ($\Delta H = -650 \pm 1.0$ kJ mol$^{-1}$) and in neutral (hydrogen carbonate) media ($\Delta H = -333.5 \pm 1.0$ kJ mol$^{-1}$). Moreover, the kinetics of the reaction are such that even at the concentrations encountered at the equivalence point, the rate of the reaction is sufficiently great to allow the automated techniques normally used in direct thermometric titrimetry to be successful.

## *Experimental*

*Apparatus.* The initial oxidation of the carbohydrates and the subsequent determination of the excess of the periodate were done in the titration vessel of a thermometric titration apparatus, similar to that previously described[9]. The basic circuit of the electrical bridge system has also been previously described[10]; the temperature sensor used was a thermistor with a nominal resistance of 10,000 ohms at 25°C.

The titrant was delivered from an LKB peristaltic pump, delivering titrant at a rate of about 0.35 cm$^3$ min$^{-1}$ (the actual rate being determined by gravimetry). The mixtures were stirred magnetically.

*Reagents.* An aqueous solution (0.1 *M*) of analytical reagent-grade sodium metaperiodate (Hopkin & Williams) was used throughout. Freshly prepared aqueous solutions (0.1–0.2 *M*) of hydrazine sulphate solutions were used as the titrant. The carbohydrates examined are listed in Table I.

*Procedure.* Dissolve a known weight of the carbohydrate (25–50 mg) in 0.01 *M* sulphuric acid (5 cm$^3$) and add a known (excess) amount of an aqueous solution of sodium metaperiodate (20 cm$^3$ of 0.1 *M* solution). Stir for 30 min, at room temperature in the insulated block of the titrator. Adjust the pH of the solution to 7–7.5 with saturated sodium hydrogen carbonate solution. When thermal equilibrium is re-established, titrate with the hydrazine sulphate solution from the automatic pump. Record the enthalpogram on a potentiometer strip recorder (f.s.d. 10 mV; chart speed 3 cm min$^{-1}$; thus 1 cm of chart length corresponds to *ca.* 0.1 cm$^3$ of titrant delivered).

## *Results and discussion*

The effects of variations in the acidity and temperature of the medium in which the oxidation of the diol takes place, and the time for completeness of oxidation, were studied. At temperatures between 20°C and 30°C, there was no appreciable difference in the rate of oxidation at any particular pH. The pH of the solution was varied between 1.5 and 3.0. The change in the rate was not great, but the optimal rate was found at pH 1.5–2.0.

The time was varied between 15 min and 60 min. All the carbohydrates used were oxidized in less than 30 min.

It was also established that, at the pH proposed for the reduction of

TABLE I

RESULTS OBTAINED FOR DIFFERENT CARBOHYDRATES

| *Compounds* | *% Recovery*[a] | | |
|---|---|---|---|
| | *100 mg (Malaprade)* | *25 mg used* | *50 mg used* |
| Arabinose | 98.9 | 99.9 | 100.1 |
| Dulcitol | 99.2 | 100.05 | 99.7 |
| Galactose | 98.2 | 98.5 | 98.2 |
| Glucose (monohydrate) | 99.6 | 101.0 | 100.5 |
| Mannitol | 99.4 | 99.4 | 99.5 |
| Mannose | 99.0 | 99.0 | 99.0 |
| Rhamnose | 99.7 | 100.2 | 100.7 |
| Ribose | 99.2 | 100.8 | 99.25 |
| Sorbitol | 98.5 | 98.9 | 99.5 |
| Xylose | 99.2 | 99.3 | 99.25 |

[a] Each result is the average of 4–5 determinations.

periodate, amounts of iodate up to 30-fold the amount of periodate were not reduced by hydrazine.

The compounds were assayed by the recommended method and also by the standard Malaprade method; for the latter, the excess of periodate was masked by molybdate, and the iodate produced was determined iodimetrically. In order to achieve an acceptable precision by this method, 100 mg of each carbohydrate were used. A comparison of the results is given in Table I.

Since galactose gave the lowest result, a standard deviation of the method was found with this carbohydrate as the analyte. Weighed aliquots (nominally 25 mg, actually between 24 and 26 mg) of galactose were assayed; the average purity of ten samples was found to be 98.47% (range 99.7–97.7%) and the standard deviation obtained was 0.211.

The use of hydrazine at pH 7–7.5, to reduce the periodate, gives only iodate ion, water and nitrogen as the products of the reduction. This obviates the possibility of reactions between any of the products of the indirect assay reaction reacting with the products of the periodate–diol reaction, so that the method has a greater potential range of uses than has the classical iodimetric method.

The method is faster than the classical Malaprade method, and has a greater precision on smaller samples. It can be used in coloured solutions which prevent the use of visual indicators and hence has a more direct use for foodstuffs analysis.

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## SHORT COMMUNICATION

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# Oxidative determination of α-hyponitrate with alkaline hexacyanoferrate(III)

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Although the reducing properties of α-hyponitrate ion (usually employed as the sodium salt, which is known as Angeli's salt, α-$Na_2N_2O_3$, sodium *N*-nitrohydroxylamate) were established long ago[1,2], only one redox reaction has been developed into a method[3] for the determination of the α-$N_2O_3^{2-}$ ion. This titration, which involves the oxidation of α-$N_2O_3^{2-}$ to nitrate with potassium permanganate, is cumbersome and time-consuming, because of the simultaneous oxidation of nitrite, which is often present in solutions of α-$Na_2N_2O_3$. The few other methods (spectrophotometric[4,5] and polarographic[6]) proposed for the determination of α-$N_2O_3^{2-}$ ion are subject to restricted operative conditions.

In the present communication, it is demonstrated that α-hyponitrate ion can be determined accurately and conveniently in alkaline solutions by oxidation at room temperature with hexacyanoferrate(III). Direct titration is possible with amperometric end-point detection, or the excess of hexacyanoferrate(III) can be back-titrated with appropriate reducing agents, such as arsenious oxide and vanadyl sulphate solution, to a potentiometric end-point. The method is advantageous because low concentrations of α-$N_2O_3^{2-}$ ion can be determined, and because nitrite ions do not interfere. The optimal conditions for the direct and indirect determination of the ion have been established. Common anions such as chloride, nitrate and sulphate do not interfere and ten-fold amounts of nitrite can be tolerated in this accurate and reproducible determination.

### *Reagents and apparatus*

Several samples of sodium α-hyponitrate were prepared by Angeli's method[7] and stored under nitrogen or vacuum; the products were characterized by potentiometric titration[8] at 1°C under nitrogen with standard hydrochloric acid, and by u.v. spectra[4] of their aqueous solutions.

Potassium hexacyanoferrate(III) (*ca.* 0.05 *M*) solutions were standardized iodometrically against sodium thiosulphate; 0.05 *N* arsenious oxide solution (in 1 *M* sodium hydroxide) was prepared in the usual way; *ca.* 0.05 *N* vanadyl sulphate solution was prepared and standardized with hexacyanoferrate(III)[9].

Voltammetric curves were recorded at 25±0.1°C with a three-electrode system and a Metrohm E261 Polarecord connected to an iR compensator (Metrohm type E446); a cell with a periodically renewed diffusion-layer bright platinum microelectrode[10] was employed. A simplified and more readily applicable version of this electrode was used for amperometric titrations—a bright platinum indicator electrode with bubbling[11] (surface of 0.08 $cm^2$), and with periodical renewal of the solution at the electrode surface by removal of 6 mm of the solution every 4 s. A standard calomel reference electrode was connected to the solution in the cell by a sintered glass bridge filled with saturated potassium chloride solution. Oxygen was removed by bubbling prepurified nitrogen through the solution. Biamperometric and potentiometric titrations were carried out with conventional apparatus.

*Preliminary tests*

It is known[1,4] that the $\alpha\text{-}N_2O_3^{2-}$ ion is stable in deaerated alkaline solution, so that all the measurements were performed under a nitrogen atmosphere and in at least 1 *M* hydroxide solution.

Preliminary voltammetric experiments showed that the $\alpha\text{-}N_2O_3^{2-}$ ion gives an ill-defined anodic wave at more positive voltages than +0.00 V. This wave, which is probably due to electrooxidation to nitrite, is not easily reproducible and unsuitable for analytical purposes. On addition of hexacyanoferrate(III) to the $\alpha\text{-}N_2O_3^{2-}$ in alkaline solution, the anodic wave ($E_{\frac{1}{2}} = +0.180$ V) of hexacyanoferrate(II) appears. When the molecular ratio between the hexacyanoferrate(III) added and the initial $\alpha\text{-}N_2O_3^{2-}$ increases just above unity, the cathodic branch of the cathanodic curve of the redox couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ appears.

Hexacyanoferrate(III) reacts with α-hyponitrate ion according to the equation:

$$Fe(CN)_6^{3-} + \alpha\text{-}N_2O_3^{2-} \rightarrow Fe(CN)_6^{4-} + NO + NO_2^- \qquad (1)$$

as suggested by Cambi[2] and verified, as follows, in the present study. The oxidation products (NO and $NO_2^-$) are both electroinactive at a platinum microelectrode in alkaline solution; only the nitrite ion can be determined voltammetrically below pH 8 at a platinized platinum electrode[12,13]. Samples of $\alpha\text{-}Na_2N_2O_3$ were reacted with an excess of hexacyanoferrate(III) in a vacuum system and both the solution and the gas evolved were examined. The quantitative formation of nitrite was tested voltammetrically with solution buffered at pH 7.6: at this pH value the oxidation of nitrite ion by hexacyanoferrate(III) ion does not occur, as blank runs showed. Purity tests and the determination of the nitric oxide evolved from reaction (1) were accomplished by i.r. analysis and by oxidation with alkaline peroxide solution[14], respectively. The results obtained are reported in Table I.

TABLE I

ANALYSIS OF $\alpha\text{-}Na_2N_2O_3$ OXIDATION PRODUCTS FROM REACTION WITH ALKALINE HEXACYANOFERRATE(III)

| $\alpha\text{-}Na_2N_2O_3$ *taken (mmol)* | $K_3Fe(CN)_6$ *added (mmol)* | *NO found (mmol)* | $NO_2^-$ *found (mmol)* |
|---|---|---|---|
| 0.82 | 1.50 | 0.80 | 0.84 |
| 0.82 | 4.00 | 0.79 | 0.82 |
| 0.65 | 1.00 | 0.62 | 0.65 |
| 0.65 | 5.00 | 0.63 | 0.64 |

In the utilization of eqn. (1) for the determination of the $\alpha$-$N_2O_3^{2-}$ ion, amperometric and biamperometric end-point detection methods were used. Up to within 2–3% of the equivalence point, the current stabilized immediately upon addition of hexacyanoferrate(III) solution. In the immediate vicinity of the equivalence point, it was necessary to wait 3–5 min for equilibrium at the 5 m*M* level. A titration at this level, corresponding to about 30 mg of $\alpha$-$Na_2N_2O_3$ in 50 ml, required less than 40 min. Trial experiments proved that the indirect determination of $\alpha$-$N_2O_3^{2-}$ ion, by back-titrating the excess of hexacyanoferrate(III) with arsenite[15] or vanadyl[9] solution, was also feasible. The results obtained were correct, the usual volumetric errors being obtained. The addition of osmium tetroxide as catalyst caused erroneous results probably because of its reduction by nitrite ion[16].

On the basis of the results obtained, the following procedures are suggested.

### *Procedures*

*Direct amperometric titration.* Place 50 ml of 1–3 *M* sodium hydroxide solution in a polarographic cell thermostatted at 25°C. Remove oxygen by bubbling prepurified nitrogen and add 30–80 mg of sodium $\alpha$-hyponitrate. Titrate with 0.05 *M* potassium hexacyanoferrate(III) solution at −0.100 V (SCE), bubbling nitrogen through the solution after each addition of the reagent. At the end-point, the reaction is rather slow and it is advisable to proceed slowly. After correction for dilution, plot the values of the mean limiting diffusion currents observed, after stabilization, against the volume of the reagent added. For the biamperometric end-point, apply 100 mV across the platinum electrodes; the titration curve is reversed-L-shaped, the rising portion of the curve corresponding to the electroreduction of the excess of titrant. The quantity of sodium $\alpha$-hyponitrate is then calculated in the usual way.

*Indirect determination.* Deaerate 50 ml of alkaline sodium $\alpha$-hyponitrate solution (containing 15–80 mg of $\alpha$-$Na_2N_2O_3$) in a 200-ml beaker, and add dropwise

TABLE II

AMPEROMETRIC AND BIAMPEROMETRIC TITRATIONS OF $\alpha$-$N_2O_3^{2-}$ ION IN 1 *M* HYDROXIDE WITH 0.0495 *M* HEXACYANOFERRATE(III) SOLUTION

| *Amperometric titration*[a] | | | *Biamperometric titration*[b] | | |
|---|---|---|---|---|---|
| *$\alpha$-$Na_2N_2O_3$ added (mg)* | *$\alpha$-$Na_2N_2O_3$ found (mg)* | *Error (%)* | *$\alpha$-$Na_2N_2O_3$ added (mg)* | *$\alpha$-$Na_2N_2O_3$ found (mg)* | *Error (%)* |
| 80.4 | 80.0 | −0.5 | 79.4 | 78.8 | −0.8 |
| 71.8 | 72.3 | +0.7 | 70.1 | 69.9 | −0.3 |
| 65.3 | 64.9 | −0.6 | 61.9 | 70.1 | +0.3 |
| 50.0 | 48.9 | −2.2 | 58.4 | 58.1 | −0.5 |
| 45.3 | 45.6 | +0.7 | 51.0 | 51.5 | +1.0 |
| 40.0 | 39.8 | −0.5 | 47.4 | 47.0 | −0.8 |
| 35.5 | 35.6 | +0.3 | 44.2 | 43.8 | −0.9 |
| 31.0 | 30.8 | −0.7 | 34.3 | 34.1 | −0.6 |

[a] Applied voltage: −0.100 V (SCE).

[b] 100 mV applied across the platinum electrodes.

TABLE III

INDIRECT DETERMINATION OF $\alpha$-$N_2O_3^{2-}$ ION IN ALKALINE SOLUTION

| $\alpha$-$Na_2N_2O_3$ taken (meq.) | $K_3Fe(CN)_6$ added (meq.) | $\frac{[Fe(CN)_6^{3-}]}{[\alpha\text{-}N_2O_3^{2-}]}$ | $As_2O_3$ or $VOSO_4$ required (meq.) | $\alpha$-$Na_2N_2O_3$ found (meq.) | Error (%) |
|---|---|---|---|---|---|
| *Back-titration with $As_2O_3$ solution* | | | | | |
| 0.3845 | 0.9925 | 2.58 | 0.6050 | 0.3875 | +0.8 |
| 0.3754 | 0.9925 | 2.64 | 0.6185 | 0.3740 | −0.4 |
| 0.3720 | 0.9925 | 2.67 | 0.6185 | 0.3740 | +0.5 |
| 0.4073 | 0.4888 | 3.66 | 1.0845 | 0.4043 | −0.7 |
| 0.3688 | 1.4888 | 4.04 | 1.1215 | 0.3670 | −0.5 |
| 0.1450 | 0.7444 | 5.12 | 0.6002 | 0.1442 | −0.6 |
| *Back-titration with $VOSO_4$ solution* | | | | | |
| 0.6486 | 1.4888 | 2.29 | 0.8417 | 0.6471 | −0.2 |
| 0.6118 | 1.4888 | 2.43 | 0.8798 | 0.6090 | −0.5 |
| 0.3978 | 0.9925 | 2.49 | 0.5921 | 0.4004 | +0.7 |
| 0.6050 | 1.9850 | 3.28 | 1.3825 | 0.6025 | −0.4 |
| 0.5821 | 1.9850 | 3.41 | 1.4001 | 0.5850 | +0.5 |
| 0.3823 | 1.9850 | 5.19 | 1.6045 | 0.3805 | −0.5 |

a known excess of 0.05 *M* hexacyanoferrate(III) solution; with continuous bubbling of nitrogen, set aside the mixture for 10 min. Add a concentrated (30%) solution of sodium hydroxide to raise the overall concentration of the alkali to about 8 *M*. Then titrate the excess of hexacyanoferrate(III) ion with 0.05 *N* arsenite or vanadyl sulphate solution, using potentiometric end-point detection[9,15]. On the basis of the quantity of arsenite or vanadyl ion equivalent to the hexacyanoferrate(III) consumed during the oxidation, the amount of sodium $\alpha$-hyponitrate can be calculated (1 ml of 0.05 *N* $As_2O_3$ (or $VOSO_4$) solution is equivalent to 6.1 mg $\alpha$-$Na_2N_2O_3$).

## *Results*

The results of some titrations of various quantities of sodium $\alpha$-hyponitrate by the above procedures are summarized in Tables II and III.

*Influence of different anions.* The influence of fairly large amounts (5%) of different anions was tested. Nitrate, chloride and sulphate do not interfere; the accuracy of the method is not affected by the presence of a large quantity (ten times that of $\alpha$-$Na_2N_2O_3$) of nitrite ion.

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## SHORT COMMUNICATION

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# Oxidized vitreous carbon indicator electrodes in acid–base titrations

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Vitreous carbon (glassy carbon) and pyrolytic graphite have both been proposed as indicator electrodes in acid–base titrations[1,2]. The electrodes are essentially inert and non-porous. They are considered to respond as oxygen electrodes, detecting the acid-dependent reduction of oxygen to water: $O_2 + 4\,H^+ + 4\,e = 2\,H_2O$. As with other solid electrodes, the absolute potential depends critically on the condition of the electrode surface and its preparation. The potential break at the end-point in the titration is reported to be small for vitreous carbon.

Vitreous carbon is attacked by electrolytically generated oxygen producing a shining black glassy surface[3]; there is evidence of attack from inside the surface. This behaviour resembles that of graphite, where the reaction is used to produce a black form of graphitic oxide[4]. Graphitic behaviour is uncharacteristic of vitreous carbon but, from chemical behaviour, it is considered that this oxidation product of vitreous carbon is also graphitic oxide in an identical or closely related form. The oxidized surface of the vitreous carbon is no longer inert, and electrodes made from it have a potential response which is different to that of the untreated material. This communication describes the use of electrodes of vitreous carbon, modified by surface oxidation in this way, as indicator electrodes for acid–base titrations.

### *Experimental*

Vitreous carbon grade V25, heat-treated at 2500°C (Le Carbone Ltd.) was obtained as 3-mm diam. rods. Electrodes were prepared by cementing the rod into 3-mm bore, thick-walled tubing with Araldite epoxy resin cement. The surface area was varied by exposing different lengths of rod. However, for reproducibility in preparation and ease of cleaning, the majority were ground flat with the end of the tube, and polished with wet carborundum paper. The construction is shown in Fig. 1. Electrical contact was made with copper wire through a bead of mercury. The electrode was sealed with more Araldite.

The exposed area (7.1 $mm^2$) was oxidized by passing (usually) 1 coulomb of electricity (5 mA for 200 s) through an electrolysis cell filled with 1 *M* sulphuric acid; vitreous carbon was used as the anode with a platinum cathode. This current density is sufficient to cause severe damage to the vitreous carbon on prolonged electrolysis. Longer electrolysis at a lower current density could be employed.

For some experiments, pairs of electrodes were made by cementing individual ones together, side by side. Occasionally, one was oxidized with the second as the cathode, which suffers no attack from the hydrogen generation.

The electrodes were normally set into glass. However, they were found to work well in fluoride solutions, in which case PTFE rod was drilled to take the vitreous carbon. Electrical connections were made as above.

Potential measurements were made on a Beckman research pH meter model 1019 or on a Corning–Eel Digital pH meter model 109, both used in the mV mode. Chemicals were of analytical-reagent grade dissolved in distilled water. All measurements were made with solutions open to the atmosphere and the solutions were stirred continuously by means of a magnetic stirrer.

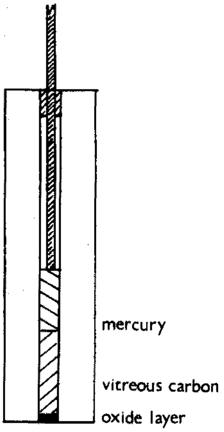
### *Results*

The untreated vitreous carbon electrode gave a linear potential response to the logarithm of the acid concentration. The electrode function was 34 mV/decade concentration at room temperature; this is higher than previously reported[1]. Reproducibility of potentials measured from day to day was poor, and in acid solution, it was difficult to achieve zero potential difference between apparently identical electrodes.

Electrodes with newly prepared oxide films had higher potentials, often more than 1 V *vs.* SCE. This behaviour is also typical of graphite, which can be "activated" by mild oxidation before use as a pH indicator electrode[5]. The potentials, however, were unstable and fell rapidly at first and then more slowly for several hours. Steady potential measurements were achieved by using electrodes which had been aged for as long as possible—at least a week—by standing in distilled water. For potentiometric titrations, however, it was adequate to soak the electrodes for a few hours only. Satisfactory results were then obtained by making incremental additions and potential readings at 1-min intervals. Less than 1 mV change in potential during the 1 min was considered satisfactory in all experiments.

The oxidized electrode, after ageing, also gave linear response to logarithmic changes in acid concentration. The smallest electrodes ground flat as described above, gave the best results after several weeks of soaking in water. Thereafter, readings were reproducible from day to day for several weeks. The potential at 1 *M* hydrochloric acid was 500 mV and the electrode function was 55 mV/decade concentration at 25°C over the range $10^{-5}$ *M*–1 *M* HCl. An exposed rod electrode 100 $mm^2$ in area gave 60 mV/decade after only a few days of soaking. Newly prepared electrodes did not show a linear potential–concentration response and the gradient rose steeply as the concentration approached 1 *M*. This is also true of untreated vitreous carbon rod used after being allowed to dry, following polishing, and used without soaking.

The electrode response was rapid, provided that the conditions above were observed, over the concentration range about 1–$10^{-5}$ *M*. In mid range, stable response took less than 1 min; in high concentration, the response took longer to become steady and the electrode exhibited a memory for the potential which was not observed at lower concentrations. This memory is a disadvantage not yet overcome and of uncertain origin. The most obvious mechanism for the potential generation is that the electrode behaves similarly to the metal oxide pH electrodes, *e.g.* $Sb/Sb_2O_3$ The 60-mV electrode function of the large electrode supports the idea of stoicheiometric equilibrium reaction. It is possible, however, that the mechanism is more complicated. The vitreous carbon has unusual properties with regard to porosity. Earlier studies[3] showed that electrolytic oxidation of vitreous carbon caused reaction to occur beneath the surface presumably because of discontinuous porosity. This was unexpected since the material was considered to be impervious to many gases. Membranes of chemically prepared graphitic oxide also appear to be strangely selective to the passage of gases, and have been used, for instance, to measure the partial pressure of water vapour in the presence of other gases[6,7]. In addition, graphitic oxide is not a good conductor of electricity and is known to have acidic functional groups and some ion-exchanger capacity which could be having an effect. High concentrations of exchangeable salts such as sodium ions caused unsteady potentials although the pH dependence of the potential was still clearly observed.



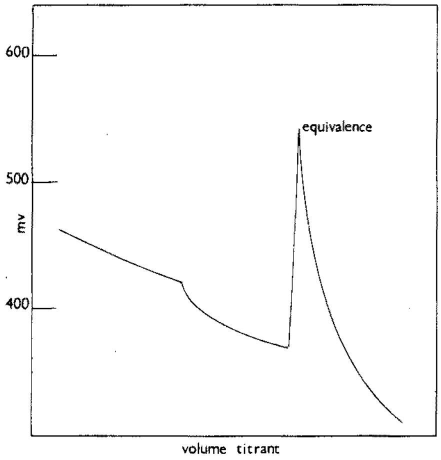


Fig. 1. The oxidized vitreous carbon electrode.

Fig. 2. Differential curve obtained in manual acid–base titration with one oxidized and one untreated vitreous carbon electrode, for 1 *M* HCl titrated with 1 *M* NaOH.

It seems unlikely that the solutions significantly penetrate the oxide film. For example, whilst the "inert" untreated vitreous carbon adopts the redox potential of pH-independent systems such as $I_2/I^-$, and is suitable as indicator in redox titrations, the oxide film electrodes do not behave in the same way. For example, in the titration of iodine with thiosulphate in neutral solution, the potential of the untreated rod *versus* a saturated calomel electrode showed a large break at the end-point, similar to that seen with a platinum wire indicator electrode. The oxidized rod showed no potential break, and the potential–volume curve was simply a shallow slope. This confirms that the unoxidized vitreous carbon does not contact the solution beneath the oxide film, despite long immersion, and also that the observed potential depends on the chemical differences in the two electrodes.

The electrodes are easily used as indicators in acid–base titrations. Special attention was given to indicator probes comprising a vitreous carbon–vitreous carbon graphitic oxide couple. This system proved suitable for the titration of strong or weak acids including hydrofluoric acid, and gave a characteristic differential signal, passing a sharp maximum at the equivalence (Fig. 2).

For 1 *M* hydrochloric acid or other strong acids, the peak height was 200 mV; the height was 100 mV at 0.1 *M*, and 50 mV at 0.01 *M*, when equimolar titrant and titrand were used. For manual titrations of 25-ml samples of 0.1 *M* acid, with increments and readings at 1-min intervals, the accuracy of the mean results was within the limitations of the glassware. The relative standard deviation of the peak maximum about the mean position was 0.26%.

Titration of smaller volumes was achieved by a semi-automatic procedure. Solution was added continuously at 0.025 $cm^3$ $s^{-1}$ by means of a Technicon Autoanalyser pump, calibrated by pumping and weighing distilled water. The potential difference was continuously recorded on chart. The time taken from switching on to peak maximum was measured by stopwatch. A 5-ml titration of hydrochloric acid (*i.e.* 200 s) was achieved with a relative standard deviation of 0.2% at a concentration of 1 *M*, and 0.46% at 0.1 *M*, compared to deviations of 1,4% and 0.9%, respectively, for the same electrode used with a saturated calomel electrode. Acetic acid (1 *M*) gave a relative standard deviation of 0.44%. No loss of sensitivity was noticed in electrodes used for more than sixty successive titrations.

## *Conclusion*

Vitreous carbon coated with graphitic oxide film seems to be suitable as parent material for a new family of potentiometric indicator electrodes. The electrodes, in the form of a simple pH probe, behave similarly to a metal/metal oxide electrode in acid solution. They are suitable for use as acid–base titration indicators, especially when used as a couple with untreated vitreous carbon rod. The electrodes are easily prepared, inexpensive, light, strong, non-toxic and resistant to chemical attack, including hydrofluoric acid.

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## SHORT COMMUNICATION

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### A simple, rapid electrochemical method for the determination of oxalic acid

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During some recent studies of the electrochemical oxidation of some pteridines in aqueous solutions[1] at the pyrolytic graphite electrode (PGE), it was necessary to determine the concentration of oxalic acid, and to ascertain the potentials at which this compound was electrochemically oxidized and the products so formed. The analyses for oxalic acid were required on mixtures that contained oxamide, oxamic acid, tetraketopiperazine and other similar oxidizable species, so that conventional titrants such as cerium(IV) or permanganate could not be used. Oxalic acid in strongly acidic solution gives rise to a polarographic reduction wave at the dropping mercury electrode (DME) at very negative potentials[2–4]. However, since oxamide[5] and tetraketopiperazine[6] also exhibit polarographic reduction waves at very negative potentials, oxalic acid could not be determined polarographically.

Several authors have indicated that oxalic acid can be electrochemically oxidized in aqueous solutions at platinum and gold electrodes[7–13]. Most workers have concluded that the oxidation is a two-electron irreversible process which yields carbon dioxide; almost all reports conclude that the undissociated form of the acid is the electroactive species[7–12], although Kornienko *et al.*[13] have proposed that only oxalate ions are electrooxidizable. When the pH of the supporting electrolyte is increased above *ca.* 2.5 (ref. 9), the oxidation of oxalic acid at platinum electrodes is inhibited either by extensive dissociation of the acid or by an adsorbed oxide layer on the electrode which prevents adsorption of oxalic acid; adsorption is apparently necessary for oxidation to proceed[9]. Literature data generally indicate that platinum or gold electrodes are rather unsatisfactory for the electrochemical determination of oxalic acid, particularly above pH 2; in fact almost all work on aqueous solutions has been carried out in 0.5 *M* sulfuric acid. Preliminary studies in this laboratory[6] showed that oxalic acid gives a very well-defined oxidation peak at the PGE in 1 *M* acetic acid; the present communication describes an investigation of the analytical applicability of this voltammetric oxidation.

### *Experimental*

*Apparatus.* Equipment used for electrochemical studies has been described elsewhere[14]. All potentials are referred to the SCE at 25°C.

Macroscale electrolyses to determine the amount of carbon dioxide liberated on electrooxidation usually involved oxidation of 25–50 mg of oxalic acid. To reduce

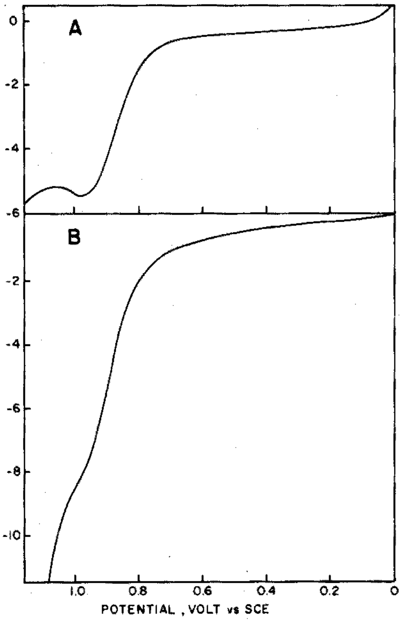


Fig. 1. Voltammogram of 0.5 m*M* oxalic acid in (A) acetate buffer pH 4.7 and (B) borate buffer pH 8.1. Voltage sweep rate 0.005 V $s^{-1}$.

TABLE I

PEAK POTENTIALS AND PEAK CURRENT FUNCTIONS OBSERVED ON VOLTAMMETRIC OXIDATION OF OXALIC ACID AT THE PGE

| *pH* | *Buffer system* | *Mean* $E_p$[a] *(V vs. SCE)* | *Mean peak current function*[a] $i_p/Acv^{\frac{1}{2}}$[b] $(\mu A\ (mM\ l^{-1})^{-1}\ cm^{-2}\ (V\ s^{-1})^{-\frac{1}{2}})$ |
|---|---|---|---|
| 0 | 0.5 *M* $H_2SO_4$ | NO[c] | |
| 1.0 | Chloride | NO | |
| 2.0 | McIlvaine ($Cl^-$)[d] | 1.04 | I[e] |
| 2.3 | 1 *M* HOAc | 1.01 | 999 |
| 3.0 | McIlvaine($SO_4^{2-}$)[f] | 1.05 | 1100 |
| 3.7 | Acetate | 0.93 | 857 |
| 4.7 | Acetate | 0.98 | 921 |
| 5.7 | Acetate | 1.01 | 728 |
| 6.0 | McIlvaine ($Cl^-$) | NO | |
| 6.0 | McIlvaine($SO_4^{2-}$) | NO | |
| 7.2 | McIlvaine($SO_4^{2-}$) | *ca.* 0.92 | I |
| 8.1 | Borax | 0.99 | 1156 |
| 8.95 | Borax | 0.98 | 1156 |
| 9.9 | Borax | 0.97 | 1022 |
| 11.1 | Borax | 0.92 | 1033 |

[a] Mean of at least three replicate measurements.

[b] $i_p$ = peak current ($\mu$A); *A* = area of PGE = 0.125 $cm^2$; *c* = concentration of oxalic acid = 0.504 m*M*; *v* = voltage sweep rate = 0.005 V $s^{-1}$.

[c] No oxidation peak observed.

[d] McIlvaine buffer prepared from phosphate, citrate and KCl.

[e] Peak very indistinct.

[f] McIlvaine buffer prepared from phosphate, citrate and $K_2SO_4$.

contamination of the supporting electrolyte with chloride ion which normally diffuses from salt bridges and reference electrode and which is oxidized at very positive potentials, a two-compartment cell was employed, one compartment for the working electrode (PGE) and one for a platinum gauze counter electrode. These compartments were separated by a fine sintered glass disc and an agar–acetic acid salt bridge. The reference electrode, a fiber-tip SCE, was inserted into the working electrode solution.

Carbon dioxide was determined by arranging a gas train as follows: nitrogen tank, Ascarite tube, water bubbling tower, electrolysis cell (150-ml capacity for working electrode compartment), dry ice trap and saturated barium hydroxide trap; this last trap consisted of two side-arm test tubes (2 × 16 cm) into which the gas passed *via* dropping pipets. The carbon dioxide liberated during the electrolysis formed barium carbonate, which was subsequently filtered on a medium-porosity Buchner funnel, washed with freshly boiled distilled water and acetone, dried at 120°C for 1 h, and weighed, so that the weight of carbon dioxide originally liberated could be calculated.

*Chemicals.* Oxalic acid dihydrate was obtained from Baker. Buffer solutions were prepared from reagent grade chemicals and normally had an ionic strength of 0.5.

### *Results and discussion*

*Voltammetry.* Oxalic acid exhibits a single voltammetric oxidation peak at the PGE between pH 2 and 11.1. The peak potential is essentially pH-independent, $E_p = 0.99 \pm 0.07$ V (Table I). No oxidation peak was observed at pH 6–7 because it was masked by background discharge. The peaks are well-defined only in acetate buffers; a pronounced inflection on background discharge is noted in borax buffers (Fig. 1) and a very ill-defined inflection in certain McIlvaine buffers, *e.g.* pH 2.0 and 7.2 (Table I).

In 0.5 *M* sulfuric acid or chloride buffer pH 1.0, the background discharge current does not become significant, under similar conditions to those in Fig. 1, until 1.1–1.2 V. Accordingly, it is apparent that the undissociated oxalic acid ($pK_{a_1} = 1.46$, $pK_{a_2} = 4.40$ (ref. 15)) is not electrochemically oxidizable at the PGE, whereas both the mono- and dianionic forms of the acid are oxidizable.

Controlled potential electrolysis and coulometry of oxalic acid in acetate buffers gave *n*-values indicating a 2*e* process (mean *n* value of $2.02 \pm 0.2$). Electrolysis of 25–50 mg of oxalic acid and determination of the carbon dioxide evolved showed that 2 moles of $CO_2$ per mole of oxalic acid were liberated.

Attempts to investigate the mechanism of the electrooxidation of oxalic acid by studying the effect of voltage sweep rate on the peak current function were inconclusive, because the oxalic acid peak shifted towards more positive potentials with increasing scan rate, and tended to merge with the background discharge current, even in acetate buffers. Meaningful measurements of peak current and peak potential at sweep rates above *ca.* 100 mV $s^{-1}$ were therefore not possible.

*Analytical utility of voltammetric peak.* The voltammetric peak of oxalic acid was very well defined and most analytically useful in acetate buffers (pH 2.3–6, Table I). Typical analytical data at pH 4.7 are shown in Table II; there is an excellent linear $i_p$ *vs.* *c* calibration curve over the range $2 \cdot 10^{-4}$–$2 \cdot 10^{-3}$ *M*. Similar calibration curves could be obtained for the oxalic acid peak in all acetate buffers, and in borax buffers at higher pH. However, because of the closeness of the peak to background discharge in borax buffers (Fig. 1B), the lower useful concentration level was *ca.* $0.5\cdot10^{-3}$ *M*. In acetate buffers, concentrations of $10^{-4}$ *M* or lower can be readily determined. In borax buffers the analytical reproducibility and accuracy was also less than in acetate media, for which the reproducibility was ±5%.

TABLE II

PEAK CURRENT *versus* CONCENTRATION RELATIONSHIP FOR OXALIC ACID

(Acetate buffer pH 4.7)

| *Oxalic acid concentration (mM)* | *Mean peak current*[a] *(μA)* | *Mean peak current*[a] *function* $i_p/Acv^{\frac{1}{2}}$ [b] $(\mu A\ cm^{-2}\ (mM\ l^{-1})^{-1}\ (V\ s^{-1})^{-\frac{1}{2}})$ |
|---|---|---|
| 0.217 | 1.65 | 860 |
| 0.434 | 3.13 | 816 |
| 0.868 | 6.63 | 864 |
| 1.302 | 9.95 | 865 |
| 1.736 | 13.18 | 859 |
| 2.170 | 16.87 | 879 |

[a] Mean of at least three replicate measurements.
[b] $A = 0.125\ cm^2$; $v = 0.005\ V\ s^{-1}$.

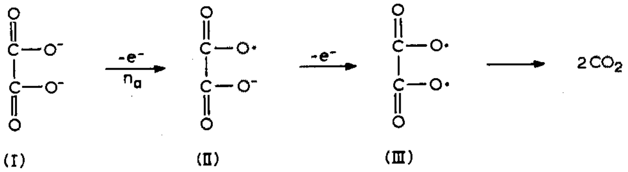
*Reaction scheme.* The mechanism of the electrochemical oxidation of oxalic acid at the PGE was not studied in detail. However, in view of the conflicting data in the literature, a few comments with respect to the electrode process at the PGE can be made. Oxalic acid is clearly electrochemically oxidized in a pH-independent process, *i.e.* protons are not directly involved. The data indicate that undissociated oxalic acid is not electrochemically oxidizable (no peak is observed below pH 2) but that both the mono- and dianionic species are oxidizable. The overall oxidation involves two electrons per molecule of oxalic acid under conditions of controlled potential electrolysis. For example, from the data obtained at pH 4.7 (Table II), the mean experimental peak current function was 857±41. The theoretical peak current function was calculated by first computing the value of $\alpha n_a$ from eqn. (1) (ref. 16).

$$\alpha n_a = \frac{0.048}{E_p - E_{p/2}} \tag{1}$$

The mean value of $\alpha n_a$ was found to be 0.36±0.04. The magnitude of the theoretical irreversible peak current was calculated from eqn. (2) (ref. 17),

$$i_p = (2.98\cdot10^5)\, n(\alpha n_a)^{\frac{1}{2}} A D^{\frac{1}{2}} v^{\frac{1}{2}} c \tag{2}$$

where all terms have their usual electrochemical significance, and *n*-values of 1 and 2 were employed. The value of the theoretical peak current function for $n=1$ was 564.5, whereas for $n=2$ it was 1129 $\mu A\ cm^{-2}\ (mM)^{-1}\ (V\ s^{-1})^{-\frac{1}{2}}$. Because of the proximity of the oxalic acid peak to background, there was some uncertainty in the values of $E_p$ and $E_{p/2}$. Nevertheless, the theoretial peak current function for $n=2$ was in reasonable agreement with the experimental value. In addition, the theoretical $n=2$ value was in good agreement with the mean experimental peak current function for oxalic acid between pH 2.3–11.1, *i.e.* 997 $\mu$A $cm^{-2}$ $(mM)^{-1}$ $(V\ s^{-1})^{-1}$ (Table I). The experimental value for $\alpha n_a$ of 0.36 indicates an $n_a$ value of 1.0, if a typical value of $\alpha$ of 0.5 is assumed, but this value for $n_a$ is extremely tentative. A reaction scheme can be proposed, however, where the oxalate dianion (or monoanion) (I) undergoes an initial 1*e* oxidation to the anion radical (II). Loss of a further electron would give the di-radical (III), which would be expected to decompose rapidly to carbon dioxide. Cyclic voltammetry at sweep rates up to 500 mV $s^{-1}$ (where it is very difficult to discern the oxidation peak of oxalic acid even in acetate buffers) gave no evidence for a reversible reduction peak or indeed of any reducible product.



*Conclusion*

Oxalic acid gives rise to a pH-independent oxidation peak at the pyrolytic graphite electrode ($E_p=0.99\pm0.07$ V *vs.* SCE) between pH 2 and 11. This peak is well-defined in acetate buffers (pH 2.3–6) and the peak current is then linearly proportional to the concentration of oxalic acid down to at least the $10^{-4}$ *M* level. Only the mono- or dianionic forms of oxalic acid are electrooxidizable. The electrode reaction is an irreversible 2*e* process giving carbon dioxide as the sole product, in essentially quantitative yield.

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*Analytica Chimica Acta*, 72 (1974) 215–219

## SHORT COMMUNICATION

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# Determination of the ammonium content in waste waters by means of the air-gap electrode

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Of the various methods for the determination of ammonia in, for example, sea, natural or waste waters, the indophenol method[1] is the most widely used procedure. On the basis of an intercalibration of methods for ammonia, NORDFORSK's working committee on water analysis has recommended the indophenol method as the standard procedure[2]. In this method the water sample is treated with alkaline hypochlorite and phenol in the presence of sodium nitroprusside, yielding a blue indophenol dye which then is measured spectrophotometrically. Although the method is very sensitive and potentially is well suited for automation, there are several limitations in making it applicable to routine analysis. The method is time-consuming as it takes 3–4 h to achieve complete colour development at room temperature, although a recently developed modified procedure has reduced the time required to *ca.* 30 min[3]. In automated operations (*e.g.*, AutoAnalyzer), the time required is further decreased by allowing the reaction to take place at elevated temperature, and by measuring the absorbance before the reaction has reached equilibrium[1]. More important, however, is the fact that the analysis is subject to serious interference from, for example, mercury and iron ions, as well as soluble sulphides[2,3]. Thus, NORDFORSK has recommended that the water samples should not be preserved by any means (such as mercury(II) or acid) and that the actual analysis ought to be carried out as soon as possible after sampling. It should be added that the use of the many reagents needed for the procedure not only makes it complicated, but also may result in high reagent blanks.

Ammonia can be determined very selectively by distillation and titration as described by Riley[4] who found that the pH value for optimal recovery of ammonia is 9.2. The procedure is very accurate above 1 p.p.m. nitrogen, but less suitable below this level owing to the possibility of titration errors. However, the long time needed per assay makes the method inappropriate as a standard procedure for series analysis. In addition, it has recently been reported that organic nitrogen compounds in waste water may decompose during distillation, thereby increasing the ammonia level[5].

In order to minimize sample handling and the likelihood of contamination, and to circumvent the interferences of the indophenol method, ammonia-specific electrodes have been suggested for the determination of ammonia in aqueous solutions[5,6]. These gas-sensing electrodes consist in principle of a hydrophobic gas-permeable membrane which separates the alkaline test solution from an internal solution of ammonium chloride of fixed molarity. A glass pH electrode and a reference electrode are immersed in the internal solution. Thus, when the electrode is placed in an alkaline test solution, ammonia can diffuse across the membrane, alter the ammonia concentration in the filling solution and so cause a pH change which is monitored by the glass electrode. However, shortcomings like clogging of the gas-permeable membrane and leakage of the inner electrolyte around the gas membrane, as recently reported to occur with the Orion ammonia electrode[7], may impair the use of such sensors. As the gas-permeable membrane must be hydrophobic, the sample solution must not contain any wetting agent[8], and therefore measurements in, for example, effluent waters, which may often contain surfactants, organic waste and particulate matter, have to be carefully considered. Furthermore, a proviso for the application of such sensors in routine analysis is that the electrode not only gives a fast response, but also rapidly recovers before the next measurement, that is, the ammonia must rediffuse easily out of the inner electrolyte solution.

All these difficulties and limitations are eliminated in the recently developed air-gap electrode[9], which has been used successfully for determinations of ammonium ion, hydrogencarbonate and urea (*via* enzymatic degradation) in full blood, plasma and serum[9,10], sulphur dioxide in wine[11], and nitrate in foodstuffs.

The air-gap electrode is based on the same principle as other gas sensors, except that it does not have any gas-permeable membrane. The membrane is replaced by an air gap which separates the electrolyte layer from the sample solution, the entire system being contained in a gas-tight measuring chamber. The electrolyte itself is adsorbed as a very thin layer (film) on the surface of the indicator electrode (*in casu* the pH electrode). The greatest advantage of this design is that the electrode never comes into direct physical contact with the sample solution, which can therefore contain components which normally affect the function of any electrode. In addition, simplicity of design, ease of renewal of electrolyte, and fast response are further advantages gained by replacing the gas-permeable membrane with the air gap.

This gas sensor was used for the determination of ammonium in waste-water samples collected at various points in a purification plant (including a nitrification unit) situated in Lundtofte, Denmark. The size of the plant is equivalent to approximately 25,000 persons, the waste water originating equally from industry and households. Besides the potentiometric assay, all samples were also measured by the indophenol and the distillation methods. The distillation method was carried out as described in *Standard Methods for the Examination of Water and Waste Water*[1], while the indophenol method was used as recommended by NORDFORSK[2]. Both methods were checked by ammonium chloride standards. During the application of the indophenol method, it was found advisable to use EDTA instead of citrate to mask the effect of the metal ions present. Furthermore, it was observed that as little as 1–2 p.p.m. sulphide gave a strong interference, and that sulphide contents above 15–20 p.p.m. decreased the relative absorbance of the measured dye to almost zero, thus seriously impairing the method.

*Experimental*

The apparatus and the air-gap electrode were the same as previously described[9,10]. Both the larger and the smaller electrode chambers, having a total volume of 8.0 ml and 1.0 ml, respectively, were used. The electrolyte solutions ($1.0 \cdot 10^{-3}$ *M* ammonium chloride for the larger electrode chamber, and $1.0 \cdot 10^{-2}$ *M* ammonium chloride for the smaller chamber) were saturated with a wetting agent (Victawet 12, Stauffer Chemical Company, U.S.A.). The electrolyte layer on the surface of the glass electrode was renewed after each measurement, by letting the air-gap electrode rest on a perspex holder, containing a sponge soaked with the electrolyte solution[9]. When not in use, the electrode was similarly stored in the electrode holder.

When the larger (macro) chamber was used, the calibration curve was obtained by pipetting 2.0 ml of the standard solution of ammonium chloride into a polyethylene beaker which fitted into the electrode chamber. A Teflon-covered magnetic stirring bar was placed into the beaker followed by 1.0 ml of 0.1 *M* sodium hydroxide. The chamber was then immediately closed by means of the body of the air-gap electrode and the magnetic stirrer was started. A steady reading of the electrode, $pH_e$, was reached within 2–3 min and read to 0.001 $pH_e$. For each standard ammonium chloride solution (1, 2.5, 5, 7.5, 10, 13, and 15 p.p.m. nitrogen), two measurements were plotted *versus* the $pH_e$ values obtained. The calibration curve was computed on a WANG 700 B Programmable Electronic Calculator provided with a WANG 702 Plotting Output Writer using a linear-regression analysis programme. The calibration curve was then used in the subsequent evaluations of the waste-water samples. With the standard solutions, a straight line was obtained with a slope of 0.9790 log (p.p.m. nitrogen)/$pH_e$, a standard deviation of 0.02 $pH_e$ (corresponding to 5%), and a regression coefficient of 0.998. When the waste-water samples were analyzed, the same procedure was used.

TABLE I

DETERMINATION OF THE AMMONIUM CONTENT IN WASTE-WATER SAMPLES COLLECTED AT FIVE DIFFERENT LOCATIONS IN A MUNICIPAL PURIFICATION PLANT

| | *N content (p.p.m. $NH_3$)* | | |
|---|---|---|---|
| *Origin of waste water samples* | *Indophenol method* | *Distillation and titration method* | *Air gap electrode (macro-chamber) method* |
| Untreated waste water | 13.55 | 13.36 | 12.93 |
| Sedimentation basin | 14.01 | 14.61 | 13.78 |
| Inlet to nitrification unit | 15.61 | 14.95 | 13.81 |
| Outlet from nitrification unit | 3.22 | 3.25 | 3.50 |
| Outlet from purification plant | 2.21 | 2.05 | 2.20 |

The calibration of the electrode and the actual waste water analysis performed with the smaller (micro) chamber were carried out by an identical procedure: 200 μl of standard ammonium chloride solution (or 200 μl of waste-water sample) was pipetted by means of an MLA Precision Pipette into the perspex micro-chamber containing a magnetic stirring bar, 200 $\mu l$ of 0.2 $M$ sodium hydroxide was added, and the chamber was immediately closed with the electrode body. Only then was the magnetic stirrer started. A steady $pH_e$ reading was reached within 1–2 min and read to 0.001 $pH_e$. For each standard (0.05, 0.1, 0.5, 1, 5 and 10 mmol $l^{-1}$), two measurements were plotted *versus* the $pH_e$ value obtained, as outlined above. With the standard solutions, a straight line was obtained with a slope of 1.003 $\log[NH_4^+]_s/pH_e$, a regression coefficient of 0.9999 and a standard deviation of 0.01 $pH_e$ (corresponding to 2.4%).

### *Results*

The results obtained by the macro-chamber procedure, compared with those of the indophenol and the titration methods, are summarized in Table I.

In order to evaluate the standard deviation on the individual determinations by the micro-chamber procedure, two waste-water samples (sampled at a different date from those used previously) were measured 4 and 8 times, respectively. The first sample (untreated waste water) was measured twice, each series consisting of 4 determinations. In the first series, the standard deviation was 0.0031 $pH_e$ and in the second one 0.0065 $pH_e$, *i.e.*, corresponding to 0.75–1.56% (the sample contained, according to the standard curve, 37.3 p.p.m. nitrogen). The second sample (water from the outlet of the purification plant) was measured 8 times, resulting in a standard deviation of 0.0081 $pH_e$, corresponding to 1.93% (the sample contained 1.90 p.p.m. nitrogen).

To check the method further, two waste-water samples which previously had been measured, were spiked with known amounts of ammonium chloride and then each measured twice again with the micro-chamber assembly. The first sample (untreated waste water), containing 28.6 p.p.m. nitrogen, was spiked with 21.4 p.p.m. nitrogen (*i.e.*, a total of 50.0 p.p.m.); it was found to contain 50.6 p.p.m. nitrogen. The second sample (outlet from the nitrification plant; the sample was collected during a cold period) was originally found to contain 5.72 p.p.m. nitrogen as ammonia; after being spiked with 2.14 p.p.m. nitrogen, the content was found to be 7.80 p.p.m., compared to the calculated value of 7.86 p.p.m. nitrogen. Thus, within experimental error, very accurate results were obtained.

### *Discussion*

It takes only a few minutes to make a determination with the air-gap electrode, and thus the time of analysis is drastically reduced compared to the conventional methods. Furthermore, the method is highly selective and is not affected by any of the interferences to which the other methods are subject. The potentiometric method should equally well be applicable to the analysis of less polluted waters, such as drinking water and sea water. As only a few waste-water samples were analyzed, this communication does not pretend to be a thorough investigation, but is rather intended to serve as a demonstration of the capacity of the electrode for this type of measurement.

The authors extend their sincere thanks to J. P. Jørgensen of the Department of Sanitary Engineering of this University for critical discussions and for his help in providing the waste-water samples; and to I. M. Johansen for her conscientious technical assistance. This work was in part supported by the Danish Natural Research Council.

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## SHORT COMMUNICATION

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# The opening up of insoluble oxides (tantalum, niobium, chromium, aluminium and others) with liquid selenium dioxide

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Selenium dioxide is a colourless solid at room temperature, which melts at about 390°C at a vapour pressure of about 9 atm[1]. It is shown here that liquid selenium dioxide is a useful solvent for a large number of "insoluble" oxides. Details are given for $Ta_2O_5$, $Nb_2O_5$, $Cr_2O_3$ and $Al_2O_3$, with directions for the preparation of aqueous solutions. The first two of these oxides are very soluble in liquid selenium dioxide, while $Cr_2O_3$ and $Al_2O_3$ form crystalline pyroselenites of low solubility, the solubility decreasing in this order. $SnO_2$ forms an even less soluble pyroselenite. The category of very soluble oxides comprises $Nb_2O_5$, $Ta_2O_5$, $Fe_2O_3$, $In_2O_3$, $Ga_2O_3$, ZnO, CdO, PbO and $Ag_2O$. Pyroselenite crystals could also be grown for most of the soluble oxides, although rapid cooling of the solution usually resulted in a glassy product. No further oxides were included in this investigation.

Pyroselenites are derived from the corresponding oxides by substituting $Se_2O_5$ for oxygen. This composition was confirmed by chemical analysis for the zinc, cadmium and gallium compounds, and follows for the aluminium and chromium compounds because their x-ray powder patterns are practically identical to that of gallium pyroselenite.

The preparation of some pyroselenites from aqueous solutions has been reported in the literature. This concerns mainly the alkali and ammonium compounds[2], except for some very old reports[3] that have not been confirmed by more recent work[4].

### *Experimental*

It should be noted that selenium dioxide is classified as a harmful substance; its vapour should not be inhaled even in trace amounts.

*$Ta_2O_5$ and $Nb_2O_5$*. The oxide (0.1 g) and about 1.5 g of selenium dioxide are placed in a 4-ml ampoule with inner and outer diameters of 10 and 13 mm, respectively, and made of pyrex glass or, preferably, quartz. If the $SeO_2$ is moist, which it usually is, it can be dried by connecting the ampoule to a rotating oil vacuum pump and heating, *e.g.* with a hair dryer; the pressure will rise and the heating is briefly continued until the pressure is back to its initial low value. The metal oxide should be added after drying, lest it be entrained by the escaping water vapour.

The ampoule is sealed under an oxygen pressure of about 0.8 atm., to prevent the dissociation of selenium dioxide into its elements at elevated temperatures. The ampoule is heated to about 420°C and may be agitated to speed up the dissolution of the metal oxide. A more convenient, though slower, method is to use an ampoule bent over about 20° and placed with the powder in the (shorter) top part, and with the bend uppermost, in a horizontal furnace with two temperature zones. Initially both zones are at 400°C; the selenium dioxide melts and most of it flows over the bend to the bottom. The bottom is then heated to 420°C and the top of the ampoule with the undissolved oxide is cooled to about 380°C; fresh selenium dioxide evaporates from the bottom, condenses at the top and flows back saturated with the oxide, until all has dissolved after about 30 min. To facilitate inspection, the furnace used was made of two coaxial quartz glass tubes with a coiled heating wire in between, the ampoule being attached to a longer glass rod, permitting rotation and movement in the furnace. On cooling, the ampoule is taken out of the furnace as soon as the yellow colour of the selenium dioxide vapour has more or less disappeared and the viscous melt is spread over the lower part of the wall of the ampoule, where it forms a glass. The ampoule is cracked below the bend and placed in a slightly wider, thick-walled test tube; to this are added 5 ml of a solution made by adding citric acid monohydrate to concentrated ammonia until the pH is about 8. The selenite glass rapidly dissolves on stirring. After the ampoule has been opened, the contents should not be left in moist air for long, lest water vapour attracted by the selenium dioxide initiates hydrolysis of the metal.

In one of the experiments, selenium dioxide crystals suddenly formed throughout the melt in an ampoule that was left to cool slowly inside the furnace. When the aqueous citrate solution was then added, tantalum hydroxide precipitated. It appears that the formation of a glassy product in the ampoule is essential to the success of the dissolution. If the glass crystallizes, the contents of the ampoule should be melted again and cooled more rapidly.

*$Cr_2O_3$ and $Al_2O_3$.* These oxides form pyroselenites that are slightly soluble in selenium dioxide. Therefore, to ensure complete conversion, the "reflux" method should be used as outlined above. Especially with $Al_2O_3$ the initial reaction product is rather bulky; in order to have sufficient selenium dioxide for circulation, no more than 20 mg of metal oxide is added to 2 g of selenium dioxide. As soon as all the oxide has been transported to the bottom (after 1 h for $Cr_2O_3$ and about 4 h for $Al_2O_3$), the ampoule is slightly tilted and the excess of selenium dioxide is distilled to the top and thus recovered straight away. The colourless crystals of aluminium pyroselenite dissolve readily in aqueous alkaline solutions. At least 25 mg of the dark green crystals of chromium(III) pyroselenite can be dissolved in a solution of 100 mg of ammonium chloride in 1 ml of 6 *M* hydrochloric acid at 100°C, resulting in a solution of a green colour characteristic of chromium(III).

## *Discussion*

The (arbitrary) list of oxides given in the first paragraph suggests that most metal oxides rapidly dissolve in, or react with, liquid selenium dioxide. Fortunately, silica in the form of quartz glass is much less reactive; after 2 g of selenium dioxide had been kept at 420°C for 16 h in a sealed quartz ampoule, only about 10 $\mu$g of silicon was detected in the selenium dioxide. Pyrex glass is attacked at about the same rate but gives rise to contamination by a larger number of elements. Contamination by silica at this rate will hardly be a problem for the majority of oxides, including $Ta_2O_5$ and $Nb_2O_5$, which, with agitation, completely dissolve in selenium dioxide in a matter of minutes, or within 30 min if the "reflux" method is used. It seems therefore that liquid selenium dioxide is a suitable agent for the dissolution of many "insoluble" oxides. At least for $Cr_2O_3$, there seems to be no alternative method that leaves the chromium in the trivalent state. The only "undissolved" oxide of those investigated is $SnO_2$. In this case a crystalline compound, presumably in tin pyroselenite, is formed which is very slightly soluble in liquid selenium dioxide and only slightly soluble in 40% hydrofluoric acid.

An attractive feature of selenium dioxide is its high vapour pressure which permits purification by sublimation. If a white product is desired, uncontaminated by elemental selenium, the vapour can be passed over a platinum catalyst[5]. Recovery of spent selenium dioxide should not be difficult. The vapour pressure at the melting point, 9 atm., is not so high as to require the use of special apparatus, although precautions against leaky or exploding ampoules are, of course, essential.

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*Analytica Chimica Acta*, 72 (1974) 223–224

# BOOK REVIEWS

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Wolfdietrich Schneider, *Neutronenmesstechnik*, de Gruyter, Berlin et New York, 1973, 454 pp., prix DM 168.—.

Les neutrons ont, aujourd'hui, non seulement un grand intérêt en physique nucléaire (réacteur nucléaire) ou en physique du solide, mais aussi, entre autre, en chimie analytique (analyse par activation), en médecine (radiobiologie) et en radiochimie.

L'auteur de l'ouvrage Neutronenmesstechnik étant directeur de l'équipe de mesure des radiations des laboratoires de recherches nucléaires Jülich GmbH, a nécessairement été confronté avec les problèmes de mesures en neutronique.

Les techniques de mesure s'étant largement développées et diversifiées, il manquait à la littérature un recueil rassemblant celles-ci et c'est maintenant chose faite par la publication de cet ouvrage. Les chapitres les plus importants sont les suivants: base des mesures en neutronique, les principaux détecteurs de neutrons, étalonnage et interprétation des résultats, pratique des mesures dans le cadre d'un réacteur nucléaire.

Le grand avantage de ce recueil est de grouper sous forme condensée l'ensemble des méthodes de mesures—ce qui n'est pas peu dire—avec une appréciation critique de leur utilisation. Bien que spécialisé, l'ampleur même du sujet traité ne permet certainement pas de développer longuement chaque sujet; aussi, une abondante et riche littérature est citée avec précision et à la bonne place, pour information et développements. L'excellente présentation de cet ouvrage, des tableaux clairement disposés et utiles aident le lecteur dans ses recherches. Néanmoins, une meilleure mise en évidence typographique des mots-clefs faciliterait une recherche rapide.

L'ensemble du recueil montre clairement que l'auteur s'est trouvé en prise directe avec les problèmes de mesures en neutronique et qu'il a voulu partager son expérience, ce qui lui a fort bien réussi. Il est hors de doute que cet ouvrage a atteint parfaitement son but et nous pouvons le recommander avec un plaisir sans réserve.

W. Haerdi et R. Beeler (Genève)

J. W. Akitt, *N.M.R. and Chemistry*, Chapman and Hall, London, 1973, ix + 182 pp., price £1.95.

This short book (182 pages) has the stated aim of providing a general introductory account of the whole field of n.m.r. spectroscopy. The approach is essentially non-mathematical and is directed towards spectral interpretation and practical applications. The presentation is very clear and the text is liberally provided with suitable illustrations, though the representation of electron delocalisation in dimethylformamide (Fig. 50) requires correction. A particularly attractive feature of the book is that the examples are chosen widely from organic, inorganic and organometallic compounds and are not limited to proton spectra. Topics discussed include nuclear relaxation, double resonance, virtual coupling, contact and pseudo-contact shifts, site exchange processes, spectral accumulation, and Fourier transform spectroscopy. However, the depth of treatment is somewhat variable; for example, more space is devoted to wiggle beats and phase-sensitive detection than to Fourier transform spectroscopy.

The preface indicates that the book is aimed at undergraduate students. It is the reviewer's experience that such courses in this country tend to deal with either simple applications of n.m.r. and other spectroscopic methods to structure elucidation (usually as part of an organic course) or with theoretical aspects. It is difficult to see this book fulfilling either of these roles. However, it is quite suitable for the postgraduate student or research chemist who is starting to use n.m.r. spectroscopy in the course of his research. The author deserves credit for producing such a good wide-ranging text at this modest price.

W. B. Jennings (Birmingham)

*Organic Reaction Mechanisms–1972*, edited by B. Capon and C. W. Rees, Interscience–John Wiley, London, 1973, x+677 pp., price £16.75.

The latest volume in this series is modelled closely on its predecessors. Chapter headings, comprehensive coverage and description of major works which have characterised earlier volumes are well-maintained. The number of references reported (well over 5,000) is about the same as last year and the size of the book is still within manageable proportions. Once again the reviewers and printers have done a good job. It is interesting to note that there will be a change of editorship next year. Professor Rees and Dr. Capon are standing down after eight years. They are to be congratulated on setting a consistently high standard: the new men, Professor Perkins and Dr. A. R. Butler, can be expected to continue in the same vein.

E. J. Forbes (Birmingham)

*Drug Analysis by Chromatography and Microscopy*, edited by E. Stahl, Ann Arbor Publishers, Ann Arbor, Mich.–John Wiley, New York, x+238 pp., price £11.25.

This is an English translation of the original German version, previously reviewed in this journal (*Anal. Chim. Acta*, 59 (1972) 331). The book is well produced, and the standard of the illustrations, especially of the numerous thin-layer chromatograms, is as high as in the original version. The only other changes are a slightly smaller size for pages and diagrams (but not the chromatograms), microscopic details printed on a yellow rather than a white background, and a hard cover. This is a book to be greatly recommended to all who are concerned with the detection and identification of drugs.

A. Townshend (Birmingham)

*(Continued from page 4 of cover)*

VOL. 72 NO. 1 ANALYTICA CHIMICA ACTA SEPTEMBER 1974

# CONTENTS

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*(Continued on inside page of cover)*