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**Publication Schedule for 1971**

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Vol. 53, No. 1	January 1971	
Vol. 53, No. 2	February 1971	(completing Vol. 53)
Vol. 54, No. 1	March 1971	
Vol. 54, No. 2	April 1971	
Vol. 54, No. 3	May 1971	(completing Vol. 54)
Vol. 55, No. 1	June 1971	
Vol. 55, No. 2	July 1971	(completing Vol. 55)
Vol. 56, No. 1	August 1971	
Vol. 56, No. 2	September 1971	
Vol. 56, No. 3	October 1971	(completing Vol. 56)
Vol. 57, No. 1	November 1971	
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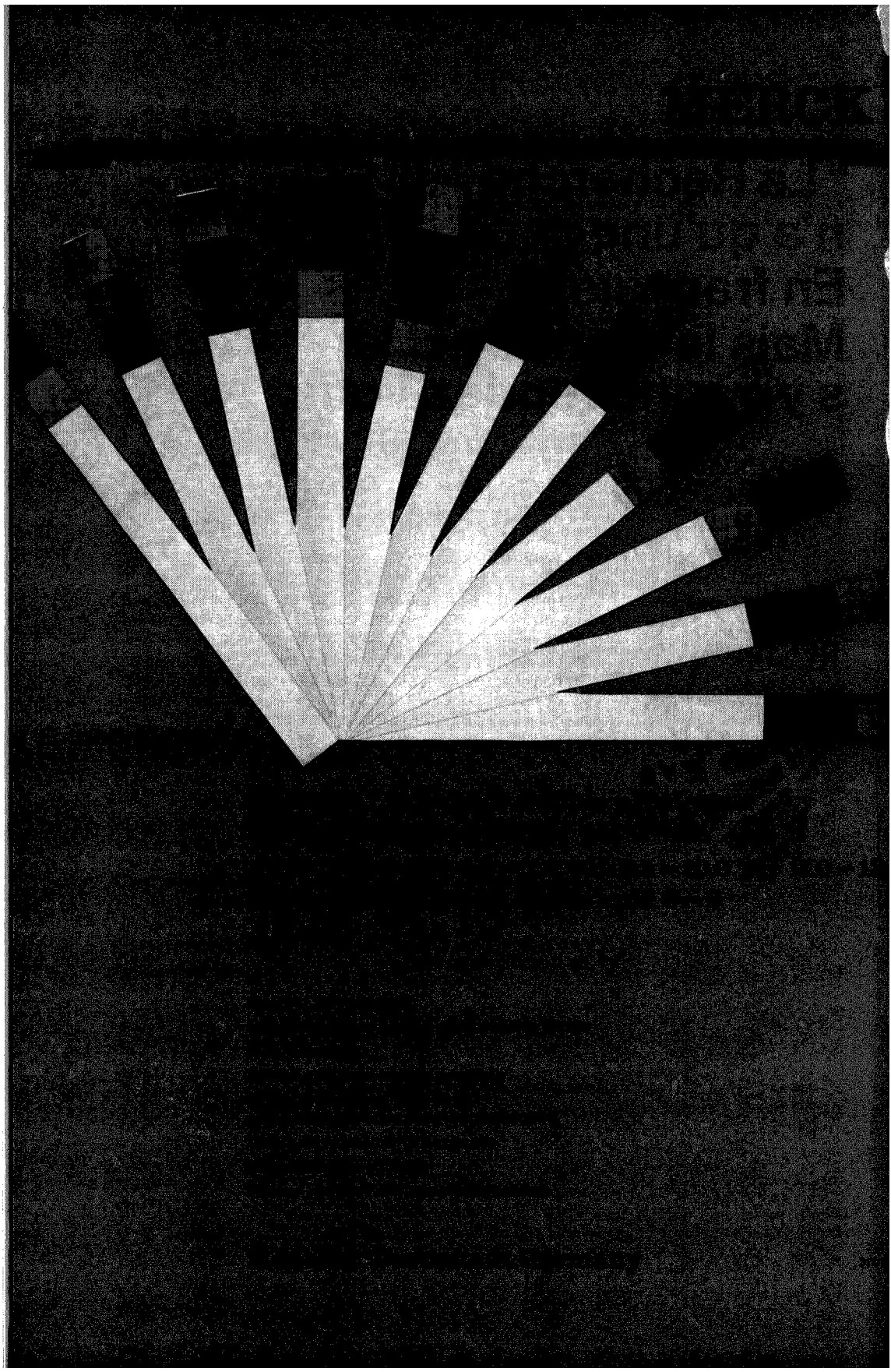
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**CHARLES V. BANKS**

**1919-1971**

Charles V. Banks was born in Blandinsville, Illinois, on March 22, 1919. He received his elementary education in the Blandinsville Public Schools, and his Bachelor of Education degree with honors from Western Illinois University, in 1941.

He went to Iowa State University in 1941 as a graduate student and received his M.S. degree in 1944 and the Ph.D. degree in 1946. He served in the U.S. Army Corps of Engineers, from 1944 to 1946, being assigned to the Manhattan District Project, and returned to Ames to continue his work with the metallurgical group concerned with the manufacture of metallic uranium. Professor Banks contributed considerably to the success of the Ames group in various research endeavors which led to the development of the first atomic bomb. At the conclusion of the war he joined the faculty of the Department of Chemistry of the University, and the staff of the newly created Ames Laboratory of the Atomic Energy Commission. His brilliance in teaching and research led to his rapid promotion; he was made full professor at the age of 35. He was appointed acting head of the Chemistry Department in 1965 and later became Senior Chemist and Section Chief for the Institute for Atomic Research.

Professor Banks' research work was concerned primarily with the development of new methods of chemical analysis for the rare elements, used in the difficult metallurgical problems involved in the development of atomic energy. This work was carried out under the joint auspices of the Department of Chemistry and the Atomic Energy Commission and involved 32 Ph.D. candidates and 9 post-doctoral fellows. The results are reported in some 130 scientific papers. In 1970, the American Chemical Society honored him with the Fisher Award, its highest honor for outstanding contributions to analytical chemistry.

Dr. Banks was a member of Sigma Xi, Phi Lambda Upsilon, Phi Kappa Phi, Alpha Chi Sigma, Kappa Delta Phi and Sigma Zeta. He was also a member of the American Chemical Society and a fellow of the Iowa Academy of Sciences and the American Association for the Advancement of Science. He had served as secretary-treasurer and chairman of the Ames Section of the American Chemical Society's Analytical Chemistry Division. He was also active on the advisory boards of *Analytical Chemistry* and *Analytica Chimica Acta*, and on many local and national committees.

His hobbies of hunting, fishing and gardening interested him in conservation and environmental problems to which his active scientific mind made many useful contributions. He is survived by his wife, whom he married in 1941, a son and a daughter.

Professor Banks was held in high esteem by analytical chemists throughout the world. His untimely death at the height of his scientific career is a loss which chemistry can ill afford.

## PROTON MAGNETIC RESONANCE STUDIES OF SOME GROUP VIII-POLYPYRIDINE COMPLEXES

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(Received 8th July 1971)

During a study of Group VIII-polypyridine chelate luminescence it became apparent that an analytical method was necessary to determine both the purity and structure of the synthetic preparations. Classical methods of analysis do not always give unambiguous results for this type of compound. As examples, melting points are hampered by sample decomposition, and elemental analyses are complicated by the presence of the metal ion and variable numbers of waters of hydration. Recent interest in the proton magnetic resonance (p.m.r.) spectroscopy of metal chelates<sup>1-5</sup> indicated that a systematic investigation was merited.

Even though the identities of the ligands in a complex are usually known with a high degree of certainty, because of the simplicity of the preparatory procedures, p.m.r. is an excellent method of verification. Also, by use of the quantitative aspects of p.m.r. it is possible to calculate the number of ligands attached to the metal ion.

In most cases the purity of the preparation can be determined to a reasonable extent. The amount of free ligand can be detected at a level greater than 1% by the fortuitous fact that it usually has peaks appearing in different spectral regions than the chelated version. Also, several species in equilibrium with one another or, more commonly, several species produced in the same preparation give an extremely complicated spectrum in contrast to the simplicity that would be expected for a single complex.

A detailed examination of the spectra reveals unusual chemical shifts that prove useful in determining the exact three-dimensional structure of the chelates. These same shifts also provide an unambiguous method of assigning a complex either a *cis* or *trans* configuration. In the case of complicated spectra, decoupling experiments can relate the peaks in such a manner that the number of magnetic environments can be established. From this, the number of nonequivalent pyridine moieties can be determined.

Not only has p.m.r. proved to be useful in the direct analysis of these complexes, but on the basis of the information about the structure, attempts can be made to explain anomalous luminescence behavior.

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## EXPERIMENTAL

*Apparatus*

The p.m.r. spectra were recorded on a Varian 100XL and/or a Varian A60 spectrometer. In some cases, because of solubility difficulties, a computer of average transients was used to increase the signal-to-noise ratio.

*Reagents*

Tris(2,2'-bipyridine)ruthenium(II) dichloride was purchased from G. Frederick Smith Chemical Co. The remaining complexes were prepared by published procedures: dichloro-bis(2,2'-bipyridine)ruthenium(II)<sup>6</sup>; ethylenediamine-bis(2,2'-bipyridine)ruthenium(II) dichloride<sup>7</sup>; bis(2,2',2''-terpyridine)ruthenium(II) diiodide<sup>8</sup>; and bis(2,2',2''-terpyridine)osmium(II) dichloride<sup>9</sup>.

*Procedure*

The concentration of the samples was usually 15% (w/v) in dimethylsulfoxide (DMSO). The complexes were relatively insoluble and had to be refluxed for 30 min and then centrifuged to remove any remaining solid. All samples were deoxygenated with prepurified nitrogen for 10 min just before their spectra were measured.

For the 100 Mc sec<sup>-1</sup> instrument, the lock signal was deuterium. The reported chemical shifts are from TMS with a 500-c.p.s. sweep width at 60 Mc sec<sup>-1</sup>. The spectra from the 100 Mc sec<sup>-1</sup> instrument are only used to clarify peak patterns.

## RESULTS AND DISCUSSION

*Tris-bidentate complexes*

The p.m.r. spectrum of free 2,2'-bipyridine in DMSO is shown in Fig. 1. The spectrum of this species has been discussed in the literature and the molecule has been shown to be in a *trans* configuration<sup>4,10,11</sup>. The assignment of the various peaks to the protons is straightforward. Since the coupling to adjacent carbons will be larger than long range coupling, the principle splittings will be two doublets, H3 and H6, and two

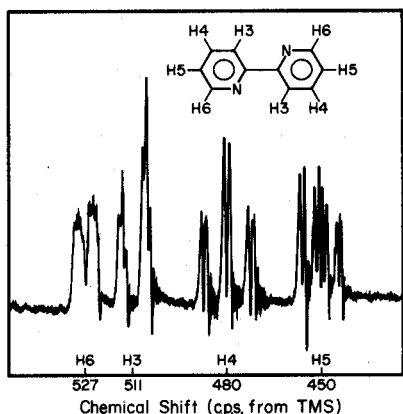


Fig. 1. Structure and p.m.r. spectrum of 2,2'-bipyridine. The spectrum is observed as a 15% (w/v) solution in DMSO-d<sub>6</sub> at 60 Mc sec<sup>-1</sup>.

triplets, H4 and H5. H3 and H5 should be the further upfield, for their group, because they are shielded by the inductive effect of the hetero-nitrogen. H3 appears abnormally downfield because, in the *trans* configuration, it is deshielded by the non-bonding electrons of the nitrogen on the opposite ring. It was experimentally found that the coupling constants for these protons do not vary significantly when the metal, ligand or solvent is changed ( $J_{3,4}=8.0$ ,  $J_{3,5}=1.2$ ,  $J_{3,6}=1.0$ ,  $J_{4,5}=7.5$ ,  $J_{4,6}=1.8$ ,  $J_{5,6}=4.8$ ). Therefore, in the preliminary analysis of the spectra of the complexes, coupling constants were used as an aid in identifying the peaks.

The p.m.r. of tris(2,2'-bipyridine)ruthenium(II) dichloride (Fig. 2) contains four distinct patterns—two doublets and two triplets. Each set of peaks can be assigned to the appropriate proton by coupling constants. The spectrum indicates one magnetic environment, therefore, all pyridine moieties must be equivalent. The general downfield shift upon chelation can be attributed to the decrease in electron charge density at the individual carbon nuclei caused by the ligand interaction with the dipositive metal ion. Such considerations would predict chemical shifts of H3=514, H4=498, H5=468 and H6=535<sup>5</sup>. From Fig. 2 it can be seen that only H4 agrees with these expectations to any degree.

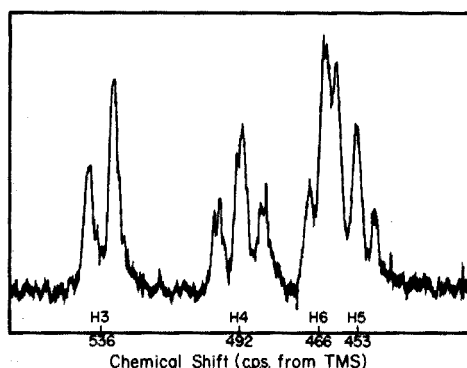


Fig. 2. P.m.r. spectrum of tris(2,2'-bipyridine)ruthenium(II) dichloride. The spectrum is observed as a 15% (w/v) solution in DMSO- $d_6$  at 60 Mc sec<sup>-1</sup>.

Because of the *cis* configuration of the ligand the H3 protons on the two rings are forced together giving rise to a strong van der Waals deshielding interaction. The order of magnitude and direction of this shift (22 c.p.s.) can be predicted from the relationship derived by Cheney<sup>12</sup> and the bipyridine crystal data of Merritt and Schroeder<sup>13</sup>. However, nothing quantitative can be established without invoking bond stretching and/or bending.

The H6 protons show a dramatic upfield shift analogous to others that have been reported. Miller and Prince<sup>14</sup> attributed this shift to a non-bonded hydrogen-metal interaction. Castellano *et al.*<sup>4</sup> felt that it was due to the diamagnetic anisotropic effect of the aromatic ring of the adjacent ligand. Recent studies of tris(2,2'-bipyridine) complexes have agreed with the latter interpretation<sup>1,5</sup>. Again, the order of magnitude and direction of the shift (-69 c.p.s.) can be predicted from the tables of Johnson and Bovey<sup>15</sup>, the bipyridine crystal data, and the ruthenium-nitrogen distance<sup>16</sup>.



### Bis-bidentate complexes

The tris-bidentate complexes presented a relatively simple structural analysis. By replacing a bipyridine molecule with other ligands, two geometric isomers are possible, *trans* and *cis*. For the *trans* compound, there would only be one magnetic environment for all four pyridine rings. The spectrum would resemble that of tris-(2,2'-bipyridine)ruthenium(II) dichloride. It would have the same four peaks corresponding to the different protons. The absorbancies would be shifted downfield because of the absence of the anisotropic effect of the neighboring ligand. Of course, the H6 proton would show the greatest downfield shift due to the absence of this effect.

The *cis* configuration is more complicated, since now the pyridines of each ligand are not magnetically equivalent. Each ligand contains one pyridine moiety which is still influenced by the adjacent ring. The chemical shifts of the protons will be about the same as those of the tris-bidentate system. The other pyridine moiety will be shifted downfield owing to the absence of the pyridine ring just as in the *trans* bis-bidentate compound.

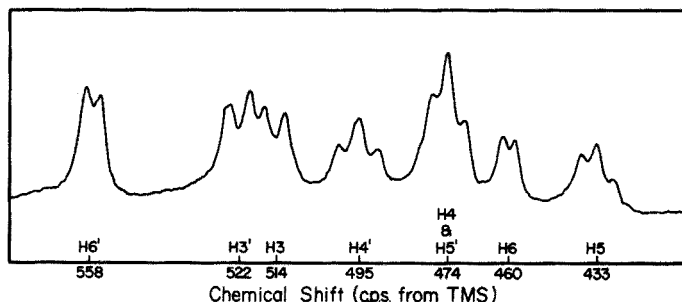


Fig. 3. P.m.r. spectrum of ethylenediamine-bis(2,2'-bipyridine)ruthenium(II). The spectrum is observed as a 15% (w/v) solution in DMSO- $d_6$  at 100 Mc  $sec^{-1}$ .

Ethylenediamine-bis(2,2'-bipyridine)ruthenium(II) dichloride was prepared to test the above hypothesis. Figure 3 is the p.m.r. spectrum of this compound. The assignments of the protons are based on coupling constants and decoupling experiments. Examination of H5' reveals unequal coupling constants, and decoupling experiments confirm the presence of two peaks. The differentiation of primed and non-primed numbers is also based on these decoupling experiments. H4 is coupled to both H3 and H5, and H5 is coupled to H6; similarly H4' to H3' and H5'; and H5' to H6'. The relative chemical shifts of H3, H4, H5, and H6 follow quite closely those in tris(2,2'-bipyridine)ruthenium(II) dichloride, and, therefore are considered to be affected by the  $\pi$ -cloud of the adjacent ligand. The non-primed numbers correspond to those protons which are not deshielded by the aromatic ring. The diamagnetic shielding affects the H3 protons only slightly, as is shown by the small chemical shift between H3 and H3'. The effect of the increasing proximity to the center of the ring current is displayed by the increasing relative chemical shift between H4 and H4', and H5 and H5'. The H6' proton is no longer affected and is seen downfield as in the free ligand spectrum. The geometry of the ethylenediamine complex is therefore a *cis* arrangement of the bipyridine molecules.

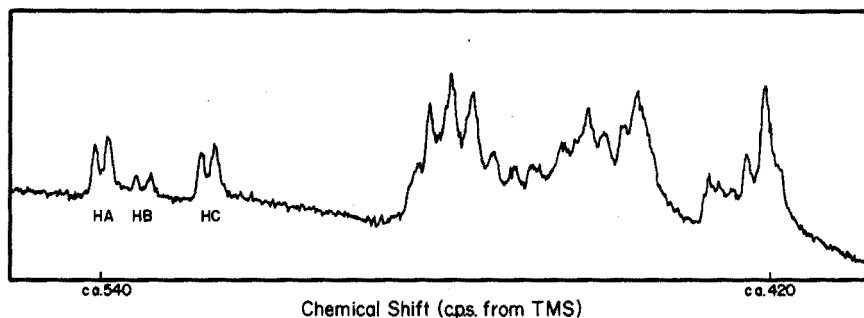


Fig. 4. P.m.r. spectrum of dichloro-bis(2,2'-bipyridine)ruthenium(II). The spectrum is observed as a saturated solution in DMSO- $d_6$  at 100 Mc  $sec^{-1}$ .

The next compound tested was dichloro-bis(2,2'-bipyridine)ruthenium(II). The spectrum (Fig. 4) is more complex than that which would be expected for the *cis* or *trans* configuration. The peaks could not be integrated because the signal-to-noise ratio was small and decoupling was infeasible due to the proximity of the peaks. There are two possible explanations for the complexity of the spectrum: both isomers are present, or there is a solvent interaction with the *cis* and/or *trans* isomer. The only clue which indicates that there may be a solvent interaction lies in the interpretation of the three peaks, HA, HB, and HC. The peaks, HA and HC, are characteristic of H6 protons in shape and coupling constant. The spectrum of the compound was run many times and only HC remained constant in the relative chemical shift from the main body of peaks. This chemical shift is the same as that of H6' from H3' in the ethylenediamine complex. The proton HA always appeared but had a slightly different chemical shift and intensity each time. The proton HB was not always observed and also varied in chemical shift and amplitude. HA could be an H6' influenced by coordinated dimethylsulfoxide and HB could be attributed to the protons of the coordinated solvent molecules<sup>17</sup>. There can be many interpretations of the spectrum, but the important fact is that there is a mixture of compounds present with possible solvent interactions.

#### *Bis-terdentate complexes*

The structure and spectrum of 2,2',2''-terpyridine (Fig. 5) can be compared to that of 2,2'-bipyridine. The conformation of the free molecule would be expected to be *trans-trans*<sup>18</sup>, owing to repulsion of the nitrogen non-bonding orbitals. The outer pyridine moieties are magnetically equivalent to those in 2,2'-bipyridine. The center ring possesses increased aromatic character because of the pyridine rings at the two and six positions, causing a slight diamagnetic shift of H3' and H4'; thus creating the complex patterns at 508 c.p.s. and 477 c.p.s. respectively. The number of lines for H3' and H4' differs from that of H3 and H4, because both H3' are equivalent and a magnetically unique H6' is absent. They appear as a doublet and a triplet respectively, with no further first order coupling. This fact will help to differentiate them in coordinated molecules.

Morgan and Burstall<sup>19</sup> proposed three possible structures for 2,2',2''-terpyridine in octahedral microsymmetry. The one in which the terpyridine is planar would appear to be the most stable, if the central atom were large enough to coordinate all

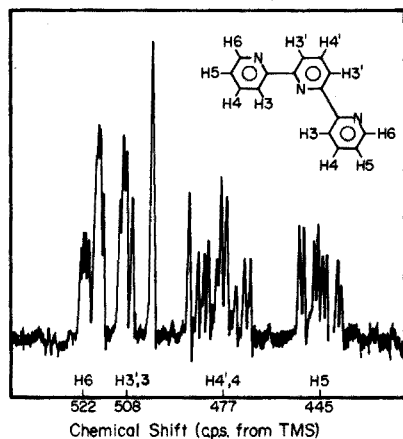


Fig. 5. Structure and p.m.r. spectrum of 2,2',2''-terpyridine. The spectrum is observed as a 15% (w/v) solution in DMSO- $d_6$  at 60 Mc  $sec^{-1}$ .

pyridine moieties. The p.m.r. spectrum of bis(2,2',2''-terpyridine)osmium(II) dichloride confirms a planar configuration of the ligand (Fig. 6). The assignments of protons were made on the basis of coupling constants and decoupling of the H4' and H3' from H3 and H4 respectively. The chemical shifts of H3' and H4' are downfield as discussed for the free ligand. It should be noted the H4 and H4' are almost chemically equivalent in the osmium complex. H6 is shifted upfield as a result of the anisotropic effect of the neighboring ligand (see the section on tris-bidentate chelates). As is the case of the free ligand, there are only two magnetic environments: that of the terminal pyridine and that of the central ring.

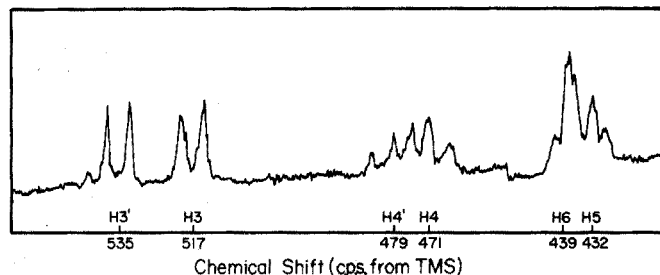


Fig. 6. P.m.r. spectrum of bis(2,2',2''-terpyridine)osmium(II) dichloride. The spectrum is observed as a 15% (w/v) solution in ethanol at 100 Mc  $sec^{-1}$ .

The spectrum of bis(2,2',2''-terpyridine)ruthenium(II) diiodide is shown in Fig. 7. A comparison of the spectrum to that for the osmium chelate indicates that there are two magnetic environments. The protons, H3, H3', H4, H5, and H6 can be assigned as before, but there is an apparent 29 c.p.s. downfield shift of H4' from H4. The near chemical equivalence of the H4(4') protons as seen in the osmium complex disappeared.

There are three configurations of the ligand that could give rise to such a change: one terminal pyridine is not bonded strongly; the two terminal pyridines

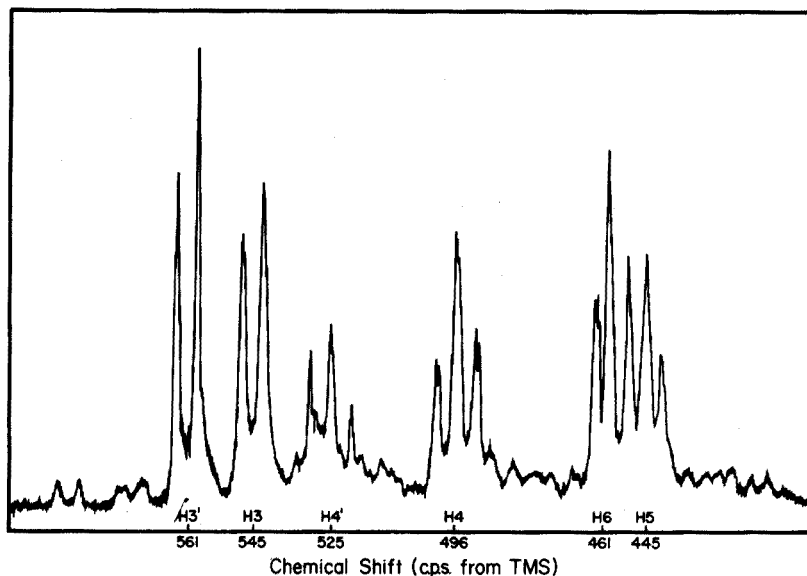


Fig. 7. P.m.r. spectrum of bis(2,2',2''-terpyridine)ruthenium(II) diiodide. The spectrum is observed as a 15% (w/v) solution in DMSO- $d_6$  at 100 Mc  $sec^{-1}$ .

are not bonded strongly; and the central pyridine is not bonded strongly. The first possibility is dismissed immediately since this would necessitate three magnetic environments instead of the observed two. On a chemical basis the last possibility can be dismissed since there seems to be no precedence for chelation where the central complexing group is not strongly bonded.

If the difference between the chemical shifts of H4 and H4' can be attributed to the decrease in electron charge density caused by the ligand interaction with the dipositive metal ion, effective charges of  $\frac{1}{6}$ ,  $\frac{2}{3}$  and  $\frac{1}{6}$  at the three nitrogen atoms can adequately explain the spectrum<sup>5</sup>. The charge difference of  $\frac{1}{2}$  would predict the observed 29-c.p.s. split between the H4(4') protons. The H3(3') protons are insensitive to this effect and would not be expected to change much. Two other features of the spectrum can be explained by a change in effective charge distribution from  $\frac{1}{2}$ ,  $\frac{1}{2}$  and  $\frac{1}{2}$  in the osmium complex to  $\frac{1}{6}$ ,  $\frac{2}{3}$  and  $\frac{1}{6}$  in the ruthenium complex. First, the increased spread between H3 and H5 of 15 c.p.s., and second, the increased spread between H5 and H6 of 9 c.p.s. in going from osmium to ruthenium.

As added proof that at least one pyridine is not strongly bonded in the ruthenium compound, Ciantelli *et al.*<sup>8</sup> have recently shown that during spectrophotometric titrations this compound exhibits monoprotic character.

#### APPLICATIONS TO LUMINESCENCE SPECTROSCOPY

Several imine chelates of  $d^6$  ions of certain group VIII metals are known to have large temperature-dependent luminescence intensities. Fink and Ohnesorge<sup>20</sup> have ascribed the absence of luminescence from iron(II)-imine chelates to the effect on the intersystem crossing rate of a temperature-dependent equilibrium between high- and low-spin states established during the lifetime of the charge-transfer excited.

state. However, they also generalized their theory to include most other luminescent chelates of this type. For at least one such chelate, tris(2,2'-bipyridine)ruthenium(II) dichloride, Lytle and Hercules<sup>21</sup> have shown this dependence to be a thermal population of a level coupled strongly to the ground state. This work indicates that the temperature dependence of several of these chelates may be explained by two additional effects. Bis(2,2',2''-terpyridine)ruthenium(II) diiodide does not emit in fluid solution at room temperature but strongly emits in a rigid glass at 77° K. It is obvious from the p.m.r. data that two of the nitrogens are only weakly bonded to the metal ion and could be photodissociated at room temperature in fluid solution. At 77° K the lack of thermal energy or the rigidity of the spectroscopic glass could inhibit any excited state depleting reaction. Dichloro-bis(2,2'-bipyridine)ruthenium(II) is an example of a complex having the possibility of solution equilibrium that would change direction and magnitude with temperature. The luminescence of this complex has been discussed in at least one paper<sup>22</sup>, but the results of this work would raise doubt about any interpretation of the spectral data.

The authors would like to thank S. A. Carlson for his participation in the early phases of the investigation.

#### SUMMARY

The p.m.r. spectra of 2,2'-bipyridine, tris(2,2'-bipyridine)ruthenium(II) dichloride, dichloro-bis(2,2'-bipyridine)ruthenium(II), ethylenediamine-bis(2,2'-bipyridine)ruthenium(II)dichloride, 2,2',2''-terpyridine, bis(2,2',2''-terpyridine)ruthenium(II) diiodide and bis(2,2',2''-terpyridine)osmium(II) dichloride have been reported and analyzed. From the p.m.r. data, the symmetry of the complex and the geometry of the ligand within the complex are predicted. In some cases, attempts to explain anomalous luminescence behavior are made on the basis of the structural analysis.

#### RÉSUMÉ

Une étude est effectuée sur les spectres de résonance magnétique (p.m.r.) de divers composés chloro-et iodo-pyridine-ruthénium(II) et osmium(II). On détermine la symétrie du complexe et la géométrie du ligand. Dans certains cas, on essaie d'expliquer le comportement anormal de la luminescence, en se basant sur une analyse de structure.

#### ZUSAMMENFASSUNG

Die p.m.r.-Spektren von 2,2'-Bipyridin, Tris(2,2'-bipyridin)ruthenium(II)-dichlorid, Dichloro-bis(2,2'-bipyridin)ruthenium(II), Äthylendiamin-bis(2,2'-bipyridin)ruthenium(II)-dichlorid, 2,2',2''-Terpyridin, Bis(2,2',2''-terpyridin)ruthenium(II)-dijodid und Bis(2,2',2''-terpyridin)osmium(II)-dichlorid werden vorgelegt und analysiert. Aus den p.m.r.-Ergebnissen werden die Symmetrie des Komplexes und die Geometrie des Liganden innerhalb des Komplexes abgeleitet. In einigen Fällen wird versucht, anomales Lumineszenzverhalten auf der Basis der Strukturanalyse zu erklären.

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## DETERMINATION OF MOLYBDENUM IN ROCKS BY EPITHERMAL NEUTRON ACTIVATION ANALYSIS

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Although neutron activation analysis exhibits a fairly high sensitivity for molybdenum, this technique has not been frequently used for the determination of molybdenum in geological material. The main reason for this is the serious interference often encountered from  $^{99}\text{Mo}$  produced by fission of uranium, and in some cases also thorium. In meteorites, where the uranium content is in general very low, molybdenum can be determined<sup>1,2</sup> without significant interference, but in silicate rocks, the uranium content is often at the same level as, or higher than, that of molybdenum, which means that a major fraction of the  $^{99}\text{Mo}$  activity induced in a rock sample on neutron irradiation may be due to uranium. The rather poor precision obtained in previous work<sup>3,4</sup> on neutron activation analysis for molybdenum in rocks clearly indicates the difficulty associated with this task.

Activation with epithermal neutrons will help considerably to reduce the fission-product interference in the case of molybdenum. This is so because  $^{98}\text{Mo}$  has a large resonance activation integral compared to its thermal neutron activation cross-section ( $I_0/\sigma_0 \approx 50$ ) while the corresponding ratio for  $^{235}\text{U}$ , regarding the (n, fission) reaction, is about 0.48. In the present work, irradiation under cadmium cover is shown to facilitate the attainment of presumably good molybdenum data for silicate rocks, even at U/Mo ratios as high as 15.

### FISSION-PRODUCT INTERFERENCE IN MOLYBDENUM DETERMINATION

The following discussion is based on the use of 67-h  $^{99}\text{Mo}$  for the neutron activation determination of molybdenum. The 14.6-min  $^{101}\text{Mo}$  may also be used, but this nuclide represents an even more unfavourable case with respect to fission-product interference.

The disintegration rate of  $^{99}\text{Mo}$  obtained by reactor neutron irradiation of natural molybdenum, is given by:

$$D(\text{Mo}) = \frac{P_{\text{Mo}}}{M_{\text{Mo}}} \theta_{98} N_0 (1 - e^{-\lambda T}) (\phi_{\text{th}} \sigma_0^{98} + \phi_{\text{epi}} I_0^{98}) \quad (1)$$

where  $P$  is the weight of element,  $M$  is its atomic weight,  $N_0$  is Avogadro's number,  $\theta_{98}$  is the fractional isotopic abundance of  $^{98}\text{Mo}$ ,  $\phi_{\text{th}}$  and  $\phi_{\text{epi}}$  are the fluxes of thermal and epithermal neutrons respectively,  $\sigma_0$  is the thermal neutron activation cross-section, and  $I_0$  is the resonance activation integral (including the "1/v tail").

The corresponding  $^{99}\text{Mo}$  activity produced by uranium fission (provided that the irradiation time is long compared to the half-lives of the precursors of  $^{99}\text{Mo}$  in the

$A=99$  fission product chain) can be expressed as follows:

$$D(U) = \frac{P_U}{M_U} N_0 Y_U^{99} (1 - e^{-\lambda T}) [\theta_{235} (\phi_{th} \sigma_f^{235} + \phi_{epi} I_f^{235}) + \theta_{238} \phi_F \sigma_F^{238}] \quad (2)$$

neglecting the fast-neutron fission of  $^{235}\text{U}$ . Here  $Y_U^{99}$  is the cumulative yield of  $^{99}\text{Mo}$  by  $^{235}\text{U}$  fission (the yield is nearly the same by reactor fast-neutron fission of  $^{238}\text{U}$ ),  $\sigma_f^{235}$  and  $I_f^{235}$  are the thermal neutron cross-section and resonance integral for the  $^{235}\text{U}(n,f)$  reaction, and  $\sigma_F^{238}$  is the reactor fast-neutron cross-section for the  $^{238}\text{U}(n,f)$  reaction. By irradiation with the whole reactor neutron spectrum, the term due to  $^{238}\text{U}$  fission will in most cases be 1–2% of the activity or less, and may be neglected. Similarly, the term  $\phi_{epi} I_f^{235}$  will in most cases contribute to only a few per cent of the total activity, and may be ignored unless very exact calculations are needed.

The epithermal flux may conveniently be expressed by means of the cadmium ratio of gold, which is the quantity commonly used to express the relative strength of the epithermal component in the reactor neutron spectrum:

$$\phi_{epi} = \frac{\phi_{th} \sigma_0^{Au}}{I_0^{Au} (R_{Cd}^{Au} - 1)} \quad (3)$$

Combination of eqns. (1), (2) and (3) and insertion of appropriate values\* for the various constants, yields:

$$\frac{D(\text{Mo})}{D(U)} \approx \frac{P_{\text{Mo}}}{P_U} \left( 0.32 + \frac{1.04}{R_{Cd}^{Au} - 1} \right) \quad (4)$$

It should be noted that the relative contribution from uranium fission to the  $^{99}\text{Mo}$  activity is very much dependent on the ratio  $\phi_{th}/\phi_{epi}$ , a fact which has sometimes been overlooked. In a virtually pure thermal neutron flux, a value of 0.32 for the ratio  $D(\text{Mo})/D(U)$  is obtained at equal weights of U and Mo, while for example in a flux with  $R_{Cd}^{Au} = 3.0$ , which is a typical value for irradiation positions used for neutron activation work in many research reactors,  $D(\text{Mo})/D(U) = 0.84$ . Therefore, if the  $^{99}\text{Mo}$  contribution from fission products is to be calculated in activation analyses for molybdenum in samples with significant uranium concentrations, it is not sufficient to know the uranium content; the cadmium ratio of  $^{197}\text{Au}$  in the irradiation position to be used, must also be known if fairly accurate corrections are to be obtained. The most accurate correction factors are probably those determined experimentally.

If activation of the sample under cadmium cover is introduced, a considerable advantage is obtained in the determination of molybdenum. In this case

$$\frac{D(\text{Mo})}{D(U)} \approx \frac{P_{\text{Mo}}}{P_U} \cdot \frac{14}{0.42 + \alpha (R_{Cd}^{Au} - 1)} \quad (5)$$

\* The following data were used in the calculations leading to eqns. (4), (5) and (7):

$$\begin{array}{ll} \sigma_0^{98} = 0.14 \text{ b}^5 & \sigma_F^{238} = 0.312 \text{ b}^7 \\ I_0^{98} = 7.1 \text{ b}^6 & \sigma_F^{232} = 0.072 \text{ b}^7 \\ \sigma_0^{Au} = 99 \text{ b}^5 & Y_U^{99} = 6.14 \%^8 \\ I_0^{Au} = 1550 \text{ b}^6 & Y_{Th}^{99} = 2.80 \%^8 \\ \sigma_f^{235} = 580 \text{ b}^5 & \\ I_f^{235} = 280 \text{ b}^6 & \end{array}$$



where  $\alpha = \phi_F / \phi_{th}$ .

Under the experimental conditions used in the present work ( $R_{Cd}^{Au} = 3.0$  and  $\alpha \approx 0.05$ ), a value of 27 was obtained for  $D(Mo)/D(U)$  at equal weights of the elements, which means that the situation is about 32 times more favourable than is the case by irradiation at the same position *without* cadmium cover. From eqn. (5), the relative uranium interference on the  $^{99}Mo$  activity is seen to be relatively independent of the actual neutron distribution, unless fluxes with high  $\alpha$  values are employed.

Thorium will also produce  $^{99}Mo$  by fast neutron-induced fission. In most cases, the contribution from  $^{232}Th$  will be insignificant compared to that of  $^{235}U$ , by irradiation with the whole reactor spectrum. In the case of epithermal activation, however, the  $^{232}Th$  contribution may in some cases be significant. The disintegration rate of  $^{99}Mo$  produced from thorium is given by the following equation:

$$D(Th) = \frac{P_{Th}}{M_{Th}} N_0 Y_{Th}^{99} (1 - e^{-\lambda T}) \theta_{232} \phi_F \sigma_F^{232} \quad (6)$$

where  $Y_{Th}^{99}$  is the cumulative fission yield of  $^{99}Mo$  by reactor fast-neutron fission of thorium and  $\sigma_F^{232}$  is the reactor fast-neutron cross-section of the  $^{232}Th(n,f)$  reaction. Combination with eqn. (1) and insertion of figures for the constants gives in the case of epithermal activation:

$$\frac{D(Mo)}{D(Th)} \approx \frac{P_{Mo}}{P_{Th}} \cdot \frac{130}{\alpha (R_{Cd}^{Au} - 1)} \quad (7)$$

In the experimental situation used in this work,  $D(Mo)/D(Th) = 1300$ , which means that the interference from thorium fission should be considered if the thorium/molybdenum ratio of the rock is higher than about 10.

From the above considerations, it can be inferred that the optimal conditions for determination of molybdenum should be obtained by activating under cadmium cover in a reactor position at some distance from the fuel elements, where the fast-neutron component is sufficiently low so that the interference from fast-neutron fission of  $^{238}U$  and  $^{232}Th$  becomes negligible. Even though the relative strength of the epithermal neutron component may also be fairly low in this position, the conditions will still be favourable, provided that the epithermal flux is large enough to induce a sufficiently high  $^{99}Mo$  activity from the molybdenum present in the samples. The  $D(Mo)/D(U)$  ratio of about 30 observed at equal amounts of the two elements by epithermal activation is maintained at fluxes with fairly high  $R_{Cd}^{Au}$  values, provided that care is taken to use a cadmium thickness sufficient to shield the thermal neutron component efficiently.

## EXPERIMENTAL

### Irradiation

Rock samples of about 100 mg were wrapped in 30 mm  $\times$  30 mm sheets of aluminium foil for irradiation. Standards were prepared by carefully evaporating aliquots of dilute solutions on the same sort of aluminium sheets. About 5  $\mu g$  of molybdenum, and 5  $\mu g$  of uranium for the determination of fission product correction, were used as standards. Cylindrical cadmium boxes of 0.7 mm thickness, 14 mm internal diameter and 10 mm internal height were used for irradiation. Seven rock samples,

two molybdenum standards, two uranium standards and two aluminium foil blanks were irradiated in one cadmium box. Simultaneously an identical set of standards was irradiated at a distance of 10 cm from the cadmium box, both sets of samples being included in the same aluminium container. Irradiations were performed for 3 days in a vertical isotope channel of the JEEP II reactor (Kjeller, Norway), in a fixed position where the thermal neutron flux was about  $1.5 \cdot 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$  and the cadmium ratio of  $^{197}\text{Au}$  was 3.0.

#### *Radiochemical separation*

After 4 days' delay, the samples were transferred to nickel crucibles containing evaporated carriers of molybdenum (10 mg), chromium (10 mg) and iron (20 mg), and fused with 2 g of sodium hydroxide pellets using an electrothermal bunsen. The fusion cake was, after cooling, dissolved in 20 ml of water and subsequently filtered through a blue ribbon filter paper for removal of insoluble hydroxides. Sodium sulphite (200 mg) was then added to the supernatant solution, and the solution was acidified with hydrochloric acid, in order to reduce chromium(VI) to chromium(III). The solution was then adjusted to pH 7–8 with ammonia solution, and after 2 h, was again filtered through a blue ribbon filter paper. The resulting supernatant solution was again acidified with hydrochloric acid, and molybdenum was precipitated with 5 ml of a solution of 0.5% (w/v)  $\alpha$ -benzoinoxime in ethanol. The solution was filtered through a membrane filter; the precipitate was washed several times with dilute hydrochloric acid and water and then transferred to a small cylindrical polyethylene vial (5 mm diameter, 30 mm length).

The aluminium foils with the standards were dissolved in 10 ml of 6 M hydrochloric acid containing 1 ml of 30% hydrogen peroxide, in the presence of molybdenum, chromium and iron carriers. After the remaining hydrogen peroxide had been boiled off, the solution was adjusted to pH 7–8 with ammonia solution and further treated in the same manner as the standards.

#### *Activity measurements*

After 2 days, to allow transient equilibrium between  $^{99}\text{Mo}$  and the  $^{99\text{m}}\text{Tc}$  daughter to be established, the  $\gamma$ -activity measurements were carried out by means of a 400-channel  $\gamma$ -spectrometer with a well-type  $3 \times 3''$  NaI (Tl) detector. The 140-keV  $\gamma$ -ray of  $^{99\text{m}}\text{Tc}$  was recorded, and Covell's method<sup>9</sup> was used for the peak area calculations.  $\gamma$ -Rays from interfering nuclides were not observed.

#### *Chemical yield determination*

Chemical yields for samples and standards were determined by re-activation. After decay of the initial  $^{99}\text{Mo}$  activity, the polyethylene vials containing the isolated precipitates were irradiated for 2 min at a flux of  $1.5 \cdot 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$  and counted for  $^{99\text{m}}\text{Tc}$  after 1 days' delay. The chemical yield was in most cases 70% or higher.

## RESULTS AND DISCUSSION

Seven standard rocks from U.S. Geological Survey were selected as test material in this work. The rocks and the values for their uranium and thorium contents used to correct for fission-product interference, are listed in Table I. Uncorrected molybdenum

TABLE I  
MOLYBDENUM CONTENT OF SOME U.S.G.S. STANDARD ROCKS (p.p.m.)

Rock	U content <sup>a</sup> (p.p.m.)	Th content <sup>a</sup> (p.p.m.)	Observed values (p.p.m.)	Corrected for U interference	Final value corrected for Th interference	Spectrophotometric method <sup>b</sup>	Neutron- activation method <sup>c</sup>
AGV-1	1.90	5.88	1.68, 1.71, 1.96, mean 1.78	1.71	1.71	1.66	10.0
BCR-1	1.80	5.60	1.22, 1.23, 1.21, mean 1.22	1.15	1.15	1.21	2.3
DTS-1	0.003 <sup>12</sup>	—	0.05, 0.04, 0.04, mean 0.04	0.04	0.04	0.04	0.2
G-2	1.93	23.3	0.20, 0.24, 0.26, mean 0.23	0.15	0.13	0.15	3.2
GSP-1	2.05	101	0.44, 0.40, 0.42, mean 0.42	0.34	0.27	0.30	5.3
PCC-1	0.005 <sup>12</sup>	—	0.02, 0.01, 0.02, mean 0.02	0.02	0.02	0.03	0.2
W-1 <sup>d</sup>	0.59	2.11	0.57, 0.63, 0.58, mean 0.59	0.57	0.57	0.52	0.7

<sup>a</sup> See ref. 10.

<sup>b</sup> See ref. 11.

<sup>c</sup> See ref. 4.

<sup>d</sup> Hamaguchi *et al.*<sup>3</sup> report values of 0.9–1.8 p.p.m. for W-1, with a mean value of 1.3 p.p.m.

values for these rocks from three different irradiations are given in the Table. In order to demonstrate the influence of uranium and thorium on the results, the mean molybdenum values for each rock are shown respectively uncorrected, corrected for uranium interference, and corrected also for thorium interference. The uranium corrections were based on the experimentally determined correction factor for each irradiation; the thorium corrections, which were necessary only in the cases of G-2 and GSP-1, which have very high Th/Mo ratios, were based on eqn. (7), assuming  $\alpha = 0.05$ .

The final values are compared in Table I with two recent sets of literature data: one by Kawabuchi and Kuroda<sup>11</sup> based on spectrophotometry following an anion-exchange separation method, and another by Laul *et al.*<sup>4</sup>, based on a neutron-activation scheme for the determination of 15 elements. Very good agreement between the data from the present work and the spectrophotometric values is evident from the Table. The data of Laul *et al.*, on the other hand, except for W-1, are higher by a factor of 2–20. These authors have evidently not determined experimentally a correction factor for the uranium interference, but have chosen a value corresponding to an  $R_{Ca}^{Au}$  of 4.0 according to eqn. (4). If their irradiation position had a more thermalized flux, their values corrected for uranium interference would approach those of the present work, but this fact alone is not sufficient to explain the differences.

The ratio  $D(\text{Mo})/D(\text{U})$  at equal amounts of elements was found to be  $0.89 \pm 0.02$  in the irradiation position used in this work, while the same ratio by irradiation under cadmium was  $27 \pm 3$ . This gives an "enrichment" factor of  $30 \pm 3$ . The corresponding figures calculated from eqns. (4) and (5) are respectively 0.84 and 27, giving an "enrichment" factor of 32. The agreement between calculated and experimental values is considered to be satisfactory.

If the errors in the uranium and thorium corrections are respectively  $\pm 10\%$  and  $\pm 20\%$ , the maximum error from fission interference should not exceed 10% even in the case of G-2, which is the least favourable one in this respect. Considering other sources of error, epithermal neutron self-shielding is not likely to occur in the first irradiation, but may to a small extent be present in the re-activation. As the chemical yield is fairly constant, however, possible shielding is expected to occur approximately to the same degree for all samples. The good agreement obtained with results from an entirely different analytical technique further indicates that systematic errors do not interfere appreciably in this work.

#### SUMMARY

A neutron-activation method for molybdenum in rocks based on epithermal activation and a simple radiochemical separation is described, and data for some standard rocks are presented. Errors caused by fission of uranium and thorium in neutron activation for molybdenum are calculated and discussed. The interference from fission product  $^{99}\text{Mo}$  is shown to be considerably dependent on the epithermal and the fast-neutron flux. Epi-cadmium activation reduces the uranium interference by a factor of 20–80 compared to activation without cadmium cover, the actual value being dependent on the cadmium ratio of gold in the irradiation position used.

## RÉSUMÉ

Une méthode par activation neutronique est proposée pour le dosage du molybdène dans des roches. Elle est basée sur une activation épithermique et une simple séparation radiochimique. Les valeurs obtenues pour quelques échantillons standards sont données. On examine les erreurs dues à la fission de l'uranium et du thorium, lors de l'activation neutronique du molybdène.

## ZUSAMMENFASSUNG

Für die Bestimmung von Molybdän in Gesteinen wird eine Neutronenaktivierungsmethode beschrieben, die auf epithermischer Aktivierung und einer einfachen radiochemischen Trennung beruht. Die Ergebnisse für einige Standardgesteine werden vorgelegt. Fehler, die durch Spaltung von Uran und Thorium bei der Neutronenaktivierung von Molybdän hervorgerufen werden, werden berechnet und diskutiert. Die Störung durch das Spaltprodukt  $^{99}\text{Mo}$  hängt erheblich vom Fluss der epithermischen und schnellen Neutronen ab. Epi-Cadmiumaktivierung vermindert die Uranstörung um einen Faktor von 20–80 im Vergleich zur Aktivierung ohne Cadmiummantel; der tatsächliche Wert hängt vom Cadmiumverhältnis zu Gold in der verwendeten Bestrahlungsposition ab.

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## DETERMINATION OF TRACE METALS IN HIGH-PURITY SILVER CHLORIDE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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High-purity silver chloride is commonly analyzed by emission spectrography. With special methods of spectral evaluation, elements may be determined in concentrations as low as 0.01 p.p.m. with 12–20% error<sup>1</sup>. Calibration curves have been established for each of 20 elements over a 0.01–10  $\mu\text{g}$  range by this technique<sup>2,3</sup>. Solvent extraction techniques followed by colorimetric measurement of each isolated element have been applied to this analytical problem for nine elements at the p.p.m. level with 10% accuracy by Concialini *et al.*<sup>4</sup>. Samples dissolved in excess of potassium iodide solution were subjected to a complex separation scheme which required large dissolved sample volumes and several extracting agents.

Solvent extraction techniques combined with atomic absorption spectroscopy allow preconcentration of impurities and a corresponding increase in signal as reported by Allan<sup>5</sup>. Frequently a single extraction is sufficient since isolation of individual impurities is not required. A summary of applications of ammonium pyrrolidine dithiocarbamate (APDC) as a chelating agent for trace metal determinations is given by Slavin<sup>6</sup>, and the extraction efficiencies of APDC are compared with those of 8-hydroxyquinoline (oxine) by Mansell and Emmel<sup>7</sup>.

Preliminary experiments with APDC extraction of trace metals from silver chloride showed extensive extraction of silver ions while oxine did not extract significant quantities of silver from ammoniacal solutions. Oxine has been used to extract magnesium into methyl isobutyl ketone (MIBK) before atomic absorption analysis of impurities in metals and in purified brine<sup>8</sup>. This chelating agent has been found to react with more metals than APDC, among which are magnesium, aluminum and copper<sup>9</sup>. Al, Cu, Fe, Mn, Ni, Mo and Sn have been extracted by oxine into chloroform and pH ranges established for each metal<sup>10</sup>. Similar studies by methods other than atomic absorption have established pH ranges for the extraction of other elements. A more complete discussion of oxine as a chelating agent can be found in a recent book by De *et al.*<sup>11</sup>

In the proposed method a concentrated ammonia solution is used to dissolve the silver chloride samples. An ultrasonic generator speeds the dissolution. Fe, Cu, Mg, Mn and Zn are then extracted as the 8-hydroxyquinolate complexes into MIBK, which are then aspirated into the burner of an atomic absorption spectrophotometer. Calibration curves were established for each element by two methods. In one, standard aqueous solutions were extracted by the proposed method. In another, standard MIBK solutions were aspirated. Since the extraction efficiency proved to be better than 95%, the two calibration curves were equivalent.

## EXPERIMENTAL

*Apparatus*

Dissolutions were performed in 25-ml volumetric flasks. Labindustries Repipetters with a reproducibility of  $\pm 0.1\%$  were used for addition of the ammonia solutions. A Branson model 520 Ultrasonic Powerpack was used to speed dissolution of the silver chloride. Atomic absorption measurements were performed on a Jarrell-Ash 82-566 atomic absorption unit equipped with model 82-385 solid-state electronic system with d.c.-pulsed Westinghouse hollow-cathode lamps. A Techtron D4-130A premix burner nebulizer assembly with an AB-51 titanium burner head was used. An air-acetylene flame was used for all samples and standards in this work.

*Reagents*

Methyl isobutyl ketone (Fisher certified grade) and 8-hydroxyquinoline (Aldrich Gold Seal zone-refined) were used.

Aztec Atomic Absorption iron standard was used; the five other standards were Fisher Certified atomic absorption standards.

U.S.P. grade ethanol and Baker reagent-grade ammonium hydroxide with heavy metals  $< 0.1$  p.p.m. were used.

Checks verified that the metals studied were present in amounts less than the detection limits with the exception of copper for which corrections were made.

*Procedure*

*Sample.* Place 2 g of silver chloride in a 25-ml volumetric flask. Add 20 ml of concentrated ammonia solution and partially immerse the flask in the ultrasonic bath. Dissolution requires *ca.* 15 min. Dilute to volume with distilled-deionized water and transfer 20 ml of the sample solution to a 60-ml separatory funnel. Add 5 ml of concentrated ammonia solution and 5 ml of 1% (w/v) oxine solution in MIBK. Shake for 1 min and allow 20 min for separation of the layers. Aspirate the MIBK layer.

*Standards.* The standards were prepared from stock aqueous solutions of the metals, by making dilutions to give 20 ml of concentrated ammonia solution per 25 ml of standard. The standards were then extracted and analyzed by the above procedure. Calibration curves are based on the concentration of metal in the ammonia solutions.

## RESULTS AND DISCUSSION

Six elements were chosen for study: Cu, Fe, Mg, Mn, Zn and Ni. It was found that nickel was not extracted by the procedure outlined above but was about 40% extracted when 5 ml of absolute ethanol was added to the solution. Alcohol either salts out nickel oxinate from the aqueous phase or solubilizes the species in MIBK. This variation of the standardized procedure opens the possibility for determination of nickel, but it has not been explored thoroughly. The present procedure applies to the remaining five elements. Sensitivities, defined as that concentration of metal which produces a 1% absorption signal, for the metals in the aqueous phase and in solid silver chloride are presented in Table I. Flame conditions were constant for all elements and no attempt was made to set up the instrument for maximum possible

TABLE I

SENSITIVITIES IN AQUEOUS SOLUTION AND SOLID SILVER CHLORIDE

Element	Aqueous ( $\mu\text{g ml}^{-1}$ )	Solid ( $\mu\text{g g}^{-1}$ )
Mg	0.005	0.06
Cu	0.015	0.19
Mn	0.010	0.13
Fe	0.013	0.16
Zn	0.020	0.25

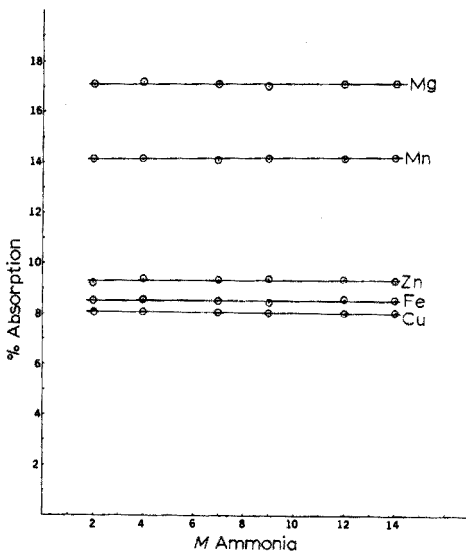


Fig. 1. Combined extraction efficiency and spectrophotometric sensitivity. Five elements Mg, Mn, Zn, Cu and Fe extracted from varying concentrations of ammonia solution. Measurements were made at the most sensitive resonance lines: 285.2, 279.5, 213.9, 324.7 and 248.3 nm, respectively.

TABLE II

RECOVERY STUDY

Element	$\mu\text{g added}$	$\mu\text{g found}^a$	% Extracted
Mg	3.0	2.90	96.6
Cu	3.0	2.90	96.6
Mn	3.0	2.91	97.0
Fe	3.0	2.86	95.3
Zn	3.0	2.85	95.0

<sup>a</sup> Average of three runs.



TABLE III  
ANALYSIS OF STANDARD SAMPLES

Mg			Cu			Mn			Fe			Zn		
$\mu\text{g}$ added	$\mu\text{g}$ found	% Error	$\mu\text{g}$ added	$\mu\text{g}$ found	% Error	$\mu\text{g}$ added	$\mu\text{g}$ found	% Error	$\mu\text{g}$ added	$\mu\text{g}$ found	% Error	$\mu\text{g}$ added	$\mu\text{g}$ found	% Error
5.0	5.00	0.0	5.0	4.88	-2.4	5.0	5.13	2.6	5.0	5.00	0.0	5.0	4.80	-4.0
5.0	5.13	2.6	5.0	4.85	-3.0	5.0	5.13	2.6	5.0	4.85	-3.0	5.0	4.90	-2.0
5.0	5.01	0.2	5.0	5.14	2.8	5.0	4.91	-1.8	5.0	4.98	-0.4	5.0	5.18	3.6
10.0	9.82	-1.8	10.0	10.33	3.3	10.0	10.38	3.8	10.0	10.30	3.0	10.0	9.50	5.0
10.0	10.38	3.8	10.0	10.00	0.0	10.0	10.22	2.2	10.0	10.05	0.5	10.0	10.00	0.0
10.0	10.10	1.0	10.0	10.32	3.2	10.0	10.21	2.1	10.0	10.00	0.0	10.0	10.10	1.0
Ave. $\pm$ 1.6			Ave. $\pm$ 2.5			Ave. $\pm$ 2.5			Ave. $\pm$ 1.2			Ave. $\pm$ 2.6		

sensitivities. The sensitivities can be improved by using larger sample sizes where available.

The extraction efficiency was studied over an ammonia concentration range of 2–14 M. Figure 1 shows the percent absorption as a function of ammonia concentration when standards of equal metal concentration were extracted into MIBK.

A study of the efficiency of the extraction step showed that all extractions were 95% or more complete with one solvent pass. Samples (3  $\mu\text{g}$ ) of each element were added to the aqueous layer and the weight of each impurity extracted into the MIBK layer was calculated by comparison with standards dissolved in MIBK. These results are given in Table II.

The described method was also checked by adding known amounts of the impurities to be determined to ammoniacal solutions of silver chloride. These solutions were then analyzed by means of calibration curves prepared as outlined earlier. From a silver chloride sample with no added metals and a reagent blank carried through the procedure, the absorbance from these sources was determined. Only copper was found in detectable amounts and the appropriate corrections were made. Zinc samples showed a background absorption which was traced to a molecular band absorption. The zinc-free reagent blank at the zinc resonance line gave the same absorption which was shown to be constant and corrections were easily made. The results for the five elements studied are summarized in Table III. Errors for individual determinations ranged from 0 to 5%. The average error for 6 determinations of an element varied from 1.2 to 2.6%.

Original investigations were made with 1% oxine dissolved in absolute ethanol as described by Suzuki *et al.*<sup>8</sup>. Sensitivities by this method were found to be less by about 50% than those of the above method. This was traced to the extraction step where it was discovered that up to 50% of the metal was left in the aqueous phase. This is presumably due to solubility of the metal 8-hydroxyquinolate in the ethanol which remains in the aqueous layer.

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#### SUMMARY

A method for determination of trace metals in silver chloride by atomic absorption spectroscopy is described. Solid silver chloride is dissolved in ammonia solution and impurities are extracted into MIBK as 8-hydroquinolate complexes. Calibration curves based on concentrations in the ammoniacal solution are prepared by the same extraction procedure. Sensitivities as low as  $0.06 \mu\text{g g}^{-1}$  with errors of less than 5% are reported. The method should prove applicable to more than the five metals selected for study.

#### RÉSUMÉ

On décrit une méthode de dosage de métaux à l'état de traces dans le chlorure d'argent, par spectroscopie par absorption atomique. Le chlorure d'argent solide est dissous dans l'ammoniaque; les impuretés sont extraites dans la méthylisobutyl-

cétone sous forme de complexes hydroxy-8-quinoléates. On arrive à des sensibilités de  $0.06 \mu\text{g g}^{-1}$  avec des erreurs inférieures à 5%. Cette méthode peut être appliquée également à d'autres métaux que les cinq qui ont été choisis pour cette étude.

#### ZUSAMMENFASSUNG

Es wird eine Methode für die Bestimmung von Spurenmetallen in Silberchlorid durch Atomabsorptionsspektroskopie beschrieben. Das feste Silberchlorid wird in Ammoniaklösung aufgelöst, und die Verunreinigungen werden mit MIBK als 8-Hydroxychinolat-Komplexe extrahiert. Die Eichkurven, bezogen auf die Konzentrationen in der ammoniakalischen Lösung, werden nach demselben Extraktionsverfahren erstellt. Es werden Empfindlichkeiten von  $0.06 \mu\text{g g}^{-1}$  mit Fehlern von weniger als 5% erreicht. Die Methode dürfte ausser auf die fünf für die Untersuchung ausgewählten Metalle auch auf andere Metalle anwendbar sein.

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## DETERMINATION OF COPPER IN SERUM WITH A GRAPHITE ROD ATOMIZER FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Of the 37 analytically detectable elements present in the human body, 26 are metallic in nature, and many are present in trace concentrations. The importance of several of these trace metals in mediating biochemical processes has prompted investigations of their physiological values and variations of these values in pathological states. Various methods have been employed for the detection and measurement of trace metals in biological materials among which is atomic absorption spectroscopy (a.a.s.).

When a.a.s. is used for the spectrometric determination of various elements, the necessary cloud of atoms is usually produced by vaporization of sample salt particles and dissociation of the resultant molecules in the flame. However, heating of the sample on a carbon rod or similar device is another means of producing a vapor of metal atoms in their ground state. In this method, a graphite rod filament is heated to a sufficiently high temperature by an electric current to effect atomization and an inert gas environment is provided to minimize oxidation.

King<sup>1</sup> employed a graphite furnace as early as 1932 for fundamental studies. L'vov<sup>2,3</sup> was the first to use such a graphite furnace for analytical studies. Woodriff and Ramelow later used a graphite tube for a.a.s. analyses with a nebulizing system<sup>4</sup>. More recently, Massmann<sup>5</sup> compared a heated graphite furnace for a.a.s. and atomic fluorescence spectroscopy (a.f.s.) measurements, and West *et al.*<sup>6-8</sup> have used a carbon filament for both a.a.s. and a.f.s. analyses. In addition, Donega and Burgess<sup>9</sup> as well as Winefordner *et al.*<sup>10</sup>, have described modified systems. More recently, Amos *et al.*<sup>11</sup> have evaluated and compared a carbon rod atomizer and a carbon tube atomizer for a.a.s. and a.f.s. and have developed methods for direct analysis of lead in blood and urine by a.f.s. While this paper was in preparation, Matousek and Stevens<sup>12</sup> published a survey study on the use of a commercial carbon rod atomizer for the measurement of magnesium, lead, iron, zinc, and copper in blood and serum.

In the present study, a graphite rod atomizer has been evaluated as a practical means of performing the direct analysis of copper in serum, and a suitable method has been worked out.

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## EXPERIMENTAL

A Perkin-Elmer AA-303 Atomic Absorption Spectrophotometer with a graphite rod atomizer substituted for the burner assembly and a potentiometric recorder readout was used for all studies. A high-intensity copper hollow-cathode discharge lamp was employed for all measurements.

In Fig. 1, the dimensions of the two types of graphite rods used are shown. The Type 1 graphite rod features a center section of reduced diameter. The ends of the rod are of larger diameter for better electrical and thermal contact with the terminals. In later work, a modified version also shown in Fig. 1 was utilized. The Type 2 graphite rod gave better performance, and lifetime was increased to over 200 measurements per rod. In Fig. 2, the graphite rod atomizer with the gas sheathing chamber is shown. Heat is localized around the center of the rod, and is dissipated quickly between analyses by water cooling the copper terminals. The gas sheathing chamber is a concentric Meker burner with provision for an outer flame sheath; it is identical to a concentric burner system described in detail by Hollander<sup>13</sup>. The gas sheathing chamber was used because it was available; however, it was not unique to the recent study. In fact, any concentric chamber which would allow the independent flow of an inner sheath of gas by the graphite rod atomizer, and the flow of an outer sheath of gas to minimize air entrainment would suffice.

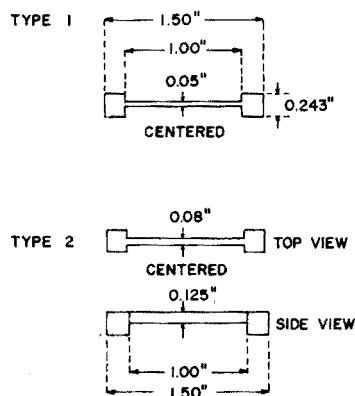


Fig. 1. Graphite rod.

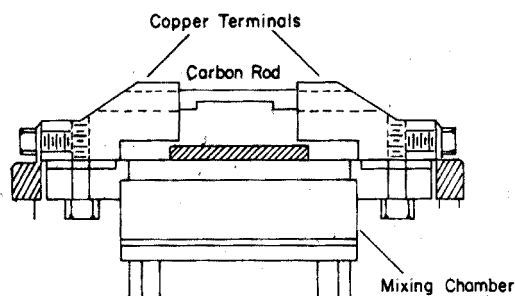


Fig. 2. Graphite rod atomizer system.

To minimize air entrainment, a laminar flame sheath surrounding the inner gas (argon in our case) flow was necessary. Optimal operation resulted from an argon flow rate of  $2 \text{ l min}^{-1}$  in the inner portion of the concentric mixing chamber, and a mixture of hydrogen and argon at a flow ratio of 12 : 7 (volume : volume) in the outer flame sheath of the chamber. Hydrogen was introduced in the inert gas stream at a sufficient rate to ignite and burn with the entrained atmospheric oxygen after the graphite rod reached a sufficiently high temperature.

To heat the graphite rod to a temperature of over  $2000^\circ$ , a current of 120 A was required. This current was provided by a Lee Associate SCR-10-250 power

supply. A timing circuit was constructed to allow a preheat period, a final vaporization and atomization period for each sample, and a final cooling period\*. The time for one complete cycle was controllable up to a maximum of 60 sec.

## RESULTS AND DISCUSSION

### Detection limits

The detection limit is defined as the lowest amount of copper which would produce a signal twice as great as the blank of distilled water under the same conditions, and was found to be 200 picograms ( $2 \cdot 10^{-10}$  g). The detection limit of 20 pg mentioned by Amos *et al.*<sup>11</sup> was an approximate extrapolated value<sup>11</sup>. The limit of detection of 0.6 pg quoted by L'vov<sup>2,3</sup> was defined as that amount of copper which would have at least one percent absorption value. The detection limit of Massmann<sup>5</sup> was 10 pg and was defined as that amount of copper producing a signal-to-noise ratio of two.

Detection limits in the order of  $10^{-12}$  g are obtained because of the small sample size involved ( $5 \mu\text{l}$ ) and the efficiency of atomization by this method.

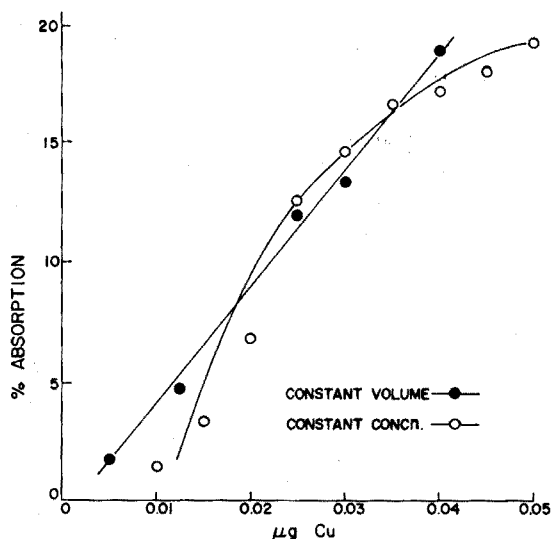


Fig. 3. Analytical curves for copper.

### Analytical curves

In Fig. 3, two analytical curves are given for copper by atomic absorption at 324.7 nm. A straight-line plot was obtained for copper by a.a.s. in the range of  $1\text{--}6 \mu\text{g ml}^{-1}$  of copper when a constant volume of  $5 \mu\text{l}$  was used. However, when the volume of the sample was varied from  $1 \mu\text{l}$  to  $10 \mu\text{l}$  for a sample which contained  $5 \mu\text{g Cu ml}^{-1}$ , a slight curvature appeared for larger sample sizes. Reduction of sensitivity for larger sample sizes of  $6\text{--}10 \mu\text{l}$  was primarily a result of the varying

\* The timing current diagram may be obtained by writing Dr. James Winefordner.

degree of soaking of the sample into the graphite rod and the variation in the placement of the sample onto the graphite rod.

#### Precision

The percent relative standard deviations ( $s_r$ ) of 5–10% for the present method compare favorably to values obtained by Massmann<sup>5</sup>, Amos *et al.*<sup>11</sup>, and L'Vov<sup>3</sup> of 4–12%, 5–8%, and 5–12%, respectively.

The  $s_r$  values for 14 replicate samples of copper containing  $1.0 \mu\text{g ml}^{-1}$  and 20 replicate samples containing  $2.5 \mu\text{g ml}^{-1}$  were 4.5%, and 10.3%, respectively. The range of  $s_r$  values was attributed to loss of copper on the syringe wall, the differing rates of diffusion of sample into the graphite rod which was a function of age and porosity of the rod, and variation in atomization rate with variation in sample coverage on the graphite rod.

#### Interferences

In studying the practical application of the method for the determination of copper in serum, an investigation of interference effects caused by the presence of matrix components in biological samples was carried out. Interference from the sample matrix is primarily a result of nonspecific absorption caused by light scattering (spectral interference) and variation of the ground atom population (chemical interference) owing to differences in sample vaporization rate. Phosphate ( $0.05 \text{ mg ml}^{-1}$ ), sodium ( $2 \text{ mg ml}^{-1}$ ), potassium ( $1 \text{ mg ml}^{-1}$ ), magnesium ( $0.02 \text{ mg ml}^{-1}$ ), and chloride (concentration of  $3.07 \text{ mg ml}^{-1}$ ) diminished the signal level for  $1.25 \mu\text{g ml}^{-1}$  of copper by 24%, 20%, 34%, 30%, and 0%, respectively. These depressions were probably a result of chemical interferences; on the other hand, calcium(II) at a concentration of  $0.05 \text{ mg ml}^{-1}$  produced an enhancement of 91%, presumably by spectral interference. Other cations— $\text{Ba}^{2+}$ ,  $\text{Rb}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Li}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Hg}^{2+}$ —at concentrations found in normal serum were also investigated as possible interferences. Slight enhancements were noted for manganese(II) and iron(III), a depression of greater than 50% was noted for barium(II), and no significant depression or enhancement was found for the other cations.

It was later shown by comparing the present method with a reference procedure that the combined effects of these ions present in serum samples produced minimal interferences in the measurement of copper. Presumably the serum matrix minimized spectral and chemical interferences.

#### Applications

A typical recorder tracing for a blank, an aqueous copper standard, and a serum sample are given in Fig. 4. Experimental conditions varied in the studies, but a general procedure was followed. Aliquots ( $5 \mu\text{l}$ ) of a sample were introduced with a Hamilton syringe on the center of the rod. With the Type 1 graphite rod, a drying time of 11 sec at 20 A, an atomization time of 3 sec at 175 A, and a cooling time of 46 sec at no current were used. These conditions compared to a drying time of 22 sec at 30–40 A, an atomization time of 3 sec at 118 A, and a cooling time of 35 sec at no current with the Type 2 graphite rod.

A comparison of values obtained by direct analyses of serum copper levels and values obtained by using Sunderman's extraction method<sup>14</sup> are given in Table I.

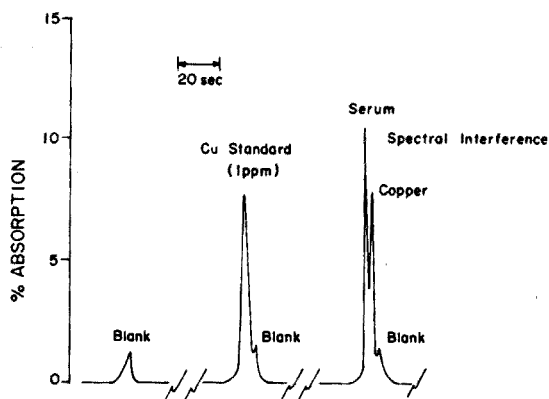


Fig. 4. Typical recorder tracings.

In the latter method, a protein-free filtrate was obtained by use of trichloroacetic acid. Comparison of values obtained by these two methods shows excellent agreement.

Percentage recoveries of copper added to straight serum and protein-free filtrates are given in Table II; slightly higher recoveries and better precision resulted when serum aliquots were used.

TABLE I

COMPARISON OF COPPER CONCENTRATIONS BY TWO TYPES OF GRAPHITE RODS

	Copper concn. ( $\mu\text{g}/100\text{ ml}$ )		$s_r$ (%)
	Type 1	Type 2	
<i>Direct analysis</i>			
Serum no. 1	110	100	7.7
Serum no. 2	142	95	
<i>Protein-free filtrate</i>			
1. Serum no. 1	96	105	7.1
2. Serum no. 2	99	112	
3. Aqueous Cu standard no. 1 (200 $\mu\text{g}/100\text{ ml}$ )	217	200	7.7
4. Aqueous Cu standard no. 2 (200 $\mu\text{g}/100\text{ ml}$ )	208	215	
5. 100 $\mu\text{g}/100\text{ ml}$ Cu added to serum no. 1	107	90	9.6
6. 100 $\mu\text{g}/100\text{ ml}$ Cu added to serum no. 2	98	85	

The copper level was measured in the serum of 13 patients taken from a group of 28 patients who had been diagnosed as having rheumatoid arthritis. It had previously been found that elevated copper levels were noted for patients with rheumatoid arthritis<sup>15</sup>. In Table III, a comparison is given of the copper levels in the sera of 28 patients measured by normal a.a.s. with a flame atomizer, and in the sera of 13 patients (from the 28 patients) measured by the present flameless a.a.s.



TABLE II

RECOVERY OF COPPER ADDED TO SERUM WITH GRAPHITE ROD a.a.s.

Number of analyses	Copper added ( $\mu\text{g}/100\text{ ml}$ )	% Recovery		$s_r$ (%)
		Range	Mean	
5 Serum samples	125-250	105-115	110	5.1
4 Serum extracts	100	85-107	95	9.6

TABLE III

COMPARISON OF SERUM COPPER LEVELS BY FLAME a.a.s. AND GRAPHITE ROD a.a.s.

Results	Flame a.a.s. <sup>16</sup>	Graphite rod a.a.s.
Number of samples	28	13
Mean serum Cu level ( $\mu\text{g}/100\text{ ml}$ )	151	167
Standard deviation	46.2	40.2

The authors wish to thank Perkin-Elmer Corporation, Norwalk, Conn., for the loan of a Model 303 Atomic Absorption Spectrophotometer. This work was partly supported by NIH 229\* H90 and AF-AFOSR-70-1880B.

## SUMMARY

A graphite rod atomizer is used to atomize copper in 5- $\mu\text{l}$  blood serum samples; measurement is made by atomic absorption spectrometry. The precision of measurement was less than 10% for all measurements of serum and aqueous samples. No interference resulted from  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{Ca}^{2+}$  in serum. Recoveries of copper from serum samples with and without deproteinization agreed within experimental error. Copper levels by the graphite atomizer atomic absorption method, in blood serum of patients diagnosed as having rheumatoid arthritis, agreed well with copper levels measured by normal flame atomic absorption spectrometry.

## RÉSUMÉ

Un atomiseur à baquette de graphite est utilisé pour l'atomisation du cuivre dans des échantillons de sérum sanguin de 5  $\mu\text{l}$ . Les mesures sont faites spectrométriquement par absorption atomique. La précision est inférieure à 10% pour toutes les mesures avec des échantillons aqueux et de sérum. Il n'y a pas d'interférence de  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$  et  $\text{Ca}^{2+}$ . Les résultats obtenus correspondent bien à ceux fournis par la spectrométrie par absorption atomique à flamme, normale.

## ZUSAMMENFASSUNG

Kupfer in Blutserum-Proben von 5  $\mu\text{l}$  wurde durch Atomabsorptionsspektrometrie unter Verwendung einer Graphitstab-Küvette bestimmt. Die Reproduzierbarkeit der Messung war bei allen Messungen von Serum- und wässrigen Proben kleiner

als 10%. Störungen durch  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$  und  $\text{Ca}^{2+}$  im Serum traten nicht auf. Die erfassten Anteile des Kupfers in enteiweissten und nicht enteiweissten Serumproben stimmten innerhalb des experimentellen Fehlers überein. Die nach der Graphitstab-Methode bestimmten Kupfergehalte des Blutserums von Patienten mit rheumatoider Arthritis stimmten mit den Kupfergehalten, die mit der gewöhnlichen Flammen-Atomabsorptionsspektrometrie ermittelt worden waren, gut überein.

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## ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

### PART VI. A STUDY OF SOME MATRIX EFFECTS

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The determination by atomic fluorescence spectroscopy (a.f.s.) of a number of metal ions in pure aqueous solution by means of a carbon filament atom reservoir has already been described<sup>1</sup>. In a more detailed study of the determination of cadmium by this technique<sup>2</sup>, many interferences were noted. In this paper, a more detailed study of matrix effects associated with the use of the carbon filament atom reservoir is presented.

#### EXPERIMENTAL

##### *Apparatus*

The spectrometer, lamps, cell and a.c. detection system have all been described previously<sup>1</sup>.

In addition a fast-response d.c. detection system has been developed to replace the a.c. amplifier of the spectrometer. The lamps are run in the d.c. mode, and the output from the photomultiplier tube is fed into a negative feedback operational amplifier circuit built round a Philbrick PF85AU amplifier (Fig. 1). The output from this circuit is then fed into the galvanometer (type BB 160A) used in the Honeywell 1706 "Visicorder" oscillograph.

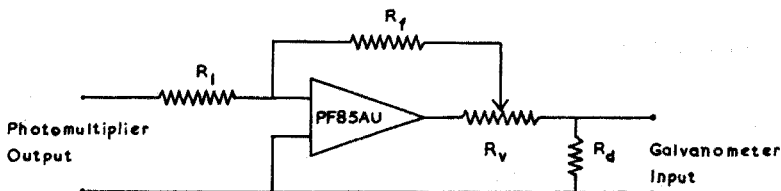


Fig. 1. Circuit diagram of the d.c. detection system.  $R_l$ , Photomultiplier load resistance;  $R_f$ , feedback resistance;  $R_v$ , variable feedback (variable gain) resistance;  $R_d$ , galvanometer damping resistance.

##### *Preparation of the solutions*

All glassware was treated as described previously<sup>1</sup>, and the chemicals were of AR grade where available. Stock solutions of the ion to be determined were prepared and diluted with deionized water immediately before use. An appropriate amount of

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“matrix material” was dissolved directly in the diluted solution of the ion to be determined. Blank solutions containing only the “matrix material” were always run, and occasionally a small correction due to impurities in the “matrix material” had to be made.

#### *Measurement of the absorption and fluorescence*

The technique for measuring the fluorescence intensity was as described previously<sup>1</sup>. For atomic absorption spectroscopy (a.a.s.) the lamp was moved to a position on the optical rail of the spectrometer and focussed to give a beam of appropriate geometry (see “Results and Discussion”) above the filament, which was aligned either along or at right angles to the optical axis.

Each result reported is the average of at least four readings.

### RESULTS AND DISCUSSION

#### *Detection system*

It was noted previously<sup>1</sup> that the rise time of the a.c. amplifier incorporated in the Techtron AA-4 Atomic Absorption Spectrometer was too long for the shortest of the signals to be detected faithfully. Therefore, a simple d.c. circuit was built around a cheap operational amplifier to enable the signals to be displayed in the d.c. mode on the oscilloscope. The rise time of this system is about 0.01 sec.

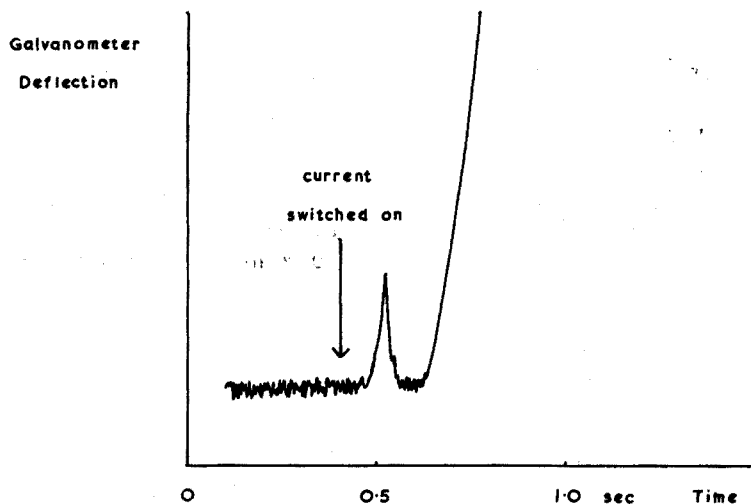


Fig. 2. Typical a.f.s. signal obtained with d.c. detection.

A typical signal obtained with this system is shown in Fig. 2. It is noted that in this system, continuum radiation from the filament is detected immediately after the atomic signal. However, interference between the two signals has not occurred for the elements that have so far been studied.

With the d.c. detection system it was found that the most sensitive signals were always obtained at the maximal filament voltage. This is because, in contrast to the a.c. system, no signal distortion occurred. Under these conditions the lifetimes of the shortest signals observed were of the order of 0.05 sec.

*Optimal conditions for analysis in a.f.s.*

Optimal conditions have already been reported for the a.c. detection of Mg, Ag, Pb, Zn, Bi, Tl and Ga<sup>1</sup>. Table I gives values for a number of other elements, together with the limits of detection (signal to noise of 2:1) and the upper limits of determination beyond which the calibration curve ceases to have an analytically useful slope. Similar results with the d.c. detection system are also given in Table I. From the Table it can be seen that, for the elements so far studied, the choice of detection system, although affecting the accuracy of reproduction of the a.f.s. peak, does not affect the analytical range of the technique.

TABLE I

OPTIMAL CONDITIONS AND USEFUL RANGE FOR THE a.f.s. DETERMINATION OF CERTAIN ELEMENTS WITH a.c. DETECTION AND d.c. DETECTION

<i>Element</i>	<i>Line (nm)</i>	<i>Lamp<sup>a</sup></i>	<i>Filament voltage (V)</i>	<i>Ar flow rate (l min<sup>-1</sup>)</i>	<i>Range<sup>b</sup> (g)</i>
<i>A.c. detection</i>					
Cd	228.80	EDL	7.2	2.5	5·10 <sup>-14</sup> –5·10 <sup>-12</sup>
Sb	231.15	EDL	9.0	2.5	10 <sup>-9</sup> –3·10 <sup>-8</sup>
Cu	324.75	HIL	12.0	1.1	10 <sup>-12</sup> –4·10 <sup>-9</sup>
Mn	279.48	HCL	12.0	2.5	5·10 <sup>-12</sup> –2·10 <sup>-9</sup>
Co	240.73	HIL	12.0	1.7	2·10 <sup>-11</sup> –6·10 <sup>-9</sup>
Ni	232.00	HIL	12.0	1.7	5·10 <sup>-12</sup> –5·10 <sup>-9</sup>
<i>D.c. detection</i>					
Bi	306.77	EDL	12.0	2.5	10 <sup>-11</sup> –10 <sup>-8</sup>
Tl	377.57	EDL	12.0	1.7	5·10 <sup>-11</sup> –2·10 <sup>-9</sup>
Cu	324.75	HIL	12.0	1.1	10 <sup>-12</sup> –4·10 <sup>-9</sup>
Mn	279.48	HCL	12.0	2.5	5·10 <sup>-12</sup> –2·10 <sup>-9</sup>
Hg	253.65	EDL	12.0	1.7	5·10 <sup>-11</sup> –10 <sup>-8</sup>

<sup>a</sup> EDL = Electrodeless discharge lamp, 2450 MHz; HIL = A.S.L. high intensity (Sullivan and Walsh type) hollow-cathode lamp; HCL = hollow-cathode lamp.

<sup>b</sup> The lower limit represents a signal/noise ratio of 2:1.

*Matrix effects in a.f.s.*

Initially, all matrix effects were studied with the matrix ion present in a 1000-fold amount, by weight, compared to the ion to be determined. The amount of the latter ion present was chosen to lie within, and towards the upper limit of, the analytical range, as it was found that interferences were most noticeable in this region. Counter ions for cation studies were chloride, sulphate, nitrate, or occasionally fluoride, and for anion studies either the free acid or the ammonium salt was used. Occasionally the sodium or potassium salt was used in cases where these elements did not appear to interfere. The results for cations, which were obtained with a.c. detection, are summarized in Table II. An interference was considered to have occurred if the signal was enhanced or suppressed by 5% or more.

Clearly, a large number of apparent suppressions occurred. No enhancements were observed. Interferences were more marked in the determinations of Bi, Cu, Mg, Pb and Tl than for Ag, Cd, Hg and Zn.

Elements that form refractory oxides, such as Al, Ti, Zr, Th, V, Cr and Mo, did not produce many interferences. This is in complete contrast to the usual case observed in flame analysis, and suggests a further possible advantage of the carbon filament

TABLE II

PERCENTAGE DEPRESSION CAUSED BY 1000-FOLD AMOUNT OF MATRIX IONS ON a. f. s. SIGNALS WITH CONVENTIONAL TOTAL AREA ILLUMINATION

Analyte	Ag	Bi	Cd	Cu	Hg	Mg	Pb	Tl	Zn
Wt. of analyte (g)	$10^{-10}$	$10^{-10}$	$10^{-12}$	$10^{-9}$	$10^{-9}$	$10^{-10}$	$2 \cdot 10^{-9}$	$10^{-9}$	$10^{-11}$
Wavelength (nm)	328.07	306.77	228.80	324.75	253.65	285.21	405.78	377.57	213.86
<i>Matrix ion</i>									
Ag <sup>+</sup>		90	0			0	70	0	60
Al <sup>3+</sup>	0	0	0	0	0	0	0	0	0
Au <sup>3+</sup>	0					0	0		
Ba <sup>2+</sup>	0			30	0	50	0		
Be <sup>2+</sup>	0					0			
Bi <sup>3+</sup>	55				70	0	75		
Ca <sup>2+</sup>	0	0	0	65		0	60	100	60
Cd <sup>2+</sup>	0	0		0	0	0	50	50	
Co <sup>2+</sup>	0						70		
Cr <sup>3+</sup>	0		0	65		95	0	0	0
Cs <sup>+</sup>						65			
Cu <sup>2+</sup>	40	35	0		0	75	65	35	0
Fe <sup>2+</sup>	0	65		65	0	80	0	0	0
Hg <sup>2+</sup>	30	0	30	0		0	0	35	
K <sup>+</sup>	0	25	0	70	0	65	65	80	0
La <sup>3+</sup>	0	0	0	0	0	0	0	0	0
Li <sup>+</sup>	0					0	30		
Mg <sup>2+</sup>	0	0	0	0			70	0	0
Mn <sup>2+</sup>	0		0	100					
Mo(VI)	0			0			0		
Na <sup>+</sup>	0		0	55	0	45	55	90	0
Nb(V)	0					65			
Ni <sup>2+</sup>	0	40	0			95	0		0
NH <sub>4</sub> <sup>+</sup>	0	0		0	0	0	0		0
Pb <sup>2+</sup>	70	90	0	0	0	0		90	0
Pd(II)	40								
Pt(IV)	0					0	0		
Rb <sup>+</sup>	0					65	50		
Sb <sup>3+</sup>	0		0	35					0
Si(IV)	0					50			
Sn <sup>2+</sup>	0						0		
Sr <sup>2+</sup>	0			60		50	0		0
Ta(V)	0								
Th <sup>4+</sup>	0	0	0	0		0	0	0	0
Ti(IV)	0	0	0	0	0	0	0	60	0
Tl <sup>+</sup>	0								
UO <sub>2</sub> <sup>2+</sup>	0						0		
VO <sub>2</sub> <sup>2+</sup>	0		0	55		0	0		0
V(V)	0								
W(VI)	0								
Zn <sup>2+</sup>	0	0	35	0	0	0	0		
Zr(IV)	0					0	20		0

atom reservoir over flames.Suppressions occurred most frequently from elements such as Ca, Cu, Fe, Hg, K, Na, Pb, and Bi. A common factor between these elements is that they all have boiling points below the maximum temperature attainable by the filament, and are, therefore, likely to be atomised along with the element being determined.

1000-fold amounts of acetate, arsenate, borate, bromide, chloride, citrate, cyanide, EDTA, fluoride, iodate, iodide, nitrate, oxalate, perchlorate, phosphate, sulphate, sulphide, sulphite, tartrate and thiocyanate were examined in the determination of silver; only phosphate and arsenate in 1000-fold amounts interfered causing signal suppressions of 65% and 70%, respectively. Representative anions were also examined for the other analytes listed in Table II. The only interference found was the suppressing effect of phosphate on magnesium (-55%). The suppressions caused by phosphate were removed when nitric acid was added to the sample.

Table III shows some matrix effects obtained on both the a.c. and d.c. detection systems. The weights of analyte and matrix ion were the same as those quoted in Table II. It can be seen that, although the response time of the latter system is much the faster, no significant differences exist between the matrix effects observed for either system.

TABLE III

A COMPARISON OF MATRIX EFFECTS IN a.f.s. OBSERVED WITH a.c.<sup>a</sup> AND d.c.<sup>b</sup> DETECTION SYSTEMS (Quantities of analyte and matrix ion as in Table II)

Analyte	Matrix ion	Percentage suppression of signal	
		A.c. system	D.c. system
Tl at 377.57 nm	Al <sup>3+</sup>	0	0
	Cd <sup>2+</sup>	50	45
	Hg <sup>2+</sup>	35	45
	K <sup>+</sup>	80	70
Bi at 306.77 nm	Cu <sup>2+</sup>	35	30
	Fe <sup>2+</sup>	65	70
	K <sup>+</sup>	25	30
	Mg <sup>2+</sup>	0	0
	Hg <sup>2+</sup>	0	0

<sup>a</sup> i.e. Slow response.

<sup>b</sup> i.e. Fast response.

Table IV shows some matrix effects on silver (1- $\mu$ g amount on 0.1 ng of silver) in both a.f.s. and a.a.s., with a.c. detection. In a.a.s. the filament was aligned along the optical bar. Instrument settings were as described previously<sup>3</sup>. Similar results were obtained for the interference of the alkali metals on magnesium. These results show that the interferences occur equally in a.a.s. and a.f.s., which suggests that the interference is due to a reduction in the ground-state population of the element determined.

Table V shows the effect on the a.f.s. signal of lead caused by reducing the sample size while maintaining a constant weight ratio of matrix ion to lead ion. It can

TABLE IV

A COMPARISON OF MATRIX EFFECTS ON SILVER AT 328.07 nm WITH a.c. DETECTION IN a.f.s. AND a.a.s. (Quantities as in Table II)

Matrix ion	Percentage suppression of signal	
	A.f.s.	A.a.s.
Bi <sup>3+</sup>	55	50
Hg <sup>2+</sup>	30	35
Cu <sup>2+</sup>	40	50
Pb <sup>2+</sup>	70	70

TABLE V

EFFECT ON THE a.f.s. SIGNAL AT 405.78 nm OF A CONSTANT 1000-FOLD AMOUNT OF VARIOUS IONS IN THE DETERMINATION OF LEAD (a.c. DETECTION)

Matrix ion	Percentage suppression of signal of	
	$2 \cdot 10^{-9}$ g of Pb	$10^{-10}$ g of Pb
Na <sup>+</sup>	55	45
K <sup>+</sup>	65	35
Mg <sup>2+</sup>	70	20

be seen that the suppression is reduced. Similar experiments carried out on other systems showed in all cases that the suppression was reduced by reducing the sample size.

The suppression by sodium of the a.f.s. signal of lead was not affected by the presence of 8-hydroxyquinoline under conditions such that the lead was in the form of a complex.

In other experiments, the sample (0.1 ng of magnesium) and matrix (100 ng of potassium) were applied separately on the filament on opposite sides of the central notch, so that they did not come into contact until the sample was vaporized. The suppression of the a.f.s. signal persisted. The same result was obtained in a more rigorous experiment designed to prevent any possibility of solution mixing by diffusion through the rod, by use of two filaments mounted one above the other with the sample on the higher and the matrix on the lower<sup>4</sup>.

From these experiments it was apparent that the suppressions occurred in the vapour phase *after* the sample had been vaporized, and were not solely due to interactions occurring on the filament.

The carbon filament atom reservoir differs from other atomisation systems such as flames or the furnaces of L'Vov<sup>5</sup> or Massmann<sup>6</sup>, in that once the atoms are produced they diffuse immediately into a cold atmosphere. Therefore, they will rapidly recombine by condensation with their own species or with other atoms present, as they lose their thermal energy. This means that condensation will be much more rapid than in other systems, *e.g.* flames, where thermal energy is supplied continuously.

It is reasonable to suppose that if the sample is atomised in the presence of a



large excess of matrix material, the lifetime of the required atoms will be reduced even further, owing to the much higher concentration of rapidly nucleating atoms which may cocrystallize or occlude the required atoms. Since the primary sources illuminate a relatively large area above the filament, the atoms will remain in the radiation path for the whole of their lifetime. If their number is decreased by condensation during the period of observation, this will be manifested in a suppression of the absorption or fluorescence signal.

In order to test this hypothesis, the apparatus was modified for a.a.s. measurements in such a way that the primary source illuminated an area only 0.5 mm high and 4 mm wide above the filament. This was achieved by placing a narrow horizontal slit in front of the source and focussing the image of this slit over the filament which is at right angles to the light beam (Fig. 3). By varying the height of the filament above

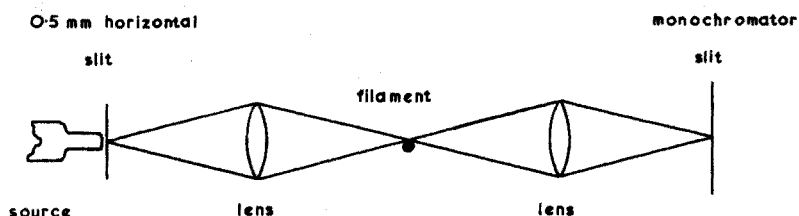


Fig. 3. Diagram of apparatus used for a.a.s. experiments with limited field viewing.

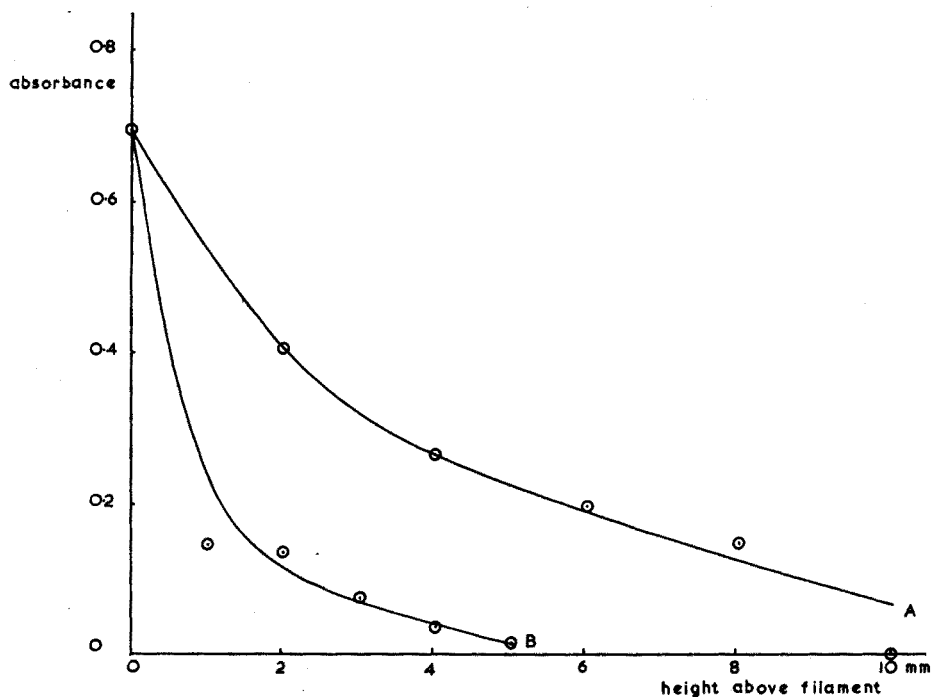


Fig. 4. Variation of the a.a.s. of lead with height of observation above filament (limited field viewing). (A) For 2 ng of lead; (B) for 2 ng of lead in the presence of 2000 ng of sodium.

the optical bar it was possible to study by absorption measurements the variation of atomic concentration as a function of height above the filament.

Two experiments were carried out. In the first, the a.a.s. signal for 2 ng of lead was observed at different heights above the filament and plotted against height of observation above the filament. The second experiment was similar but was conducted with 2 ng of lead in the presence of 2000 ng of sodium. The 217.00-nm line for lead was used with d.c. detection and an argon flow rate of 1.1 l min<sup>-1</sup>. The results are shown in Fig. 4.

For pure lead solution, the atomic population decays approximately exponentially as the height above the filament is increased, atoms persisting for about 8–10 mm above the filament. However, in the presence of sodium, the atomic population decays very much more rapidly, although immediately above the surface of the filament the atomic population is the same. Finally, the a.a.s. signals for those two samples were recorded with the horizontal slit removed. A 55% suppression by sodium was observed, equal to the suppression observed in a.f.s.

TABLE VI

MATRIX EFFECTS IN a.a.s. WITH A 0.5-mm HORIZONTAL SLIT IN FRONT OF THE PRIMARY SOURCE, AND d.c. DETECTION  
(1000-fold weight amount of matrix ion. Percentage change of signal)

Analyte	Ag	Mg	Pb	Cu
Wavelength (nm)	328.07	285.21	217.00	324.75
Wt. of analyte (g)	10 <sup>-10</sup>	10 <sup>-10</sup>	5 · 10 <sup>-10</sup>	10 <sup>-9</sup>
Filament voltage	12.0	12.0	12.0	9.6
Ar flow rate (l min <sup>-1</sup> )	1.7	1.7	1.7	1.1
Slit (μm)	300	200	200	25
<i>Matrix ion</i>				
Ag <sup>+</sup>			-50	
Ba <sup>2+</sup>		0		0
Bi <sup>3+</sup>	0		-40	
Ca <sup>2+</sup>			0	-25(0 <sup>b</sup> )
Cd <sup>2+</sup>			0	
Co <sup>2+</sup>			-15(0 <sup>a</sup> )	
Cr <sup>3+</sup>		-70		-50(-20 <sup>b</sup> )
Cu <sup>2+</sup>	0	0	0	
Fe <sup>2+</sup>		-25(0 <sup>a</sup> )		-55(-10 <sup>b,c</sup> )
Hg <sup>2+</sup>	+ 5			
K <sup>+</sup>		0	-30(0 <sup>a</sup> )	-25(0 <sup>b</sup> )
Li <sup>+</sup>			0	
Mg <sup>2+</sup>			0	
Mn <sup>2+</sup>				-60(-40 <sup>b,c</sup> )
Na <sup>+</sup>			0	0
Ni <sup>2+</sup>		-25(0 <sup>a</sup> )		
Pb <sup>2+</sup>	-45			
Sr <sup>2+</sup>		0		- 5
VO <sup>2+</sup>				0
Zr(IV)			0	

<sup>a</sup> 500-fold amount of matrix ion.

<sup>b</sup> 1000-fold amount on 5 · 10<sup>-10</sup> g of analyte.

<sup>c</sup> Argon flow rate of 2.5 l min<sup>-1</sup>.

It was concluded from these observations that a.a.s. measurements made immediately above the filament should be relatively interference-free. Table VI shows results for the a.a.s. of silver, magnesium, lead and copper with a horizontal slit in front of the hollow-cathode lamp focussed to give an image grazing the surface of the filament, *i.e.* with limited field viewing. Instrument settings used are also shown. The hollow-cathode lamps were all run at maximal current, and relatively wide slits were used, because the light entering the monochromator was of course considerably reduced.

All the systems reported in Table VI suffered from severe interference under the conventional a.a.s. or a.f.s. arrangement, *i.e.*, with viewing of total population of atoms. However, with the arrangement described above, in every case, the interference was either removed completely or substantially reduced.

It appears, therefore, that the above arrangement is a useful practical means for operating the carbon filament atom reservoir under reasonably interference-free conditions. Preliminary studies have shown that the sensitivities obtained in a.a.s. with this arrangement are good, as are the detection limits if the primary source is bright enough. The amount of light entering the slit in this arrangement is of course low, and therefore the use of a high-intensity lamp is recommended. A more detailed study of a.a.s. with the proposed arrangement is currently being made<sup>7</sup>.

We are grateful to Laporte Titanium Ltd. for assistance and support of this programme, and to the S.R.C. for the provision of a CAPS award for I.S.M. and for a Research Assistantship for R.G.A.

#### SUMMARY

A study is made of the effects of 62 ions present in 1000-fold amounts on the determination of  $10^{-9}$ – $10^{-11}$  g amounts of Ag, Bi, Cd, Cu, Hg, Mg, Pb, Tl and Zn by atomic fluorescence spectroscopy with a carbon filament in an argon atmosphere, with high-intensity hollow-cathode lamps or electrodeless discharge lamps as sources of excitation.Suppressions of signal which occur are shown to be due to gas-phase interaction between the atomic species concerned and the cloud of condensing elements. Re-investigation of these matrix effects by atomic absorption with the filament cell and a limited area viewing technique shows that most of the interferences can be avoided if only the space extending 0.5 mm upward from the filament is illuminated.

#### RÉSUMÉ

Une étude est effectuée sur l'influence de 62 ions (présents en concentration 1000 fois supérieure) sur le dosage de Ag, Bi, Cd, Cu, Hg, Mg, Pb, Tl et Zn ( $10^{-9}$  à  $10^{-11}$  g) par spectroscopie de fluorescence atomique, à l'aide d'un filament de carbone, dans une atmosphère d'argon, avec des lampes à cathode creuse de haute intensité, ou avec des lampes à décharge sans électrode, comme sources d'excitation. Un autre examen de l'influence de ces matrices, par absorption atomique, montre que la plupart des interférences peuvent être évitées en limitant la distance d'avec le filament à 0.5 mm.

## ZUSAMMENFASSUNG

Es wurde der Einfluss von 62 in 1000-fachem Überschuss vorliegenden Ionen auf die Bestimmung von  $10^{-9}$ – $10^{-11}$  g Ag, Bi, Cd, Cu, Hg, Mg, Pb, Tl und Zn durch Atomfluoreszenz-Spektroskopie untersucht. Es wurden ein Graphit-Heizfaden in einer Argonatmosphäre und als Anregungsquellen hochintensive Hohlkathodenlampen oder elektrodenlose Entladungslampen verwendet. Die auftretenden Signalunterdrückungen werden durch Gasphasen-Wechselwirkung zwischen den beteiligten Atomspezies und der Wolke kondensierender Elemente hervorgerufen. Die erneute Untersuchung dieser Matrixeffekte durch Atomabsorption mit der Heizfadenküvette unter Anwendung der Methode des begrenzten Sichtfeldes zeigt, dass die meisten Störungen vermieden werden können, wenn nur ein Bereich von 0.5 mm oberhalb des Heizfadens beleuchtet wird.

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*Anal. Chim. Acta*, 57 (1971) 271–280

## ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

### PART VII. ATOMIC ABSORPTION UNDER LIMITED FIELD VIEWING CONDITIONS

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In previous parts of this series<sup>1-3</sup>, a large number of matrix effects have been reported for the atomic fluorescence spectroscopic (a.f.s.) and atomic absorption spectroscopic (a.a.s.) determination of metals with the carbon filament atom reservoir. It was possible to remove or reduce the severity of all these interferences by carrying out a.a.s. measurements in such a way that an area extending only 0.5 mm above the filament was illuminated<sup>2,3</sup>.

Since this arrangement appeared promising from a practical point of view, a more general study of a.a.s. with the carbon filament under these limited viewing conditions was made.

#### EXPERIMENTAL

A Varian Techtron AA4 atomic absorption spectrophotometer was used in conjunction with ASL high-intensity (Sullivan-Walsh) hollow-cathode lamps operated in a d.c. mode. The Visicorder oscillograph was used as discussed earlier<sup>3</sup>, and the Varian Techtron amplifier was replaced by a rapid response d.c. negative feedback operational amplifier<sup>3</sup>. A 20,000 pF damping capacitor was placed across the input terminals.

#### *Carbon filament units*

Enclosed<sup>4</sup> and open<sup>1</sup> units were used as described before. The horizontal slit placed between the filament and the spectrometer slit was 0.5 mm high and 4 mm long<sup>3</sup>. The argon flow rate was *ca.* 1.7 l min<sup>-1</sup> in the open cell and *ca.* 1.4 l min<sup>-1</sup> in the enclosed cell.

The operating conditions for the various elements are as follows:

Pb:  $\lambda = 217.1$  nm. Spectrometer slit, 0.66 nm. Lamp current, 15 mA primary and 300 mA secondary. An EHT of 800 V was applied to the photomultiplier when the horizontal slit was used and 550–600 V when it was not used.

$\lambda = 283.3$  as above but with EHT = 575 V.

Cu:  $\lambda = 324.75$  nm and 327.4 nm. Spectrometer slit, 0.165 nm. Lamp current, 20 mA primary and 300 mA secondary. EHT = 675 V.

Ni:  $\lambda = 341.5$  nm. Spectrometer slit, 0.495 nm. Lamp current, 25 mA primary and 500 mA secondary. EHT = 725 V.

$\lambda = 231.1$  nm. Spectrometer slit, 0.66 nm. Lamp current as before. EHT = 800 V.

Al:  $\lambda = 308.2$  nm. Other conditions as for Ni at 231.1 nm but with 20 mA primary and 400 mA secondary lamp currents.

The technique of sample application has been described previously<sup>4</sup>.

## RESULTS

### *Detection system*

In these studies, the fast-response d.c. detection system described previously<sup>3</sup> was used; although the signal distortion that occurred with the slow-response a.c. detection system did not seriously affect the a.f.s. results<sup>3</sup>, it caused spurious a.a.s. results. The rise times of the a.c. and d.c. detection systems were *ca.* 0.2 and 0.01 sec, respectively. However, noise from the source in a.a.s. was not tolerable with d.c. detection, and, therefore, a limited amount of capacitance was introduced across the input terminals of the d.c. detector<sup>3</sup>. The optimal value for this capacitance was found to be 20,000 pF for a load resistance of 1 M $\Omega$ . Under these conditions the rise time was increased to 0.05 sec.

A further problem with the d.c. detection system is the possibility of interference from filament continuum radiation. Although this did not occur in the a.f.s. studies, the somewhat different nature of the signals in a.a.s. (Fig. 1) require the signal and continuum to be clearly separated in order that it may be stated categorically that interference has not occurred.

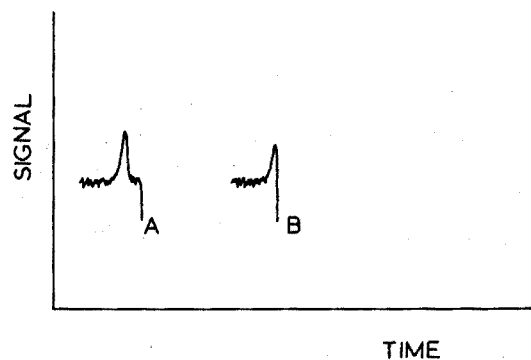


Fig. 1. A.a.s. signals obtained with the carbon filament and d.c. detection. (A) Satisfactory signal; (B) showing possible interference from continuum. The signal duration at half-peak width was *ca.* 0.05 sec.

### *Filament voltage*

In every case, except for aluminium, maximal absorption with the d.c. detection system was observed with maximal filament voltage. However, with aluminium, it was found necessary to reduce the filament voltage to 95% of its maximal value in order to prevent interference with the signal by continuum emission from the filament. The effect of filament voltage on the a.a.s. of lead and aluminium is shown in Fig. 2.

### *Comparison of enclosed and unenclosed cells*

In the initial work with the carbon filament, an enclosed cell was used<sup>4</sup>. However, this was subsequently replaced by an unenclosed cell in which the filament

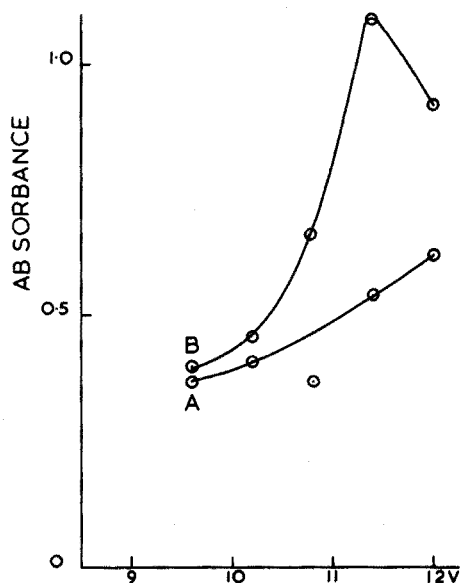


Fig. 2. Variation of a.a.s. with filament voltage. (A) Pb; (B) Al.

is surrounded by a sheath of inert gas<sup>1</sup>. A comparison of the two cells in the determination of lead (Table I) shows that in each case the sensitivity is very slightly improved with the unenclosed cell. Moreover, owing to the increased intensity of the primary light beam that now does not pass through two silica windows, there is an improve-

TABLE I

COMPARISON OF SENSITIVITIES (1% ABSORPTION) AND LIMITS OF DETECTION (SIGNAL: NOISE OF 2) FOR THE a.a.s. OF LEAD UNDER DIFFERENT EXPERIMENTAL CONDITIONS<sup>a</sup>

Wavelength (nm)	Gas	Enclosed system			Unenclosed system		
		Gas flow rate (l min <sup>-1</sup> )	Sensitivity (g)	Limit of detection (g)	Gas flow rate (l min <sup>-1</sup> )	Sensitivity (g)	Limit of detection (g)
217.00	Ar	1.4	10 <sup>-11</sup>	10 <sup>-10</sup>	1.7	7·10 <sup>-12</sup>	5·10 <sup>-11</sup>
217.00	N <sub>2</sub>	1.7	1.3·10 <sup>-11</sup>	1.7·10 <sup>-10</sup>	2.0	10 <sup>-11</sup>	8·10 <sup>-11</sup>
217.00 <sup>a</sup>	Ar	1.4	2.9·10 <sup>-11</sup>	10 <sup>-10</sup>	1.7	2.6·10 <sup>-11</sup>	4·10 <sup>-11</sup>
283.31	Ar	1.4	2.1·10 <sup>-11</sup>	7·10 <sup>-11</sup>	1.7	1.6·10 <sup>-11</sup>	4·10 <sup>-11</sup>
283.31	N <sub>2</sub>	1.7	2.8·10 <sup>-11</sup>	1.5·10 <sup>-10</sup>	2.0	2.3·10 <sup>-11</sup>	6·10 <sup>-11</sup>

<sup>a</sup> No horizontal slit used.

ment in the detection limits by a factor of about 2. This observation, and the considerably greater ease of operation of the unenclosed system, suggests that this system is superior. A further advantage of the unenclosed system is that the 45-sec period allowed for purging the enclosed cell<sup>4</sup> may be omitted without affecting the reproducibility. The lifetime of a carbon filament with this system is shorter, but may be somewhat lengthened by using higher gas flow rates, without affecting the results.

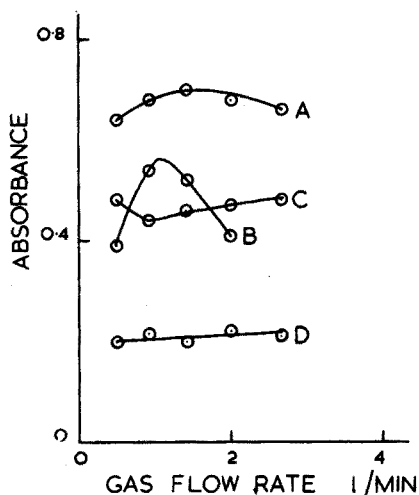


Fig. 3. Variation of a.a.s. with gas flow rate. (A) Pb, unenclosed cell, argon; (B) Pb, enclosed cell, argon; (C) Cu, unenclosed cell, argon; (D) Cu, unenclosed cell, nitrogen.

#### Nature of flow gas

Table I shows slight adverse effects, on both sensitivity and limit of detection in the a.a.s. of lead, when nitrogen replaces argon. Since the thermal conductivity of the two gases is similar, this effect has been ascribed to the greater specific heat of nitrogen ( $0.2477 \text{ cal g}^{-1}$  for  $\text{N}_2$  and  $0.1253 \text{ cal g}^{-1}$  for Ar at  $15^\circ \text{C}$ ). It has, of course,

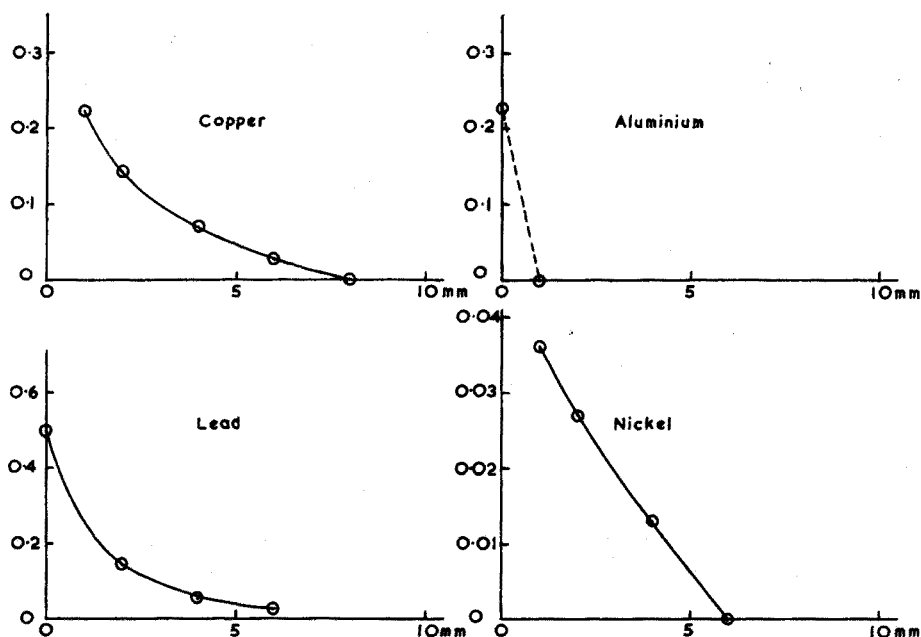


Fig. 4. Plots of absorbance against height of observation above filament.



TABLE II  
OPTIMAL CONDITIONS, SENSITIVITIES (1% ABSORPTION) AND LIMITS OF DETECTION (SIGNAL: NOISE OF 2) FOR  
THE a.s. DETERMINATION OF METALS WITH LIMITED FIELD VIEWING

Element	Line (nm)	HIL current		Monochromator slit ( $\mu\text{m}$ )	Filament voltage (V)	Ar flow rate ( $\text{l min}^{-1}$ )	Height of observation	Sensitivity (g)	Limit of detection (g)
		prim (mA)	sec (mA)						
Pb	217.00	15	300	200	12.0	1.7	Gr <sup>a</sup>	$7 \cdot 10^{-12}$	$5 \cdot 10^{-11}$
	283.31	15	300	200	12.0	1.7	Gr	$1.6 \cdot 10^{-11}$	$4 \cdot 10^{-11}$
Cu	324.75	20	300	50	12.0	1.1	1 mm <sup>b</sup>	$3.3 \cdot 10^{-11}$	$5 \cdot 10^{-11}$
	327.40	20	300	50	12.0	1.1	1 mm	$6 \cdot 10^{-11}$	$7 \cdot 10^{-11}$
Ni	341.48	25	300	100	12.0	2.0	1 mm	$2.4 \cdot 10^{-10}$	$3 \cdot 10^{-10}$
Al	308.22	20	400	200	11.4	2.5	Gr	$6 \cdot 10^{-10}$	$10^{-9}$

<sup>a</sup> Image of slit grazing filament.

<sup>b</sup> Image of slit 1 mm above filament.

already been noted that choice of flow gas had a marked spectroscopic effect on the a.f.s. (but not the a.a.s.) of cadmium<sup>1</sup>.

#### *Gas flow rate*

Figure 3 shows the effect of gas flow rate on the a.a.s. of lead and copper under limited viewing conditions. Apparently, with the unenclosed cell the signals obtained are virtually independent of gas flow rate. The curve obtained for the enclosed cell is similar to that described previously<sup>4</sup>.

#### *Lamp current, slit and wavelength*

Because the intensity of the light beam is considerably reduced by the horizontal slit used to achieve limited viewing, all the high-intensity hollow-cathode lamps were operated at maximum current. The largest possible monochromator slit widths, which did not cause loss of sensitivity or serious continuum interference, were used. The choice of line depended in this instance as much on the brightness of the line as on its sensitivity. For instance, a very slightly better limit of detection for lead was obtained with the 283.31-nm line than with the more sensitive 217.00-nm line (Table II). The only nickel line of sufficient brightness or sufficiently isolated from other lines to permit an acceptable bandpass to be used was the 341.48-nm line, which originates from a state 0.025 eV above the ground state<sup>6</sup>.

#### *Variation of height of illumination above filament*

Figure 4 shows the effect on the a.a.s. signal, of varying the height of illumination above the filament; a 0.5-mm wide band of light was used in each case. For nickel, copper and lead the atomic population decays in a roughly exponential fashion with increasing height; for lead and copper, free atoms persist for about 6 mm above the filament, whereas for nickel, no atoms are found more than 4 mm above the filament. In the case of aluminium, however, atoms are only found in the area immediately above the filament. Earlier attempts to determine aluminium on the carbon filament without the use of a horizontal slit, either by a.a.s. or a.f.s., were not successful<sup>7</sup>, and this was presumably because the general area illuminated did not contain any aluminium atoms. For aluminium and lead, the optimal position for making measurements is immediately above the filament and some continuum interference must be accepted; but for nickel and copper the best position is 1 mm above the filament, where the continuum signal can be largely avoided (Table II).

#### *Effect of the horizontal slit*

Table I shows that if the horizontal slit is removed, the sensitivity of the method towards lead is reduced by a factor of 3 to 4. This arises because, when the horizontal slit is used, it is possible to view only that area where the atomic population is at its densest, *i.e.* immediately above the filament. This improvement in sensitivity does not extend to the detection limit, owing to the higher noise levels associated with the higher photomultiplier EHT settings used. These are required, of course, because of the low intensity of primary radiation.

#### *Analytical results*

Optimal conditions for analysis, sensitivities and limits of detection are

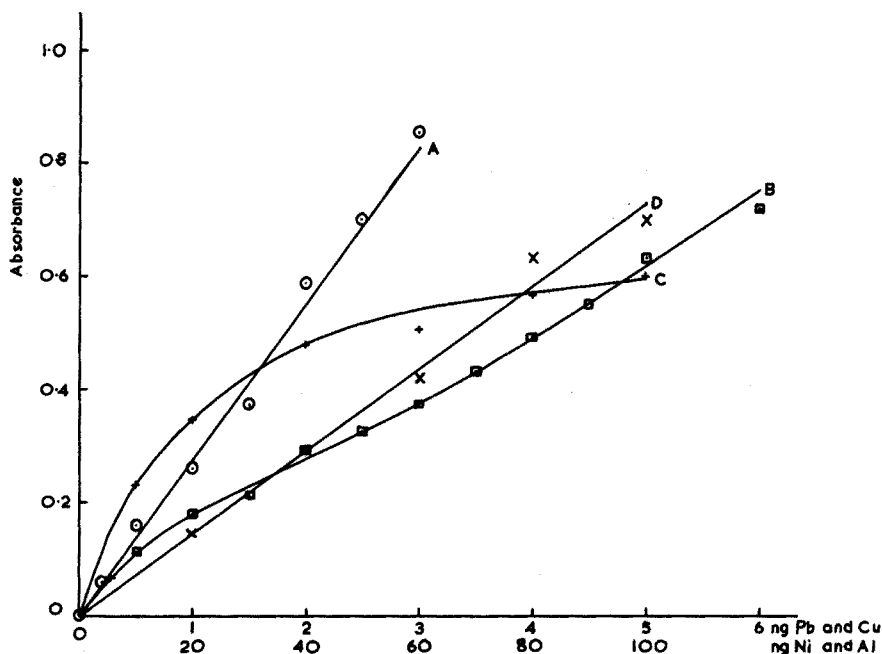


Fig. 5. Calibration curves (A) Lead, 283.31 nm; (B) copper, 324.75 nm; (C) nickel; (D) aluminium.

summarized in Table II. Calibration curves, obtained under the conditions given in Table II, are shown in Fig. 5. Each point on these curves is the average of 3 separate determinations. The precision associated with each determination was of the order of  $\pm 3\%$ , i.e., the same as that obtained in a.f.s.<sup>4</sup>

The upper limits of determination were not probed extensively, although with nickel, at 341.48 nm, severe curvature in the calibration graph set in above 20 ng. With copper, at 222.57 nm, the upper limit is 30 ng. With larger amounts, the copper is incompletely volatilized before the continuum signal from the filament occurs. Any inadvertent overloading of the filament with copper can, of course, be resolved by strongly heating the filament between determinations.

## DISCUSSION

One of the principal advantages of the carbon filament atom reservoir over other flameless methods of atomization is its simplicity of construction and operation. However, a previous disadvantage of the method, which resulted in a large number of matrix effects<sup>3</sup>, and also in the failure to detect some metals, such as aluminium, chromium and vanadium<sup>7</sup>, was that once the atoms are produced, no further heat is supplied to them, and they rapidly condense. Earlier studies<sup>2,3</sup> showed that by placing a horizontal slit across the primary source in a.a.s., the method could be made relatively interference-free for a number of metals.

This limited field viewing technique is also successful in improving the general performance of the carbon filament in a.a.s., namely by increasing the sensitivity of the determination of lead and making the determination of aluminium possible. The

sensitivities and precision obtained with this simple system compare very favourably with those obtained by the heated graphite tube method of Manning and Fernandez<sup>8</sup>, although the apparatus is considerably simpler.

The principal disadvantage of the apparatus at present is the low intensity of light entering the monochromator. However, it should be possible, either by using more intense primary sources or by redesigning the optical system to increase the amount of light entering the monochromator, and this should result in further improved limits of detection.

#### SUMMARY

The atomic absorption spectroscopy of copper, lead, nickel and aluminium with the carbon filament atom reservoir under conditions such that only an area extending 0.5 mm above the filament is irradiated, is described. The sensitivity for lead under these arrangements is improved, and the determination of aluminium is made possible.

#### RÉSUMÉ

On décrit une méthode spectroscopique par absorption atomique pour le dosage du cuivre, du plomb, du nickel et de l'aluminium; elle consiste à utiliser un atomiseur à filament de carbone et à irradier la zone à 0.5 mm du filament seulement. On peut ainsi améliorer la sensibilité du plomb et doser l'aluminium.

#### ZUSAMMENFASSUNG

Die Atomabsorptionsspektroskopie von Kupfer, Blei, Nickel und Aluminium mittels einer Graphitheizfadenvkuvette wurde unter Bedingungen untersucht, bei denen nur ein Bereich von 0.5 mm oberhalb des Heizfadens bestrahlt wird. Die Empfindlichkeit für Blei wird bei dieser Anordnung verbessert, und es wird die Bestimmung von Aluminium ermöglicht.

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## QUANTITATIVE X-RAY DIFFRACTION ANALYSIS BY A DIFFRACTION-FLUORESCENCE TECHNIQUE

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The fundamental equation relating the intensity of the diffracted X-rays to the absorptive properties of the compound in a multicomponent system is<sup>1</sup>:

$$I_1/(I_1)_0 = x_1 \mu_1 / \{x_1(\mu_1 - \mu_m) + \mu_m\} \quad (1)$$

If the total mass absorption coefficient of the sample is expressed as  $\mu_T$ , this equation can be written in the form<sup>2</sup>:

$$I_1/(I_1)_0 = x_1 \mu_1 / \mu_T \quad (2)$$

where  $I_1/(I_1)_0$  = the ratio of the intensity diffracted at a definite Bragg angle of component 1 in a mixture to that of component 1 in the pure state,

$x_1$  = the weight fraction of component 1,

$\mu_1$  = the mass absorption coefficient of the pure component 1, and

$\mu_T$  = total mass absorption coefficient of the sample, including component 1.

If the value  $\mu_T$  can be determined, then it is possible to provide an alternative method to replace the well-known methods of X-ray diffraction analysis which involve calibration curves, internal standards and active dilutions. The method which is proposed here has certain advantages, especially for laboratories where samples submitted for analysis vary widely in chemical composition, although its precision is generally less than that obtained by the conventional method.

### EXPERIMENTAL

The mass absorption coefficients were measured on a Philips semi-automatic PW 1220 fluorescence spectrometer, with molybdenum and silver tubes, a lithium fluoride crystal and the scintillation counter. The diffractometer used was a Philips PW 1010 unit, with a proportional and scintillation counter and pulse-height discrimination. The divergence and scatter slits were usually  $1^\circ$ , and the receiving slit was 0.1 mm. The X-ray radiations (50 kV, 20 mA) were nickel-filtered Cu  $K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) and zirconium-filtered Mo  $K\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ).

All the samples were ground, and only the sieve fractions with a particle size of 40–80  $\mu\text{m}$  were used. After grinding, all samples were pressed into disks ( $7 \text{ tons cm}^{-2}$ ), if necessary with the addition of 5–10% graphite or Mowiol (Farbwerke Hoechst AG), a polyvinyl alcohol.

## RESULTS

*Determination of mass absorption coefficients*

For the experimental direct determination of the mass absorption coefficient, several methods have been proposed.

1. Measurement of the absorption of monochromatic X-ray radiation through the sample<sup>3-5</sup>. This method gives satisfactory results but is time-consuming and needs a special sample holder.

2. Measurement of the background of the sample in the neighbourhood of the diffracted peaks<sup>6,7</sup>. However, as has been shown in X-ray spectroscopic analysis<sup>8</sup>, the validity of this measurement is very limited, and good results have been obtained only in some special cases.

3. Utilization of the coherent or incoherent scattered lines or their ratio<sup>9-12</sup>.

In the present work, this third method was preferred for determination of the mass absorption coefficients. The advantage of using Mo or Ag K-radiation rather than  $W L\alpha$  has been previously shown<sup>13</sup>. The intensities of coherent (Raleigh) scattered radiation and incoherent (Compton) scattered radiation, and the intensity ratio of Mo  $K\alpha/K\beta$  and Ag  $K\alpha/K\beta$  (with background correction) were plotted against the mass absorption coefficient for a wide range of materials.

The best results were obtained with the incoherent diffused Mo  $K\alpha$  radiation (Fig. 1). For calculation of the mass absorption coefficients, data from the International Tables<sup>14</sup> for X-ray crystallography were used. For establishment of the calibration curve (Fig. 1), care must be taken to use only very pure compounds.

Experiments carried out with low concentrations of elements of medium atomic number (Ni, Cr, Zn) in a silica matrix showed that the total concentration

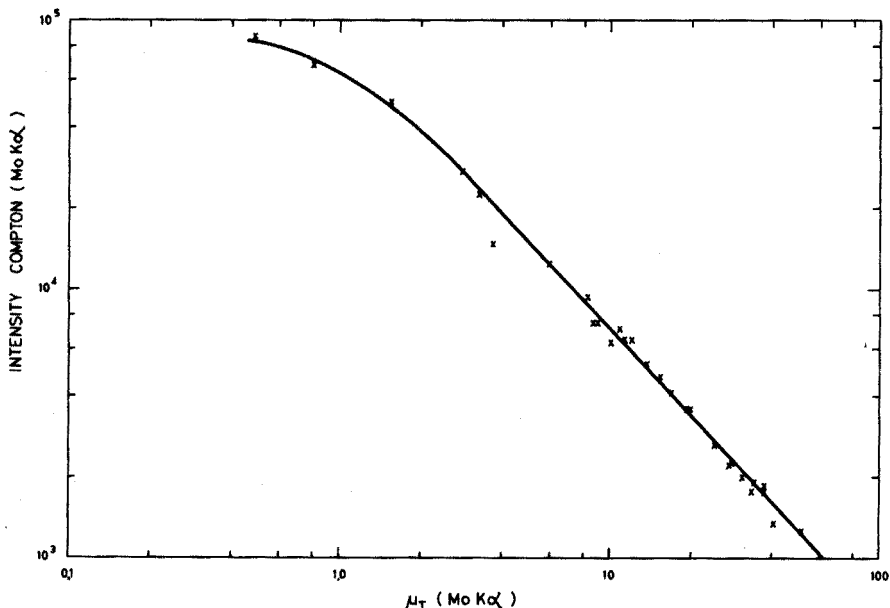


Fig. 1. Calibration curve for the determination of the mass absorption coefficients, established using *e.g.*: C, BeO, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, NaCl, CaSO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>-C mixtures, NiO, Cu.

must not exceed 0.02%, otherwise the effect on the Compton peak intensity cannot be neglected. To eliminate the influence of packing density, only samples with a particle size of 40–80  $\mu\text{m}$  must be used. The water content of the samples provided a further source of error so that dehydration of all calibration compounds was essential. Finally, interferences of the Compton line with first- or second-order emission lines (for instance  $\text{UL}\beta_4$ ,  $\text{Nb K}\alpha$ ) had to be avoided.

Although there should be no differences in the intensities of scattered radiation from crystalline and amorphous compounds for a large aperture of the X-ray primary radiation<sup>15</sup>, a slight difference was found between crystalline and amorphous samples of alumina; this difference was about 10% for the  $\text{Mo K}\alpha$  and about 3% for the  $\text{Mo K}\alpha$  Compton radiation.

With the aid of the calibration curve shown in Fig. 1, the mass absorption coefficients of several test mixtures were determined. The results (Table I) indicated an average relative error of about 5%.

TABLE I

COMPARISON BETWEEN CALCULATED AND FOUND VALUES OF MASS ABSORPTION COEFFICIENTS

Sample no.	$\mu$ Mo $\text{K}\alpha$ calculated	$\mu$ Mo $\text{K}\alpha$ found
1	3.69	3.6
2	7.11	7.2
3	8.91	9.3
4	9.70	10.2
5	12.42	13.3
6	14.89	13.8
7	17.20	18.2
8	17.61	19.0
9	19.30	19.5
10	20.25	18.9
11	24.78	25.2
12	25.89	26.0
13	34.48	35.5
14	34.30	35.5

#### *X-ray diffraction measurements*

When the mass absorption coefficients had been obtained, the validity of eqn. (2) was checked by means of synthetic prepared samples. Two systems were studied: the binary system  $\text{NaCl-CuCl}$  and the ternary  $\text{Fe}_2\text{O}_3\text{-Fe-C}$  system. The latter system is of practical interest in the determination of iron oxides in deposits of corrosion products from water-cooled nuclear reactors.

Since the total mass absorption coefficients were determined for  $\text{Mo K}\alpha$  radiation, and in diffraction measurements  $\text{Cu K}\alpha$  is the most frequently used radiation, these absorption coefficients had to be transferred to this wavelength. As is well known, for a given element, between two absorption discontinuities, the mass absorption coefficient varies inversely with wavelength, approximately as  $\lambda^3$ . When this conversion factor for the transformation of the absorption coefficients from  $\text{Mo K}\alpha$  to  $\text{Cu K}\alpha$  radiation was calculated for different elements, it was found to have a mini-

imum value of 2.09 for beryllium and a maximum value of 2.89 for aluminium. Accordingly, if the general composition of the sample is not known, large errors are possible in transforming the mass absorption coefficients from Mo  $K\alpha$  to Cu  $K\alpha$  radiation. When an average factor of about 2.8 was used, then only semi-quantitative results could be obtained for the systems studied. Furthermore, transforming the mass absorption coefficient values determined for Mo  $K\alpha$  radiation to Cu  $K\alpha$  radiation is only possible for compounds with  $\mu_T$  values for Mo  $K\alpha$  radiation ranging from 0.1 to about 45. However, when the same wavelength (Mo  $K\alpha$  radiation) was used, satisfactory results were obtained (Table II), with a relative error between 1 and 8%.

TABLE II

ANALYSIS OF TEST MIXTURES

Matrix	Composition (%)	Found (%)
CuCl	NaCl 10.0	10.8
CuCl	NaCl 20.0	19.1
CuCl	NaCl 40.0	39.5
C	Fe 10.0	9.4
C	Fe <sub>2</sub> O <sub>3</sub> 10.0	9.2
Fe <sub>2</sub> O <sub>3</sub> +C	Fe 20.0	21.5
Fe <sub>2</sub> O <sub>3</sub> +C	Fe 30.0	31.4
Fe+C	Fe <sub>2</sub> O <sub>3</sub> 10.0	9.3
Fe+C	Fe <sub>2</sub> O <sub>3</sub> 40.0	38.2

## DISCUSSION

Quantitative X-ray diffraction phase analyses by means of intensity-concentration relationships, the mass absorption coefficient of the sample being determined by the Mo  $K\alpha$  Compton scattered radiation in an X-ray fluorescence arrangement, can give good results. With regard to diffraction measurements, the use of Mo  $K\alpha$  radiation has the general disadvantage of giving lower dispersion and a lower P/B ratio than are obtained with Cu  $K\alpha$  radiation. However, this statement is not true for the investigated iron oxide system; with these samples, both the continuous spectrum and the Cu  $K\alpha$  line excite the iron in the sample, producing a high fluorescent background which filtering will not reduce.

Owing to the possible errors in transferring the  $\mu_M$  value from one wavelength to another, a single wavelength for both absorption and diffraction measurements is in general indicated; Mo  $K\alpha$  radiation seems to be the best choice.

This method can replace the internal standard technique in most cases. The disadvantages of the conventional method, such as difficulties in finding a suitable internal standard, dilution of the sample and homogeneity problems in the mixing procedure are eliminated. The obvious disadvantage, of course, is that the X-ray diffraction laboratory must be equipped with an X-ray fluorescence arrangement. But in general in an X-ray laboratory these two techniques are available. The use of Cu  $K\alpha$  Compton radiation for the determination of the mass absorption coefficients on a diffractometer is of course possible, but then a modification of the diffraction arrangement is necessary, and the disadvantages of using Cu  $K\alpha$  Compton radiation as opposed to Mo  $K\alpha$ -Compton, still exist.



The author is very grateful to Mr. M. Ooms, who carried out a part of the experimental work.

## SUMMARY

Quantitative X-ray diffraction analysis by means of the basic relationship relating the intensity of the diffracted X-rays to the absorption properties of the sample is described. The mass absorption coefficient is determined from the Mo  $K\alpha$  Compton diffused radiation on an X-ray fluorescence spectrometer. The average relative error for the mass absorption coefficient determination was found to be about 5%. Analyses of synthetic mixtures (NaCl-CuCl and  $Fe_2O_3$ -Fe-C) gave a relative error of 1-8%, depending on the concentration.

## RÉSUMÉ

On décrit une méthode d'analyse quantitative par diffraction aux rayons-X. L'erreur relative moyenne pour la détermination du coefficient d'absorption est d'environ 5%. Des analyses de mélanges synthétiques (NaCl-CuCl et  $Fe_2O_3$ -Fe-C) fournissent des déviations relatives de 1 à 8%, suivant la concentration.

## ZUSAMMENFASSUNG

Es wird eine quantitative Röntgenbeugungsanalyse unter Anwendung der grundlegenden Beziehung zwischen der Röntgenbeugungsintensität und den Absorptionseigenschaften der Probe beschrieben. Der Massenabsorptionskoeffizient wird aus der Mo  $K\alpha$ -Compton-Streustrahlung an einem Röntgenfluoreszenzspektrometer ermittelt. Der mittlere relative Fehler bei der Bestimmung des Massenabsorptionskoeffizienten war etwa 5%. Die Analysen von synthetischen Gemischen (NaCl-CuCl und  $Fe_2O_3$ -Fe-C) ergaben je nach Konzentration eine relative Standardabweichung von 1-8%.

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## FLUORESCENCE AND METALLIC VALENCY STATES

### PART VI. DETERMINATION OF VANADIUM WITH BENZOIC ACID

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No method has yet been reported for the determination of vanadium based on production of fluorescence. The fluorescence detection of vanadium (2.5 p.p.m.) with resorcinol<sup>1</sup> and the catalytic determination of vanadium (0.1–100  $\mu\text{g}/5$  ml) involving fluorescence-quenching through titrimetry<sup>2</sup> have been reported. A sensitive catalytic method<sup>3</sup> (0.1–8 p.p.b.) with gallic acid has been used for water analysis, but a close temperature control ( $\pm 0.5^\circ$ ) for 1 h is necessary.

Many spectrophotometric methods for vanadium have been proposed for the determination of p.p.m. levels of vanadium<sup>4</sup>. Atomic absorption and atomic fluorescence spectrometric detection limits are 40 p.p.b.–1.0 p.p.m.<sup>5</sup>, but 5 p.p.b. of vanadium in lake water has been determined by atomic absorption after extraction of the dichlorooxine–vanadium chelate with *n*-butyl acetate<sup>6</sup>. Neutron activation analysis<sup>7</sup> has been applied to the determination of vanadium (1–10 p.p.b.) in natural waters after chloroform extraction of the vanadium–oxine complex.

Recent studies<sup>8–10</sup> in this laboratory have been concerned with the determination of p.p.b. levels of transition metals based on fluorescence production. This paper describes a simple fluorimetric method for the determination of vanadium with benzoic acid.

#### EXPERIMENTAL

##### *Apparatus, reagents and solutions*

An Aminco-Bowman spectrophotofluorimeter was used for recording excitation and emission spectra.

A Vortex mixer (Scientific Industries, Inc.) coupled with a 1-min timer and a constant voltage transformer was used for mixing solutions with zinc amalgam.

The stock reagent solutions ( $2 \cdot 10^{-2}$  M,  $2 \cdot 10^{-3}$  M and  $5 \cdot 10^{-3}$  M) were prepared by dissolving benzoic acid (99.99% NBS standard) in 2 ml of 1 + 1 ammonia solution and diluting with twice-distilled water to ca. 50 ml. This solution was adjusted to ca. pH 4 with 3 M hydrochloric acid before dilution to 250 ml in a volumetric flask with twice-distilled water.

The stock vanadium solution ( $1.0 \text{ mg ml}^{-1}$ ) was prepared by dissolving vanadium pentoxide (0.4464 g of 99.98% analytical reagent) in 1–2 ml of concentrated ammonia solution; after dilution to ca. 50 ml with twice-distilled water, the solution was neutralized with 1 + 1 hydrochloric acid to ca. pH 5 and diluted to 250 ml with dis-

tilled water. Vanadium solutions (10, 1, 0.1 p.p.m.) were prepared as required from this standard.

The acetate buffer, pH 5.2, contained 100 ml of 1 *M* sodium acetate and 20 ml of 1 *M* hydrochloric acid in a volume of 250 ml.

The 2.0% (w/v) solution of sodium sulfite was prepared by dissolving 2.0 g of sodium sulfite (Analar grade) in 100 ml of 5% methanol (fluorimetric grade).

The zinc amalgam was prepared as previously described<sup>10</sup>.

### Procedure

To 1 ml of solution (pH 4–5) containing  $5 \cdot 10^{-3}$ – $4 \mu\text{g}$  of vanadium in a 10-ml volumetric flask, add 1 ml of  $2 \cdot 10^{-3}$  *M* reagent solution and 0.5 ml of acetate buffer. Add 0.5 ml of zinc amalgam from a 10-ml burette; mix immediately for 2 min using a Vortex mixer coupled with a timer and constant voltage transformer. Dilute the solutions to the mark with freshly prepared sodium sulfite solution. Measure the fluorescence intensity at 410 nm using an excitation wavelength of 300 nm. A reagent blank should be run concurrently.

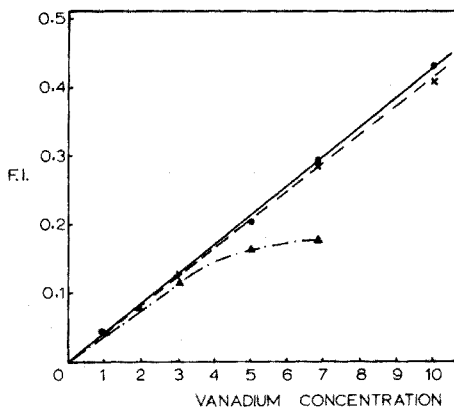


Fig. 1. Calibration curves. F.I. is the meter multiplier setting · % fluorescence intensity. (●—●) 1–10 p.p.b., (× — ×) 10–100 p.p.b. (F.I. = × 10), (▲—▲) 100–500 p.p.b. (F.I. = × 100).

Typical calibration curves are shown in Fig. 1. Under slightly different conditions (1 ml of  $5 \cdot 10^{-3}$  *M* reagent, 0.4 ml of buffer pH 4.4 and 0.6 ml of zinc amalgam with 3 min of mixing in the reaction system), a straight-line calibration graph was obtained over the range 0.5–5 p.p.b. of vanadium.

## RESULTS AND DISCUSSION

### Factors affecting fluorescence intensity

The factors affecting fluorescence in this reaction were similar to those described previously for iron<sup>10</sup>

Good results were obtained at pH 5.2 and there was no appreciable change in fluorescence intensity down to pH 4.0. Above pH 5.5 precipitation took place during mixing with the amalgam; for 10 p.p.b. of vanadium the fluorescence intensity was 41 at pH 5.2, 40 at pH 4.8, 42 at pH 4.4, and 39 at pH 4.0 (MM 0.01 and S 0.0). If

less than 0.3 ml of buffer solution was added in the procedure, precipitation occurred during the mixing with the amalgam; the fluorescence intensity decreased as the buffer concentration was increased. For 10 p.p.b. of vanadium the fluorescence intensity was 52 with 0.4 ml, 40 with 0.5 ml, 28 with 0.7 ml and 24 with 1.0 ml of acetate buffer added. Reproducible results were obtained with 0.5 ml of buffer solution for 0.5–400 p.p.b. of vanadium.

The fluorescence intensity varied with the mixing time with the amalgam; the longer the mixing time, the higher the fluorescence intensity. For 10 p.p.b. of vanadium the net fluorescence intensity was 24 after 1-min mixing with amalgam, 40 after 2 min, and 50 after 3 min (after 3 min of mixing precipitation occasionally occurred). Good fluorescence intensity and a linear relationship for 0.5–400 p.p.b. of vanadium were obtained with 2-min mixing; 3-min mixing gave higher fluorescence intensity and is recommended for determining 0.5 to 5 p.p.b. of vanadium. The manner of mixing with the amalgam was important for reproducible results; the vortical motion of the amalgam along the flask wall (by placing the flask directly into neoprene cup of the mixer) ensured reproducibility during the mixing process.

The fluorescence intensity of the blank increased with increasing reagent concentration and the intensity differences between blank and vanadium sample also increased; for example, for 10 p.p.b. of vanadium and 1 ml of  $1 \cdot 10^{-3} M$ ,  $2 \cdot 10^{-3} M$ , or  $5 \cdot 10^{-3} M$  reagent, the intensity difference was 22, 41 and 62, respectively, at the same instrument setting. A  $2 \cdot 10^{-3} M$  concentration of benzoic acid was used for the concentration range of 0.5–400 p.p.b. of vanadium;  $5 \cdot 10^{-3} M$  reagent is recommended for the 0.5–5 p.p.b. range because of better sensitivity.

Figure 2 shows the effect of the amalgam and buffer on the fluorescence intensity; 0.5–0.6 ml of the amalgam and 0.5 ml buffer are recommended for best results.

Sodium sulfite in methanol was added after mixing with the zinc amalgam to stabilize the fluorescence intensity; the intensity for 10 p.p.b. of vanadium remained constant at 39–40 for 30 min when a 2% solution of sodium sulfite in 5% methanol was used as the diluting solution. Dilution with distilled water or an aqueous sodium sulfite solution resulted in an increase in fluorescence intensity with time. Dilution with 1, 2 or 3% sodium sulfite in 5, 10 or 20% methanol gave the same results and a 2% solution is therefore recommended in the procedure.

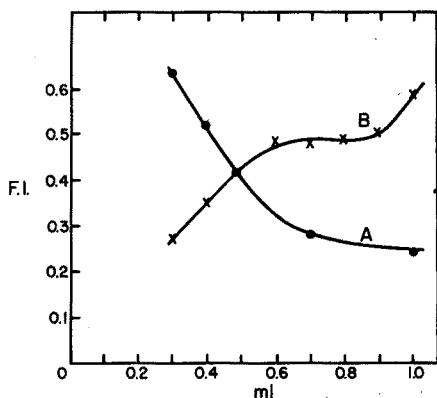


Fig. 2. Effect of amounts of amalgam and buffer on the F.I. of 10 p.p.b. of vanadium. (A) Buffer; (B) amalgam.

### Range and precision

The fluorescence intensity was a linear function of concentration for 0.5 to 400 p.p.b. of vanadium. Samples containing 10.0 p.p.b. of vanadium in synthetic water<sup>11</sup> were analyzed by the above procedure, and  $10.0 \pm 0.5$  p.p.b. (6 determinations) were found.

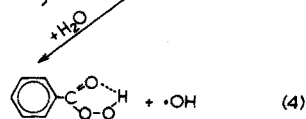
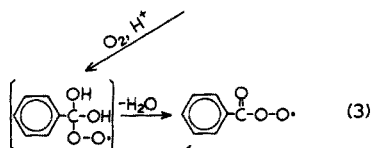
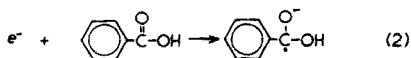
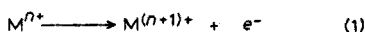
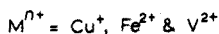
### Interferences

Vanadium (10 p.p.b.) was successfully determined in the presence of large amounts (at least 10 p.p.m.) of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Similarly, 200-fold amounts of  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and 30-fold amounts of  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Mo}^{3+}$  did not interfere. Although titanium(IV) gave no fluorescence itself, there was an increase in the vanadium fluorescence when titanium was present and only 20 p.p.b. of titanium(IV) could be tolerated when determining 10 p.p.b. vanadium. The fluorescence intensity increased in the presence of p.p.b. of iron, and iron must be absent.

Trace amounts of vanadium were separated from iron by ion-exchange<sup>12</sup> before determination by the above procedure. Results, although occasionally satisfactory, were inconsistent. At the p.p.b. level, further studies are necessary to devise better procedures to eliminate environmental contamination (for example, air dust contamination during evaporation after separation of vanadium).

### Nature of reaction

The fluorescent species obtained in reacting vanadium with benzoic acid in the presence of zinc amalgam and oxygen was similar to that previously described for iron<sup>10</sup>. It was suggested that the fluorescent product is the result of an electron-transfer process; the fluorescence may originate from peroxybenzoic acid formed in the reaction by:



Peroxybenzoic acid

As further proof that peroxy acid formation is responsible for fluorescence, the monoperoxyphthalic acid was prepared from phthalic anhydride<sup>13</sup>; the monopero-



von Zinkamalgam hervorgerufen wird. Die meisten der üblichen Ionen stören nicht; Eisen(III) und Titan(IV) stören. Ein Reaktionsmechanismus wird vorgeschlagen.

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## SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM WITH 4-(2-PYRIDYLAZO)RESORCINOL BY EXTRACTION OF TETRAPHENYLPHOSPHONIUM AND ARSONIUM SALTS

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In weakly acidic solution vanadium reacts with 4-(2-pyridylazo)resorcinol, PAR, and the visible spectra show a maximum at 545 nm. The colored complex formed is most stable at pH 5–6. The reaction is very sensitive and was first applied for a spectrophotometric determination in 1965<sup>1–3</sup>. Under similar conditions, PAR reacts with a number of other metal ions. However, diaminocyclohexanetetraacetic acid (DCTA) can destroy the majority of metal–PAR complexes and the vanadium reaction with PAR in presence of DCTA becomes reasonably selective, but less sensitive<sup>3</sup>. However, ions of Ti, Zr, Nb, Ta and U, that are frequently present in analytical systems with vanadium, still interfere. Vanadium reacts with PAR also in presence of hydrogen peroxide, forming complexes that enable a rather selective determination in acidic media, but the sensitivity of such a determination is significantly decreased<sup>4,5</sup>.

The vanadium–PAR ratio of 1:1 has been found for the colored complex species formed in aqueous solutions<sup>3,6,7</sup>. In the presence of hydrogen peroxide in acidic media (pH 3) the presence of a complex containing hydrogen peroxide molecule was reported, but in solutions with pH above 3 the species studied did not contain peroxide. The existence of anionic<sup>6</sup> or cationic<sup>7</sup> vanadium(V)–PAR complexes has been proposed in aqueous solutions, but in general, according to different literature reports, the nature of the colored species formed is not well understood. In an investigation of tartrate–vanadium–PAR systems, we have observed that with tetraphenylphosphonium or arsonium chloride, the “color” can be easily extracted with chloroform or similar solvents. The absorbance of the organic phase is very stable and is thus suitable for spectrophotometric determination.

### EXPERIMENTAL

#### *Reagents*

4-(2-Pyridylazo)resorcinol (Merck, monosodium salt), tetraphenylphosphonium and tetraphenylarsonium chlorides (Analar grade, Fluka) and chloroform (with 1% ethanol) were used. Acetate buffer (pH 5.5) was prepared as 1 M sodium acetate solution, to which a few drops of anhydrous acetic acid were added, and the pH was adjusted with a pH meter. All the other reagents used were Analar grade.

*Standard solution of vanadium(V)* ( $1 \cdot 10^{-2}$  M). Prepare by dissolving am-



monium vanadate (1.17 g) in 1 l of hot distilled water. The solution was standardized by gravimetric determination of vanadium with cupferron and heating the precipitate to vanadium pentoxide<sup>8</sup>. Solutions of lower concentrations were obtained by dilution.

#### Apparatus

Absorbance measurements were taken on a Beckman Spectrophotometer, Model DU-2, and visible spectra were recorded on a Perkin Elmer 137UV Spectrophotometer.

#### Spectrophotometric determination of vanadium

To the solution (5 ml) containing 2–20  $\mu\text{g}$  of vanadium, add 0.1 M sodium tartrate solution (2 ml), acetate buffer pH 5.5 (2 ml), and  $2 \cdot 10^{-3}$  M solution of PAR (2.5 ml). Leave the reaction mixture at room temperature for 30 min and then transfer to a separatory funnel. Extract twice with 5 ml of a chloroform–acetone mixture (5:1), containing  $10^{-3}$  M tetraphenylphosphonium or arsonium chloride. Shake for about 1 min and separate the layers. Collect the organic phase in a volumetric flask (10 ml) and fill up with the organic phase. Measure the absorbance at 560 nm.

#### Determination of $(\text{C}_6\text{H}_5)_4\text{X}-\text{Y}-\text{PAR}$ ratio in organic phase

The absorbance of the chloroform–acetone phase was measured at 560 nm. The ionic strength of the aqueous phase was kept constant at pH 5.5–6.0. The ratio was determined by Job's method of continuous variation, mole ratio method, and slope ratio method. Concentrations used are given in Figs. 5–7. Results for the  $(\text{C}_6\text{H}_5)_4\text{P}-\text{V}-\text{PAR}$  system only are shown, since identical behaviour was observed for systems containing tetraphenylarsonium chloride.

## RESULTS

It was found that the vanadium–PAR complex formed in the aqueous solutions at pH 5–6 can be quantitatively extracted by tetraphenylphosphonium and arsonium

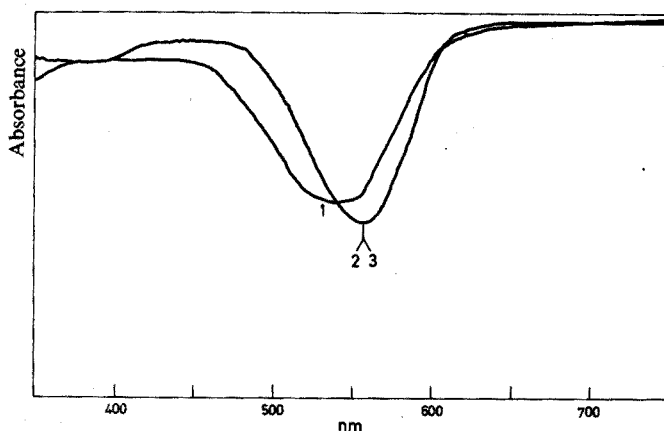


Fig. 1. Visible spectrum of vanadium–PAR complex. (1) Aqueous solution. (2,3) Organic phase, obtained by extraction with tetraphenylphosphonium or arsonium chloride.

chloride, respectively, in chloroform, acetone or other similar solvent mixtures. The visible spectrum of the organic phase shows a bathochromic shift of 15 nm compared to the aqueous phase, and maximum absorbance occurs at 560 nm. Spectra are shown in Fig. 1. PAR, itself, on the other hand, shows a hypsochromic shift in the organic phase, the maximum occurring at 20 and 10 nm lower wavelength in chloroform-acetone (5:1) and pure chloroform solution, respectively. A small hyperchromic effect is also observed. The color intensity of the organic phase in the region of maximum absorption is increased by about 10% compared to the aqueous phase intensity.

Dependence of the extraction upon pH was studied and it was found that in the pH region where the vanadium-PAR complex is stable, the pH of the aqueous solution has no effect on the absorbance of the organic phase (Fig. 2).

Acetate buffer was used in order to maintain optimal pH in aqueous solution. Sodium and acetate ions have no influence on the vanadium-PAR reaction, but they change significantly the ionic strength of the solution, which in turn may affect the distribution coefficient in the extraction procedure. For this reason dependence of sodium acetate concentration on extraction was studied. Experiments showed that in the range  $1 \cdot 10^{-4}$ – $1 \cdot 10^{-1}$  M, sodium acetate concentration has no influence on the absorbance of the organic phase, and thus on distribution coefficient. The extraction is therefore independent of buffer concentration. Results are shown in Table I.

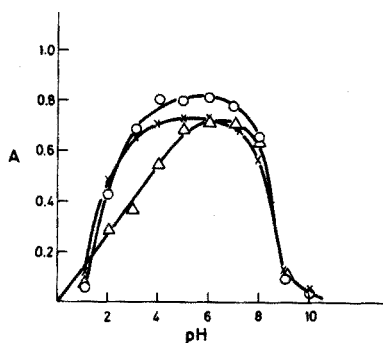


Fig. 2. Dependence of extraction upon pH. ( $\Delta$ ) Aqueous system V-PAR at  $\lambda_{\max} = 545$  nm. ( $\circ$ ) Organic phase, system  $(C_6H_5)_4P$ -V-PAR at  $\lambda_{\max} = 560$  nm. ( $\times$ ) Organic phase, system  $(C_6H_5)_4As$ -V-PAR at  $\lambda_{\max} = 560$  nm.

TABLE I

EXTRACTION DEPENDENCE ON THE BUFFER CONCENTRATION  
( $c_V = c_{PAR} = 2 \cdot 10^{-5}$  M;  $c_{(C_6H_5)_4XCl} = 2 \cdot 10^{-4}$  M)

Na acetate (moles $l^{-1}$ )	$A_{560}$	
	$(C_6H_5)_4AsCl$	$(C_6H_5)_4PCl$
—	0.556	0.560
$1 \cdot 10^{-4}$	0.550	0.560
$1 \cdot 10^{-3}$	0.558	0.563
$1 \cdot 10^{-2}$	0.560	0.560
$1 \cdot 10^{-1}$	0.560	0.565

*Organic phase composition*

It was observed that addition of acetone to chloroform favors the extraction by increasing the distribution coefficient. The optimal solution proved to be a chloroform–acetone mixture of 5:1. Compared to the extraction with chloroform alone, layers are separated better and faster, and a smaller excess of onium salts is needed. However, with a large excess of onium salts present, quantitative extraction is achieved for different chloroform–acetone mixtures as well, as shown in Table II.

TABLE II

ABSORBANCE DEPENDENCE ON CHLOROFORM–ACETONE RATIO

 $(c_V = c_{PAR} = 2 \cdot 10^{-5} M; c_{(C_6H_5)_4XCl} = 1 \cdot 10^{-3} M)$ 

Chloroform–acetone ratio	$A_{560}$	
	$(C_6H_5)_4AsCl$	$(C_6H_5)_4PCl$
10:0	0.606	0.620
9:1	0.625	0.629
8:1	0.635	0.632
7:1	0.626	0.629
6:1	0.630	0.623
5:1	0.630	0.640
4:1	0.629	0.629
3:1	0.615	0.623
2:1	0.600	0.631
1:1	0.588	0.608

*Reagent concentration*

It was shown that absorbance of the organic phase depends upon the PAR concentration in water. Maximal absorbance was observed for a vanadium–PAR ratio of 1:2 and above this value the color intensity was independent of reagent concentration (Fig. 3). However, for quantitative extraction, a vanadium–onium salt ratio of 1:5–1:10 is needed, as shown in Fig. 4.

Tetraphenylphosphonium chloride proved to have some advantages over tetraphenylarsonium chloride. The layers are separated better and easier, and the sensitivity and precision of the determination seem to be slightly improved.

*Interference of foreign ions*

The influence of foreign ions on the determination of vanadium was studied for 17 cations that may generally appear with vanadium in analytical systems, as well as for some common anions and masking agents. Results are shown in Tables III and IV. Among the cations studied, which under given conditions react with PAR in aqueous solutions, only cobalt and gallium (and copper to a small extent) are extracted

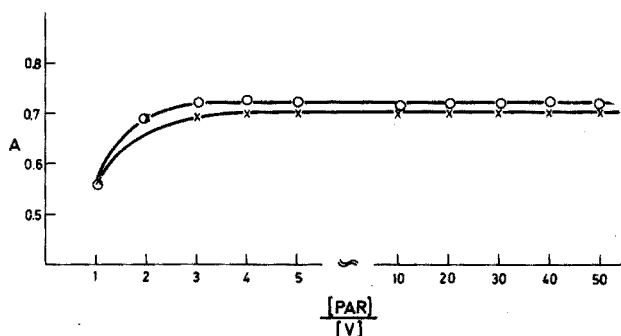


Fig. 3. Dependence of the absorbance of organic phase on the concentration of PAR in the aqueous phase.  $c_V = 2 \cdot 10^{-5} M$ .  $c_{(C_6H_5)_4XCl} = 1 \cdot 10^{-3} M$ . (O) X = P, (x) X = As.

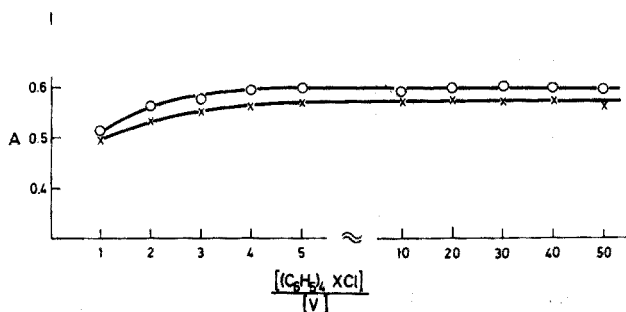


Fig. 4. Dependence of the absorbance of organic phase on tetraphenyl-onium salt concentration.  $c_V = c_{PAR} = 2 \cdot 10^{-5} M$ . (O) Phosphonium, (x) arsonium salt.

TABLE III

INFLUENCE OF DIVERSE CATIONS ON DETERMINATION OF VANADIUM

( $c_V = 2 \cdot 10^{-5} M$ ;  $c_{PAR} = 2 \cdot 10^{-4} M$ ;  $c_{(C_6H_5)_4XCl} = 1 \cdot 10^{-3} M$ ;  $c_{Nb_2C_4H_4O_6} = 2 \cdot 10^{-2} M$ )

Metal ion	Vanadium-metal ion ratio	$A_{560}$	
		$(C_6H_5)_4AsCl$	$(C_6H_5)_4PCl$
—	1: 0	0.760	0.770
Al(III)	1:200	0.769	0.765
Ca(II)	1:200	0.751	0.759
Mg(II)	1:200	0.758	0.750
Mn(II)	1:200	0.783	0.779
Cd(II)	1:100	0.700	0.705
Zr(IV)	1:100	0.720	0.730
Ti(IV)	1:100	0.772	0.758
Nb(V)	1: 10	0.700	0.705
U(VI)	1: 10	0.754	0.758
Cu(II)	1: 20	0.875	0.872
Pb(II)	1: 20	0.740	0.739
Bi(III)	1: 20	0.710	0.718
Zn(II)	1: 2	0.707	0.709
Ni(II)	1: 2	0.721	0.703
Co(II)	1: 2	>2	>2
Ga(III)	1: 2	1.425	1.430
Ta(V)	1: 2	0.750	0.755

TABLE IV

INFLUENCE OF DIVERSE ANIONS ON DETERMINATION OF VANADIUM  
 ( $c_V = 1.8 \cdot 10^{-5} M$ ;  $c_{PAR} = 2 \cdot 10^{-4} M$ ;  $c_{(C_6H_5)_4XCl} = 1 \cdot 10^{-3} M$ )

Anion	Vanadium-anion ratio	$A_{560}$	
		$(C_6H_5)_4AsCl$	$(C_6H_5)_4PCl$
Acetate	1:10000	0.636	0.629
Chloride	1:10000	0.628	0.628
Sulfate	1:10000	0.618	0.622
Phosphate	1:10000	0.491	0.481
	1: 1000	0.604	0.612
	1: 100	0.618	0.623
Nitrate	1:10000	0.422	0.410
	1: 1000	0.597	0.402
	1: 100	0.612	0.611
Fluoride	1: 100	0.632	0.630
	1: 10	0.635	0.629
Cyanide	1: 1000	0.630	0.608
	1: 100	0.628	0.608
	1: 10	0.630	0.563
Tartrate	1:10000	0.375	0.382
	1: 1000	0.595	0.597
	1: 100	0.628	0.622
	1: 10	0.620	0.625
Oxalate	1: 1000	0.200	0.218
	1: 100	0.580	0.590
	1: 10	0.600	0.604
Citrate	1: 1000	0.486	0.487
	1: 100	0.602	0.600
EDTA	1: 1000	—	—
	1: 100	0.027	0.025
DCTA	1: 1000	0.225	0.238
	1: 100	0.506	0.505
	1: 10	0.575	0.574

TABLE V

COMPARISON OF DIFFERENT METHODS OF DETERMINATION OF VANADIUM WITH PAR IN PRESENCE OF OTHER METAL IONS

( $c_V = 2 \cdot 10^{-5} M$ ;  $c_{PAR} = 2 \cdot 10^{-4} M$ ;  $c_{\text{metal ion}} = 4 \cdot 10^{-5} M$ ;  $c_{(C_6H_5)_4PCl} = 1 \cdot 10^{-3} M$ ;  $c_{Na_2C_4H_4O_6} = c_{DCTA} = 2 \cdot 10^{-2} M$ )

Metal ion added	$A_{545}$		$A_{560}$ (org. phase, $(C_6H_5)_4PCl$ )
	$(H_2O, Na_2C_4H_4O_6)$	$(H_2O, DCTA)$	
—	0.660	0.448	0.730
Cu(II)	1.450	0.460	0.729
Pb(II)	1.030	0.453	0.740
Co(II)	1.320	0.596	>2
Bi(III)	1.396	0.454	0.738
Ti(IV)	0.775	0.482	0.741
Zr(IV)	0.778	0.682	0.725
Nb(V)	>2	1.21	0.730
Ta(V)	1.13	0.960	0.720
U(VI)	0.92	0.980	0.758
Ga(III)	1.25	0.460	1.300

into the organic phase. Since all the other ions that form stable complexes with PAR in aqueous phase remain in water, they do not interfere with this determination of vanadium in chloroform-acetone solutions, provided that excess of the reagent is present in aqueous phase.

Results given in Table V illustrate the advantages of vanadium determination with PAR extraction, compared to absorbance measurements of the aqueous phase, carried out at 560 nm. Data in the first column refer to absorbance of aqueous solutions, containing tartrate and metal ions in the same concentration as the solutions used for extraction. Absorbance of the corresponding organic phase is shown in the third column. Data in the second column refer to the color intensity of aqueous solutions of the same composition, but containing DCTA instead of tartrate as masking agent. The results show that the procedure described here is far more selective than the methods based on absorbance measurements in aqueous solutions. Vanadium determinations in tartaric acid solutions have little selectivity. Addition of DCTA is helpful for several systems, but severe interference is still caused by zirconium, niobium, tantalum and uranium ions, as well as by larger concentrations of cobalt and titanium. Among the ions investigated only cobalt and gallium were found to interfere by being simultaneously extracted with vanadium.

#### *Sensitivity and reproducibility of the method*

The optimal concentration range for vanadium determination by the described procedure was found to be  $0.2\text{--}1.6 \mu\text{g V ml}^{-1}$ . Beer's law is obeyed in this range; the absorbance for  $1.6 \mu\text{g V ml}^{-1}$  was found to be *ca.* 1.100. The molar absorptivity at 560 nm amounts to  $3.9 \cdot 10^4$ . The reproducibility of the method, expressed by standard deviation on the basis of 30 determinations, is  $0.2\%$ – $2\%$ , depending on the vanadium concentration.

#### *Identification of colored species in solution*

The vanadium-PAR ratio in the colored species present in aqueous solutions has been reported<sup>3,6,7</sup> as 1 : 1. The present studies confirmed this result. The presence of the onium salts used here does not alter the position of the band or the intensity of the spectrum of the aqueous phase. In addition, the molar ratio for the onium-

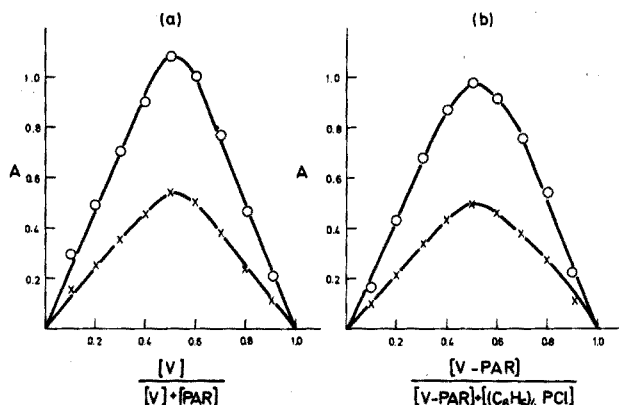


Fig. 5. Determination of complex composition by Job's method. (a) ( $\times$ )  $c_V + c_{\text{PAR}} = 4 \cdot 10^{-5} \text{ M}$ . ( $\circ$ )  $c_V + c_{\text{PAR}} = 8 \cdot 10^{-5} \text{ M}$ . (b) ( $\times$ )  $c_{V-\text{PAR}} + c_{(\text{C}_6\text{H}_5)_4\text{PCl}} = 4 \cdot 10^{-5} \text{ M}$ . ( $\circ$ )  $c_{V-\text{PAR}} + c_{(\text{C}_6\text{H}_5)_4\text{PCl}} = 8 \cdot 10^{-5} \text{ M}$ .

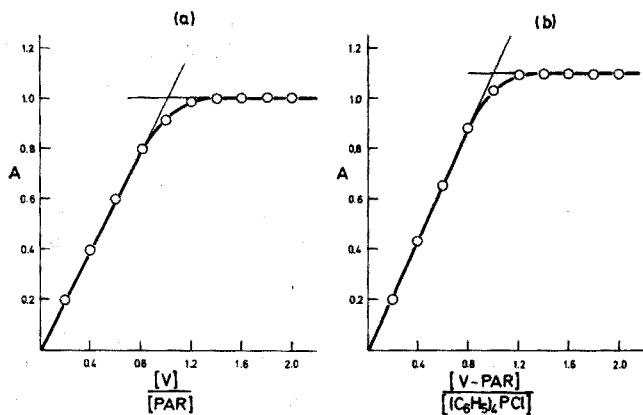


Fig. 6. Determination of complex composition by mole-ratio method. (a)  $c_V = 2.5 \cdot 10^{-5} M$ ,  $c_{(C_6H_5)_4PCl} = 1 \cdot 10^{-3} M$ . (b)  $c_V = c_{PAR}$ ,  $c_{(C_6H_5)_4PCl} = 5 \cdot 10^{-5} M$ .

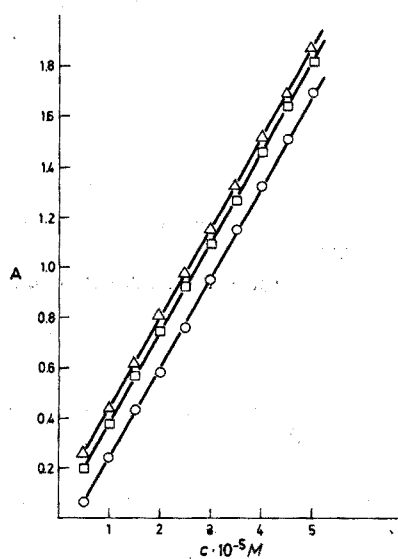


Fig. 7. Determination of complex composition by slope-ratio method. (○)  $c_{PAR} = c_{(C_6H_5)_4PCl} = 2 \cdot 10^{-3} M$ ;  $c_V$  is varied. (□)  $c_V = c_{(C_6H_5)_4PCl} = 2 \cdot 10^{-3} M$ ;  $c_{PAR}$  is varied. (△)  $c_V = c_{PAR} = 2 \cdot 10^{-4} M$ ;  $c_{(C_6H_5)_4PCl}$  is varied.

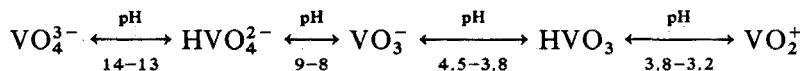
vanadium-PAR species in the organic phase was found to be 1 : 1 : 1. Results are shown in Figs. 5-7.

#### DISCUSSION

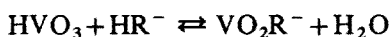
Solution studies have shown that the tetraphenyl-onium-vanadium-PAR ratio in the organic phase amounts to 1 : 1 : 1. This result shows that an anionic vanadium(V) complex, bearing one negative charge, must be present in aqueous solutions. Most probably this species is  $VO_2R^-$ , for  $PAR = H_2R$ , and  $R = C_{11}H_7N_3O_2^-$ . On addition of onium salts, a complex of the formula  $[(C_6H_5)_4X][VO_2R]$ ,

X = P, As, is formed which is transferred into the organic phase.

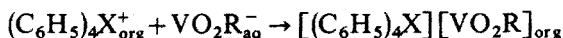
The composition of the vanadium(V) species in aqueous solutions strongly depends upon pH and metal concentration. For metal concentrations in the region of  $10^{-5}$  M and smaller, the presence of several monomeric forms is expected, and the pH-dependent equilibria among them<sup>9,10</sup> are shown below.



Accordingly, the  $\text{VO}_3^-$  ion would be expected to prevail under the conditions employed for the determination of vanadium with PAR (pH 5.5). However, other monomeric vanadium(V) ions are also present, as part of the complex equilibria involved. On the other hand, PAR under the given conditions is expected to be present primarily in the  $\text{HR}^-$  form<sup>11-15</sup>. It is possible that some of the less abundant vanadium(V) species react with the  $\text{HR}^-$  form of PAR and, being consumed by complex formation, are regenerated by equilibria requirements. Reactions of the type given below can be assumed:



The colored dioxo-PAR-vanadate(V) ion is then extracted into the organic phase by an ion-pair formation mechanism:



From chloroform solutions we have actually been able to separate crystalline compounds that correspond to this composition<sup>16</sup>.

Although tetraphenyl-onium salts have been extensively used in spectrophotometric determination of metals in combination with some other reagents, such as thiocyanates, catechol, etc., the procedure described above seems to be the first procedure based on a combination of these salts with an azo reagent such as PAR.

The authors wish to thank Lj. Marić for help in experimental procedures. The experimental work was done at the University of Zagreb.

#### SUMMARY

A spectrophotometric determination of vanadium with 4-(2-pyridylazo)-resorcinol, PAR, is described, based on the extraction of the V-PAR complex by tetraphenylphosphonium or tetraphenylarsonium chloride. Absorbance in a chloroform-acetone mixture shows a better selectivity and sensitivity compared with other spectrophotometric methods for vanadium with PAR in aqueous media. The composition of the colored complex and the mechanism of the extraction are discussed.

#### RÉSUMÉ

Un dosage spectrophotométrique du vanadium est décrit, basé sur l'extraction du complexe vanadium-4-(2-pyridylazo)résorcinol par le chlorure de tétraphénylphosphonium ou de tétraphénylarsonium. L'absorption en milieu chloroforme-acétone présente une meilleure sélectivité et une meilleure sensibilité, comparées à



celles obtenues pour d'autres méthodes spectrophotométriques du vanadium, en milieu aqueux. On examine la composition du complexe coloré et le mécanisme d'extraction.

#### ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Bestimmung von Vanadin mit 4-(2-Pyridylazo)resorcin, PAR, beschrieben, die auf der Extraktion des V-PAR-Komplexes mit Tetraphenylphosphonium- oder Tetraphenylarsoniumchlorid beruht. Die Extinktion in einem Chloroform-Aceton-Gemisch zeigt eine bessere Selektivität und Empfindlichkeit im Vergleich zu anderen spektrophotometrischen Methoden für Vanadin mit PAR in wässrigen Medien. Die Zusammensetzung des gefärbten Komplexes und der Extraktionsmechanismus werden diskutiert.

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## DETERMINATION OF SUBMICROGRAM AMOUNTS OF IODIDE BY ITS CATALYTIC EFFECT ON THE SUBSTITUTION REACTION OF MERCURY(II)-PAR COMPLEX WITH CyDTA

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Kinetic methods of analysis which utilize reactions involving metal complexes have been discussed by several authors<sup>1</sup>. Olson and Margerum<sup>2</sup> have reported an interesting coordination chain reaction which is catalyzed by trace amounts of EDTA. Based on a careful study on the mechanism of the reaction, Margerum *et al.*<sup>3,4</sup> succeeded in developing new methods for the determination of submicrogram quantities of various metals. Cabello-Tomas and West<sup>5</sup> reported that the reaction of slightly aged zirconyl chloride with xylenol orange is catalyzed by substoichiometric amounts of fluoride, arsenate, sulfate, citrate or oxalate. In an earlier paper<sup>6</sup>, ligand substitution reactions involving 4-(2-pyridylazo)resorcinol (PAR) and ethyleneglycol bis(2-amino-ethylether)-N,N,N',N'-tetraacetic acid (EGTA) have been proposed for the differential determination of various metals.

For the catalytic determination of submicrogram amounts of iodide, methods based on the redox reactions of iron(III) thiocyanate and sodium nitrite<sup>7,8</sup> and of pyrocatechol violet and hydrogen peroxide<sup>9</sup> have been reported.

In the present paper a new kinetic method of analysis is proposed for the determination of submicrogram amounts of iodide. The method is based on the following ligand substitution reaction:



which is catalyzed by iodide as low as  $10^{-8}$  M. CyDTA denotes 1,2-cyclohexane-diamine-N,N,N',N'-tetraacetic acid.

### RESULTS AND DISCUSSION

If PAR and CyDTA are abbreviated as  $\text{H}_2\text{par}$  and  $\text{H}_4\text{cydta}$ , respectively, the rate equation of the ligand substitution reaction of the mercury(II)-PAR complex with CyDTA in the presence of iodide is expressed as follows<sup>10</sup>:

$$-\frac{d[\text{Hg}(\text{par})_2^{2-}]}{dt} = k_{0(\text{H},\text{PAR},\text{I})}[\text{Hg}(\text{par})_2^{2-}][\text{Hcydta}^{3-}] \quad (2)$$

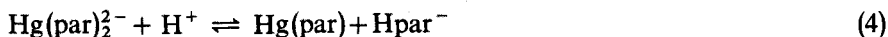
where  $k_{0(\text{H},\text{PAR},\text{I})}$  refers to a conditional rate constant involving concentrations of hydrogen ion, PAR and iodide. Careful study of the kinetics of this reaction showed the following relationship:

$$k_{0(\text{H,PAR,I})} = \frac{k_1[\text{H}^+] + k_2 + k'_{3,1}[\text{H}^+][\text{I}^-]}{[\text{Hpar}^-]} \quad (3)$$

where  $k'_1$ ,  $k'_2$  and  $k'_{3,1}$  refer to conditional rate constants. It is obvious from eqn. (3) that, under conditions where PAR is present in large excess and the pH is constant, the conditional rate constant  $k_{0(\text{H,PAR,I})}$  is a linear function of the concentration of iodide. This provides the basis of the determination of submicrogram amounts of iodide by means of the ligand substitution reaction of the mercury(II)-PAR complex with CyDTA. Details of the kinetics and mechanism of this reaction have been reported<sup>10</sup>.

#### Effect of pH

As is apparent from eqn. (3), hydrogen ion accelerates the ligand substitution reaction. If the pH is lower than 8, the substitution reaction is too fast to be followed by a conventional method. The predominant species of the mercury(II)-PAR complex is the form  $\text{Hg}(\text{par})_2^{2-}$ . At pH lower than 8, the 1:2 mercury(II)-PAR complex dissociates to yield the 1:1 mercury(II)-PAR complex:



Thus, pH values above 8.5 are preferable. On the other hand, very high pH leads to hydrolysis of the mercury(II)-PAR complex. The rate of hydrolysis of the mercury-PAR complex depends on the concentration of hydrogen ion; above pH 10.5, hydrolysis is immediate, but below pH 9.2, hydrolysis is negligible at least for 120 sec. Accordingly, the pH range of 8.5-9.2 is recommended.

#### Effect of concentration of reactants

The rate of hydrolysis of the mercury(II)-PAR complex decreases with increasing concentrations of PAR, hence a relatively high concentration of PAR is preferable. Concentrations of PAR higher than  $10^{-4}$  M are necessary to form quantitatively the 1:2 mercury(II)-PAR complex in the pH range 8.5-9.2.

The rate of ligand substitution of the mercury(II)-PAR complex is of first order with respect to the concentration of CyDTA. The ligand substitution reaction is too fast at high concentrations of CyDTA, whereas at very low concentration of CyDTA, the mercury(II)-PAR complex is not completely substituted by CyDTA. A CyDTA concentration of  $2 \cdot 10^{-5}$  M is recommended.

Relatively high concentrations of mercury(II) lead to improved sensitivity. For optimal sensitivity and precision, a mercury(II) concentration of  $4 \cdot 10^{-6}$  M is recommended.

The stability constant of the iodo-complex of mercury(II) is high, hence the mercury(II)-PAR complex is substituted by iodide at a higher concentration than  $2 \cdot 10^{-7}$  M. This results in a decrease in absorbance at the start of the reaction.

#### Calibration curve

The plot of the absorbance change ( $A_{30,0} - A_{30,1}$ ) at 30 sec after the initiation of reaction against iodide concentration, where  $A_{30,0}$  and  $A_{30,1}$  denote the absorbances at  $t=30$  sec in the absence of iodide and in the presence of iodide, respectively, was found to be a straight line passing through the origin for the range  $0-10 \cdot 10^{-8}$  M iodide.

Concentrations as low as  $10^{-8}$  M can be determined. For  $10^{-7}$  M iodide concentrations, the  $(A_{30,0}-A_{30,t})$  value was 0.225 at pH 8.94 and  $25^{\circ}$ .

#### Effect of diverse ions

With a thorough knowledge of the kinetics of the reaction system, the following elements are expected to interfere with the determination of iodide: complexing agents for mercury(II), and metals forming complexes with CyDTA and/or PAR.

The conditional rate constants ( $k'_{3,x}$ ) for chloride, bromide and iodide are as follows<sup>10</sup>:  $k'_{3,Cl} = (4.5 \pm 0.2) \cdot 10^9 M^{-2} \text{ sec}^{-1}$ ,  $k'_{3,Br} = (3.2 \pm 0.1) \cdot 10^{11} M^{-2} \text{ sec}^{-1}$ ,  $k'_{3,I} = (5.6 \pm 0.2) \cdot 10^{14} M^{-2} \text{ sec}^{-1}$ , i.e.  $k'_{3,Cl} : k'_{3,Br} : k'_{3,I} = 7.9 \cdot 10^{-6} : 5.6 \cdot 10^{-4} : 1$ . This suggests that iodide can be determined in the presence of a  $10^4$ -fold excess of chloride or a  $10^2$ -fold excess of bromide. Table I summarizes the effect of diverse ions on the determination of iodide. Sulphate, nitrate and fluoride cause no interference. Chloride and bromide do not interfere with the determination of iodide at least up to  $5 \cdot 10^{-4}$  M and  $10^{-5}$  M, respectively. Interference from cations can be eliminated by passing the sample solution through a column of a cation-exchange resin before the determination of iodide. Table I shows that cations are satisfactorily removed by this procedure.

TABLE I

EFFECT OF DIVERSE IONS

Ions added	Concentration (M)	Iodide taken ( $\cdot 10^{-8}$ M)	Iodide found ( $\cdot 10^{-8}$ M)	Recovery (%)
F <sup>-</sup>	$5 \cdot 10^{-3}$	4.3	4.3	100
	$10^{-2}$	4.3	4.5	105
Cl <sup>-</sup>	$5 \cdot 10^{-4}$	4.3	4.6	107
	$2.5 \cdot 10^{-3}$	4.3	5.5	128
Br <sup>-</sup>	$10^{-5}$	4.3	4.5	105
	$5 \cdot 10^{-5}$	4.3	6.4	149
NO <sub>3</sub> <sup>-</sup>	$5 \cdot 10^{-3}$	4.3	4.3	100
SO <sub>4</sub> <sup>2-</sup>	$5 \cdot 10^{-3}$	4.3	4.6	107
HPO <sub>4</sub> <sup>2-</sup>	$10^{-4}$	4.3	4.6	107
Ca <sup>2+</sup>	$10^{-4}$	3.7	3.7	100
Mg <sup>2+</sup>	$10^{-4}$	3.7	3.4	92
Zn <sup>2+</sup>	$10^{-5}$	3.7	4.0	108
Mn <sup>2+</sup>	$10^{-5}$	3.7	3.9	105
Fe <sup>3+</sup>	$10^{-5}$	3.7	3.7	100
Cu <sup>2+</sup>	$10^{-5}$	3.7	3.9	105
Al <sup>3+</sup>	$10^{-5}$	3.7	3.7	100
NH <sub>4</sub> <sup>+</sup>	$10^{-5}$	3.7	3.4	92
Mixture of above cations		3.7	3.4	92

#### Determination of iodide in rain water

Table II shows results of the determination of iodide in rain water by the present method and the iron(III) thiocyanate-nitrite method<sup>8</sup> for comparison. The results obtained by both methods agree satisfactorily.

#### EXPERIMENTAL

##### Reagents

**Mercury(II) nitrate.** A  $10^{-2}$  M stock solution of mercury(II) was prepared by

TABLE II

DETERMINATION OF IODIDE IN RAIN WATER

Sample	Iodide found ( $\cdot 10^{-8} M$ )	Procedure
Rain water	3.1 } 3.2 } 3.4 }	Present method
Rain water and $1.9 \cdot 10^{-8} M$ iodide	5.3 }	
Rain water	3.1 } 3.3 } 3.2 }	

dissolving the calculated amount of commercial G. R. mercury(II) nitrate in 1 M perchloric acid. Solutions of lower concentration were prepared by suitable dilution with water. The mercury concentration was determined by a standard EDTA solution with xylenol orange as indicator.

*CyDTA.* The acid form of CyDTA (Dojindo Co., Ltd.) was dissolved in sodium hydroxide solution and CyDTA was precipitated by adding perchloric acid. The purified CyDTA was dissolved in 2 equivalents of sodium hydroxide. The CyDTA solution was standardized with a standard zinc(II) solution with Erio T as indicator.

*Sodium iodide.* Sodium iodide (G. R.) was recrystallized twice from distilled water. The sodium iodide crystals were washed with ether and benzene, and then dried *in vacuo* at room temperature. The sodium iodide solution was standardized by a standard silver nitrate solution with eosin as indicator.

*Cation-exchange resin.* Amberlite IR 120-B exchanger was used to eliminate cations in a sample solution.

The preparation of all other reagents (sodium hydroxide, PAR, borax and boric acid) have been described previously<sup>11</sup>.

### Apparatus

The following instruments were used: a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer; a Hitachi Model QPD-53 recorder; a Radiometer PHM-4d (Copenhagen) with a Type G 202 B glass electrode and K 401 calomel electrode; a Sharp Model TEB-10 thermoelectric circulating bath.

### Recommended procedure

Pass a sample solution through a column of cation-exchange resin at a rate of  $1 \text{ ml min}^{-1}$ ; reject the first 20 ml of the effluent. Take 50 ml of the sample solution containing no more than  $2 \cdot 10^{-7} M$  iodide in a 100-ml silica beaker placed in a cell compartment thermostated at  $25^\circ$ , and add 10 ml of borate-boric acid buffer solution (pH 9), 23 ml of distilled water, 10 ml of  $10^{-3} M$  PAR solution and 2 ml of  $2 \cdot 10^{-4} M$  mercury(II) solution. Start the reaction by mixing 5 ml of  $4 \cdot 10^{-4} M$  CyDTA solution into the sample solution containing the mercury(II)-PAR complex within 1 min after the addition of mercury(II) solution. Follow the reaction automatically, recording the transmittance at 500 nm as a function of time. Determine the concentration of iodide from the calibration curve previously constructed. Be careful to keep the pH constant, using the same buffer as for construction of the calibration curve.

## SUMMARY

A kinetic method for the determination of submicrogram amounts of iodide is described. The method is based on the catalytic effect of iodide on the ligand substitution reaction of the mercury(II)-4-(2-pyridylazo)resorcinol complex with 1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid. Iodide concentrations as low as  $10^{-8}$  M can be determined. Chloride and bromide do not interfere at least up to  $5 \cdot 10^{-4}$  M and  $10^{-5}$  M, respectively. Cationic interferences can be removed by preliminary ion exchange.

## RÉSUMÉ

On décrit une méthode pour le dosage des iodures (en quantité de l'ordre du submicrogramme). Elle est basée sur l'action catalytique des iodures dans la réaction de substitution du complexe mercure(II)-4-(2-pyridylazo)réSORCINOL avec l'acide 1,2-cyclohexanediamino-N,N,N',N'-tétraacétique. Chlorure ( $5 \cdot 10^{-4}$  M) et bromure ( $10^{-5}$  M) ne gênent pas. Les interférences cationiques peuvent être éliminées par traitement préliminaire sur échangeur d'ions.

## ZUSAMMENFASSUNG

Es wird eine kinetische Methode für die Bestimmung von Submikrogramm-Mengen Jodid beschrieben. Die Methode beruht auf der katalytischen Wirkung von Jodid auf die Ligandensubstitutionsreaktion des Quecksilber(II)-4-(2-Pyridylazo)-resorcin-Komplexes mit 1,2-Cyclohexandiamin-N,N,N',N'-tetraessigsäure. Es können Jodidkonzentrationen bis zu  $10^{-8}$  M herab bestimmt werden. Chlorid und Bromid unterhalb  $5 \cdot 10^{-4}$  M bzw.  $10^{-5}$  M stören nicht. Kationische Störungen können durch vorhergehenden Ionenaustausch entfernt werden.

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## A SPECTROPHOTOMETRIC DETERMINATION OF MALIC ACID IN THE PRESENCE OF GLYCOLIC, GLYOXYLIC AND DIGLYCOLIC ACIDS

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The colorimetric molybdate bleaching method for  $\alpha$ -hydroxy acids, published by Matulis and Guyon<sup>1</sup>, was applied to the determination of malic acid by Bewich and Greener<sup>2</sup>. This procedure was investigated but malic acid could not be differentiated from other  $\alpha$ -hydroxy acids by this method. However, it was noted that diglycolic acid did not bleach the molybdate solution. Likewise, the cerium(IV) sulfate oxidation method proposed by Willard and Young<sup>3-5</sup> gives the total  $\alpha$ -hydroxy acid present. In the colorimetric method of McFadden and Howes<sup>6</sup>, glyoxylic acid can be determined in the presence of glycolic acid by reaction of the phenylhydrazone with potassium hexacyanoferrate(III), but malic acid is not mentioned. A preliminary survey of the usefulness of this procedure for the possible differentiation of glyoxylic acid in the presence of malic acid demonstrated that it was not applicable. Samuelson *et al.*<sup>7,8</sup> employed ion-exchange chromatography and AutoAnalyzer technology to demonstrate the separation of a variety of systems including glycolic and glyoxylic acid by simultaneous dual analysis with chromic acid and carbazole. This type of analysis is both expensive and time-consuming and a shorter, simpler method was needed.

The method employed and described here is an extension of the work reported by Coe<sup>9</sup>, whereby the temperature-sensitive reactivities of malic, glycolic and diglycolic acids with pyrogallol in sulfuric acid permit the spectrophotometric analysis for malic acid in the presence of glycolic, diglycolic and glyoxylic acids.

### EXPERIMENTAL

#### *Apparatus*

Absorbance measurements were made with a Perkin-Elmer 202 recording spectrophotometer with matched  $1.000 \pm 0.0002$  cm quartz cells. Water and oil bath temperatures (other than 100° temperatures) were maintained with an I<sup>2</sup>R apparatus attached to a knife heater which supplied intermittent heat to the liquid contained in a battery jar and stirred by an air motor. Most of the constant heat was supplied by a hot plate.

#### *Reagents*

A solution (3 mg ml<sup>-1</sup>) of pyrogallol in concentrated sulfuric acid was prepared daily, by adding 1.5 g of pyrogallol to a dry 500-ml flask containing a Teflon

stirring bar and adding about 250 ml of sulfuric acid, stirring with a magnetic stirrer until dissolved (about 45 min), then diluting to the mark with sulfuric acid.

#### *Recommended method*

In order to analyze for combined malic, glycolic and diglycolic acids, it is necessary to carry out the pyrogallol-sulfuric acid reaction at 100°. Also, since either acid may be determined in the absence of the other, separate calibration curves at this temperature are necessary. When it is desired to analyze for malic acid only, the reaction is carried out at 50° and a calibration curve for malic acid at this temperature is made.

#### *Preparation of calibration curves*

*Color development at 100°.* Prepare separate calibration curves by adding 1 ml each of solutions of 0.05, 0.1, 0.2 and 0.4 mg ml<sup>-1</sup> of malic, glycolic and diglycolic acids to 26-mm o.d. test tubes equipped with T joints and calibrated at the 16-ml mark. With a 25-ml syringe add the pyrogallol solution to the 16-ml mark with sufficient force to mix thoroughly during the acid addition. Prepare a blank using 1 ml of water and 15 ml of the pyrogallol solution and mix in the same way. Add the T plugs and carefully mix. Heat for 30 min at 100° in a steam bath, remove, cool in an ice bath and read the absorbance at 365 nm, against the blank as a reference. Plot absorbance versus milligrams for each of the acids.

*Color development at 50°.* Use the same procedure as that for 100° except use 1 ml each of 0.4, 0.8, 1.6 and 3.2 mg ml<sup>-1</sup> solutions of malic acid. After addition of the pyrogallol solution, heat in a water bath at 50° for 30 min. Cool, read and plot the absorbances versus milligrams of malic acid.

#### *General procedure*

Dissolve the sample, if necessary, and dilute the samples to be assayed at 100° so as to contain an estimated 0.2–0.4 mg of malic acid per ml. For samples to be analyzed at 50° the samples should be diluted to contain 1.5–3.0 mg ml<sup>-1</sup>. A dilution of up to 5-fold can be made after color development on samples where the absorbance is excessive with the developed blank solution without introducing appreciable error into the final analysis. Scan the visible region of the spectra from 350 to 750 nm for the presence of glycolic or diglycolic acid bands. If either or both are present, repeat the analysis at 50° to eliminate the reaction of the glycolic and diglycolic acids with the pyrogallol.

## RESULTS AND DISCUSSION

#### *Method of addition of pyrogallol solution*

Pouring the pyrogallol solution into the test tubes containing the 1 ml of solution to be assayed did not always give complete reproducibility of the colored reaction product. This was due to inhomogeneous mixing or layer formation during addition of the pyrogallol mixture. To avoid the problem, the pyrogallol solution was added with a syringe to insure uniform mixing. Cooling of both solutions before and during mixing in an ice bath had no additional effect.



*Effect of time and temperature*

Figure 1 shows the comparative absorbances for equal concentrations of malic, glycolic and diglycolic acids when reacted with the pyrogallol reagent at 50, 75 and 100° for 1 h. Figures 2–4 show the actual calibration curves for these three acids when reacted at 100° for 30 min, 50° for 30 min, and 50° for 1 h. It is obvious that in the analysis for malic acid in the presence of those acids, the 50° reaction conditions will give a minimum of interference from glycolic and diglycolic acids.

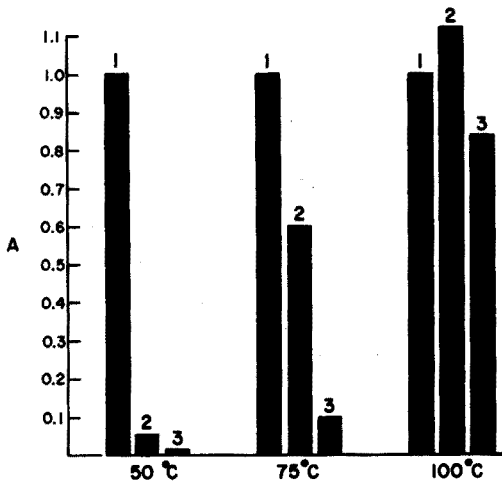


Fig. 1. Relative absorbance at 365 nm for (1) malic acid, (2) glycolic acid, (3) diglycolic acid.

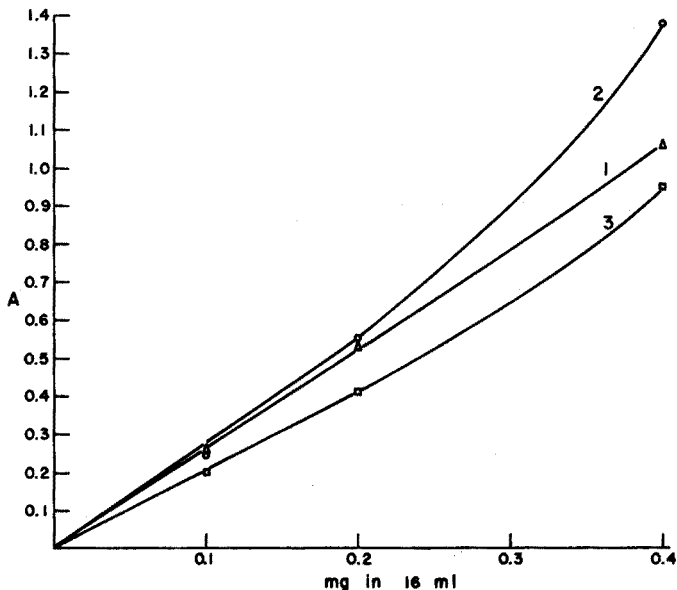


Fig. 2. Calibration curves at 100°, 30 min reaction time, for (1) malic acid, (2) glycolic acid, (3) diglycolic acid.

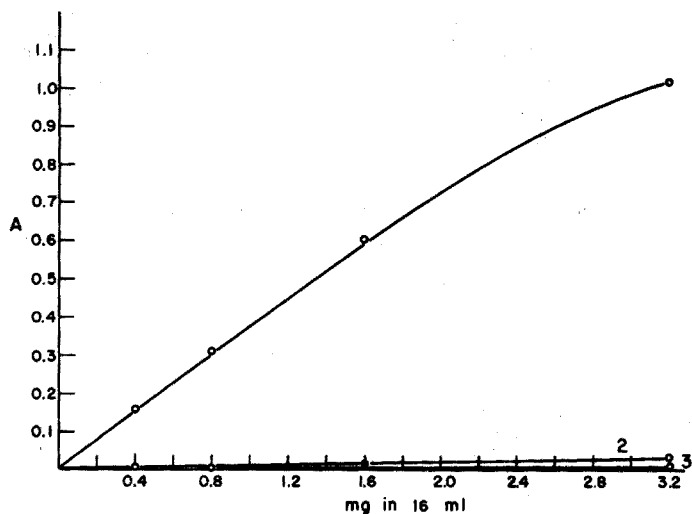


Fig. 3. Calibration curves at 50°, 30 min reaction time, for (1) malic acid, (2) glycolic acid, (3) diglycolic acid.

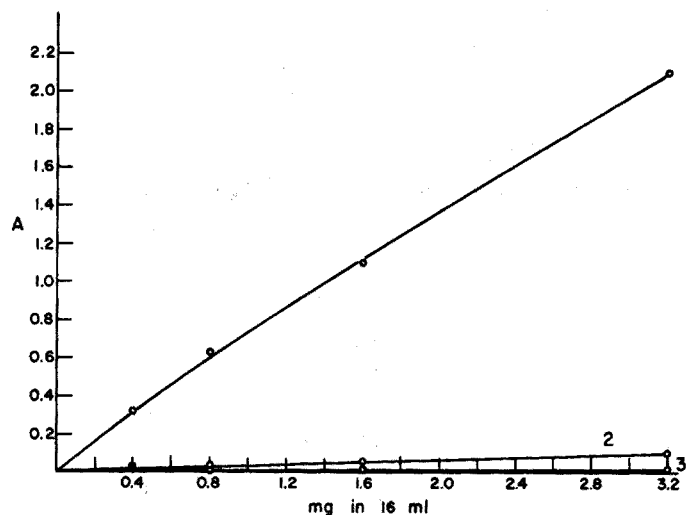


Fig. 4. Calibration curves at 50°, 1 h reaction time, for (1) malic acid, (2) glycolic acid, (3) diglycolic acid.

### Spectra

The visible region of the spectra of the pyrogallol-sulfuric acid reaction products obtained at 100° for 30 min for the three acids under study are shown in Fig. 5. The difficulties of interpreting the malic acid content in this mixture are apparent. However, by determining the total malic, glycolic and diglycolic acids by means of the 100° reaction conditions and then determining the malic acid content by means of the 50° reaction conditions, an estimate of the combined glycolic-diglycolic acid content can be made.

Since glyoxylic acid absorbs at 590 nm and does not absorb significantly at

365 nm the presence of this acid in the malic-glycolic-diglycolic system can easily be detected.

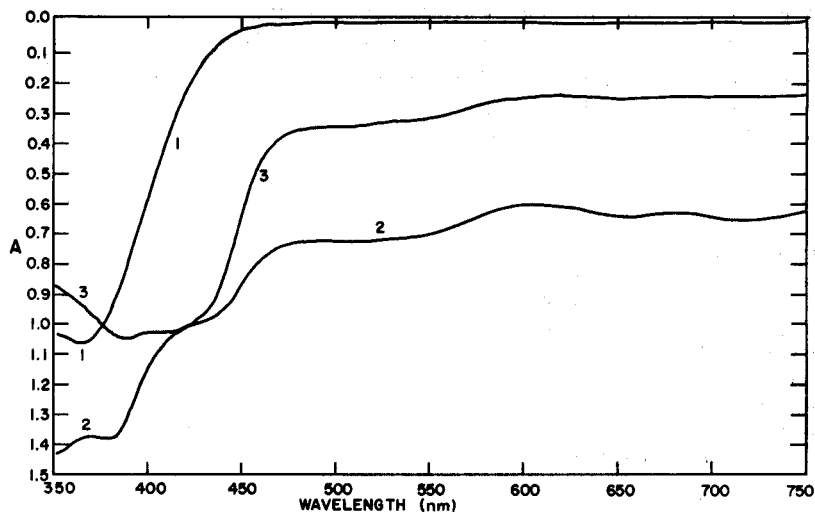


Fig. 5. Spectra of equal concentrations of (1) malic acid, (2) glycolic acid, (3) diglycolic acid, 30 min reaction time.

### Interferences

The following compounds were tested at the maximum concentrations shown for the 1 ml of sample used in the analysis, and no interferences were found: hexafluorosilicic acid (75 mg), formic acid, ethanol, ethyl acetate and maleic acid (0.4 mg each). Both 1,3- and 1,6-hexanediol interfered at the 0.2-mg level with both exhibiting an absorbance maximum at 395 nm.

### SUMMARY

The optimal reaction temperature ( $50^{\circ}$ ) for the reaction of malic acid with pyrogallol in sulfuric acid in the presence of glycolic and diglycolic acid was obtained; the determination of malic acid is possible under these conditions. Additionally, the concentration of combined glycolic and diglycolic acids can be determined by again reacting the mixture with pyrogallol-sulfuric acid at higher temperatures ( $100^{\circ}$ ).

### RÉSUMÉ

On propose une méthode spectrophotométrique rapide pour le dosage de l'acide malique, en présence d'autres  $\alpha$ -hydroxy-acides. Elle est possible, grâce au fait que l'acide malique réagit avec le pyrogallol, dans l'acide sulfurique à des températures plus basses que les autres  $\alpha$ -hydroxy-acides (soit  $50^{\circ}$ ). Les acides glycolique et diglycolique peuvent être dosés à des températures plus élevées ( $100^{\circ}$ ).

## ZUSAMMENFASSUNG

Die optimale Reaktionstemperatur (50°) für die Reaktion von Äpfelsäure mit Pyrogallol in Schwefelsäure in Gegenwart von Glykol- und Diglykolsäure wurde ermittelt; die Bestimmung von Äpfelsäure ist unter diesen Bedingungen möglich. Zusätzlich kann die Konzentration von Glykol- und Diglykolsäure zusammen bestimmt werden, indem das Gemisch mit Pyrogallol-Schwefelsäure bei höheren Temperaturen (100°) erneut umgesetzt wird.

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## SELECTIVE EXTRACTION OF MOLYBDENUM(V) THIOCYANATE WITH N-BENZYLANILINE

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The reduction of acidic solutions of molybdate by tin(II) chloride in the presence of thiocyanate is probably the most widely used spectrophotometric method for the determination of molybdenum. The intense amber or orange-red molybdenum(V) thiocyanate complex is presumably an oxypentathiocyanatomolybdenum(V)<sup>1-4</sup> of the formula  $[\text{MoO}(\text{SCN})_5]^{2-}$ . Because this reaction is kinetically and mechanistically complex, careful regulation of the many variables in the system is required to achieve analytical reproducibility. To circumvent these complications of the tin(II) chloride reduction, several investigators have recommended so-called "one-electron" reducing agents such as copper(I) chloride<sup>5</sup>, hydrazonium sulphate<sup>6,7</sup>, thioglycollic acid<sup>8</sup>, dihydroxymaleic acid<sup>9</sup>, thiourea<sup>10</sup>, ascorbic acid<sup>11</sup> and acetone<sup>12</sup>. Another approach was used by Wilson and McFarland<sup>13</sup>, in which molybdenum(VI) is reduced to molybdenum(V) by tin(II) chloride in dilute hydrochloric acid and the excess of tin(II) is completely oxidized by perchlorate. Silver and mercury metal reductors<sup>14,15</sup> in 3 M hydrochloric acid have also been used. The method based on the use of copper(I) chloride as reducing agent, with acetone-water as the reaction medium, is said to be superior to any other thiocyanate method, but this method has a number of drawbacks in practice. Firstly, after the initial reduction of molybdenum, a little tin(II) chloride must be added to reduce copper(II) which otherwise would give a colour with thiocyanate. Secondly, in the presence of large amounts of copper, this element is precipitated as the thiocyanate<sup>16</sup> and tends to collect at the interface between the inorganic and organic phases, contaminating the extract. Thirdly, the original volume of the sample solution must not exceed a few milliliters and iron cannot be present in more than minute amounts.

Several organic solvents have been recommended for the extraction of the molybdenum(V) thiocyanate complex so as to provide a separation of molybdenum from accompanying elements and also to increase the sensitivity and stability of the reaction product. The extraction of molybdenum(V) thiocyanate complex with tetraphenylarsonium chloride<sup>17</sup>, 3,4-dichlorobenzyltriphenylphosphonium chloride<sup>18</sup> and tricaprilmethylammonium chloride<sup>13</sup> has been claimed as suitable for the photometric determination of molybdenum, after extraction into chloroform. But co-extracted with molybdenum in these methods are rhenium, palladium, platinum and tungsten<sup>19</sup>. Tungsten, can, however, be retained in the aqueous phase by adding tartrate or citrate.

Owing to the serious interference of platinum<sup>20</sup>, solutions for test cannot be prepared in contact with platinum, *e.g.*, by fusion or evaporation in platinum vessels. Certain other metals<sup>21</sup> such as silver, mercury, gold, tellurium and selenium interfere seriously giving insoluble products. A literature survey<sup>19</sup> also shows that other extraction methods, besides the popular thiocyanate methods, are also not selective<sup>19</sup>. These include the extraction of molybdenum complexes of dithiol<sup>22</sup>, benzoin- $\alpha$ -oxime<sup>23-26</sup>, cupferron<sup>27,28</sup>, oxine<sup>29</sup>, acetylacetone<sup>30</sup> and also extraction of molybdenum with alkylphosphates<sup>31</sup> and 2-thenoyltrifluoroacetone<sup>32</sup>.

Considering the above limitations of the thiocyanate method and the serious interferences of the metal ions listed, even in the extraction methods for molybdenum, the present investigation was undertaken to develop a more practicable method for the spectrophotometric determination of molybdenum. This paper reports the selective extraction of molybdenum(V) thiocyanate with *N*-benzylaniline in a mixture of chloroform and isoamyl alcohol from sulphuric acid and hydrochloric acid media. Chloroform alone can be used if the complex is extracted from hydrochloric acid medium. The complex is quantitatively extracted from 1.8 *M* sulphuric acid or 2.8 *M* hydrochloric acid media. Molybdenum(VI) is quantitatively reduced to molybdenum(V) by excess of thiourea or by the addition of copper(II) sulphate and excess of thiourea in 1.8 *M* sulphuric acid or 2.8 *M* hydrochloric acid media. The latter system is essential for the reduction of iron(III) to iron(II). The separation of organic and inorganic phases is very rapid. Most cations and anions do not interfere. Tungsten, niobium and tantalum, in the presence of tartrate or citrate, cause no interference. A large amount of niobium, tantalum and titanium can be tolerated in the presence of fluoride. The method is simple, accurate, rapid and selective. The method was used for the analysis of molybdenum in diverse synthetic mixtures.

## EXPERIMENTAL

### Apparatus

Absorbances were measured with a Bausch and Lomb Spectronic 20, with the accessory 0.5-in diameter test tubes, and a Hilger Uvispek spectrophotometer, with 1.0-cm cells.

### Reagents

Analytical-grade reagents were used without purification. Niobium and tantalum solutions were prepared by fusion of their oxides with potassium pyrosulphate and dissolution of the fused mass in hot tartaric acid. All standard solutions were prepared in double distilled water.

*Molybdenum standard solution.* Dissolve 0.0750 g of dried molybdenum trioxide in 5–10 ml of 0.1 *M* sodium hydroxide, dilute with water to *ca.* 100 ml, make slightly acidic with hydrochloric acid and make up to 500 ml. This solution contains 100  $\mu\text{g}$  Mo ml<sup>-1</sup>. Prepare a dilute solution containing 10  $\mu\text{g}$  Mo ml<sup>-1</sup> in 0.1 *M* hydrochloric acid by suitable dilution of the stock solution.

*N-Benzylaniline (Fluka).* A 9% (w/v) solution in redistilled chloroform (E. Merck) was used.

*Thiourea solution.* Prepare a 10% (w/v) solution by dissolving thiourea (E. Merck) in water and filtering the solution.

*Tin(II) chloride solution.* Prepare a 10% (w/v) solution by dissolving tin(II) chloride dihydrate crystals in ca. 100 ml of 1 M hydrochloric acid. Add a few pieces of tin and filter the solution twice. Prepare a fresh solution weekly.

#### *Procedure*

Transfer an aliquot of solution containing upto 50  $\mu\text{g}$  of molybdenum to a 100-ml separatory funnel. Add 10 ml of 9 M sulphuric acid or 14 ml of 10 M hydrochloric acid and 1.5 ml of aqueous 5% (w/v) copper sulphate pentahydrate solution. Cool the solution to room temperature. Add 15 ml of the thiourea solution and swirl the solution for 1 min. Now add 2 ml of aqueous 50% (w/v) potassium thioxanate solution and dilute to 50 ml with water. Keep the solution for 10 min. Add 10 ml of the extractant mixture containing 2 ml of the N-benzylaniline solution and 8 ml of (6+2) chloroform-isoamyl alcohol mixture. Shake the separatory funnel vigorously for 1 min and allow the aqueous and organic phases to separate. If iron (about 120 mg) is present, add 4 ml of tin(II) chloride solution to the aqueous layer, reshake the separatory funnel for another minute, and allow the phases to separate again. Transfer the organic layer to a 10-ml volumetric flask and make up to 10 ml with chloroform. Filter the extract through a Whatman No. 1 filter-paper and measure the absorbance at 466 nm against a similarly treated blank.

#### RESULTS AND DISCUSSION

##### *Quantitative conversion of molybdate(VI) to oxypentathiocyanatomolybdenum(V) in dilute sulphuric acid and hydrochloric acid media and its extraction*

Molybdenum(VI) was quantitatively reduced to molybdenum(V) in 1.8 M sulphuric acid or 2.8 M hydrochloric acid by excess of thiourea. The addition of copper(II) sulphate before the addition of thiourea accelerated the reduction of molybdenum(VI) to molybdenum(V). The addition of copper(II) sulphate and thiourea was essential for the reduction of iron which generally accompanies molybdenum. The formation of orange-red molybdenum(V) thiocyanate was completed within 10 min in 1–2% potassium thiocyanate solution, although an excess of thiocyanate up to 10% had no deleterious effect on the formation of the complex. The complex was quantitatively extracted with N-benzylaniline into chloroform-isoamyl alcohol mixture (8:2) from 1.8 M sulphuric acid or 2.8 M hydrochloric acid media. Chloroform alone could be used as a solvent when the extraction of the molybdenum(V) thiocyanate complex was achieved from hydrochloric acid medium. N-Benzylaniline thiocyanate crystallised out from sulphuric acid medium, but these crystals were highly soluble in isoamyl alcohol. The separation of organic and aqueous phases was very rapid. The orange-red complex showed maximum absorption at 466 nm, which is characteristic of oxypentathiocyanatomolybdenum(V). The complex was stable and obeyed Beer's law in the range 0–50  $\mu\text{g}$  of molybdenum per ml. The molar absorptivity of the complex was  $16380 \pm 190$ .

##### *Interferences*

Numerous cations and anions were examined by applying the method to fixed amounts of molybdenum in the presence of increasing quantities of the ions being studied. The tolerance limits for various diverse ions (Table I) represent the

TABLE I

DETERMINATION OF 20.0  $\mu\text{g}$  OF MOLYBDENUM IN THE PRESENCE OF DIVERSE IONS

<i>Diverse ion</i>	<i>Amount tolerated (mg)</i>	<i>Diverse ion</i>	<i>Amount tolerated (mg)</i>
Hg(II)	40	Ba(II)	100 <sup>b</sup>
Ag(I)	40	Sr(II)	100 <sup>b</sup>
Au(III)	20	W(VI)	20 <sup>c</sup>
Pd(II)	20	V(V)	25
Pt(IV)	20	Ti(IV)	50 <sup>d</sup>
Rh(III)	20	Th(IV)	50
Ru(III)	20	Nb(V)	20 <sup>d</sup>
Os(VIII)	10	Ta(V)	20 <sup>d</sup>
Ir(IV)	15	Tl(I)	40
Cu(II)	30	Te(IV)	25
Cd(II)	20	Cr(VI)	30
Sb(III)	20 <sup>a</sup>	Cr(III)	30
Bi(III)	20	Sc(III)	25
Pb(II)	40 <sup>a,b</sup>	In(III)	30
Fe(III)	120	Re(VII)	20
Al(III)	50	Ga(III)	15
Be(II)	20 <sup>a</sup>	Nd(III)	20
Zr(IV)	20	Sm(III)	20
Ce(III)	20	Fluoride	100
U(VI)	20	Borate	100
Zn(II)	100	Nitrate	100
Mn(II)	50	Phosphate	3,500
Co(II)	6	Citrate	10,000
Ni(II)	100	Tartrate	10,000
Ca(II)	100 <sup>b</sup>	Oxalate	10,000
Mg(II)	200	Arsenate	100
Sn(II)	200	Silicate	100
		EDTA	150

<sup>a</sup> In presence of tartrate ions.<sup>b</sup> In hydrochloric acid media.<sup>c</sup> In presence of citrate ions.<sup>d</sup> In presence of fluoride ions.

concentration of foreign ions in the presence of which the absorbance of molybdenum(V) thiocyanate complex solution obtained was within  $\pm 1.5\%$  of the expected value.

It is evident that most cations do not interfere at the levels studied. Iron(III) formed an intense red thiocyanate complex which was readily extracted by N-benzyl-aniline. To use the extraction method, iron had to be reduced to iron(II), which does not form coloured complexes with thiocyanate. Although iron(III) was effectively reduced in the presence of copper(II) sulphate and thiourea, on shaking the aqueous



phase with the extractant, the organic layer became slightly coloured owing to the atmospheric oxidation of iron(II). The addition of sufficient tin(II) chloride solution to the aqueous layer and re-shaking of the separated phases, eliminated completely the extracted iron(III) thiocyanate; the molybdenum(V) thiocyanate complex was not affected. This treatment allowed the determination of molybdenum in the presence of large amounts of iron. Niobium, tantalum and tungsten did not interfere in the presence of citrate or tartrate. Palladium(II), platinum(II, IV), silver, gold(III), copper(II), bismuth(III), mercury(II), cadmium, rhodium(III), vanadium(V), tellurium(IV), ruthenium(III), osmium(IV, VIII), chromium(III, VI), titanium(III), manganese(II), indium(III), nickel, thorium(IV), zirconium(IV), uranium(VI), cerium(III, IV) and Be(II) at the milligram level did not interfere. No interference was observed when the mole ratio of cobalt to molybdenum was 500. Selenium(IV) was precipitated as elemental selenium in the presence of thiourea and, therefore, must be removed. Calcium, barium, strontium and lead which form poorly soluble molybdates, could be dissolved in hydrochloric acid and then molybdenum determined by the above method. Lead was kept in solution by the presence of excess of 50% tartaric acid solution. Antimony did not interfere in the presence of tartrate.

Most anions at the milligram level did not interfere. Phosphate, tartrate, citrate, oxalate, chromate, dichromate, arsenate, perchlorate and borate did not cause any interference. A considerable amount of fluoride could be tolerated. This tolerance of fluoride helped to remove the interference of large amounts of uranium, titanium, niobium and thorium. Tungstate and sulphate which produced considerable interference in the method of Wilson and McFarland<sup>13</sup> did not interfere.

#### CONCLUSIONS

The proposed method is simple, rapid, selective and reproducible; it is useful for the determination of molybdenum in the presence of large amounts of associated diverse ions, compared to the conventional thiocyanate method. None of the experimental conditions is highly critical. Palladium, platinum, rhodium, rhenium, gold and tellurium, which interfere in the well known thiocyanate method, do not cause any interference in the proposed method.

#### SUMMARY

N-Benzylaniline in chloroform-isoamyl alcohol mixture is shown to be a selective extraction reagent for molybdenum(V) thiocyanate complex in 1.8 M sulphuric acid or 2.8 M hydrochloric acid media. Few cations interfere. Palladium, platinum, rhodium, gold, rhenium, and tellurium which interfere seriously in the conventional extraction thiocyanate method do not interfere. Phosphate, oxalate, citrate, tartrate, borate, arsenate, dichromate, chromate and vanadate do not interfere. Beer's law is obeyed in the range 0-50  $\mu\text{g Mo ml}^{-1}$ . The molar absorptivity of the extracted orange-red complex is  $16380 \pm 90$ . The method is simple and rapid and effects a clean cut separation.

## RÉSUMÉ

La N-benzylaniline, dissoute dans un mélange chloroforme-alcool isoamylique, constitue un réactif d'extraction sélectif pour le complexe thiocyanate-molybdène(V), en milieu acide sulfurique 1.8 M ou acide chlorhydrique 2.8 M. La plupart des cations ne gênent pas. Palladium, platine, rhodium, or, rhénium et tellure, qui gênaient considérablement lors de la méthode conventionnelle au thiocyanate, n'interfèrent pas dans ce cas. Phosphate, oxalate, citrate, tartrate, borate, arséniate, dichromate, chromate et vanadate ne gênent pas. La loi de Beer s'applique de 0 à 50  $\mu\text{g Mo ml}^{-1}$ . Le coefficient d'extinction molaire du complexe rouge orange est de  $16380 \pm 90$ . Cette méthode est simple et rapide.

## ZUSAMMENFASSUNG

N-Benzylanilin in Chloroform-Isoamylalkohol-Gemisch ist ein selektives Extraktionsreagenz für den Molybdän(V)-Thiocyanat-Komplex in 1.8 M Schwefelsäure oder 2.8 M Salzsäure. Wenige Kationen stören. Palladium, Platin, Rhodium, Gold, Rhenium und Tellur, die bei der konventionellen Thiocyanat-Extraktionsmethode ernsthaft stören, rufen keine Störung hervor. Ebenso wenig stören Phosphat, Oxalat, Citrat, Tartrat, Borat, Arsenat, Dichromat, Chromat und Vanadat. Das Beersche Gesetz ist im Bereich 0–50  $\mu\text{g Mo ml}^{-1}$  erfüllt. Der molare Extinktionskoeffizient des extrahierten orangefarbenen Komplexes ist  $16380 \pm 90$ . Die Methode ist einfach und schnell und bewirkt eine scharfe Abtrennung.

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## SPECTROGRAPHIC MICRODETERMINATION OF REFRACTORY ELEMENTS IN URANIUM

DIRECT SPARK EXCITATION OF A BPHA-CHLOROFORM EXTRACT WITH A SOLUTION TRANSPORT SYSTEM\*

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Uranium compounds are analyzed spectrographically for the refractory elements: Mo, Nb, Ta, Ti, W, Zr, and Hf<sup>1</sup>. The elements are extracted from hydrochloric acid solution by a solution of BPHA (N,N-phenylbenzohydroxamic acid) in chloroform. The extract is evaporated, acid-digested, and ignited. The final residue is dissolved in a mixture of hydrofluoric and hydrochloric acids and excited by means of the rotating disk technique<sup>2</sup>. The ignition step, however, causes the vaporization of some of the volatile metal chelates and also the conversion of some of the extracted species into insoluble oxides. These are serious disadvantages since their effect yields low analytical results.

Johnson<sup>3</sup> reported an analysis for boron with a solution transport system in which an acid solution was fed at a constant rate with a syringe pump through a hollow electrode and excited with a spark source. This solution transport system now has been evaluated and applied for the listed refractory elements in uranium. The direct spark excitation of the extract is an improvement over the rotating disk procedure because the ignition step with its inherent disadvantages—volatilization of metal chelates and formation of insoluble oxides—has been eliminated. The extract is also easier to handle, and the results are more accurate and precise than those obtained with the rotating disk technique.

### EXPERIMENTAL

#### *Apparatus*

Major equipment required includes: a Bausch and Lomb dual-grating spectrograph with a 30,000 line/in grating in the 230.0–310.0 nm range, first order; a B&L illuminator; a NSL SpecPower with cathode oscillograph; a variable speed Sage syringe pump No.237-1; a Zeebac No. 2204 laminar flow Atmo-Jet with ceramic nozzle; a Met Bay No. 1132 M electrode; an Ultra Carbon No. U7-1509 flat-end counter electrode; 5-ml glass Luer-Lok syringes (Fisher No. 14-820); No. 20, Yale stainless

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Luer-Lok needles (Sargeant No. S-79435-G); Teflon tubing of 0.034 in i.d. and 0.012 in wall (Bel-Art No. 21195); and a Burrell shaker with adapters for 125-ml separatory funnels.

### Reagents

All reagents were reagent grade. Argon, nitrogen, oxygen, and dry air were used. *N,N*-Phenylbenzohydroxamic acid (Eastman Organic Chemicals No. 7297) was used as a 0.5 % (w/v) solution in chloroform.

### Standards

All standard stock solutions were  $100 \mu\text{g ml}^{-1}$ , and dilutions were made, as required, in 12 *M* hydrochloric acid.

*Molybdenum*. Dissolve 0.0920 g of SpecPure  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 500 ml of 12 *M* hydrochloric acid.

*Niobium*. Dissolve 0.07153 g of SpecPure  $\text{Nb}_2\text{O}_5$  in 500 ml of 18 *M* sulfuric acid.

*Tantalum*. Fuse 0.06105 g of SpecPure  $\text{Ta}_2\text{O}_5$  with 5 g of potassium hydrogen-sulfate, dissolve in 100 ml of 10% (w/v) tartaric acid in distilled water, and dilute to 500 ml with distilled water.

*Titanium*. Dissolve 0.0500 g of SpecPure titanium sponge in 500 ml of 12 *M* hydrochloric acid.

*Tungsten*. Dissolve 0.0897 g of Mallinckrodt Analytical Reagent Grade  $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  in 500 ml of 12 *M* hydrochloric acid.

*Zirconium*. Fuse 0.06754 g of SpecPure  $\text{ZrO}_2$  with 5 g of potassium hydrogen-sulfate; dissolve in 100 ml of 10% (w/v) tartaric acid in distilled water, and dilute to 500 ml.

*Hafnium*. Fuse 0.05896 g of SpecPure  $\text{HfO}_2$  with 5 g of potassium hydrogen-sulfate; dissolve in 100 ml of 10% (w/v) tartaric acid and dilute to 500 ml.

*Internal standard stock* ( $13.5 \mu\text{g Hf ml}^{-1}$ ). Dilute 67 ml of the hafnium stock solution to 500 ml with 12 *M* hydrochloric acid.

### Recommended procedure

Weigh up to 6 g of uranium in the form of  $\text{U}_3\text{O}_8$ ,  $\text{UO}_2$ ,  $\text{UO}_2(\text{NO}_3)_2$ , or  $\text{UO}_2\text{F}_2$  into a 200-ml platinum dish. Dissolve the sample in 10 ml of 8 *N* nitric acid. Uranyl nitrate or uranyl fluoride can be dissolved in distilled water. Cover uranium dioxide samples during dissolution. Add 10 ml of water and 10 ml of concentrated hydrofluoric acid, and carefully add 15 ml of concentrated sulfuric acid to the dish. Fume the sample to dryness to expel fluoride and nitrate ions. Cool the fumed sample and dissolve the residue in 20 ml of 6*M* hydrochloric acid. Transfer the solution to a 125-ml separatory funnel. Rinse the dish with two 20-ml portions of concentrated hydrochloric acid and combine the rinses with the sample. Add 2 ml ( $27 \mu\text{g}$ ) of the hafnium internal standard solution and mix the sample thoroughly.

Add 20 ml of the 0.5% BPHA-chloroform stock solution to the funnel. Stopper and shake the funnel for 10 sec and then release the pressure. Clamp the stopper in the funnel and place the funnel, upside down, in a plastic bag. Clamp the inverted funnel on the shaker and extract the sample. Contact the sample for 10 min and then allow 10 min for the layers to separate. Drain the lower organic layer into a 50-ml platinum dish. Add 5–10 ml of chloroform to the raffinate to rinse any chloroform extract from

the side of the funnel and the top of the acid layer, and combine with the extract.

Evaporate the extract to about 1 ml under infrared lamps. If the sample is baked, the volatile metal chelates may vaporize. Rinse down the side of the dish with 2–3 ml of chloroform and allow the sample to air-dry. Place 1.8 ml of chloroform in the dish, using an automatic pipette. Cover the dish with a watch glass and gently swirl the solution until all of the residue is dissolved and thoroughly mixed. Draw the sample up into a 5-ml syringe. Eject solution out of the syringe to remove all air from the barrel and needle. Rinse the needle tip with chloroform. Prepare the spectrograph.

Spectrographic conditions:

Analytical gap	3 mm
Fish tail	4.5 mm
Grating	230.0 nm to 310.0 nm, first order
Illuminator	100% transmission
Slit	10 $\mu\text{m}$
Step filter	100%/10%

Power source:

Voltage	195 V a.c.
Capacitance	0.0012 $\mu\text{F}$
Inductance	300 $\mu\text{H}$
Resistance	0 $\Omega$
R.F. current	3.2 A
Spark Power No. 2	
Sparks/half-cycle	22
Auxiliary gap	3 mm
Pre-exposure time	5 sec
Exposure time	2 min

Photographic conditions

Emulsion type	SA-1
Developing time	3 min
Stop time	20 sec
Fix time	1 min

Adjust the power source to deliver 22 sparks/half-cycle with carbon electrodes, before exciting the sample. Re-adjustment of the source during excitation or over a series of 10–12 excitations is not normally necessary.

Place one end of a 15-in length of Teflon tubing into the larger orifice of the No. 1132 electrode. Run the tubing and electrode through the top of the water cooled Atmo-Jet in the arc stand and clamp the electrode in the electrode clip. Adjust the analytical gap to 3 mm, keeping the top of the ceramic nozzle  $\frac{1}{8}$  inch below the top of the capillary electrode. Use an Ultra Carbon No. U7-1509 flat-end counter electrode. Each end can be used for separate analyses.

Connect the loose end of the Teflon tubing to the syringe. Force the sample solution into the tubing up to 2 in from the lower end of the electrode and clamp the syringe on the syringe pump. Set the argon flow rate to 10 l  $\text{min}^{-1}$  and turn on the syringe pump, adjusted to deliver 0.5 ml  $\text{min}^{-1}$ . Begin the excitation when a droplet appears on the top end of the electrode.

Process the photographic plate and determine the densities of the applicable lines. Determine the intensity ratios, and evaluate the results with either working curve plots or working curve plots adapted to a calculating board.

## RESULTS AND DISCUSSION

The effects of inert atmospheres, optical parameters, electrical parameters, and solution flow rates were investigated. The goals were to obtain a spectrum with a high signal-to-background ratio, a background between 85 and 100% transmission in the area of interest (230.0–310.0 nm, first order), and a detection limit of about  $1 \mu\text{g ml}^{-1}$  in chloroform.

### Inert atmosphere

Several sheath gases were investigated as inert atmospheres to determine their effect on the spectrum. Various mixtures of argon, nitrogen, oxygen, and dry air were used for this purpose at flow rates ranging from 4 to  $15 \text{ l min}^{-1}$ . Twenty  $\mu\text{g}$  of tantalum in 60 ml of 10 M hydrochloric acid were extracted into 20 ml of 0.5% BPHA–chloroform. The chloroform was evaporated under infrared lamps, and the residues dissolved in 2 ml of chloroform. These solutions were drawn into syringes and passed through a 3-mm spark gap, using the normal excitation conditions for the rotating disk spark<sup>1</sup>,

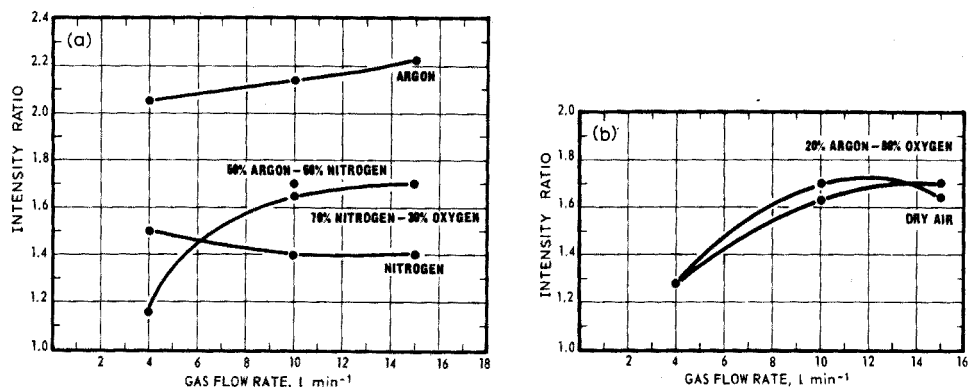


Fig. 1. Effect of atmosphere on intensity ratio of the Ta 206.357-nm line and background.

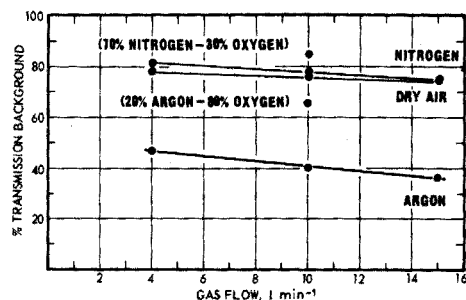


Fig. 2. Effect of atmosphere on transmission background.

at a rate of  $0.2 \text{ ml min}^{-1}$  for 5 min. The effect on the signal-to-background ratios is shown in Fig. 1. Signal-to-background ratios were obtained for the Ta 260.357-nm line and the adjacent background.

Oxygen present at a level greater than 20%, in any mixture, caused excessive sputtering and flaming. An argon atmosphere provided the highest signal-to-background ratios and was chosen for use, even though, as Fig. 2 shows, its characteristic background is the highest. To determine the appropriate flow rates, samples containing  $35 \mu\text{g Hf ml}^{-1}$  and  $5 \mu\text{g Ta ml}^{-1}$  were excited at argon flow rates of  $4\text{--}15 \text{ l min}^{-1}$ . No significant effect on the Ta/Hf intensity ratios was observed. An argon flow rate of  $10 \text{ l min}^{-1}$ , therefore, was chosen for this procedure since a rate greater than  $7 \text{ l min}^{-1}$  is recommended for the operation of the Atmo-Jet.

### Optical conditions

A 100% transmission on the illuminator in conjunction with a  $10\text{-}\mu\text{m}$  slit was used because it minimized background intensities while providing line intensities high enough for use. For making the calibration curves, a 100%/10% split-field lens was chosen to obtain a wide working range for the encountered metal concentrations.

### Electrical parameters

The electrical parameters were evaluated by exciting several BPHA-chloroform extracts containing  $10 \mu\text{g Ta ml}^{-1}$  with a  $10\text{-}\mu\text{m}$  slit and 100% transmission of the illuminator. Capacitance and voltage changes were made to obtain a range of 5 to 40 sparks/half-cycle. Reducing the capacitance and increasing the sparks/half-cycle resulted in lower background intensities and higher signal-to-background ratios, as shown in Fig. 3. Relatively high voltages were required to obtain 30 or 40 sparks/half-cycle and reproducibility was poor. For best reproducibility, 22 sparks/half-cycle was selected as the optimum spark setting.

When the inductance was changed from 50 to  $500 \mu\text{H}$  at 22 sparks/half-cycle, the background intensity decreased. An inductance of  $300 \mu\text{H}$  gave the best results with respect to the background intensity and the signal-to-background ratio.

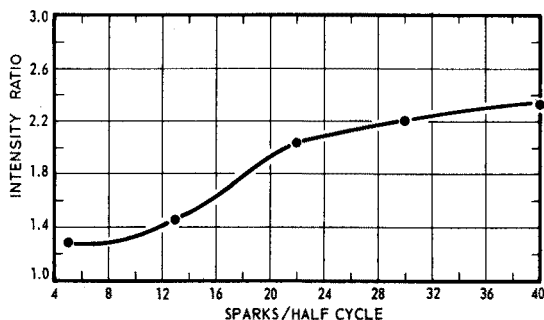


Fig. 3. Effect of variation of sparks/half-cycle on the intensity ratio of the Ta 260.357-nm line and background.

### Solution flow rates

The effect on the spectrum was evaluated for solution flow rates of  $0.2\text{--}0.75 \text{ ml min}^{-1}$ . Argon, at  $4 \text{ l min}^{-1}$ , was used as the inert atmosphere along with a  $10\text{-}\mu\text{m}$



slit and 100% transmission on the illuminator. Samples containing  $5 \mu\text{g Ta ml}^{-1}$  in 2 ml of chloroform were excited, and exposure times were adjusted so that only 1.0 ml of chloroform was excited. The sparks/half-cycle were increased from 22 to 40 at each flow rate.

Figure 4 shows that the background intensity decreased as solution flow rates were increased. This is probably caused by lower excitation temperatures because of the cooling effect of the solution. An increase in solution flow rates also affected the signal-to-background ratios, as shown in Fig. 5. At 22 sparks/half-cycle, a  $0.5 \text{ ml min}^{-1}$  rate produced a spectrum with low background intensity and high signal-to-background ratios. At lower solution flow rates, the background intensity above  $260.0 \text{ nm}$  was too high, and above  $0.5 \text{ ml min}^{-1}$ , the signal-to-background ratios were too low.

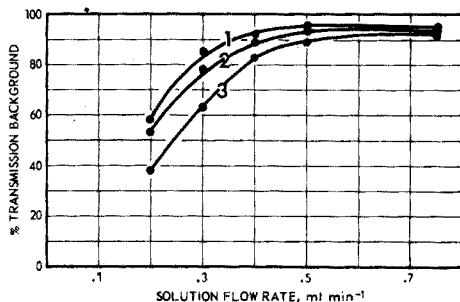


Fig. 4. Effect of solution flow rate on % transmission background. For each half-cycle, curve 1 corresponds to 40 sparks, 2 to 30 sparks and 3 to 22 sparks.

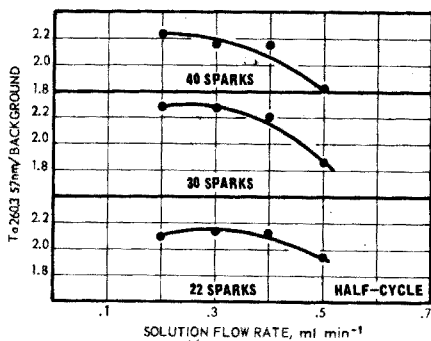


Fig. 5. Effect of solution flow rate on signal/noise ratio.

### Internal standard

The BPHA solution in chloroform extracts Mo, Nb, Ta, Ti, W, Zr, Hf, and V from 10 M hydrochloric acid; therefore, vanadium and hafnium were possibilities for internal standards. Vanadium, however, presents an interference on some of the selected analytical lines, and a high concentration of vanadium is necessary to produce desirable internal standard lines. Maintaining the vanadium in the pentavalent state, which is necessary for its extraction, is also difficult. Hafnium, therefore, was chosen as the internal standard since it is rarely found in our samples and since it is quantitatively extracted<sup>4</sup>, except in the presence of fluoride ion. Its chemical and excitation

properties are similar to those of the refractory elements of interest, and only a small amount of hafnium ( $15 \mu\text{g ml}^{-1}$  of chloroform) is necessary to obtain the exposure index of 40% transmission on the 10% step of the filter. Also, there are several useful hafnium lines such as 264.1406, 277.3357, and 282.0224 nm. The Hf 264.1406-nm line was chosen because of its proximity to most of the analytical lines of interest.

### Working curves

Working curves were established with samples containing 1–1000  $\mu\text{g}$  total of each metal. The samples were prepared and excited as described above. The intensity

TABLE I

STATISTICAL EVALUATION OF WORKING CURVE DATA

Element line	Minimum detection limit ( $\mu\text{g ml}^{-1}$ )	Concentration range ( $\mu\text{g ml}^{-1}$ )	Split field lens step (%)	Intensity ratio (mean)	Determinations	Standard deviation (%)
Mo 253.8455	5.0	5.0	100	0.25	13	17
		50.0	100	2.70	17	8.5
		100.0	10	0.43	12	10
		555.0	10	1.97	4	10
Mo 268.4143	0.5	0.5	100	0.20	10	12.5
		10.0	100	3.26	10	6
		10.0	10	0.33	17	7
		50.0	10	2.62	13	9.5
Nb 259.0944	1.0	1.0	100	0.15	13	7
		10.0	100	1.73	15	4
		30.0	10	0.35	18	6
		100.0	10	1.35	16	8.5
Nb 309.4183	1.0	1.0	10	0.24	13	10.5
		15.0	10	2.97	12	7
Ta 260.3573	4.5	5.0	100	0.36	11	14
		30.0	100	3.34	14	13
		30.0	10	0.31	10	12.5
		100.0	10	1.10	12	5.5
Ta 243.2701	10.0	10.0	100	0.29	12	7.5
		100.0	100	3.32	10	10.5
Ti 288.4107	10.0	10.0	10	0.23	13	5
		100.0	10	1.95	16	6
Ti 308.8025	0.5	0.5	10	0.22	11	8.5
		10.0	10	2.68	16	7
W 239.7091	3.5	5.0	100	0.30	13	9
		100.0	100	3.90	9	6
		100.0	10	0.31	12	7.5
		555.0	10	1.88	4	2
Zr 253.2460	5.0	5.0	100	0.17	9	17
		100.0	100	4.19	12	8
		100.0	10	0.28	10	11.5
		555.0	10	2.03	4	7
Zr 256.8873	0.5	0.5	100	0.24	13	9
		10.0	100	3.98	12	7
		10.0	10	0.40	6	3.5
		50.0	10	2.15	12	4

ratios were calculated from the selected analytical line intensities and the Hf 264.1406-nm line intensity on the 10% step of the filter. All analytical line intensities were background corrected where the background transmission values were 97% or less.

Table I presents the working curve data. The minimum detection limits are given in  $\mu\text{g}$  of metal per ml of chloroform. The concentration ranges shown were investigated, but these are not necessarily the limits on each line. The mean of the intensity ratios is given along with the standard deviation, in percent, for the specified number of determinations at each concentration. The element lines shown were chosen because they are generally free of interferences and because of their usefulness in terms of the concentration ranges obtainable with them. The detection limits are better for all the elements, except tantalum, than those obtained with the rotating disk technique. The standard deviation (average) for all the elements in the 2–10  $\mu\text{g ml}^{-1}$  range obtained with the new technique is about 9%, compared to 12.5% with the rotating disk technique<sup>5</sup>. Figure 6 shows some working curves obtained with the solution transport system.

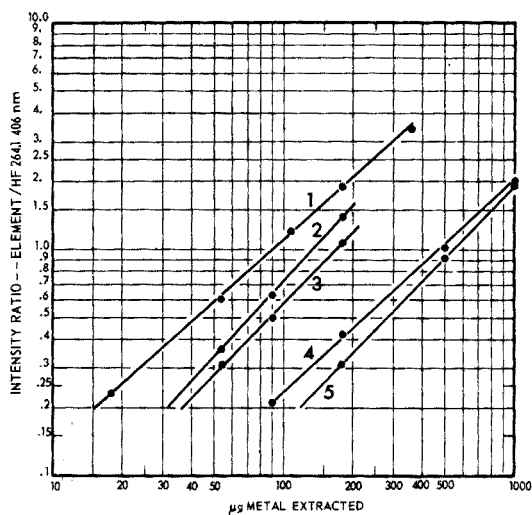


Fig. 6. Analytical working curves. (1) Ti 288.4107 nm; (2) Nb 259.0944 nm; (3) Ta 260.3573 nm; (4) Mo 253.8455 nm; (5) W 239.7091 nm. 10% steps.

### *Analysis of uranium standards*

Uranium metal standards containing Mo, Nb, Ti, and Zr were analyzed by wet-chemical methods, the rotating disk technique, and the solution transport system; the results are given in Table II. The zirconium results obtained by the solution transport method are higher than those obtained by the chemical and rotating disk techniques. A possible explanation for these low results is that all three methods use the BPHA-chloroform extraction; consequently, vaporization of the zirconium chelates could account for zirconium loss. Furthermore, the problem of chelate vaporization was unknown when these samples were analyzed. For the other elements, the results of the solution transport technique agree with chemical analysis, which is generally more accurate than the spectrographic analysis.

TABLE II

ANALYSIS OF URANIUM STANDARDS

Sample	Element	Wet chemical ( $\mu\text{g g}^{-1}$ )	Rotating disk ( $\mu\text{g g}^{-1}$ )	Solution transport ( $\mu\text{g g}^{-1}$ )
1	Mo	148	n.d. <sup>a</sup>	142
	Nb	81	64	76
	Ti	18	27	19
	Zr	68	69	84
2	Mo	154	n.d.	131
	Nb	74	64	83
	Ti	18	40	18
	Zr	66	80	82
3	Mo	157	n.d.	140
	Nb	86	68	79
	Ti	17	23	17
	Zr	70	79	85
4	Mo	148	n.d.	135
	Nb	83	63	82
	Ti	18	23	18
	Zr	67	69	82
5	Mo	152	n.d.	133
	Nb	86	69	80
	Ti	18	24	17
	Zr	80	77	80

<sup>a</sup> Not determined.

## SUMMARY

A procedure for the microdetermination of Mo, Nb, Ta, Ti, W, and Zr in uranium is described. These metals are extracted from uranium in 10 M hydrochloric acid with BPHA (N,N-phenylbenzohydroxamic acid) in chloroform and the extract is spark-excited directly by means of a solution transport system. Hafnium is added to the sample before extraction and acts as a chemical and spectral internal standard. The solution transport system overcomes the problem of low results obtained in the rotating disk technique because of metal chelate vaporization and insoluble oxide formation in the ignition step. The extract is easier to handle and requires one-third less time for a single analysis than other spectrographic procedures for these metals. The detection limits are better than those obtained with the rotating disk method except for tantalum. These limits range from 0.9  $\mu\text{g Ta}$  per g U to 0.1  $\mu\text{g Mo}$  per g U. The standard deviation (average) for all elements in the 2–10  $\mu\text{g}$  range obtained with the solution transport system is about 9%, compared to 12.5% with the rotating disk procedure.

## RÉSUMÉ

On décrit une méthode spectrale avec système de transport de la solution pour le microdosage de Mo, Nb, Ta, Ti, W et Zr dans l'uranium. Ces métaux sont extraits de l'uranium en milieu acide chlorhydrique 10 M, au moyen de BPHA (acide N,N-

phénylbenzohydroxamique) dans le chloroforme. Le hafnium est ajouté à l'échantillon avant l'extraction; il agit comme étalon interne, chimique et spectral. Les limites de détection sont meilleures que celles obtenues à l'aide de la méthode du disque tournant, sauf pour le tantale:  $0.9 \mu\text{g Ta/g U}$  à  $0.1 \mu\text{g Mo/g U}$ .

#### ZUSAMMENFASSUNG

Es wird ein Verfahren für die Mikrobestimmung von Mo, Nb, Ta, Ti, W und Zr in Uran beschrieben. Diese Metalle werden aus 10 M salzsauren Uranlösungen mit BPHA (N,N-Phenylbenzohydroxamsäure) in Chloroform extrahiert. Der Extrakt wird unmittelbar unter Verwendung eines Lösungstransportsystems einer Funkenanregung unterworfen. Vor der Extraktion wird der Probe Hafnium zugesetzt, das als chemischer und spektraler innerer Standard dient. Das Lösungstransportsystem schaltet das Problem der zu niedrigen Ergebnisse aus, die bei der Rädchenmethode durch die Metallchelaterverdampfung und Bildung unlöslicher Oxide bei der Entzündung erhalten werden. Der Extrakt ist leichter zu handhaben und erfordert ein Drittel weniger Zeit für eine einzelne Analyse als andere spektrographische Verfahren für diese Metalle. Mit Ausnahme von Tantal sind die Nachweisgrenzen besser als bei der Rädchenmethode. Sie liegen zwischen  $0.9 \mu\text{g Ta/g U}$  und  $0.1 \mu\text{g Mo/g U}$ . Die mit dem Lösungstransportsystem für alle Elemente im Bereich  $2\text{--}10 \mu\text{g}$  erhaltene Standardabweichung ist (im Mittel) 9% im Vergleich zu 12.5% bei der Rädchenmethode.

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## COMPLEX FORMATION OF LANTHANUM(III) OR CERIUM(III) WITH 3-AMINOMETHYLALIZARIN-N,N-DIACETIC ACID AND FLUORIDE

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Some years ago Belcher *et al.*<sup>1</sup> introduced the first positive colour reaction for fluoride ion, which is based upon the formation of a ternary complex of fluoride with cerium(III), lanthanum(III), or any other suitable rare earth ion, and 3-aminomethylalizarin-N,N-diacetic acid (alizarin complexan, alizarin fluorine blue).

From the use of the method of continuous variations, Leonard and West<sup>2</sup> concluded that the (1:1) cerium(III)-alizarin complexan chelate reacted with one fluoride ion, the latter ion replacing one of the two coordinated water molecules remaining on the cerium atom. However, the curve of continuous variation reproduced by the latter authors exhibits some features which do not seem to be in complete accordance with the conclusions drawn. Firstly, the curve has a maximum, not at the middle, as would be expected from the mole ratio 1:1 given by the authors, but displaced to higher mole fractions of the binary reactant. Secondly, one of the curve branches is not drawn to the end-point; as pointed out by the authors, the extension made a negative intercept on the extinction axis.

Investigations of the composition of the ternary cerium system were also made by Jeffrey and Williams<sup>3</sup>. From a ternary continuous-variations diagram these authors suggested the composition (fluorine)<sub>4</sub>:(cerium)<sub>5</sub>:(alizarin complexan)<sub>4</sub>.

Belcher and West<sup>4</sup> reported that an extended calibration curve for fluoride made a negative intercept on the extinction axis. This observation was confirmed by Hanocq and Molle<sup>5</sup> and by the present authors. However, by preparing and measuring solutions with very low contents of fluoride the calibration curve has been found<sup>6</sup> to approach the origin parabolically.

Leonard and Nagi<sup>7</sup> studied the analytical utility of bimetallic ternary complexes of alizarin complexan.

Laird and Leonard<sup>8</sup> determined the dissociation constants of alizarin complexan.

From the above survey, and from the fact that nothing was found in the literature on the application of the continuous variations method to ternary systems, it appeared that further studies were required.

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## EXPERIMENTAL

*Apparatus*

For absorbance measurements Cary 14 and Zeiss PMQ II spectrophotometers and 0.5-, 1-, 2-, 4- and 5-cm cells were employed.

*Reagents*

The alizarin complexan was obtained from Fluka AG, and the lanthanum(III) oxide (purity 99.9%) and cerium metal (purity > 99.8%) from Koch-Light Laboratories, Ltd. All other chemicals were of reagent-grade quality.

*Preparation and investigations of the ligand*

Preliminary investigations of the ligand indicated that the product was impure\*. The reagent was purified in the following way: 1.0 g of alizarin complexan was suspended in 50 ml of 0.1 M sodium hydroxide solution, undissolved material was separated by filtration on a glass filter crucible, and 0.1 M hydrochloric acid was added dropwise to the filtrate until an orange precipitate was formed. The precipitate was collected on a glass filter crucible, washed with ice water and dried in vacuum over solid potassium hydroxide.

The purity of the preparation was checked by elemental analysis and alkali-metric titration. Analytical results: found 54.1% C, 4.7% H, 3.4% N and 37.8% O; required for  $C_{19}H_{15}O_8N \cdot 2H_2O$ , 54.2% C, 4.5% H, 3.3% N and 38.0% O.

*Standard solutions*

*Alizarin complexan standard solution* ( $5 \cdot 10^{-4}$  M). 0.2105 g of the purified product was suspended in about 30 ml of water, 0.1 M sodium hydroxide solution was added dropwise while stirring until a clear solution was obtained, and 0.1 M hydrochloric acid was then added until the colour changed from violet to red (pH about 6); the solution was finally diluted to 1 l with water. In alkaline solution the ligand was found to be unstable.

*Lanthanum(III) standard solution* ( $10^{-3}$  M). 0.3258 g of the oxide was dissolved in about 10 ml of concentrated hydrochloric acid, and the solution was diluted to 1 l with water.  $5 \cdot 10^{-4}$  M solutions were prepared by dilution.

*Cerium(III) standard solution* ( $10^{-2}$  M). 1.4012 g of the metal was dissolved in about 10 ml of concentrated hydrochloric acid, and the solution was diluted to 1 l with water.  $5 \cdot 10^{-4}$  M solutions were prepared by dilution.

*Fluoride standard solution* ( $5 \cdot 10^{-3}$  M). 0.2099 g of sodium fluoride was dissolved in water and the solution was diluted to 1 l; it was stored in a plastic bottle.  $5 \cdot 10^{-4}$  M solutions were prepared by dilution.

A stock aqueous 1.0 M solution of potassium nitrate was prepared.

Buffer solutions (pH 4.50, 5.50 and 6.50) were prepared from acetic acid and sodium acetate.

*Ionic strength*

During the photometric measurements, the ionic strength was kept relatively

\* In a commercial product used by Laird and Leonard<sup>8</sup>, traces of alizarin were detected.

constant by maintaining a concentration of 0.10 *M* potassium nitrate and low concentrations of ligand, metal and fluoride ion.

#### STUDIES OF THE BINARY SYSTEMS

The complex formation of alizarin complexan with lanthanum(III) or cerium(III) was first studied by recording absorption curves.

The solutions were prepared by pipetting into 100-ml volumetric flasks 10 ml of  $5 \cdot 10^{-4}$  *M* ligand standard solution, 1 ml of buffer solution (pH 4.50, 5.50 or 6.50), 10 ml of inert salt solution and 10 ml of  $5 \cdot 10^{-4}$  *M* lanthanum or cerium standard solution. Water was added to a volume of about 90 ml, and the pH was checked and, if necessary, adjusted by the addition of acid or alkali, before the solutions were finally diluted to volume with water. Blanks containing the proper amounts of ligand, buffer, inert salt and adjusted to the appropriate pH were also prepared.

Figure 1 shows the curves for the lanthanum system; the curves for the cerium system were practically identical.

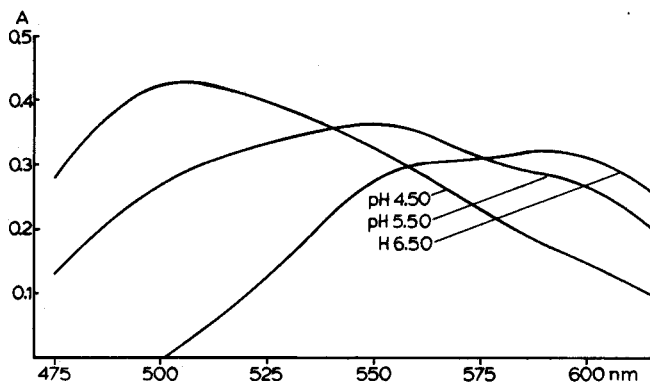


Fig. 1. Absorption curves of the lanthanum(III)-alizarin complexan complex recorded at pH 4.50, 5.50 and 6.50. Concentration of both reactants  $5 \cdot 10^{-5}$  *M*.

At pH 4.50 a binary complex with an absorption maximum at about 505 nm predominated, but the solutions also contained small amounts of another species with an absorption maximum at about 590 nm. At pH 6.50 the latter complex predominated.

Absorption curves of the binary cerium system have been recorded<sup>2,4,5</sup>, but no curves were found for the lanthanum system. Previous studies concentrated upon elucidating the complex formation at pH values about 4, and the species predominating at pH about 6.50 does not seem to have been detected. However, a closer inspection of earlier absorption curves<sup>2,4,5</sup> showed that some of them exhibit a shoulder around 600 nm, this indicating the presence of the second species.

The method of continuous variations was then applied to the binary systems. Solutions for photometric measurements were prepared by pipetting into 100-ml volumetric flasks 1 ml of buffer solution (pH 4.50, 5.50 or 6.50),  $v_1$  ml of  $5 \cdot 10^{-4}$  *M* alizarin complexan solution,  $20 - v_1$  ml of  $5 \cdot 10^{-4}$  *M* lanthanum or cerium standard solution and 10 ml of inert salt solution. After dilution to about 90 ml, the pH was



checked and, if necessary, adjusted, and the solutions were made up to volume with water. Blanks were prepared in a similar way, but without metal ion. The measurements were made at 500 nm.

At pH 4.50 both systems exhibited distinct maxima at the mole fraction 0.5, the curves had no inversions, and the gradients at the end-points had a finite value; these features clearly pointed to the presence of a complex with the composition 1:1.

From the other curves (pH 5.50 and 6.50) no definite conclusions could be drawn. However, all curves had a maximum between mole fractions corresponding to the 1:1 complex and a compound of two metal ions with one ligand molecule. It was assumed that these solutions contained a mixture of the 1:1 complex with species containing two or more metal ions. Unfortunately, it was not possible to find pH conditions under which the unknown complex(es) predominated.

The straight-line method of Asmus<sup>9</sup> was then applied to the lanthanum system. Series of solutions with pH 4.50, 5.50 or 6.50 were prepared; in all series the content of ligand (L) was maintained constant and in excess, while the concentration of lanthanum (La) was varied. Assuming a complex of the form  $La_mL_n$ , the series at pH 4.50 gave the value  $m = 1$ .

The series at the two higher pH values gave no straight lines, this again indicating the existence of mixtures of two or more species.

Because of the difficulties encountered in keeping lanthanum in solution, the method could not be applied to mixtures containing an excess of metal ion.

The method introduced by Klausen<sup>10</sup> was used to calculate the conditional constant of the binary lanthanum complex at pH 4.50. This constant was found to be  $3.6 \cdot 10^4$ .

#### STUDIES OF THE TERNARY SYSTEMS

The study of the ternary systems started by recording series of absorption curves. The solutions were prepared by pipetting into 100-ml volumetric flasks 1 ml of buffer solution (pH 4.50, 5.50 or 6.50), and 10 ml each of  $5 \cdot 10^{-4}$  M standard solutions of lanthanum or cerium, of alizarin complexan and of fluoride; after the addition of inert salt solution, controlling and, if necessary, adjusting the pH, the mixtures were diluted to 100 ml with water. The solutions were measured against blanks prepared in the same way, but without fluoride.

The curves recorded for the two systems were practically identical; those for the lanthanum system are reproduced in Fig. 2.

The absorption curves exhibited two maxima, one—not changing with the pH—at about 575 nm, and the other varying with the pH from 612 nm to 617 nm. The latter maximum is the one normally recommended for the spectrophotometric determination of fluoride. At higher pH the maximum at the higher wavelength became more predominant. It was assumed that in the pH range 4.50–6.50 one ternary complex predominated in solutions containing the three reactants in equimolar amounts.

With regard to the position of the absorption maxima, the present curves for the ternary cerium and lanthanum systems are practically identical with those reproduced in previous papers; the absorption curves for the ternary lanthanum complex have been recorded by Greenhalgh and Riley<sup>11</sup>. The relative height of the two maxima of the cerium complex varies in the different investigations; direct comparison

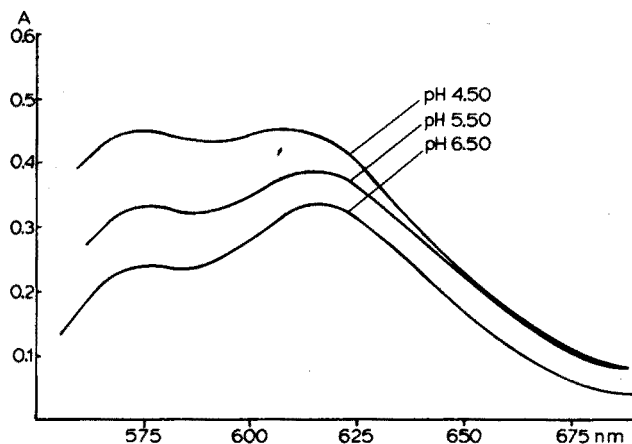


Fig. 2. Absorption curves of the lanthanum(III)-alizarin complexan-fluoride complex at pH 4.50, 5.50 and 6.50. Concentration of the three reactants  $5 \cdot 10^{-5} M$ .

is difficult because some of the curves are not corrected for the absorption of the ligand.

As nothing was found in the literature on the applicability of the method of continuous variations to the study of ternary systems, it was considered of interest to plot some theoretical curves.

Let  $M$ ,  $L$  and  $F$  represent the metal, the alizarin complexan and the fluoride ions, present in the total concentrations  $c_M$ ,  $c_L$  and  $c_F$ , respectively. The complex formation of the binary compound of composition  $ML$  with fluoride is then represented by the equation:



with the conditional stability constant

$$K = \frac{[(ML)_m F_n]}{[(ML)]^m [F]^n}$$

The dissociation of the binary monomer should also be considered, consequently



with the conditional stability constant

$$k = \frac{[ML]}{[M][L]} \quad (3)$$

Let  $c$  represent the constant sum of the concentrations of the reactants  $ML$  and  $F$ . The mole fraction of fluoride ( $x$ ) in the mixtures is then  $x = c_F/c$ .

The values  $y$ ,  $Z_T$  and  $Z_B$  are now introduced, these being defined by:

$$y = [(ML)_m F_n]/c \quad Z_T = [ML]_T/c \quad Z_B = [ML]_B/c$$

the parentheses  $[ML]_T$  and  $[ML]_B$  referring to the concentration of the binary complex in the ternary and binary mixtures, respectively.

The following equations describe the ternary system:

$$Z_T = 1 - x - my + \frac{1}{2} \frac{1}{kc} \left\{ (1 - x - my) \frac{1}{kc} + \frac{1}{4} \left( \frac{1}{kc} \right)^2 \right\}^{\frac{1}{2}} \quad (4)$$

$$Z_T^m (x - ny)^n - \frac{1}{Kc^{m+n-1}} y = 0 \quad (5)$$

$$Z_B = 1 - x + \frac{1}{2} \frac{1}{kc} - \left\{ (1 - x) \frac{1}{kc} + \frac{1}{4} \left( \frac{1}{kc} \right)^2 \right\}^{\frac{1}{2}}$$

the latter equation following from theoretical consideration given elsewhere<sup>10</sup>.

By selecting values for  $m$  and  $n$ ,  $1/kc$  and  $1/(Kc^{m+n-1})$ , it is possible to calculate  $y$ ,  $Z_T$  and  $Z_B$  as functions of  $x$  by means of a computer.

The absorbance difference ( $A$ ) between solutions of the ternary and the binary complexes (both solutions having the same concentration of metal and alizarin complexan) when measured against distilled water can be shown to be

$$A = \varepsilon_T cl \left( y - \frac{\varepsilon_B}{\varepsilon_T} (Z_B - Z_T) \right) \quad (6)$$

$\varepsilon_T$  and  $\varepsilon_B$  representing the molar absorptivities of the ternary complex  $(ML)_m F_n$  and the binary complex  $ML$ , respectively, and  $l$  the path length. Similarly, the equation

$$A_B = \varepsilon_B cl Z_B \quad (7)$$

gives the absorbance of solutions of the binary complex.

When the molar absorptivities are known, eqn. (6) can be used to plot theoretical continuous variations curves for ternary systems.

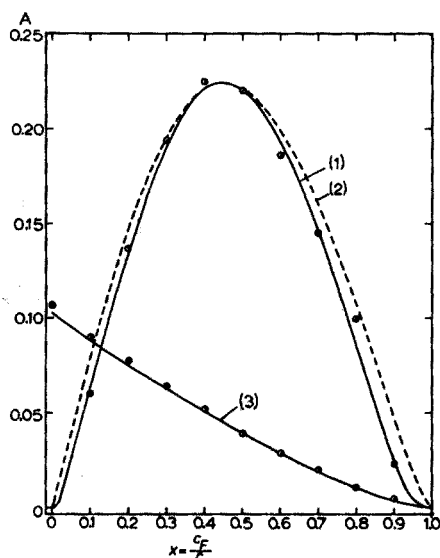


Fig. 3. Continuous variations curves for the lanthanum(III)-alizarin complexan-fluoride system. (1) Theoretical curve for the  $(LaL)_2F_2$  complex; (2) theoretical curve for the  $(LaL)F$  complex; (○) experimental points recorded at pH 4.50; (3) theoretical calibration curve for the blank solutions of the binary  $LaL$  complex.

The method of continuous variations was then applied to the lanthanum-alizarin complexan-fluoride system; however, curves were only recorded for solutions maintained at pH 4.50. The solutions were prepared by pipetting into 100-ml volumetric flasks 1 ml of buffer solution pH 4.50,  $v_1$  ml of  $5 \cdot 10^{-4}$  M alizarin complexan and lanthanum or cerium standard solutions,  $20 - v_1$  ml of  $5 \cdot 10^{-4}$  M fluoride standard solution and 10 ml of inert salt solution. The pH was controlled and the solutions were diluted to 100 ml with water. The measurements were made at 610 nm against two series of blanks containing the proper amounts of ligand, metal, buffer and inert salt solution.

In Fig. 3 the experimental points are given, as well as two theoretical curves, one for the complex  $(ML)_2F_2$ , the other for  $(ML)L$ . By adjusting the values of  $\epsilon_T$  and  $\epsilon_B$ , the two theoretical curves were constructed to pass through the experimental point for  $x = 0.5$ .

The two theoretical curves represent the best possible fit to the experimental points, the fitting procedure being based upon varying the stability constant  $K$  of the ternary complex; the present value of the conditional constant of the binary complex ( $k = 3.6 \cdot 10^4$ ) was used in these calculations.

Supposing a ternary complex of the composition  $(LaL)_2F_2$ , the conditional constant (valid at pH 4.50 and ionic strength 0.1 M  $KNO_3$ ) from the curve of the best fit was calculated to be  $6.3 \cdot 10^{13}$ .

#### DISCUSSION

The present investigation of the complex formation of lanthanum(III) or cerium(III) with alizarin complexan confirmed the results of previous authors<sup>2</sup>, *viz.* that at pH 4.50 the reactants formed the compounds  $LaL$  or  $CeL$ . At the pH values 5.50 and 6.50 both systems seemed to contain mixtures of the 1:1 species with complexes containing two or more metal ions per ligand molecule.

The present work further demonstrated that the ternary complex formed at pH 4.50 between lanthanum(III), alizarin complexan and fluoride cannot be of the simple type  $LaLF$  suggested by other authors, but has the more complex composition  $(LaL)_2F_2$ .

From Fig. 3 it appears that curves of continuous variations of the form  $(ML)_2F_2$  are characterized by having a maximum, not in the middle, but displaced to higher mole fractions of the binary reactant, the displacement increasing with decreasing values of the binary stability constant. Both curve branches exhibit inversions and have horizontal tangents at the end-points.

Figure 3 shows that complexes of the form  $(ML)F$  also have continuous variations curves with a displacement of the maximum; at high mole fractions of fluorine the curve has an inversion and approaches the end-point parabolically, whereas at low mole fractions of fluorine the curve has no inversion and the tangent at the end-point has a finite value. From the latter important and distinguishing feature and from the fact that the theoretical curve for  $m = n = 2$  fits much better to the experimental points than the curve for  $m = n = 1$ , it was concluded that the ternary lanthanum complex has the composition  $(LAL)_2F_2$ .

It is also important to note that the calibration curve in Fig. 3 for the contribution from the binary complex is curved, not straight, as given by Leonard and West<sup>2</sup>.

The experimental points are again plotted with the curve of the best fit calculated from the conditional constant for the binary complex ( $k = 3.6 \cdot 10^4$  at pH 4.50).

The structure of the ternary complex  $(LaL)_2F_2$  may be explained by assuming a ring-formed dimer  $La_2L_2$  to which two fluoride ions are attached. A possible structure is shown in Fig. 4.

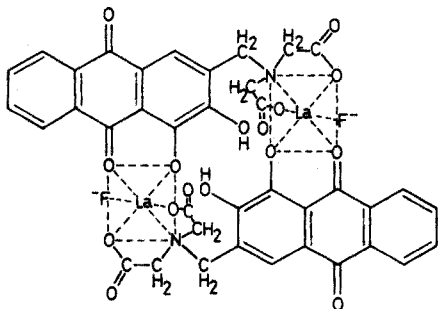


Fig. 4. Structure suggested for the  $(LaL)_2F_2$  complex.

A possible reaction mechanism is that the dimer lanthanum(III)-alizarin complexan chelate reacts with two fluoride ions, each of the two latter ions replacing the single water molecule remaining on the lanthanum atom.

It is interesting to note that Leonard and Nagi<sup>7</sup>, in their study of the complex formation of alizarin complexan with lanthanum(III) and nickel(II) concluded by assuming the presence of the ternary compound  $LaNiL_2$ . These authors did not discuss the structure of this mixed complex which could also be of the present ring-formed type.

#### SUMMARY

The complex formation in aqueous solution of lanthanum(III) or cerium(III) with 3-aminomethylalizarin-N,N-diacetic acid (alizarin complexan, L) and fluoride (F) was studied by spectrophotometry. At pH 4.50 the metals react with alizarin complexan to form the compounds  $LaL$  or  $CeL$ ; the conditional constant of  $LaL$  is  $3.6 \cdot 10^4$ . At pH 5.50 and 6.50 both systems contained a mixture of the 1:1 species with complexes containing two or more metal ions per ligand molecule.

The ternary metal-alizarin complexan-fluoride systems were studied by recording absorption and continuous variations curves, and plotting theoretical curves of continuous variations for various  $ML$ -fluoride complexes. The results showed that the ternary complexes have the composition  $(ML)_2F_2$ , the conditional constant at pH 4.50 being  $6.3 \cdot 10^{13}$  for the lanthanum complex. It is shown theoretically that ternary complexes of the form  $(ML)_2F_2$  and  $(ML)F$  are characterized by having continuous variations curves with maxima displaced to higher mole fractions of the binary reactant. The differences between the curves for the two types are discussed. The ternary complex probably consists of a ring-formed dimer  $La_2L_2$  with one fluorine atom attached to each of the two metal atoms.

## RÉSUMÉ

Une étude spectrophotométrique est effectuée sur la formation de complexes du lanthane(III) ou du cérium(III) avec l'acide amino-3-méthylalizarine-N,N-diacétique (L) et un fluorure (F). Au pH 4.50, il y a formation de composés LaL ou CeL; en présence de fluorure, on obtient des complexes ternaires de composition  $(ML)_2F_2$  avec une constante conditionnelle de  $6.3 \cdot 10^{13}$  pour le complexe de lanthane. Il est probable que le complexe ternaire soit constitué par un dimère  $La_2L_2$  avec un atome de fluor, fixé à chacun des deux atomes métalliques.

## ZUSAMMENFASSUNG

Die Komplexbildung in wässriger Lösung von Lanthan(III) oder Cer(III) mit 3-Aminomethylalizarin-N,N-diessigsäure (Alizarincomplexan, L) und Fluorid (F) wurde spektrophotometrisch untersucht. Bei pH 4.50 reagieren die Metalle mit Alizarincomplexan unter Bildung der Verbindungen LaL oder CeL; die bedingte Bildungskonstante von LaL ist  $3.6 \cdot 10^4$ . Bei pH 5.50 und 6.50 enthielten beide Systeme ein Gemisch der 1:1-Spezies mit Komplexen, in denen zwei oder mehr Metallionen pro Ligandmolekül vorlagen.

Die ternären Metall-Alizarincomplexan-Fluorid-Systeme wurden durch Aufnahme von Absorptionskurven und Kurven der stetigen Veränderung sowie durch Auftragung theoretischer Kurven der stetigen Veränderung für verschiedene ML-Fluorid-Komplexe untersucht. Die Ergebnisse zeigten, dass die ternären Komplexe die Zusammensetzung  $(ML)_2F_2$  haben; bei pH 4.50 ist die bedingte Konstante für den Lanthankomplex  $6.3 \cdot 10^{13}$ . Es wird theoretisch gezeigt, dass ternäre Komplexe der Form  $(ML)_2F_2$  und  $(ML)F$  durch Kurven der stetigen Veränderung gekennzeichnet sind, deren Maxima zu höheren Molenbrüchen des binären Reaktanten verschoben sind. Die Unterschiede zwischen den Kurven der beiden Typen werden diskutiert. Der ternäre Komplex besteht wahrscheinlich aus einem ringförmigen Dimeren  $La_2L_2$  mit einem Fluoratom, das mit jedem der beiden Metallatome verknüpft ist.

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## THE COMPLEX FORMATION OF IRON(III) AND ALUMINIUM(III) WITH 2-HYDROXY-1,3-DIAMINOPROPANE-N,N,N',N'-TETRAACETIC ACID

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Recently, HPDTA (2-hydroxy-1,3-diaminopropane-N,N,N',N'-tetraacetic acid) and its complex formation with several metal ions have received considerable attention<sup>1-13</sup>. The chelates of all the metals so far reported are mononuclear, except for that of lead(II), for which Jokl and Majer<sup>7</sup> proposed a binuclear complex.

For aluminium(III) Smith<sup>1</sup> has reported the value of the stability constant for a 1:1 complex, and Springer *et al.*<sup>9</sup> have investigated the complex formation with iron(III) by spectrophotometric measurements in the ultraviolet region. However, none of these authors has reported binuclear complexes with the metal ions.

The present work was carried out in order to determine the composition and stability constant of complexes with iron(III) and aluminium(III). In this connection a computer program for determining the complexes present in potentiometric pH titrations was elaborated.

### EXPERIMENTAL

#### *Apparatus*

A Beckman Research Model pH-meter equipped with glass and calomel electrodes was used to determine the pH of the solutions. Duplicate runs gave satisfactory reproducibilities. The pH meter was standardized against 0.05 M potassium hydrogenphthalate (pH 4.008 at 25°) and as a secondary buffer 0.01 M borax (pH 9.180 at 25°) was used. The pH measurements were assumed to give the activity of the hydrogen ion according to Bates<sup>14</sup>. pH values were determined in nitric acid solutions of known concentration (ionic strength 0.1 M with KNO<sub>3</sub> and temperature 25°). The activity coefficient,  $f_{H^+}$ , was established as 0.80 according to the equation  $[H^+] = 10^{-pH}/f_{H^+}$ . The activity coefficient was assumed to be constant over the entire pH range used in this study (pH 3-9).

Spectrophotometric measurements were performed with a Zeiss spectrophotometer PMQ II with 5.000-cm cells.

#### *Reagents and standard solutions*

**HPDTA.** This was prepared as described by Smith *et al.*<sup>15</sup>. After a fractional pH crystallization, the product was recrystallized from water and dried in vacuum over calcium chloride. Analysis of the purified product showed that it was sufficiently pure (found: 39.0% C, 8.4% N and 6.1% H; calculated for HPDTA·H<sub>2</sub>O: 38.8% C, 8.2% N and 5.9% H). The molarity of a  $2 \cdot 10^{-3}$  M stock solution (0.3403 g in 500 ml)

was checked by potentiometric titration with standard sodium hydroxide solution. The titrations were performed in presence and in absence of excess calcium(II), giving end-points at 4 and 3 equivalents of base added, respectively.

*Standard aluminium(III) solution.* Super-pure 99.997% aluminium was dissolved in dilute nitric acid. The excess of free acid in this solution was determined by titration of a 1:1 aluminium(III)-EDTA mixture (disodium salt) with sodium hydroxide. The excess of acid is thus equivalent to the added sodium hydroxide minus an amount corresponding to the neutralization of two hydrogen ions per aluminium chelate.

*Standard iron(III) solution.* Reagent-grade iron(III) nitrate was dissolved in water containing nitric acid in order to prevent hydrolysis. The iron concentration was determined gravimetrically, and the excess of free acid was determined as in the aluminium standard solution.

*Standard sodium hydroxide.* A saturated sodium hydroxide solution was diluted with boiled, distilled water and standardized by potentiometric titration against potassium hydrogen iodate. The titration curves showed that the standard solution was practically free of carbonate.

All other chemicals were of reagent grade.

#### *Titration procedure*

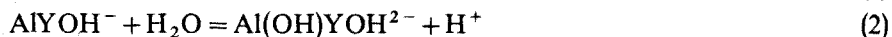
Potentiometric pH titrations of HPDTA in absence and in presence of metal ions were done with sodium hydroxide solution. Titrations of mixtures of metal with HPDTA were done with various amounts of metal, the initial concentration of HPDTA being equal to  $10^{-3}$  M in all the solutions. The initial volumes of all the solutions were 50 ml, and the ionic strength was 0.1 M ( $\text{KNO}_3$ ). The temperature was maintained at  $25^\circ \pm 0.1^\circ$  by using a thermostated titration vessel.

## RESULTS AND DISCUSSION

### *Potentiometric titrations*

Titration curves of HPDTA alone and of mixtures with aluminium(III) and iron(III) both in the ratios 1:1 and 2:1, are plotted in Fig. 1. The volumes of added sodium hydroxide were corrected for the amounts of base corresponding to the neutralization of strong acid in the metal ion solutions.

*The aluminium(III)-HPDTA system.* The titration curve for the mixture aluminium(III)-HPDTA in mole ratio 1:1 (curve 2) shows two inflexions, one at  $a=4$  and the other at  $a=5$ . This is most likely due to the formation of a 1:1 complex  $\text{AlYOH}$ , which subsequently is hydrolyzed to a hydroxo complex  $\text{Al(OH)YOH}$ .



$\text{H}_4\text{YOH}$  denotes HPDTA where OH resembles the hydroxy group in the molecule. The titration curve for the 2:1 mixture of aluminium(III) and HPDTA (curve 4) exhibits two inflexions at  $a=6$  and  $a=7$ . Titration curves of 3:1 mixtures (not shown) were similar but displaced by three equivalents of base. A precipitate ( $\text{Al(OH)}_3$ ) was observed in the latter solutions. These experiments indicate the formation of binuclear chelates, and the following reactions were assumed for the first inflexion ( $a=6$ )



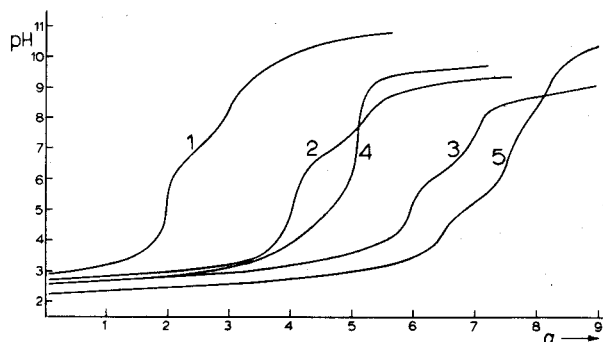
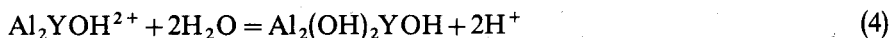
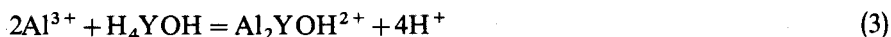


Fig. 1. Potentiometric titration curves.  $10^{-3}$  M HPDTA solutions containing 0.1 M  $\text{KNO}_3$  and: (1) no metal ion; (2)  $10^{-3}$  M Al(III); (3)  $2 \cdot 10^{-3}$  M Al(III); (4)  $10^{-3}$  M Fe(III); (5)  $2 \cdot 10^{-3}$  M Fe(III).  $a$  = moles of NaOH per mole HPDTA.

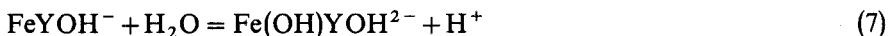
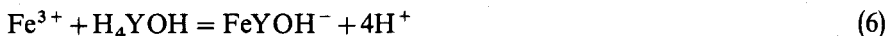


and for the last inflexion ( $a = 7$ )

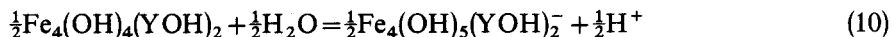
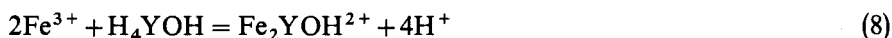


This interpretation involves the formation of hydroxo complexes in rather acidic solution (pH 3.5), a case which has rarely been reported<sup>16</sup>.

*The iron(III)-HPDTA system.* The titration curves for the iron(III)-HPDTA mixtures are rather different from the aluminium(III)-HPDTA curves. The 1:1 titration curve (curve 4) shows only one inflexion at  $a = 5$ . The curve shows, however, an indication of a buffer region from  $a = 4$  to  $a = 5$ . The curve can be explained by assuming the following reactions:



the last reaction corresponding to the buffer region. For the 2:1 mixture (curve 5) three inflexions occurred on the titration curve at  $a = 6\frac{1}{2}$ ,  $7\frac{1}{2}$  and 8. To explain these inflexions it is necessary to consider polynuclear complexes, and hydroxo complexes in acidic medium. The structure of these complexes probably involves hydroxo bridges between the iron ions. The following complex formations can be indicated:



The complex to the right of eqn. (9) can also be formulated as  $\text{Fe}_2(\text{OH})_2\text{YOH}$ .

These three reactions explain the inflexion at  $a = 6\frac{1}{2}$ . The other inflexions can be explained by assuming further formation of hydroxo complexes, ending up with  $\frac{1}{2}\text{Fe}_4(\text{OH})_8(\text{YOH})_2$  ( $=\text{Fe}_2(\text{OH})_4\text{YOH}$ ) at  $a = 8$ . The exact stoichiometry of all these complexes must be considered as uncertain. It was not possible to verify these 2:1

complexes by calculating the stability constants. However, spectrophotometric titrations with the use of an indicator show as mentioned later, the formation of a rather stable iron(III)-HPDPA complex with a mole ratio of 2:1 at pH 2.90. A continuous variations study<sup>17</sup> also indicates 2:1 complexes.

Titration of solutions containing more than two equivalents of iron(III), strangely enough, gave no precipitation until a content higher than 8:1 was used. Several solutions with compositions from 3:1 to 8:1 at pH 5–9 were kept for weeks without any precipitation occurring. Titration curves of the solutions resembled the 2:1 curve displaced by 3 equivalents. Subsequent addition of an iron(III) solution to a HPDPA solution, the pH being kept constant at 6.60 with sodium hydroxide, showed no precipitation until the mole ratio 8:1 was reached. When the same experiment was performed at pH 4.25 or pH 9.00, a precipitate appeared at a 12:1 mole ratio. When sodium hydroxide was added to a 9:1 or 10:1 mixture, a precipitate appeared at about pH 5, but redissolved at about pH 8. All the solutions with an iron(III) content of less than 8:1 were quite stable, and it was not possible to obtain precipitation in them, even when they were stored for months at room temperature, or for weeks at 80°. An infrared spectrum of the dried precipitate showed strong absorption at 1640  $\text{cm}^{-1}$ , corresponding to a carbonyl stretching frequency, thus indicating the precipitation of a HPDPA complex. An adequate explanation to this phenomenon is not easy to give, but it seems most likely that the iron(III) ions add on to the 2:1 (4:2) complex, to form complexes of relatively low stability by hydroxyl ion bridges. The stability is, however, high enough to prevent precipitation of iron(III) hydroxide.

#### Spectrophotometric measurements

In order to establish the mole ratio between metals and ligand in the complexes, a few spectrophotometric titrations were performed. The experimental details were as follows for aluminium(III)-HPDPA<sup>18</sup>. To a series of 50-ml volumetric flasks 5 ml of  $10^{-3}$  M aluminium(III) solution, 20 ml of 0.1 M acetate buffer pH 4.1, 2 ml of  $5 \cdot 10^{-4}$  M chrome azurol S indicator and different volumes of  $10^{-3}$  M HPDPA solution were pipetted. The solutions were diluted to the exact volume, kept in a water-bath at 60° for 15 min, cooled to room temperature and measured in the spectrophotometer. The heating was done in order to obtain stable conditions. The absor-

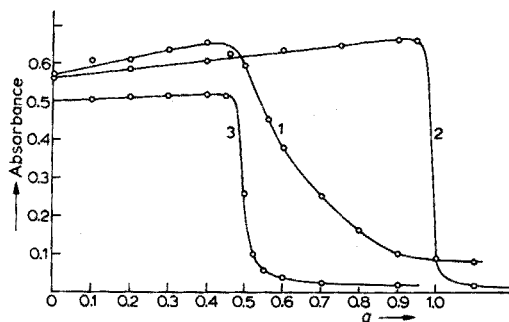


Fig. 2. Absorbance of aluminium(III) and iron(III) solutions containing chrome azurol S as indicator and various amounts of ligand, measured against indicator blank solutions. (1) Al(III)-HPDPA (pH 4.1, wavelength 545 nm); (2) Al(III)-EDTA (pH 4.1, wavelength 545 nm); (3) Fe(III)-HPDPA (pH 2.9, wavelength 570 nm).  $a$  = moles of ligand per mole metal ion.

bances were measured against similar solutions mixed as above but without aluminium. For reference, a similar titration was performed with EDTA as ligand.

In the case of iron(III)-HPDTA, the experiments were carried out in the same way but with different concentrations and pH. The details were<sup>19</sup>: in 50-ml volumetric flasks were placed 2 ml of  $5 \cdot 10^{-3}$  M iron(III) solution, 1 ml of  $5 \cdot 10^{-4}$  M chrome azurol S solution, 5 ml of  $\text{KNO}_3$  solution and different volumes of  $10^{-3}$  M HPDTA solution. After dilution to 48 ml with water, the pH was adjusted to 2.90 with dilute nitric acid or sodium hydroxide. The solutions were diluted to exact volume and the absorbances were measured against blank solutions without iron(III).

Figure 2 shows the three titration curves. With aluminium(III) the difference between HPDTA and EDTA as ligand can be seen. The latter ligand forms a 1:1 complex, whereas HPDTA forms a 2:1 complex which, from the slope of the curve, is not very stable. With iron(III), however, the curve is very steep and demonstrates a 2:1 complex of relatively high stability.

### Stability constants

*Description of the calculations.* In order to verify the assumptions mentioned above on the stoichiometry of the complexes, and to establish values of the corresponding stability constants and protonation constants, theoretical titration curves were calculated, with the computer CDC 3300 at this University. The working principle of the computer programs\* was the same as introduced by Sillén and Ingri<sup>20,21</sup>: on the basis of the suggested complexes, and a corresponding set of chosen equilibrium constants, a theoretical titration curve was calculated. This curve was then compared with the experimental curve by calculating a "root-mean-square" (RMS) error sum. The equilibrium constants were then varied to minimize this error sum. Different complexes were tried, and those which did not lead to further decrease in the RMS error sum were discarded.

The "root-mean-square" error sum used in this work was defined as:

$$U = \left[ \frac{1}{n} \sum (a_{\text{calc}} - a_{\text{exp}})^2 \right]^{\frac{1}{2}}$$

where  $a_{\text{exp}}$  is the amount of added moles of sodium hydroxide per mole of ligand at any pH value on the experimental titration curve,  $a_{\text{calc}}$  is the corresponding calculated value, and  $n$  is the number of experimental points used.

The mixtures of metal ion and ligand are completely defined by the equations:

$$c_s = \alpha[\text{YOH}] + \gamma_{11}[\text{MYOH}] + \gamma_{21}[\text{M}_2\text{YOH}] \quad (11)$$

$$c_M = \sigma[\text{M}] + \gamma_{11}[\text{MYOH}] + 2\gamma_{21}[\text{M}_2\text{YOH}] \quad (12)$$

$$c_s g = \beta[\text{YOH}] - \tau[\text{M}] + \delta_{11}[\text{MYOH}] + \delta_{21}[\text{M}_2\text{YOH}] \quad (13)$$

where  $c_s$  and  $c_M$  are the total concentrations of ligand and metal, respectively, and  $g$  is the average number of moles of protons bound per mole of ligand, *e.g.* "the true degree of neutralization" of Schwarzenbach<sup>22</sup>.

\* The computer programs written by the authors in FORTRAN IV can be used for 1:1 and 2:1 mixtures of metal ions and ligands (up to hexaprotonated ligands), considering 1:1 and 2:1 complexes in both mixtures. Hydrogen and hydroxo complexes can also be considered. On request, a photocopy of the programs can be obtained from the authors.

Here

$$g = N - a_{\text{calc}} + ([\text{OH}] - [\text{H}])/c_s \quad (14)$$

The charge signs are omitted for simplification.  $N$  is the number of protons available for dissociation from the ligand. The side reaction coefficients  $\alpha$ ,  $\beta$ ,  $\sigma$  and  $\tau$  are defined according to Ringbom<sup>23</sup> by the equations:

$$\alpha = [\text{H}]^4/k_1k_2k_3k_4 + [\text{H}]^3/k_2k_3k_4 + [\text{H}]^2/k_3k_4 + [\text{H}]/k_4 + 1$$

$$\beta = 4[\text{H}]^4/k_1k_2k_3k_4 + 3[\text{H}]^3/k_2k_3k_4 + 2[\text{H}]^2/k_3k_4 + [\text{H}]/k_4$$

$$\sigma = 1 + \lambda_{11}/[\text{H}] + \lambda_{12}/[\text{H}]^2 + 2\lambda_{22}[\text{M}]/[\text{H}]^2$$

$$\tau = \lambda_{11}/[\text{H}] + 2\lambda_{12}/[\text{H}]^2 + 2\lambda_{22}[\text{M}]/[\text{H}]^2$$

where  $k_1$ – $k_4$  are the acid dissociation constants of the ligand (here written for a tetra-protonated acid) and  $\lambda_{11}$ ,  $\lambda_{12}$  and  $\lambda_{22}$  are the hydrolytic dissociation constants of the metal ion (here forming the complexes  $\text{MOH}$ ,  $\text{M}(\text{OH})_2$  and  $\text{M}_2(\text{OH})_2$ ). The remaining coefficients  $\gamma_{11}$ ,  $\delta_{11}$ ,  $\gamma_{21}$  and  $\delta_{21}$  take account of the protolytic side reactions of the 1:1 and the 2:1 complexes, respectively. Thus:

$$\gamma_{11} = K_{11}^1 K_{11}^2 [\text{H}]^2 + K_{11}^1 [\text{H}] + 1 + K_{11}^3/[\text{H}] + K_{11}^3 K_{11}^4/[\text{H}]^2 + K_{11}^3 K_{11}^4 K_{11}^5/[\text{H}]^3$$

$$\delta_{11} = 2K_{11}^1 K_{11}^2 [\text{H}]^2 + K_{11}^1 [\text{H}] - K_{11}^3/[\text{H}] - 2K_{11}^3 K_{11}^4/[\text{H}]^2 - 3K_{11}^3 K_{11}^4 K_{11}^5/[\text{H}]^3$$

$$\gamma_{21} = K_{21}^1 K_{21}^2 [\text{H}]^2 + K_{21}^1 [\text{H}] + 1 + K_{21}^3/[\text{H}] + K_{21}^3 K_{21}^4/[\text{H}]^2 + K_{21}^3 K_{21}^4 K_{21}^5/[\text{H}]^3$$

$$\delta_{21} = 2K_{21}^1 K_{21}^2 [\text{H}]^2 + K_{21}^1 [\text{H}] - K_{21}^3/[\text{H}] - 2K_{21}^3 K_{21}^4/[\text{H}]^2 - 3K_{21}^3 K_{21}^4 K_{21}^5/[\text{H}]^3$$

In this work the protolytic constants involved (with superscribed numbering) are

$$K_{11}^1 = \frac{[\text{MHYOH}]}{[\text{MYOH}] \cdot [\text{H}]} \quad K_{21}^1 = \frac{[\text{M}_2\text{HYOH}]}{[\text{M}_2\text{YOH}] \cdot [\text{H}]}$$

$$K_{11}^2 = \frac{[\text{MH}_2\text{YOH}]}{[\text{MHYOH}] \cdot [\text{H}]} \quad K_{21}^2 = \frac{[\text{M}_2\text{H}_2\text{YOH}]}{[\text{M}_2\text{HYOH}] \cdot [\text{H}]}$$

$$K_{11}^3 = \frac{[\text{M}(\text{OH})\text{YOH}] \cdot [\text{H}]}{[\text{MYOH}]} \quad K_{21}^3 = \frac{[\text{M}_2(\text{OH})\text{YOH}] \cdot [\text{H}]}{[\text{M}_2\text{YOH}]}$$

$$K_{11}^4 = \frac{[\text{M}(\text{OH})_2\text{YOH}] \cdot [\text{H}]}{[\text{M}(\text{OH})\text{YOH}]} \quad K_{21}^4 = \frac{[\text{M}_2(\text{OH})_2\text{YOH}] \cdot [\text{H}]}{[\text{M}_2(\text{OH})\text{YOH}]}$$

$$K_{11}^5 = \frac{[\text{M}(\text{OH})_3\text{YOH}] \cdot [\text{H}]}{[\text{M}(\text{OH})_2\text{YOH}]} \quad K_{21}^5 = \frac{[\text{M}_2(\text{OH})_3\text{YOH}] \cdot [\text{H}]}{[\text{M}_2(\text{OH})_2\text{YOH}]}$$

The stability constants for the complexes are defined as:

$$K_{11} = \frac{[\text{MYOH}]}{[\text{M}] \cdot [\text{YOH}]} \quad K_{21} = \frac{[\text{M}_2\text{YOH}]}{[\text{M}]^2[\text{YOH}]}$$

Within this set of complexes defined by their constants it was possible to construct the computer program calculating the theoretical titration curve, and the RMS error sum  $U$  for any value of the constants. From eqns. (11)–(13),  $g$  was calculated and then  $a_{\text{calc}}$  from eqn. (14) at every experimental pH as a function of all the constants. The values of the constants were then varied individually until a minimum in  $U$  was reached, then the next one was varied to give a minimum, etc. If a complex did not lower the minimum of  $U$ , it was considered not to be present in the solution in question, and the constant was put equal to zero.

#### Dissociation constants of HPDTA

The dissociation constants of the ligand were determined from the titration curve (Fig. 1), by a variation procedure similar to the method described above. These constants have been calculated by several authors under slightly varying conditions. The literature data and the present results are listed in Table I.

TABLE I

DISSOCIATION CONSTANTS FOR HPDTA

$pk_1$	$pk_2$	$pk_3$	$pk_4$	Remarks	Ref.
1.55	2.48	6.90	9.48	20°, 0.1 M (KCl)	3
2.0	3.36	6.85	9.70	30°, 0.1 M (KCl)	5
2.3	2.6	7.00	9.60	20°, 0.1 M (KCl)	6
1.78	2.47	6.93	9.44	20°, 0.1 M (KCl)	7
1.8	2.4	6.90	9.41	20°, 0.1 M (KNO <sub>3</sub> )	8
1.6	2.60	6.96	9.49	25°, 0.1 M (KNO <sub>3</sub> )	10
1.85	2.90	7.10	9.70	20°, 0.1 M (KCl)	11
1.6	2.52	6.96	9.48	25°, 0.1 M (KNO <sub>3</sub> )	This work

#### Results for the Al(III)–HPDTA system

The equilibrium constants of Kubota<sup>24</sup> for the reaction of aluminium(III) with water were used ( $\lambda_{11} = 10^{-5}$ ,  $\lambda_{22} = 5.3 \cdot 10^{-7}$ ,  $\lambda_{12}$  was set equal to zero). In all the calculations activity corrections in pH measurements were made, the activity coefficient determined above (experimental section) being used.  $pK_w = 14.00$  was used for the ionic product of water.

The titration curve for the 1:1 mixture was used for the calculations on the 1:1 complexes. The function  $U$  gave the best minimum when the complexes  $\text{AlYOH}$ ,  $\text{Al(OH)YOH}$  and  $\text{Al(OH)}_2\text{YOH}$  were considered. The introduction of hydrogen complexes such as  $\text{AlHYOH}$  or 2:1 complexes in the calculations gave no decrease in the value of  $U$ . It was therefore assumed that neither of these complexes was present in the 1:1 mixtures in measurable concentrations. The results on the equilibrium constants are given in Table II. All the constants not mentioned were found equal to zero (no improvement of  $U$ ).

The calculation of 2:1 complexes was performed with data from the titration of the 2:1 mixture, and the best minimized value of  $U$  was obtained when the curve

was explained by the complexes  $\text{Al}_2\text{YOH}$ ,  $\text{Al}_2(\text{OH})\text{YOH}$ ,  $\text{Al}_2(\text{OH})_2\text{YOH}$  and  $\text{Al}_2(\text{OH})_3\text{YOH}$  (Table II). It must be pointed out here that the value  $\log K_{21}^1 = -1.0$  means that the complex  $\text{Al}_2(\text{OH})\text{YOH}$  is formed in very acidic solution, making the constant uncertain. It is here best to use the combined constant  $\log(K_{21}^1 \cdot K_{21}^2) = -4.55$ , because this constant can be calculated with greater certainty.

TABLE II

THE STABILITY CONSTANTS OF THE HPDTA COMPLEXES OF ALUMINIUM(III) AND IRON(III)

Complex	Defined constant	Al(III)		Fe(III)	
		Log of constant	RMS error	Log of constant	RMS error
MYOH	$K_{11}$	15.2	0.034	17.2	0.025
M(OH)YOH	$K_{11}^3$	-6.70		16.6 <sup>a</sup>	
M(OH) <sub>2</sub> YOH	$K_{21}^4$	-8.70		-4.55	
M <sub>2</sub> YOH	$K_{21}$	16.6	0.051	-9.30	
M <sub>2</sub> (OH)YOH	$K_{11}^3$	-1.0 <sup>b</sup>		21.3 <sup>a</sup>	
M <sub>2</sub> (OH) <sub>2</sub> YOH	$K_{21}^4$	-3.55 <sup>b</sup>			
M <sub>2</sub> (OH) <sub>3</sub> YOH	$K_{21}^5$	-6.20			

<sup>a</sup> Determined by spectrophotometric measurements at pH 2.90 in a continuous variations study<sup>17</sup>.

<sup>b</sup> The combined constants are  $\log(K_{21}^1 \cdot K_{21}^2) = -4.55$ .

*Results for the Fe(III)-HPDTA system.* The data from the titration of the 1:1 mixture were first used for calculation. The constants of Hedström<sup>25</sup> were used for the reaction of iron(III) with water ( $\lambda_{11} = 9.0 \cdot 10^{-4}$ ,  $\lambda_{12} = 4.9 \cdot 10^{-7}$ ,  $\lambda_{22} = 1.19 \cdot 10^{-3}$ ). The best minimum in  $U$  was obtained when the complexes  $\text{FeYOH}$ ,  $\text{Fe(OH)YOH}$  and  $\text{Fe(OH)}_2\text{YOH}$  were considered. Here again, the inclusion of 2:1 complexes such as  $\text{Fe}_2\text{YOH}$  did not affect the results appreciably. When  $\log K_{21}$  was higher than 21.5, the value of  $U$  increased.

When the 2:1 titration curve was used for the iron(III) system, it was possible to calculate a theoretical curve with the assumed 2:1 complexes mentioned above (eqns. 8-10). However, in this case, the function  $U$  did not go through a minimum when  $K_{21}$  was increased, but only approached a low value when  $\log K_{21}$  exceeded 20. This seems to mean that the constant is greater than  $\log K_{21} = 20$ , but the value cannot be established by these measurements because the complexes are too stable. By spectrophotometric measurements<sup>17</sup> the value  $\log K_{21} = 21.3$  was obtained.

The titration curves of all these complexes might also be explained by assuming dissociation of the proton in the hydroxyl group of HPDTA, as pointed out by Jokl and Majer<sup>7</sup> for the lead(II) system. For example, the corresponding 1:1 complexes (eqns. 1-2) will then be  $\text{AlHYO}^-$  and  $\text{AlYO}^{2-}$ , and the corresponding 2:1 complexes (eqns. 3-5)  $\text{Al}_2\text{HYO}^{2+}$ ,  $\text{Al}_2(\text{OH})\text{YO}$  and  $\text{Al}_2(\text{OH})_2\text{YO}^-$ . The difference between the two sets of complexes is stoichiometrically only one molecule of water, and it is not possible to distinguish between them by the present experimental methods. Nevertheless, all the calculations were repeated on the assumption that all of the complexes, or only one of them, were of this kind, both for the aluminium(III) and the iron(III)

systems. As expected, it did not improve the RMS error sum  $U$ . However, the question still remains open, and may be studied by other methods.

## SUMMARY

The complex formation between 2-hydroxy-1,3-diaminopropane- $N,N,N',N'$ -tetraacetic acid (HPDTA) and aluminium(III) and iron(III) was investigated by potentiometric titration and spectrophotometry. The existence of metal ion-HPDTA complexes of the composition 1:1 and 2:1 together with hydroxo complexes of the same species, was shown by computer calculation on the titration curves. The stability constants defining the corresponding complex equilibria are reported. The abnormal behavior of solutions containing excess of iron(III) is described.

## RÉSUMÉ

Une étude est effectuée par titrage potentiométrique et spectrophotométrie sur la formation des complexes entre acide hydroxy-2-diamino-1,3-propane- $N,N,N',N'$ -tétraacétique (HPDTA) et l'aluminium(III) ou le fer(III). L'existence des complexes métal-HPDTA de composition 1:1 et 2:1 est mise en évidence par calcul avec ordinateur sur les courbes de titrage. Les constantes de stabilité sont données. On décrit les anomalies de solutions renfermant un excès de fer(III).

## ZUSAMMENFASSUNG

Die Komplexbildung zwischen 2-Hydroxy-1,3-diaminopropan- $N,N,N',N'$ -tetraessigsäure (HPDTA) und Aluminium(III) sowie Eisen(III) wurde mittels potentiometrischer Titration und Spektrophotometrie untersucht. Durch Auswertung der Titrationskurven mit einem elektronischen Rechner wurde die Existenz von Metallion-HPDTA-Komplexen der Zusammensetzung 1:1 und 2:1 zusammen mit Hydroxokomplexen derselben Spezies nachgewiesen. Die Stabilitätskonstanten der entsprechenden Komplexgleichgewichte werden vorgelegt. Das ungewöhnliche Verhalten von Lösungen mit überschüssigem Eisen(III) wird beschrieben.

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## ACID-BASE STRENGTHS IN *m*-CRESOL

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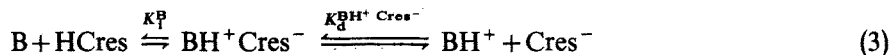
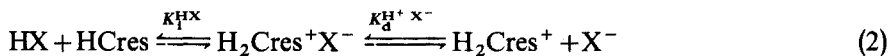
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The strength of an acid in solution depends on properties of the solvent such as its dielectric constant and basicity. In order to study the relation between the acidity of a compound and the basicity of the solvent the simplest way is to compare the acid strengths of a compound in solvents with the same dielectric constants. The dielectric constants of *m*-cresol and pyridine are almost the same, *viz.* 12.29 and 12.3 respectively at 25°. Thus the difference in acid strengths of a compound in the two solvents should be explained by the fact that *m*-cresol has weakly protogenic properties whereas pyridine has weakly protophilic properties. The acid strength in pyridine of a number of compounds is already known<sup>1,2</sup>. From the determination of the acid strength in *m*-cresol for these compounds, the influence of the basicity of the solvent can be found.

If it is assumed that *m*-cresol shows self-dissociation



the dissociation equilibria for acids and bases in this solvent resemble those in acetic acid<sup>3</sup>



For conductimetric and potentiometric studies the overall dissociation equilibria are more important



These overall dissociation constants,  $K_{\text{HX}}$  and  $K_{\text{B}}$ , were determined from conductimetric experiments and from potentiometric titrations.

### EXPERIMENTAL

#### *Chemicals.*

*m*-Cresol. This solvent (Merck, "Zur Synthese") was purified by keeping it in contact with activated molecular sieve 3A (Union Carbide) for 48 h, distillation at

200° under nitrogen and again drying over molecular sieve for 48 h. Solutions with this *m*-cresol were prepared under dried nitrogen. The water content of the solutions prepared in this way was below 0.01% (Karl Fischer titration).

**Acids.** Solutions of hydriodic, hydrobromic and hydrochloric acids were prepared by bubbling the dry gases (Baker) through *m*-cresol. Picric acid (Merck), 2,4-dinitrobenzenesulfonic acid (Eastman Kodak), benzenesulfonic acid (Riedel de Haan), benzoic acid (Merck), acetic acid (Merck), and iodoacetic acid (Merck) were used as received (reagent grade). 2,4,6-Trinitrobenzenesulfonic acid (K & K) was recrystallized from alcohol/ether before use.

**Bases.** Aniline (Merck, reagent grade),  $\alpha$ -naphthylamine (Merck, reagent grade), strychnine (Merck, reagent grade), morpholine (Merck, reagent grade), butylamine (Fluka, reagent grade), triethylamine (Koch-Light, reagent grade), dimethylaminoazobenzene (Merck, indicator grade) and methyl orange (Merck, indicator grade) were used as received.

**Salts.** The salts of tetramethylguanidine (TMG) with various acids were prepared by neutralizing the tetramethylguanidine in ethanol with the acid and recrystallizing the product that was formed twice from ethanol/ether.

In some cases the purity of the salt was checked by determination of the nitrogen-, sulfur- or chloride-content. The results are given below:

TMG-hydrochloric acid, m.p. 208° : %Cl 23.45 theor., 23.53 found ; %N 27.72 theor., 27.86 found.

TMG-benzenesulfonic acid, m.p. 145° : %S 11.61 theor., 11.80 found ; %N 15.38 theor., 14.59 found.

TMG-picric acid, m.p. 130° : %N 24.41 theor., 24.45 found.

Morpholine-2,4-dinitrobenzenesulfonic acid, m.p. 260° : %S 9.56 theor., 9.45 found ; %N 12.53 theor., 12.39 found.

TMG-hydrobromic acid, m.p. 188° ; TMG-2,4-dinitrobenzenesulfonic acid, m.p. 145°.

### Apparatus

In the conductimetric experiments a Radiometer conductivity cell type CDC 114 was used in combination with the Radiometer conductivity meter type CDM 2<sup>d</sup>. The conductivity measurements were carried out at  $20 \pm 0.1^\circ$ . The cell constant was determined to be 0.539 cm with freshly prepared potassium chloride solutions.

For the potentiometric titrations a Radiometer glass electrode, type G2222C was used. An Ag/AgCl electrode filled with a saturated solution of tetramethylammonium chloride in *m*-cresol was used as a reference electrode. When not in use the glass electrode was stored in an aqueous buffer pH 7. The potentiometric titration curves were recorded with a Radiometer titration assembly consisting of recorder SBRc, pH meter PHM26 and titrator TT111. Titration curves were reproducible within  $\pm 5$  mV.

## RESULTS

### Conductivity measurements

The specific conductivities of acids, bases and salts were determined in *m*-cresol for dilution series of these compounds. From these measurements overall

TABLE I  
CONDUCTIVITY MEASUREMENTS IN *m*-CRESOL<sup>a</sup>

2,4-Dinitrobenzenesulfonic acid		Tetramethylguanidine		Hydrochloric acid		TMG-2,4-dinitrobenzenesulfonic acid		Morpholine	
Conc. 10 <sup>3</sup>	$\Lambda$	Conc. 10 <sup>3</sup>	$\Lambda$	Conc. 10 <sup>3</sup>	$\Lambda$	Conc. 10 <sup>3</sup>	$\Lambda$	Conc. 10 <sup>3</sup>	$\Lambda$
0.100	835	0.0916	4960	0.657	127	0.100	3060	1.38	87.1
0.200	788	0.183	4110	1.31	92	0.200	2740	2.76	63.9
0.300	772	0.274	3690	1.97	71	0.300	2440	4.13	51.5
0.400	742	0.366	3370	2.63	53	0.400	2200	5.51	45.4
0.500	724	0.458	3180	3.29	48	0.500	2060	6.89	41.9
0.700	649	0.549	3060	3.94	45	0.600	2020	8.27	37.1
1.00	603	0.732	2720	5.26	37	0.800	1770	11.0	34.5
2.00	468	0.916	2560	6.57	32	1.00	1640	13.8	33.0
3.00	411	1.83	1830	13.1	29	2.00	1300	27.6	21.9
4.00	369	2.74	1620	19.7	21	3.00	1150	41.3	18.2
5.00	343	3.66	1460	26.3	18	4.00	1030	55.1	15.6
6.00	323	4.58	1350	32.9	18	5.00	970	68.9	14.1
7.00	306	5.49	1250	39.4	16	6.00	924	82.7	13.0
10.0	280	9.16	1050	52.6	21	8.00	810	110	11.1
20.0	230	18.3	931	65.7	16	10.0	723	138	10.2
30.0	208	27.5	850	$A_0$	3550 <sup>b</sup>	$A_0$	4850	$A_0$	5800 <sup>b</sup>
40.0	197	36.6	851	$K_{HX}$	$3.8 \cdot 10^{-7}$	$K_{BH^+X^-}$	$1.0 \cdot 10^{-4}$	$K_B$	$2.8 \cdot 10^{-7}$
50.0	200	45.8	850						
60.0	191	54.9	816						
70.0	193	73.2	790						
80.0	187	91.6	753						
$A_0$	1460	$A_0$	9400						
$K_{HX}$	$1.3 \cdot 10^{-4}$	$K_B$	$5.7 \cdot 10^{-5}$						

<sup>a</sup> Concs. in mol. l<sup>-1</sup>;  $\Lambda$  in ohm<sup>-1</sup>. cm<sup>2</sup>. eq<sup>-1</sup>. 10<sup>3</sup>.

<sup>b</sup>  $A_0$  calculated from eqn. (6).

dissociation constants in *m*-cresol of the compounds were calculated by the Fuoss and Kraus method<sup>4</sup>. In the calculations the value 12.5 for the dielectric constant<sup>5</sup> and the value 0.208 P for the viscosity<sup>6</sup> of *m*-cresol were used.

For various compounds the equivalent conductance became constant at higher concentrations. This can be explained by the formation of triple ions<sup>7</sup>. The formation constants of these triple ions were estimated for a number of acids by the method given by French and Roe<sup>8</sup>. In the calculations of the dissociation constants of benzenesulfonic acid and hydrochloric acid, it was necessary to calculate the equivalent conductivity of these compounds at zero concentration from the formula:

$$(A_0)_{\text{HX}} = (A_0)_{\substack{\text{2,4-dinitro-} \\ \text{benzene-} \\ \text{sulfonic} \\ \text{acid}}} - (A_0)_{\substack{\text{TMG-2,4-} \\ \text{dinitro-} \\ \text{benzene-} \\ \text{sulfonic} \\ \text{acid}}} + (A_0)_{\text{TMGHX}} \quad (6)$$

A typical part of the experimental and calculated data is given in Table I.

Table II gives the collected dissociation constants in *m*-cresol determined by conductivity measurements. The triple ion formation constants  $K_{\text{HX}_2^-}$  are given in Table III for a number of acids.

TABLE II

DISSOCIATION CONSTANTS IN *m*-CRESOL DETERMINED CONDUCTIMETRICALLY

Compound	Dissoc. const. <sup>a</sup>	Compound	Dissoc. const.
2,4-Dinitrobenzenesulfonic acid	$1.3 \cdot 10^{-4}$	<i>n</i> -Butylamine	$1.5 \cdot 10^{-5}$
Hydrobromic acid	$4.4 \cdot 10^{-5}$	Morpholine	$2.8 \cdot 10^{-7}$
Hydriodic acid	$4.1 \cdot 10^{-5}$	TMG-benz. sulf. acid	$2.7 \cdot 10^{-5}$
Benzenesulfonic acid	$5.5 \cdot 10^{-7}$	TMG-2,4-dinitrobenz. sulf. acid	$1.0 \cdot 10^{-4}$
Hydrochloric acid	$3.8 \cdot 10^{-7}$	TMG-picric acid	$1.7 \cdot 10^{-4}$
2,4,6-Trinitrobenzenesulfonic acid	$2.6 \cdot 10^{-4}$	TMG-hydrochloric acid	$3.7 \cdot 10^{-5}$
Tetramethylguanidine	$5.7 \cdot 10^{-5}$	TMG-hydrobr. acid	$3.7 \cdot 10^{-5}$
Triethylamine	$3.0 \cdot 10^{-5}$	Morpholine-2,4-dinitrobenz. sulf. acid	$8.6 \cdot 10^{-5}$

<sup>a</sup> In mol · l<sup>-1</sup>.

TABLE III

TRIPLE ION FORMATION CONSTANTS  $K_{\text{HX}_2^-}$  DETERMINED FROM CONDUCTIVITY MEASUREMENTS

Compound	$K_{\text{HX}_2^-}$
2,4-Dinitrobenzenesulfonic acid	$1 \cdot 10^3$
Hydrobromic acid	$5 \cdot 10^2$
Hydriodic acid	$3 \cdot 10^2$
2,4,6-Trinitrobenzenesulfonic acid	$3 \cdot 10^3$

<sup>a</sup> In mol<sup>-1</sup> · l.

### Potentiometric titrations

The curves of the potentiometric titrations of an acid HX with a base B in *m*-

cresol could be explained, if it is assumed that besides acid-dissociation (eqn. 4), base-dissociation (eqn. 5) and self-dissociation (eqn. 1), the following equilibria also occur.



The assumption of the formation of  $\text{HX}_2^-$ , necessary for the explanation of the titration curves, is in agreement with the conductimetric results.

*Calibration of the glass electrode.* The curve for the titration of hydrobromic acid with tetramethylguanidine in *m*-cresol was calculated up to about the equivalence point by the method described earlier<sup>1</sup>. In this calculation the values of  $K_{\text{HX}}$ ,  $K_{\text{HX}_2^-}$ ,  $K_{\text{B}}$  and  $K_{\text{BH}^+ \text{X}^-}$  determined from the conductivity measurements were used.

From the formula

$$E_{\text{mV}} = E_0 - 59 \text{ pH} \quad (9)$$

with

$$\text{pH} = -\log a_{(\text{H}_2\text{Cres}^+)} \quad (10)$$

for the behaviour of the glass electrode, the value of  $E_0$  was determined from the calculated and experimental curve of this titration. The results are given in Table IV.

*Determination of the self-dissociation constant of m-cresol.* The self-dissociation constant of *m*-cresol,  $K_s$ , was determined from the part after the equivalence point of

TABLE IV

CALIBRATION OF THE GLASS ELECTRODE WITH THE TITRATION OF 4.00 ml OF 0.0391 *N* HYDROBROMIC ACID WITH 0.1004 *N* TETRAMETHYLGUANIDINE

ml TMG	pH calculated	mV	$E_0$ calculated (mV)
0.125	2.40	846	987
0.250	2.57	831	973
0.375	2.59	826	976
0.500	2.63	821	976
0.625	2.72	811	972
0.750	2.82	801	967
0.875	2.94	796	970
1.000	3.08	776	959
1.050	3.14	771	956
1.125	3.25	771	964
1.175	3.33	766	963
1.250	3.47	756	961
1.325	3.65	746	961
1.375	3.80	741	965
1.400	3.88	731	960
1.425	3.98	726	961
1.450	4.10	721	963
1.475	4.25	716	967
1.500	4.44	701	963
	Mean value of $E_0$		966

the curve of the titration of hydrobromic acid with tetramethylguanidine. Then the titration curve was calculated with various values of  $K_s$  (Fig. 1). The value  $2 \cdot 10^{-19}$  gave the best fit between calculated and experimental titration curve.

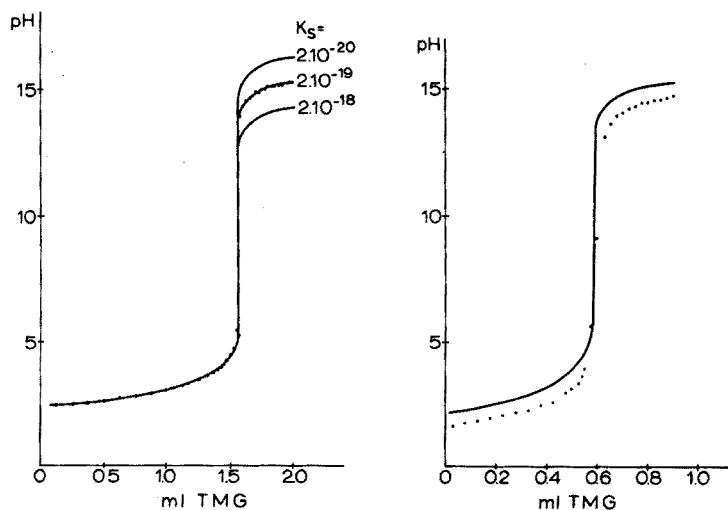


Fig. 1. Titration of 4.00 ml of 0.0391 *N* hydrobromic acid with 0.1004 *N* tetramethylguanidine in *m*-cresol. (.....) Experimental curve; (—) calculated curve.

Fig. 2. Titration of 3.00 ml of 0.0213 *N* hydriodic acid with 0.1072 *N* tetramethylguanidine. (.....) Experimental curve; (—) calculated curve.

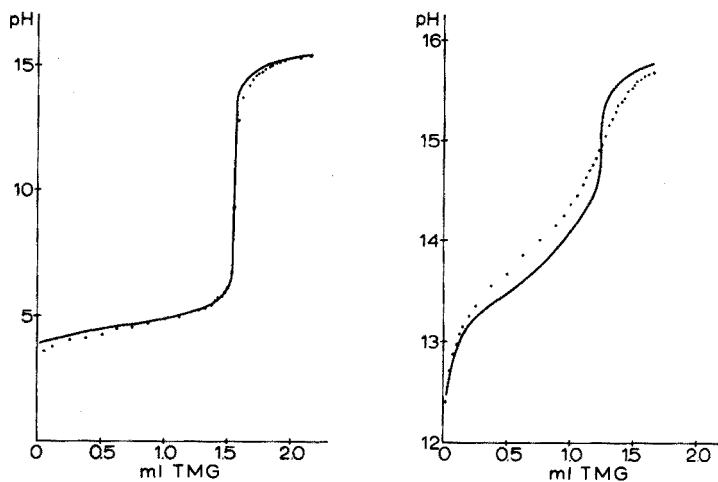


Fig. 3. Titration of 4.00 ml of 0.0250 *N* benzenesulfonic acid with 0.0645 *N* tetramethylguanidine. (.....) Experimental curve; (—) calculated curve.

Fig. 4. Titration of 2.0 ml of 0.0720 *N* benzoic acid with 0.1164 *N* tetramethylguanidine. (.....) Experimental curve; (—) calculated curve.

TABLE V

ACID-DISSOCIATION CONSTANTS AND TRIPLE ION FORMATION CONSTANTS FROM POTENTIOMETRIC TITRATIONS

Compound	$K_{\text{HX}}$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$K_{\text{HX}_2^-}$ ( $\text{l}\cdot\text{mol}^{-1}$ )
2,4,6-Trinitrobenzenesulfonic acid	$10^{-5}$	$10^3$
2,4-Dinitrobenzenesulfonic acid	$10^{-4}$	$10^3$
Hydriodic acid	$10^{-4}$	$10^4$
Benzenesulfonic acid	$10^{-6}$	$10^2$
Hydrochloric acid	$10^{-6}$	$10^3$
Picric acid	$10^{-12}$	$10^2$
Iodoacetic acid	$10^{-13}$	—
Benzoic acid	$10^{-15}$	—
Acetic acid	$10^{-16}$	—

*Potentiometric determination of dissociation constants of acids and bases.* The curves of the potentiometric titrations of various acids with tetramethylguanidine were determined with a calibrated glass electrode. From these curves the dissociation constants of the acids ( $K_{\text{HX}}$ ) and the formation constants of  $\text{HX}_2^-$  ( $K_{\text{HX}_2^-}$ ) were found in the following way. The known values of  $K_{\text{B}}$ ,  $K_{\text{s}}$ ,  $K_{\text{BH}^+\text{X}^-}$  and estimated values of  $K_{\text{HX}}$  and  $K_{\text{HX}_2^-}$  were applied in equilibria (1), (4), (5), (7) and (8), in order to calculate the titration curves. In the cases where  $K_{\text{BH}^+\text{X}^-}$  was not known from conductivity measurements, a value of  $10^{-4}$  was used. The estimated values of  $K_{\text{HX}}$  and  $K_{\text{HX}_2^-}$  were changed by one pK-unit at a time until the best fit between calculated and experimental titration curve occurred. Some typical examples of the titration curves are given in Figs. 2, 3 and 4. The results are summarized in Table V.

The dissociation constants of several bases were determined from the curves of the titrations of the bases with 2,4-dinitrobenzenesulfonic acid. Here the curves

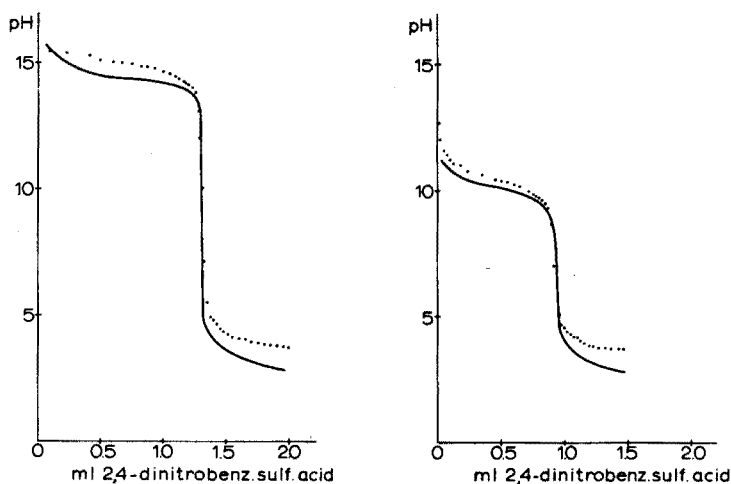


Fig. 5. Titration of 3.0 ml of 0.0439 *N* *n*-butylamine with 0.100 *N* 2,4-dinitrobenzenesulfonic acid. (.....) Experimental curve; (—) calculated curve.

Fig. 6. Titration of 2 ml of 0.04588 *N* aniline with 0.100 *N* 2,4-dinitrobenzenesulfonic acid. (.....) Experimental curve; (—) calculated curve.

were also calculated with the equilibria (1), (4), (5), (7) and (8). In the calculations, an estimated value of  $K_B$  was used, while for the other equilibrium constants the earlier determined values were used. Some typical titration curves of bases are represented in Figs. 5 and 6. The results are given in Table VI.

TABLE VI

BASE-DISSOCIATION CONSTANTS FROM POTENTIOMETRIC TITRATIONS

Compound	$K_B$
Triethylamine	$7 \cdot 10^{-5}$
<i>n</i> -Butylamine	$2 \cdot 10^{-5}$
Morpholine	$2 \cdot 10^{-6}$
Strychnine	$2 \cdot 10^{-6}$
Aniline	$2 \cdot 10^{-10}$
$\alpha$ -Naphthylamine	$2 \cdot 10^{-10}$
Methyl orange	$2 \cdot 10^{-8}$
Dimethylaminoazobenzene	$2 \cdot 10^{-8}$

## DISCUSSION

In the conductivity measurements as well as the potentiometric titrations, it is necessary to assume the formation of the complex  $HX_2^-$  to explain the experimental results. It is improbable that in *m*-cresol  $HX_2^-$  is a homoconjugate because this medium is a good hydrogen bond donor<sup>9</sup>. A triple ion of the form  $X^-H^+X^-$  is more probable. The fact that the formation constant  $K_{HX_2^-}$  of these complexes is large for those compounds which are completely ionized in *m*-cresol (determined spectrophotometrically for 2,4-dinitrobenzenesulfonic acid) is in agreement with this.

In cases in which dissociation constants were determined from potentiometric titrations as well as from conductivity measurements, the results are in agreement with each other (Table VII).

As pyridine and *m*-cresol have almost equal dielectric constants, the difference between the  $pK_a$  value in *m*-cresol and the  $pK_a$  value in pyridine for different acids

TABLE VII

COMPARISON OF  $pK$  VALUES FROM CONDUCTIVITY MEASUREMENTS AND POTENTIOMETRIC TITRATIONS

Compound	$pK_{HX}/pK_B$ titr.	$pK_{HX}/pK_B$ cond.	$K_{HX_2^-}$ titr.	$K_{HX_2^-}$ cond.
2,4,6-Trinitrobenzenesulfonic acid	5	3.6	$10^3$	$3 \cdot 10^3$
2,4-Dinitrobenzenesulfonic acid	4	3.9	$10^3$	$1 \cdot 10^3$
Hydriodic acid	4	4.4	$10^4$	$3 \cdot 10^2$
Hydrobromic acid	4.4	4.4	$5 \cdot 10^2$	$5 \cdot 10^2$
Benzenesulfonic acid	6	6.3	$10^2$	
Hydrochloric acid	6	6.4	$10^3$	
Morpholine	5.7	6.6		
<i>n</i> -Butylamine	4.7	4.8		
Triethylamine	4.2	4.5		



TABLE VIII

COMPARISON OF  $pK_a$  VALUES IN *m*-CRESOL, PYRIDINE AND WATER

Compound	$pK_a$ (cresol)	$pK_a$ (pyr)	$pK_a$ ( $H_2O$ )	$pK_a$ (cresol) - $pK_a$ (pyr)
2,4,6-Trinitrobenzene-sulfonic acid	3.6 <sup>a</sup>		—	
2,4-Dinitrobenzene-sulfonic acid	3.9 <sup>a</sup>		—	
Hydriodic acid	4.4 <sup>a</sup>	3.4 <sup>b</sup>	—	1.0
Hydrobromic acid	4.4 <sup>a</sup>	4.4 <sup>b</sup>	—	0.0
Benzenesulfonic acid	6.3 <sup>a</sup>		—	
Hydrochloric acid	6.4 <sup>a</sup>	5.7 <sup>b</sup>	—	0.7
Picric acid	12 <sup>c</sup>	3.0	0.4	9.0
Iodoacetic acid	13 <sup>c</sup>		3.1	
Benzoic acid	15 <sup>c</sup>	11	4.2	4
Acetic acid	16 <sup>c</sup>	12	4.8	4
Dimethylaminoazobenzene $H^+$	11 <sup>c</sup>		3.5	
Methyl orange $H^+$	11 <sup>c</sup>		3.8	
$\alpha$ -Naphthylamine $H^+$	9 <sup>c</sup>		3.9	
Aniline $H^+$	9 <sup>c</sup>		4.6	
Strychnine $H^+$	13 <sup>c</sup>		8.0	
Morpholine $H^+$	12.1 <sup>a</sup>	3.5	9.6	8.6
<i>n</i> -Butylamine $H^+$	13.9 <sup>a</sup>	5.5	10.6	8.4
Triethylamine $H^+$	14.2 <sup>a</sup>	3.8	10.8	10.4
TMG $H^+$	14.5 <sup>a</sup>	9.6	12.3	4.9

<sup>a</sup> From conductivity.<sup>b</sup> Reference 10.<sup>c</sup> From titrimetric experiment.

should be independent of charge type of the acid. For the ammonium-type acids and picric acid, this turned out to be so (Table VIII).

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## SUMMARY

For various acids and bases dissociation constants were determined conductimetrically in *m*-cresol. A glass electrode was calibrated by means of some compounds with dissociation constants known from conductivity measurements. Potentiometric titrations with this calibrated glass electrode gave dissociation constants of some other acids and bases in *m*-cresol. The value  $2 \cdot 10^{-19}$  was found for the self-dissociation constant of *m*-cresol. From the difference  $pK_a$  (cresol) -  $pK_a$  (pyridine) for those compounds having acid or base strengths which are not levelled either in pyridine or *m*-cresol, it was found that the solvent *m*-cresol has a basicity about 8 pK units less than that of pyridine.

## RÉSUMÉ

On a déterminé les constantes de dissociation de divers acides et bases par conductométrie dans le *m*-crésol. Au moyen de quelques composés ayant une constante de dissociation mesurée par voie conductométrique une électrode de verre a été calibrée. Des titrages potentiométriques à l'aide de cette électrode ont donné les constantes de dissociation d'autres acides et bases en *m*-crésol. Ainsi on a obtenu une valeur de  $2 \cdot 10^{-19}$  pour l'autodissociation du *m*-crésol. En partant de la différence  $pK_a(\text{crésol}) - pK_a(\text{pyridine})$  pour les composés ayant des acidités ou basicités qui ne sont nivellées ni en pyridine, ni en *m*-crésol, on a trouvé que la basicité du *m*-crésol est d'environ 8 unités de  $pK$  inférieure à celle de la pyridine.

## ZUSAMMENFASSUNG

Die Dissoziationskonstanten verschiedener Säuren und Basen in *m*-Kresol wurden konduktometrisch bestimmt. Mit Hilfe einiger Verbindungen, deren Dissoziationskonstanten aus Leitfähigkeitsmessungen bekannt sind, wurde eine Glaselektrode geeicht. Potentiometrische Titrationsen mit dieser geeichten Glaselektrode ergaben Dissoziationskonstanten einiger anderer Säuren und Basen in *m*-Kresol. Für die Eigendissoziationskonstante von *m*-Kresol wurde der Wert  $2 \cdot 10^{-19}$  gefunden. Aus der Differenz  $pK_a(\text{Kresol}) - pK_a(\text{Pyridin})$  jener Verbindungen, deren Säure- oder Basestärken noch in Pyridin noch in *m*-Kresol nivelliert wurden, ergab sich, dass die Basizität des Lösungsmittels *m*-Kresol etwa 8  $pK$ -Einheiten geringer als die von Pyridin ist.

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## SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF TIN IN ROCKS, SEDIMENTS AND SOILS

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Investigation of the geochemical behaviour of tin has been restricted by the lack of suitable analytical methods for trace amounts of the element. Spectrographic determination has been used<sup>1,2</sup>, but is subject to interference and often is not sufficiently sensitive<sup>3</sup>. The most reliable results have been obtained by neutron activation analysis<sup>4</sup>, but for many laboratories the method is inconvenient. Tin is one of the less satisfactory elements for determination by neutron activation<sup>5</sup>, and the sensitivity of the spectrophotometric method described here is comparable with that of recent neutron activation analyses<sup>6</sup>. Spectrophotometric methods are more convenient and can be made highly selective by the use of preliminary purification procedures. Many spectrophotometric reagents have been used for tin<sup>7</sup>, but none has proved completely satisfactory, particularly for submicrogram amounts.

The use of phenylfluorone as a spectrophotometric reagent for 5–50  $\mu\text{g}$  of tin was introduced by Luke<sup>8</sup>, and a modified procedure for 0–3  $\mu\text{g}$  was described by Smith<sup>9</sup>. Onishi and Sandell<sup>10</sup> used dithiol for the determination of tin in rocks and sediments and obtained results similar to recent values<sup>2</sup>, though they reported difficulties for amounts of tin less than 0.5  $\mu\text{g}$ . Catechol violet was used for tin determination by Ross and White<sup>11</sup>, and Newman and Jones<sup>12</sup> developed the use of this reagent for the determination of tin previously purified by solvent extraction as tin(IV) iodide. In the present work, problems arose in the use of catechol violet, but the solvent extraction of tin(IV) iodide was modified to allow determination of 0–3  $\mu\text{g}$  of tin with phenylfluorone.

In analysis for tin it is necessary to avoid loss of tin by hydrolysis or by volatilization of tin(IV) chloride (b.p. 114°). Hydrolysis of tin(IV) is rapid in solutions less than 0.7 *M* in hydrochloric acid or less than 0.1 *M* in sodium hydroxide<sup>13</sup>; the hydrolysis products polymerize and are removed from solution in colloidal particles that may become difficult to redissolve. Traces of tin are widely distributed and special care is needed to minimize contamination from reagents and apparatus. In this work materials were dissolved in hydrochloric acid or hydrochloric–hydrofluoric acids, with or without hydrogen peroxide, under conditions designed to prevent loss of volatile tin compounds, and to minimize contamination. After dissolution of the sample, tin was separated from the major constituents by anion-exchange chromatography, and from other potentially interfering elements by solvent extraction of the iodide, then determined spectrophotometrically with phenylfluorone.

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### *Sample dissolution*

The water content was determined on a portion of the sample material by heating at 110° to constant weight. Dried and ground samples (< 100  $\mu\text{m}$  mesh) were examined by different dissolution methods.

Fusion with sodium or potassium hydroxide or mixtures of both<sup>14</sup> was studied; 0.5 g of clay with added tin-119m tracer and 2 g of the hydroxides was heated in a nickel crucible in a muffle furnace at 700°. The best recovery obtained when the fused mass was dissolved in water was 85%. It is possible that the behaviour of the tracer was not representative of the tin in the sample, but because of low tin recovery, and contamination with nickel from the crucibles, the method was not used.

Dissolution of silicates in hydrofluoric-sulphuric acid mixture has been used in preparation for tin determinations<sup>15</sup>. The recovery of tin from such solutions was examined by adding tin-119m tracer to 10 ml of concentrated sulphuric acid and 2 ml of 40% hydrofluoric acid in a 100-ml Teflon beaker; the covered beaker was heated in a boiling waterbath overnight, and the solution was diluted to a standard volume. The recovery calculated from counts of aliquots was found to be 75%. A similar solution taken from the waterbath and evaporated to fuming under an infrared lamp gave a recovery of 70% of the tin tracer. Loss of tin was attributed to volatilization and further experiments were carried out in closed vessels. Teflon is favoured for the vessels<sup>16</sup> and is essential for decomposition at high temperatures<sup>17</sup>, but polyethylene<sup>18</sup> or polypropylene<sup>17</sup> bottles may be used and are cheaper. The use of closed polypropylene bottles to prevent loss of volatile tin compounds allowed the use of hydrochloric-hydrofluoric acid solutions with subsequent separation of tin from the major components by anion exchange.

When the recommended procedure (p. 375) was applied, dissolution was apparently complete in 30 min, but heating was continued overnight. With materials high in silica a secondary precipitate of gelatinous flakes formed after prolonged heating. With soils and sediments containing organic matter, 5 ml of 50% hydrogen peroxide was added to degrade the organic matter, reducing the possibility of interference at a later stage and assisting in the liberation of bound tin. The sulphuric-hydrofluoric-peroxide mixture attacks polypropylene very rapidly and should be avoided. Experiments with tin-119m tracer showed that there was no measurable loss of tin from these solutions heated for 24 h in the vented bottles. For limestones and ferromanganese materials, the dissolution was carried out in 6 M hydrochloric acid only, and the residue was separated by centrifugation. This procedure retained in solution calcium and magnesium which would otherwise precipitate as the fluorides. The residue, mainly clastic material, was treated separately as a silicate sample.

### *Ion-exchange separation and solvent extraction*

Separation of tin(IV) from other ions by anion-exchange chromatography has been reported<sup>15,19</sup>, and the effect of added hydrofluoric acid was examined. Amberlite IR-400 resin was used as described under *Experimental*, the initial sample solution being 6 M in hydrochloric acid. Experiments with tin-119m tracer under the recommended conditions showed that elution was complete in 1 M sulphuric acid and that the presence of up to 10 ml of 40% hydrofluoric acid did not affect the recovery of tin from solutions that were initially 6 M in hydrochloric acid. In cases where a secondary precipitate was formed during dissolution of the sample, flow through the

column was impeded, but the precipitate largely redissolved in the solutions used to wash the column.

Purification of tin by solvent extraction of tin(IV) iodide from 4.5 M sulphuric acid into toluene and back-extraction into sodium hydroxide was examined. Newman and Jones<sup>12</sup> obtained recoveries of 95–100% for amounts of tin greater than 5  $\mu\text{g}$  using this method. Recoveries of about 80% were obtained in the present work when tin-119m tracer was used with 0–5  $\mu\text{g}$  of added stable tin. Varying the amount of toluene used in the first extraction did not improve the overall recovery of tin. The recovery of tin was found to vary with the concentration of iodide in the initial solution (Table I), and for 0–10  $\mu\text{g}$  of tin recovery was quantitative from solutions 4.5 M in sulphuric acid and 0.83 M in iodide. Higher concentrations of the iodide gave a precipitate of potassium sulphate that reduced the tin recovery. Back-extraction was made into dilute sodium hydroxide solution.

TABLE I

EFFECT OF IODIDE CONCENTRATION ON RECOVERY OF TIN-119m TRACER FROM 50 ml OF 4.5 M SULPHURIC ACID

KI added (ml of 5 M KI)	1	2	5	10	20
KI concentration (M)	0.10	0.19	0.46	0.82	1.43
Tin recovered (%)	68	73	81	100	95

#### Spectrophotometric determination

Tin was determined spectrophotometrically with phenylfluorone<sup>9</sup>. Beer's law was obeyed for 0–3  $\mu\text{g}$  of tin. Interference effects of some ions were examined by adding the ion to 50 ml of 4.5 M sulphuric acid, extracting and measuring the absorbance by the recommended procedure. There was no interference from the following ions:

2000  $\mu\text{g}$  Fe(III)

100  $\mu\text{g}$  Mn(II)

25  $\mu\text{g}$  each of Al(III) Bi(III) Cd(II) Co(II) Cu(II) Cr(III)  
 Cr(VI) Ga(III) Ge(IV) Hg(II) In(III) Mo(VI)  
 Ni(II) Pb(II) Se(VI) Tl(III) U(VI) V(V)  
 W(VI) Zn(II)

5  $\mu\text{g}$  each of As(III) Sb(III)

Some interference was found from arsenic and antimony: 50  $\mu\text{g}$  of arsenic(III) was equivalent to 0.13  $\mu\text{g}$  of tin, and 50  $\mu\text{g}$  of antimony(III) was equivalent to 0.19  $\mu\text{g}$  of tin. The present results are in agreement with earlier work<sup>12,20</sup>, the interference from 50  $\mu\text{g}$  of arsenic(III) or antimony(III) being close to the limit of detection of the method.

#### Accuracy and precision

Recovery of tin through the complete procedure was examined with tin-119m tracer and stable tin. The recovery of tin tracer added to 1 g of each of the following was quantitative: basalt, granite, soil, and red clay; limestone, and ferromanganese materials dissolved in 6 M hydrochloric acid also gave quantitative recovery of tin tracer. Recovery of stable tin added to reagent blanks and to 1-g samples of clay material was determined spectrophotometrically and found to be quantitative.

Six replicate blanks put through the complete procedure had a mean absor-

bance of 0.265, with a standard deviation of 0.0058. With a calibration slope of 0.155 absorbance units per  $\mu\text{g Sn}$ , the limit of detection (three times the standard deviation of the blank) was 0.11  $\mu\text{g}$  of tin. Six replicate determinations made on 1-g samples of a basalt (U.S.G.S. BCR-1) gave a mean value of 1.81 p.p.m. with a coefficient of variation of 1.8%. The values found for the U.S.G.S. Standard Rocks are compared with other values<sup>23-26</sup> in Table II.

TABLE II

VALUES FOR TIN IN U.S.G.S. STANDARD ROCKS (p.p.m.)

	Spectrophotometric Present method	Spectrographic		Neutron activation	
		<i>Le Riche</i> (1967)	<i>Blackburn</i> <i>et al.</i> (1971)	<i>Das et al.</i> (1970)	<i>Schmidt</i> (1971)
G-2	1.32	1.4	3.0	1.2	2.0
GSP-1	4.35	5.5	5.9	4.5	8.6
AGV-1	3.03	3.6	3.5	3.0	5.65
PCC-1	0.88	1.2	3.6	0.5	1.68
DTS-1	0.74	1.1	3.5	0.5	0.68
BCR-1	1.81	1.5	4.2	1.5	2.71

## EXPERIMENTAL

*Apparatus*

Absorbances were measured with a Pye-Unicam SP 500 Series II spectrophotometer with 4-cm glass cells. An E.I.L. Model 30C pH meter with dual microelectrode was used when adjusting the pH of solutions. Gamma counts were made with a well-type NaI crystal with photomultiplier and I.D.L. 1700 scaler.

Plastic laboratory ware was used where possible, including plastic chromatography columns<sup>21</sup> and separating funnels<sup>22</sup>. For sample dissolution 500-ml polypropylene bottles with vented screw saps were held upright on a boiling waterbath. Completely sealed bottles inflated, and this was overcome by drilling a 1.5 mm diameter hole in the cap. The final solutions were made up in Quickfit 15-ml stoppered test-tubes calibrated at 14.0 ml by adding 14 ml of water by pipette and marking with a diamond.

Samples were ground in an alumina mill with a Glen Creston 280 grinder. Soft materials were ground by hand in an agate mortar.

*Anion-exchange column*

Amberlite IR-400 (100-200 mesh) resin was washed with deionized water to remove fines, and packed into plastic columns to give a bed 1 cm in diameter and 10 cm long. The column was conditioned by passing 20 ml of 6 M hydrochloric acid, and was used only once.

*Reagents*

Reagents used were of analytical grade. Water was distilled then passed through a mixed-bed ion-exchange column. Some solutions were purified before use and stored

in polyethylene bottles.

**6 M Hydrochloric acid.** Add 550 ml of 11 M acid to 450 ml of water, cool, and pass through anion-exchange resin.

**Toluene.** Shake 1 l of toluene with 250 ml of 1 M sodium hydroxide, separate and discard the aqueous layer; shake the toluene with 100 ml of 1 M sulphuric acid, separate and keep the toluene.

**50% Hydrogen peroxide.** Select a batch low in tin, or remove the tin by adding 1 ml of 1 M sulphuric acid to 100 ml of peroxide solution and passing through Zeo-Karb 225 resin.

**Phenylfluorone (0.004% w/v in ethanol).** Dissolve 4.0 mg of phenylfluorone in 10 ml of ethanol containing 5 drops of 4.5 M sulphuric acid, and make up to 100 ml with ethanol. Prepare immediately before use.

**Tin stock solution (200  $\mu\text{g Sn ml}^{-1}$  in 3.5 M sulphuric acid).** Dissolve 0.1000 g of tin in 25 ml of hot concentrated sulphuric acid. Add a further 75 ml of acid, and make up to 500 ml with water.

**Tin standard solution (1.00  $\mu\text{g Sn ml}^{-1}$ ).** Dilute 2.5 ml of tin stock solution to 500 ml with 0.1 M sulphuric acid immediately before use.

### Procedure

Dry the material in a desiccator over silica gel at room temperature, and grind in an alumina mill to pass a 100  $\mu\text{m}$  nylon mesh. Weigh accurately up to 1 g of ground material containing not more than 3  $\mu\text{g}$  of tin. Weigh a second sample of about 0.1 g into a tared crucible and determine the weight loss on drying at 110° to constant weight. Transfer the main sample to a 500-ml polypropylene bottle, and add 20 ml of 11 M hydrochloric acid and 5 ml of 40% hydrofluoric acid. Close the screw cap and support the bottle on a waterbath. Heat the waterbath to boiling and continue heating overnight. Cool the bottle, add 10 ml of water and transfer the sample solution along with any precipitate to a prepared anion-exchange column at a flow rate of 1 ml  $\text{min}^{-1}$ . Wash the bottle twice with 10-ml volumes of 6 M hydrochloric acid and pass the washings through the column. Wash the column successively with 25 ml of 6 M hydrochloric acid, 25 ml of N citric acid, and 25 ml of water. Elute the tin in 45 ml of 1 M sulphuric acid, collect in a 50-ml polyethylene measuring cylinder, stand this in cold water and add 9.7 ml of concentrated sulphuric acid to bring the solution to 4.5 M in sulphuric acid.

Transfer this solution to a separating funnel, and add 10 ml of 5 M potassium iodide and 10 ml of toluene. Extract tin(IV) iodide into the toluene by shaking for 2 min. Separate and discard the aqueous layer, and wash the toluene with 5 ml of a solution made by adding 10 ml of 5 M potassium iodide to 50 ml of 4.5 M sulphuric acid, but do not shake. Back-extract the tin into 5 ml of 1 M sodium hydroxide by shaking for 1 min; separate the aqueous layer into a graduated tube. Extract the toluene a second time with 2 ml of 0.1 M sodium hydroxide, shaking for 30 sec, separate the aqueous layer and add it to the graduated tube. Adjust the pH of the combined extracts to  $1.00 \pm 0.05$  by dropwise addition of 4.5 M sulphuric acid, using a pH meter, and add a drop of 5% ascorbic acid solution to decolourise liberated iodine. Add 5 ml of the phenylfluorone solution and make up to the mark with water. Mix well and allow to stand at room temperature for 2 h. Read the absorbance at 525 nm in a 4-cm cell with water in the reference cell. Determine the amount of tin present

by reference to a calibration graph prepared at the same time.

Prepare the calibration solutions by adding aliquots of standard tin solution ( $1.00 \mu\text{g Sn ml}^{-1}$ ) to 5 ml of 1 *M* sodium hydroxide in graduated tubes, adjusting the pH to 1.00 and continuing as described for the samples. Duplicate reagent blanks, prepared by carrying out the whole procedure without added sample, should be processed with each batch of samples. Six samples and duplicate blanks make a convenient batch. Calculate the results as p.p.m. tin on the oven-dry material.

For samples containing organic matter, dissolve the sample in 20 ml of 11 *M* hydrochloric acid, 5 ml of 40% hydrofluoric acid and 5 ml of 50% hydrogen peroxide; it is then necessary to add only 5 ml of water to make the solution 6 *M* in hydrochloric acid before passing it through the column. For limestones, and ferromanganese minerals, dissolve the sample in 20 ml of 6 *M* hydrochloric acid by shaking at room temperature overnight. Centrifuge, and pass the solution through the column. Wash the residue twice with 10-ml volumes of 6 *M* hydrochloric acid, centrifuge and pass the washings through the column; then proceed by washing the column as described above. Treat the residue separately as a silicate material.

## RESULTS

The method described here allowed the detection of as little as 0.1 p.p.m. of tin in geological materials. Results for different types of material given in Tables II and III illustrate the scope of the method. A more extensive account of the application of the method in a study of the geochemistry of tin will be published elsewhere.

TABLE III

TIN CONCENTRATIONS FOUND IN ENVIRONMENTAL MATERIALS

	<i>HCl</i> soluble	Residue	Total (p.p.m.)
<i>Limestones</i>			
Limestone (Ohio)	0.60	0.65	1.25
Dolomite (Ohio)	0.08	0.15	0.23
Marble (Perthshire)	0.24	0.57	0.81
<i>Soils (Soil Survey of Great Britain)</i>			
Brown earths	Bu 79/2		0.7
	C 64/3		0.3
	De 98/2		2.1
	Cn 64/3		0.9
Gley soil	Cn 80/3		2.8
<i>Marine materials</i> ( <i>British Museum - Natural History</i> )			
Red clay	M 306 (Pacific Ocean)		2.4
Red clay	M 290		8.8
Manganese nodule	M 2028 (Blake Plateau)		2.3
Manganese nodule	M 313 (N. Pacific)		4.1

## DISCUSSION

Except in regions of tin mineralization or contamination, rocks, sediments and soils generally contained less than 5 p.p.m. of tin. This method was developed to



measure these levels and is not recommended for tin ores or materials rich in cassiterite. Very recently, new sets of values for the U.S.G.S. standard rocks became available and results up to June 1971 are given in Table II. There is good agreement between the present results and the earlier spectrographic results of Le Riche<sup>23</sup>. The more recent spectrographic results of Blackburn *et al.*<sup>24</sup> show an apparently uniform tin concentration in five of the six standard rocks which is not in accord with the other sets of results. There is also considerable difference between the two sets of results obtained by neutron activation analysis; those of Das *et al.*<sup>25</sup> are very similar to those of Le Riche and to the present results. The values found by Schmidt<sup>26</sup> are all about twice those of Das *et al.*

Results for other materials cannot be compared directly with previous reports but the limestones analysed contained approximately equal amounts of tin in the acid-soluble and insoluble fractions. The total tin at 0.2–1.3 p.p.m. was similar to that reported for limestones by Debrabant<sup>27</sup>. The results for red clays from the Pacific Ocean agree with the results of Hamaguchi *et al.*<sup>4</sup> who found 2.9–7.5 p.p.m. tin in similar material from this region. Values for tin in ferromanganese concretions agree with the levels of 1.5–6.2 p.p.m. found in a range of these nodules by Ahrens *et al.*<sup>28</sup>. There are no reliable data for tin in soils. Careful examination of the present method, with tin-119m tracer to check that tin was recovered quantitatively, under conditions giving low blanks, and measuring the possible interference of other ions, indicated its likely accuracy. This was supported by the agreement with the best values reported by other workers for the U.S.G.S. standard rocks.

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#### SUMMARY

A spectrophotometric method for the determination of traces of tin in geological materials is described. The sample is dissolved in HCl, HCl–HF, or HCl–HF–H<sub>2</sub>O<sub>2</sub> in a polypropylene bottle under conditions preventing loss of volatile tin compounds. Tin is separated from major constituents by anion-exchange chromatography, then purified by solvent extraction of tin(IV) iodide, and determined with phenylfluorone. The limit of detection was 0.1 p.p.m. and the coefficient of variation at the 1.8-p.p.m. level was 1.8%. Results for rocks, soils, red clays and ferromanganese materials are given. Tin values for the U.S.G.S. standard rocks range from 0.74 p.p.m. in DTS-1 to 4.4 p.p.m. in GSP-1, and these are compared with previous values.

#### RÉSUMÉ

On décrit une méthode spectrophotométrique pour le dosage de traces d'étain dans des matériaux géologiques. L'échantillon est dissous dans HCl, HCl–HF, ou HCl–HF–H<sub>2</sub>O<sub>2</sub> dans une bouteille de polypropylène, dans des conditions permettant d'éviter des pertes en composés d'étain volatils. L'étain est séparé de la plupart des

constituants par chromatographie sur échangeur anionique, puis purifié par extraction dans un solvant, sous forme d'iodure d'étain(IV) et dosé avec la phénylfluorone. La limite de détection est de 0.1 p.p.m.; le coefficient de variation est de 1.8% pour 1.8 p.p.m. Des résultats sont donnés pour diverses substances, avec comparaison avec des roches standards.

#### ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode für die Bestimmung von Spuren Zinn in geologischen Materialien beschrieben. Die Probe wird in HCl, HCl-HF oder HCl-HF-H<sub>2</sub>O<sub>2</sub> in einer Polypropylenflasche unter Vermeidung eines Verlustes flüchtiger Zinnverbindungen gelöst. Zinn wird von den Hauptbestandteilen durch Anionenaustausch-Chromatographie abgetrennt, dann durch Solventextraktion von Zinn(IV)-jodid gereinigt und mit Phenylfluoron bestimmt. Die Nachweisgrenze war 0.1 p.p.m. und der Variationskoeffizient im 1.8 p.p.m.-Bereich 1.8%. Die Ergebnisse für Gesteine, Böden, rote Tone und Eisen-Mangan-Materialien werden vorgelegt. Die Zinnwerte für die U.S.G.S.-Standardgesteine reichen von 0.74 p.p.m. in DTS-1 bis 4.4 p.p.m. in GSP-1 und werden mit früheren Werten verglichen.

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## ANION-EXCHANGE SEPARATION AND SPECTROGRAPHIC DETERMINATION OF RARE EARTHS IN PLUTONIUM WITH LITHIUM FLUORIDE-SILVER CHLORIDE CARRIER

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The use of plutonium as a reactor fuel requires the determination of traces of rare-earth elements. Emission spectrographic methods are suitable because of their high sensitivity. However, direct excitation of milligram amounts of plutonium does not give the necessary sensitivity, and there is spectral interference of plutonium lines on the analytical lines for the rare earths. This difficulty has been overcome by chemically separating the rare earths from large amounts of plutonium by ion-exchange or solvent-extraction methods; the rare earths are then determined spectrographically by a copper spark<sup>1-4</sup> or d.c. arc<sup>5-7</sup> method. In the method developed in this laboratory for the determination of rare earths in uranium<sup>8</sup>, it was observed that use of a mixture of lithium fluoride and silver chloride as carrier in a d.c. arc resulted in high sensitivity. This paper describes the results obtained when this carrier was used for the determination of rare earths in plutonium after their separation by anion exchange. The influence of plutonium and some common impurities on the detection limits is also discussed.

### EXPERIMENTAL

Spec-pure chemicals (Johnson-Matthey, Ltd., London) were used for the preparation of stock solutions and carrier.

#### *Preparation of standards*

Analytical-grade hydrochloric and nitric acids and water were distilled twice in a quartz distillation unit before use. The rare-earth oxides were ignited at 800° for 1 h before their dissolution in 3 M hydrochloric acid for the preparation of individual stock solutions; a master solution was then prepared containing 0.25 mg ml<sup>-1</sup> of each of the rare earths except promethium and thulium. From the master solution, a set of seven standard solutions was prepared to give a concentration of rare earths in the range 0.01–1.0 µg per 20 µl. The solutions also contained 0.5 µg of thulium per 20 µl which, because of its absence in plutonium samples, was used as an internal standard.

#### *Preparation of carrier*

A carrier mixture containing 25% lithium fluoride, 25% silver chloride and 50% ultrapure spectroscopic graphite powder (200 mesh) was prepared by grinding

weighed amounts in an agate mortar. As silver chloride becomes flaky on grinding, small amounts of liquid nitrogen were added to make it brittle before grinding. After the moisture had been removed by heating under an infrared lamp, lithium fluoride and graphite powder were added and grinding was completed.

#### *Chemical separation procedure*

Anion exchange was used for the separation of rare earths from plutonium. Pure plutonium (100 mg) in 7.2 *M* nitric acid was used for the standardization of the chemical separation procedure. Known amounts of rare earths and 2.5  $\mu\text{g}$  of thulium (as internal standard) were added to the plutonium solution. Plutonium was converted to plutonium(IV) by adding 10–15 drops of 30% hydrogen peroxide and heated under an infrared lamp to remove excess of hydrogen peroxide. The solution was passed at a rate of 10 drops per min through a Dowex 1–X4 (50–100 mesh) ion-exchange column (1 cm diameter, 15 cm length) conditioned with 7.2 *M* nitric acid. The column was washed with six column volumes of 7.2 *M* nitric acid. Plutonium was retained on the column and the rare-earth impurities were collected in the effluent. The plutonium in the effluent was estimated by  $\alpha$ -counting to be 0.006% of the amount loaded.

The quantitative recovery of rare earths by this separation procedure was checked radiochemically with  $^{152-154}\text{Eu}$  and  $^{177}\text{Lu}$  tracers. The  $\gamma$ -activity in the effluent was determined with a sodium iodide detector. For other rare earths, percentage recovery was estimated by the spectrographic method.

#### *Preparation of sample*

The effluent containing the rare earths was evaporated to near dryness, and 1 ml of a (1 + 1) mixture of concentrated nitric acid and perchloric acid was added and evaporated to destroy any organic matter from the column. The residue was dissolved in a small volume of 3 *M* hydrochloric acid and transferred to a quartz conical tube; the solution was then evaporated to dryness and finally dissolved in 200  $\mu\text{l}$  of 3 *M* hydrochloric acid.

#### *Spectrographic procedure*

The samples were excited in a glass chamber inside a glove box. The arc was at a distance of 185 cm from the slit of the spectrograph. The image of the arc was focussed on an intermediate screen with an adjustable aperture, kept at 48 cm from the slit, by means of a spherical lens of focal length 26 cm. The aperture in the screen was adjusted to cut off the radiation from the electrode tips from the subsequent parts of the optical train. A second cylindrical lens was used to focus the light beam on the slit of the spectrograph. The aperture of the collimating mirror was reduced to  $3 \times 15$  cm to reduce the spectral background. Aliquots of 20  $\mu\text{l}$  of each standard and 40  $\mu\text{l}$  of the sample solution were loaded in duplicate on 10 mg of carrier mixture in the electrode craters after wetting it with a drop of ethanol. The electrodes were dried under an infrared lamp. The spectra were photographed under the conditions given in Table I.

## RESULTS AND DISCUSSION

Studies with the tracers  $^{152-154}\text{Eu}$  and  $^{177}\text{Lu}$ , added to 100 mg of plutonium

TABLE I

## APPARATUS AND SPECTROGRAPHIC OPERATING CONDITIONS

Spectrograph	Hilger E-456, 3.4 meter Ebert Plane Grating.
Grating	1200 grooves $\text{mm}^{-1}$ ; blazed at $1 \mu\text{m}$ in first order.
Reciprocal linear dispersion	$0.8 \text{ \AA} \text{ mm}^{-1}$ in third order; $1.25 \text{ \AA} \text{ mm}^{-1}$ in second order.
Wavelength ranges	316.0–350.0 nm third order; 388.0–444.0 nm second order.
Internal standard, thulium	342.563 nm, 424.215 nm.
Slit width	0.012 mm.
Slit height	2.5 mm.
Filter	None.
Electrodes	The electrodes were prepared from graphite rods supplied by Ultra-Carbon Corporation, U.S.A.
Sample (+)	Ultrapure graphite ST-45, 4.76 mm diameter, 20 mm long, 2.5 mm crater depth and 3.17 mm crater diameter.
Counter (–)	Ultrapure graphite ST-40, 3.17 mm diameter, 25 mm long, pointed.
Arc chamber atmosphere	80% argon and 20% oxygen with a flow rate of $20 \text{ l} \cdot \text{min}^{-1}$ for second-order setting.
Analytical gap	4 mm (not kept constant during arcing).
Excitation unit	Hilger source unit FS 131.
D.c. arc current	13 A.
Exposure time	1 min.
Photographic emulsion	Kodak B-10 (SA-I); $10.2 \times 25.4 \text{ cm}$ , two plates.
Plate development	Kodak D-19 at $18^\circ$ ; 3 min. 30 sec.
Plate calibration	Seven-step rotating sector, iron arc, exposure 30 sec.
Microphotometer	Hilger non-recording microphotometer.
Calculator	Respectra calculator.

TABLE II

## ANALYTICAL LINE PAIRS AND ESTIMATION RANGES

Element	Analytical line (nm)	Range (p.p.m.) <sup>a</sup>	Element	Analytical line (nm)	Range (p.p.m.) <sup>a</sup>
Cerium	401.239	5–50	Dysprosium	340.780	2.5–50
	422.260	5–50		404.598	2.5–50
Praseodymium	422.533	5–50	Holmium	339.898	5–50
Neodymium	401.225	5–50		404.543	2.5–50
	424.737	2.5–50	Erbium	326.478	1.25–50
Samarium	428.078	2.5–50		400.797	1.25–25
Europium	397.199	0.5–5	Ytterbium	328.937	0.5–5
Gadolinium	335.048	1.25–50		398.799	0.5–2.5
	342.247	0.5–25	Lutetium	335.956	1.25–12.5
Terbium	332.440	5–50			
	427.851	12.5–50			

<sup>a</sup> p.p.m. values are obtained for a  $40\text{-}\mu\text{l}$  aliquot of effluent from a 100-mg plutonium sample concentrated to  $200 \mu\text{l}$ .

TABLE III  
PRECISION AND ACCURACY

<i>Element</i>	<i>Average concentration found<sup>a</sup> (p.p.m.)</i>	<i>Standard deviation</i>	<i>Coefficient of variation</i>
Cerium	5.4	0.799	11.7
Praseodymium	5.3	0.571	10.8
Neodymium	5.4	0.344	6.4
Samarium	5.3	0.333	6.1
Europium	5.4	0.383	7.1
Gadolinium	4.9	0.558	11.4
Terbium	5.5	0.507	9.2
Dysprosium	5.0	0.433	8.7
Holmium	5.0	0.374	7.5
Erbium	4.8	0.383	8.0
Ytterbium	4.6	0.445	9.7
Lutetium	4.8	0.343	7.2

<sup>a</sup> Initial concentration of each rare-earth element was 5 p.p.m. Eight spiked plutonium samples were analyzed. Each element was determined in duplicate.

TABLE IV  
COMPARISON OF DETECTION LIMITS OF RARE EARTHS IN PLUTONIUM  
(Results given as  $\mu\text{g}$  on electrode)

<i>Element</i>	<i>Copper spark method</i>			<i>D.c. arc method</i>			<i>Present investigation</i>
	<i>Ref. 1</i>	<i>Ref. 3</i>	<i>Ref. 4<sup>a</sup></i>	<i>Ref. 5</i>	<i>Ref. 6</i>	<i>Ref. 7<sup>a</sup></i>	
Ce	0.03	2.0	0.30	1.0	2.0	—	0.10
Pr	0.03	—	0.20	—	—	—	0.10
Nd	0.03	—	0.30	—	—	2.5	0.05
Pm	0.1	—	—	—	—	—	—
Sm	0.05	0.2	0.03	0.1	1.0	2.5	0.05
Eu	0.002	0.05	0.05	0.1	—	0.25	0.01
Gd	0.02	0.5	0.05	0.1	0.2	0.5	0.01
Tb	0.1	—	0.15	—	—	5.0	0.1
Dy	0.02	0.1	0.03	0.1	0.1	0.25	0.05
Ho	0.02	—	0.15	—	—	2.5	0.05
Er	0.01	—	0.10	0.1	0.1	2.5	0.025
Tm	0.02	—	0.10	—	—	0.25	—
Yb	0.001	—	0.03	—	—	0.05	0.001
Lu	0.001	—	0.03	0.5	—	0.25	0.025

<sup>a</sup> Calculated from p.p.m. values and experimental details given in the reference.

and separated by the anion-exchange separation described, showed recoveries of 98.6% and 99.9%, respectively. Spectrographic determination of the other rare earths confirmed the suitability of the chemical procedure for the separation. The analytical lines used and the appropriate ranges are given in Table II. The precision and accuracy of the method are indicated in Table III. The coefficient of variation ranged from 6 to 12% for different elements.

The lowest detectable amounts of rare earths in plutonium reported in the literature are compared in Table IV with those obtained in the present investigation. It can be seen that the present detection limit for gadolinium is lower than the previously reported limits. The detection limits obtained here for all the other elements are similar to those of spark methods and are 2–50 times lower than those of d.c. arc methods.

#### *Influence of other elements*

In the chemical separation procedure, microgram quantities of plutonium and some common impurities like Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Ni, Pb, U and Zn may accompany the rare earths. Accordingly, the influence of these ions on the limits of detection and on the precision and accuracy of the proposed method was investigated. To study the effect on the detection limits and slope of the working curves, varying amounts of each rare earth (0.01–1.0  $\mu\text{g}$ ) were added to a constant amount of 10  $\mu\text{g}$

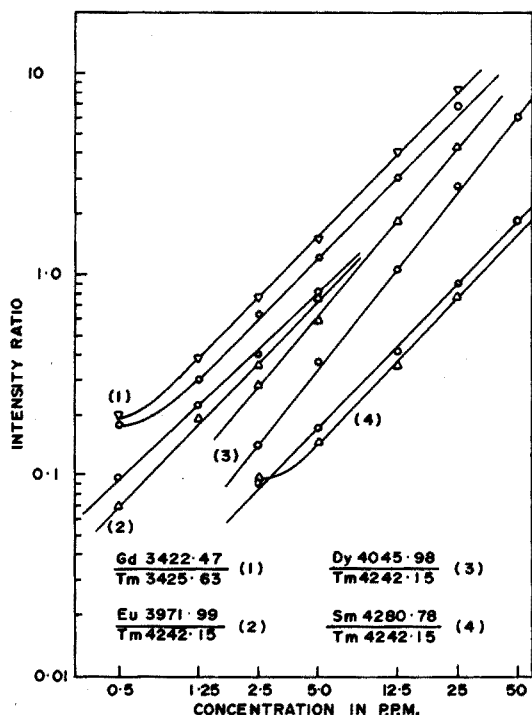


Fig. 1. Working curves of some rare earths in the absence and presence of plutonium and 13 non-rare earth elements. (○) In absence of non-rare earth elements; (△) in presence of 500 p.p.m. each of Pu and 13 other elements.

each of plutonium and 13 non-rare earth elements. These were loaded in triplicate on 10-mg charges of the carrier and photographed under the conditions mentioned earlier. Few of the detection limits for the rare earths were affected. However, for cerium, gadolinium and holmium determined with the lines 401.239, 335.048 and 404.543 nm, respectively, the limits were higher by a factor of two in the presence of these elements.

The working curves were drawn in the coordinate system  $\log(I_{RE \text{ line}}/I_{Tm \text{ line}})$  vs.  $\log(\text{concentration})$  without and with 500 p.p.m. (10  $\mu\text{g}$ ) of each of plutonium and 13 non-rare earth elements. These are shown in Fig. 1 for some of the rare earths. Table V gives the equations for the working curves; it can be seen that the slopes of the lines Pr 422.298 nm, Nd 424.737 nm, Sm 428.078 nm, Gd 342.247 nm, Dy 404.598 nm, Ho 339.898 nm, Er 400.797 nm and Yb 328.937 nm are not affected significantly whereas those of other lines are appreciably altered.

TABLE V

EQUATIONS FOR WORKING CURVES IN THE ABSENCE AND PRESENCE OF 13 NON-RARE EARTH ELEMENTS

Element	Analytical line (nm)	Equation for working curve <sup>a</sup>	
		In the absence of 13 impurity elements	In the presence of 10 $\mu\text{g}$ each of 13 impurity elements
Cerium	401.239	$\log y = 0.97 \log x - 1.74$	$\log y = 0.84 \log x - 1.62$
	422.260	$\log y = 0.87 \log x - 1.68$	$\log y = 0.97 \log x - 1.78$
Praseodymium	422.298	$\log y = 1.18 \log x - 1.67$	$\log y = 1.22 \log x - 1.65$
	401.225	$\log y = 1.01 \log x - 1.25$	$\log y = 1.22 \log x - 1.65$
Neodymium	424.737	$\log y = 1.08 \log x - 1.79$	$\log y = 1.03 \log x - 1.64$
	428.078	$\log y = 1.03 \log x - 1.49$	$\log y = 1.03 \log x - 1.56$
Samarium	397.199	$\log y = 0.94 \log x - 0.74$	$\log y = 1.03 \log x - 0.85$
Europium	335.048	$\log y = 1.04 \log x - 0.83$	$\log y = 1.22 \log x - 1.01$
	342.247	$\log y = 0.95 \log x - 0.58$	$\log y = 1.01 \log x - 0.51$
Terbium	332.440	$\log y = 1.01 \log x - 1.31$	$\log y = 0.77 \log x - 0.87$
	Dysprosium	340.780	$\log y = 1.13 \log x - 0.88$
404.598		$\log y = 1.25 \log x - 1.35$	$\log y = 1.18 \log x - 1.03$
Holmium	339.898	$\log y = 1.07 \log x - 1.05$	$\log y = 1.00 \log x - 0.88$
	404.543	$\log y = 1.28 \log x - 1.99$	$\log y = 1.61 \log x - 2.43$
Erbium	326.478	$\log y = 1.03 \log x - 0.60$	$\log y = 1.16 \log x - 0.71$
	400.797	$\log y = 0.98 \log x - 0.57$	$\log y = 0.99 \log x - 0.89$
Ytterbium	328.937	$\log y = 1.15 \log x + 0.80$	$\log y = 1.19 \log x + 0.81$
	398.799	$\log y = 1.71 \log x + 0.58$	$\log y = 1.06 \log x + 0.46$
Lutetium	335.956	$\log y = 1.48 \log x - 0.36$	$\log y = 1.66 \log x - 0.31$

<sup>a</sup>  $x$  represents concentration, and  $y$  represents  $I_{RE \text{ line}}/I_{Tm \text{ line}}$ .

In order to decide the permissible levels of the impurity elements, the change in intensity ratio of rare earth analytical lines caused by the presence of varying amounts of these elements was studied. To a constant amount (0.1  $\mu\text{g}$ ) of each rare earth, varying amounts of each impurity element (2–30  $\mu\text{g}$ , i.e. 100–1500 p.p.m.) were added on 10-mg charges of the carrier. The effect on the  $I_{RE \text{ line}}/I_{Tm \text{ line}}$  ratios for triplicate determinations is shown in Table VI. It can be seen that with each of the 13 elements at the 2- $\mu\text{g}$  level, the change in intensity ratio ranges from 0–20% for all the rare earths. With 4  $\mu\text{g}$  and 10  $\mu\text{g}$  the changes are below 25% for all the rare earths



TABLE VI

INFLUENCE OF PLUTONIUM AND OTHER NON-RARE EARTH ELEMENTS ON THE INTENSITY RATIO OF INDIVIDUAL RARE EARTH—THULIUM LINES

Element and analytical line (nm)	Intensity ratio in absence of non-rare earth elements	Intensity ratio in presence of different amounts of plutonium and 13 non-rare earth elements on electrode				
		2 $\mu\text{g}$ 100 p.p.m. each	4 $\mu\text{g}$ 200 p.p.m. each	10 $\mu\text{g}$ 500 p.p.m. each	20 $\mu\text{g}$ 1000 p.p.m. each	30 $\mu\text{g}$ 1500 p.p.m. each
Ce 401.239	0.17	0.14	0.14	0.14	0.16	0.16
422.260	0.06	0.05	0.06	0.06	0.10	0.13
Pr 422.533	0.12	0.11	0.16	0.23	0.42	0.86
Nd 401.225	0.21	0.17	0.21	0.19	0.25	0.27
424.737	0.11	0.09	0.11	0.11	0.18	0.27
Sm 428.078	0.18	0.15	0.21	0.19	0.29	0.32
Eu 397.199	0.59	0.57	0.60	0.69	0.65	0.62
Gd 335.048	0.92	1.06	0.81	0.69	0.73	0.61
342.247	1.24	1.33	1.17	1.21	1.00	1.04
Tb 332.440	0.49	0.44	0.68	0.74	1.46	1.14
Dy 340.780	0.70	0.79	0.52	0.41	—	—
404.598	0.89	0.89	0.64	0.89	1.11	1.71
Ho 339.898	0.80	0.72	1.17	1.02	1.81	1.42
404.543	0.05	0.05	0.06	0.06	0.08	—
Er 326.478	1.56	1.50	1.53	1.21	1.09	0.98
400.797	1.59	1.27	1.35	0.77	0.93	0.71
Lu 335.956	5.91	6.69	5.15	5.63	3.05	2.86

except praseodymium and terbium. With higher amounts of impurities the intensity ratio changes are greater than 30% for all the rare earths except europium and gadolinium.

The high sensitivity obtained in the present method permits the determination of rare earths at concentrations less than one p.p.m. when a very limited amount of the sample is available as in the case of actinides. It has an added advantage that larger quantities can be loaded on the electrode compared to the spark method where the amount is severely limited.

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## SUMMARY

An emission spectrographic method for the determination of traces of rare earths in plutonium with a LiF-AgCl carrier is described. The rare earths are separated from plutonium by anion exchange, concentrated and estimated. Thulium is used as an internal standard. The lowest detectable amounts are Yb 0.001  $\mu\text{g}$ ; Eu, Gd 0.01  $\mu\text{g}$ ; Er, Lu 0.025  $\mu\text{g}$ ; Nd, Sm, Dy, Ho 0.05  $\mu\text{g}$ ; Ce, Pr, Tb 0.1  $\mu\text{g}$ . The effect of microgram amounts of plutonium and thirteen common impurities on detection limits and determination is described. The coefficient of variation ranges from 6 to 12% for different elements.

## RÉSUMÉ

Une méthode spectrographique par émission est décrite pour le dosage de traces de terres rares dans le plutonium, avec un entraîneur LiF-AgCl. Les terres rares sont séparées d'avec le plutonium par échangeur anionique. Le thulium est utilisé comme étalon interne. Les limites inférieures décelables sont Yb 0.001  $\mu\text{g}$ ; Eu, Gd 0.01  $\mu\text{g}$ ; Er, Lu 0.025  $\mu\text{g}$ ; Nd, Sm, Dy, Ho 0.05  $\mu\text{g}$ ; Ce, Pr, Tb 0.1  $\mu\text{g}$ . On examine l'influence de microquantités de plutonium et de 13 impuretés courantes, sur les limites d'identification et de dosage. Le coefficient de variation est de l'ordre de 6 à 12% pour différents éléments.

## ZUSAMMENFASSUNG

Es wird eine emissionsspektrographische Methode für die Bestimmung von Spuren Seltener Erden in Plutonium unter Verwendung eines LiF-AgCl-Trägers beschrieben. Die Seltenen Erden werden von Plutonium durch Anionenaustausch abgetrennt, angereichert und bestimmt. Thulium wird als innerer Standard verwendet. Die geringsten nachweisbaren Mengen sind Yb 0.001  $\mu\text{g}$ ; Eu, Gd 0.01  $\mu\text{g}$ ; Er, Lu 0.025  $\mu\text{g}$ ; Nd, Sm, Dy, Ho 0.05  $\mu\text{g}$ ; Ce, Pr, Tb 0.1  $\mu\text{g}$ . Der Einfluss von Mikrogramm-Mengen Plutonium und von dreizehn üblichen Verunreinigungen auf die Nachweisgrenzen und auf die Bestimmung wird beschrieben. Der Variationskoeffizient beträgt 6 bis 12% für die verschiedenen Elemente.

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## CATION EXCHANGE IN FORMIC ACID-DIMETHYL SULPHOXIDE MEDIA

SEPARATION OF THORIUM FROM URANIUM, YTTRIUM, LANTHANUM AND CERIUM

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Dimethyl sulphoxide (DMSO) offers numerous advantages as an eluant in cation-exchange chromatography: it has a complex-forming tendency with almost all metal ions, contains no ionizable protons and has a fairly high dielectric constant ( $\epsilon=47.5$ ). It has therefore found some interesting analytical applications recently. Janauer in a preliminary study<sup>1</sup> reported the  $K_d$  values of some important metal ions in aqueous DMSO systems. Janauer *et al.*<sup>2</sup> also studied solvent uptake in aqueous DMSO and achieved some important separations, *e.g.*  $\text{Ni}^{2+}$  from  $\text{Pd}^{2+}$ , and  $\text{In}^{3+}$  from  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$ . Diehl *et al.*<sup>3</sup> studied the behaviour of  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Sn}^{4+}$  and  $\text{Zn}^{2+}$  on a cation-exchange resin (Bio Rad AG 50-X8) in DMSO-hydrochloric acid-water systems. On the basis of  $K_d$  values they predicted the possibility of separating these cations from mixtures. The anion-exchange behaviour of several cations in methanol-hydrochloric acid-DMSO-water systems has been explored by Fritz and Lehoczy<sup>4</sup>, who showed the usefulness of these systems by separating various mixtures of metal ions. Phipps<sup>5</sup> has studied the selectivity sequence of monovalent anions on an anion-exchange resin in DMSO systems. Earlier studies<sup>6,7</sup> have shown that formic acid offers unusual possibilities in cation-exchange chromatography and zirconium can be separated from thorium and hafnium by cation exchange in formic acid media. It was therefore decided to study formic acid-DMSO systems so that the properties of the two systems might be advantageously combined. As a result some important cation separations in DMSO have been achieved and many important separations appear to be possible in the mixed systems.

### EXPERIMENTAL

#### Apparatus

A borosilicate column of 0.6 cm internal diameter was used. Spectrophotometric studies were performed on Bausch and Lomb Spectronic 20. A temperature-controlled "SICO" shaker was used for distribution studies.

#### Chemicals

All the cation solutions of appropriate concentrations (3% of total ion-exchange capacity) were prepared from their chlorides or nitrates (A.R. grade) in demineralized water with addition of some acid to prevent hydrolysis. Stock solutions

were standardized with  $10^{-2}$  M EDTA<sup>8</sup>.

Dimethyl sulphoxide\*, formic acid, and acetone (B.D.H., Ltd., London, England) were of reagent grade. All other reagents used were of analytical grade.

Dowex 50W-X8 resin (20–50 mesh, H<sup>+</sup> form) was washed with 3 M hydrochloric acid and demineralized water, and then air-dried. Its exchange capacity was found to be 3.08 meq g<sup>-1</sup>.

### Distribution studies

Distribution coefficients ( $K_d$ ) of metal ions were determined in the following

TABLE I

COMPARISON OF  $K_d$  VALUES OF METAL IONS IN DIFFERENT ORGANIC SOLVENTS

Cation	Solvent		
	Dimethyl sulphoxide	Acetone	Formic acid
Mg(II)	69.00	10040.0	10500.0
Ca(II)	217.00	T.A. <sup>a</sup>	T.A.
Sr(II)	314.00	T.A.	T.A.
Ba(II)	—	—	T.A.
Cu(II)	333.3	—	4760.0
Pb(II)	—	4750.0	7450.0
Bi(III)	117.00	1060.0	2870.0
Zn(II)	100.0	50.0	6950.0
Cd(II)	448.0	98.7	4083.3
Fe(III)	54.00	—	5083.3
Mn(II)	110.0	4250.0	5100.0
Ni(II)	81.0	—	4950.0
Co(II)	10.0	4750.0	4590.0
Al(III)	26.00	T.A.	T.A.
Y(III)	23.0	T.A.	T.A.
La(III)	30.0	T.A.	T.A.
Pr(III)	18.0	—	2590.0
Nd(III)	24.0	—	T.A.
Ce(III)	40.0	350	T.A.
Th(IV)	0.0	28.0	409.0
Zr(IV)	0.0	—	0.0
Hf(IV)	0.0	—	14.0
Ti(IV)	240.0	—	—
VO(II)	287.5	T.A.	—
Cr(III)	T.A.	T.A.	—
UO <sub>2</sub> (II)	71.0	—	—

<sup>a</sup> T.A. = Total adsorption.

\* DMSO migrates rapidly through the skin carrying dissolved materials with it. These materials may be toxic inorganic ions, organic toxicants, or radioactivities like plutonium—thereby posing serious health problems to the uninitiated. The analyst should wear rubber gloves and carefully avoid contact of the DMSO with the skin. In case of contact, the skin should be washed immediately with water.

solvents: 85% formic acid; dimethyl sulphoxide; acetone; and DMSO-85% formic acid in 9:1, 8:2, 6:4, 5:5, 4:6 and 2:8 ratios.

The air-dried cation exchanger (100 mg) was equilibrated in 25 ml of the solvent containing the cationic species by constant shaking for 6 h<sup>3</sup> at 30 ± 1° in a temperature-controlled shaker. The concentration before and after equilibration was determined by titration with EDTA.  $K_d$  values were calculated by the following relation

$$K_d = \frac{(I_R - F_R) \cdot 25}{0.1 \cdot F_R}$$

where  $I_R$  denotes the volume of 10<sup>-2</sup> M EDTA (ml) required before equilibrium and  $F_R$  is the volume of 10<sup>-2</sup> M EDTA required after equilibrium. The amounts of titanium(IV) and uranium(VI) before and after equilibrium were determined spectrophotometrically by the well known peroxide methods. The distribution coefficients for metal ions in the first three solvents are given in Table I, while the results for the DMSO-85% formic acid systems are plotted in Figs. 1-3.

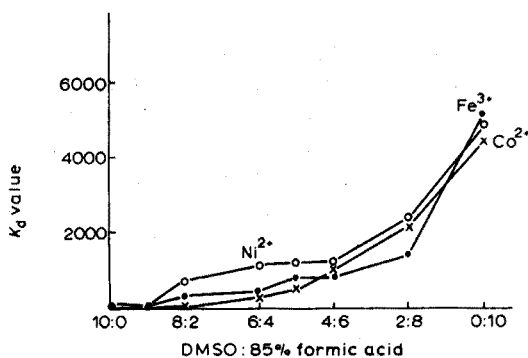


Fig. 1.  $K_d$  value as a function of DMSO-formic acid-water systems

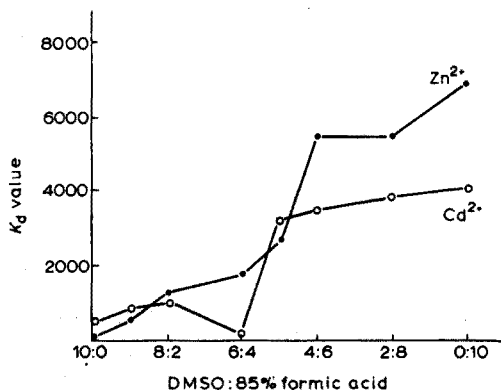


Fig. 2.  $K_d$  value as a function of DMSO-formic acid-water systems.

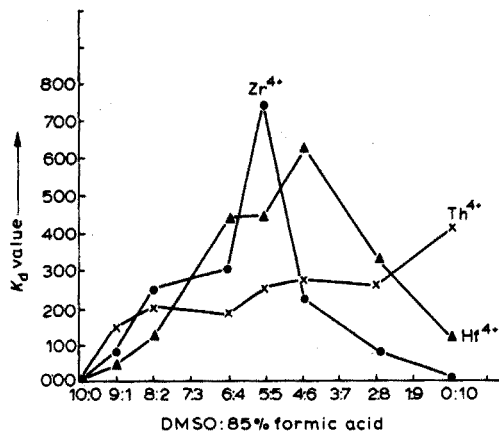


Fig. 3.  $K_d$  value as a function of DMSO-formic acid-water systems.

### Column separations

An elution technique was followed. A slurry of 1.5 g of resin in demineralized water was poured into the column which had a glass wool plug at the bottom. The resin bed was washed with 3 M hydrochloric acid and then with demineralized water until the effluent was acid-free. The resin bed was then saturated with DMSO by passing 50 ml of the eluant. A mixture of the cations was prepared in 5.0 ml of DMSO and was loaded onto the column. On elution with DMSO at a flow rate of 2 ml min<sup>-1</sup>, thorium appeared in the eluate. The column was then washed with demineralized water and the retained species was eluted with 2 M nitric acid at a flow rate of 0.7 ml min<sup>-1</sup>. Some quantitative binary cation separations are summarized in Table II.

TABLE II

SEPARATION OF THORIUM FROM URANIUM AND SOME LANTHANIDE ELEMENTS

Sample no.	Mixture	Eluant	Eluate vol. (ml)	Amount taken (mg)	Amount recovered (mg)
1	Th <sup>4+</sup>	DMSO	40.0	3.25	3.20
	UO <sub>2</sub> <sup>2+</sup>	2.0 M HNO <sub>3</sub>	60.0	0.42	0.42
2	Th <sup>4+</sup>	DMSO	40.0	3.25	3.25
	La <sup>3+</sup>	2.0 M HNO <sub>3</sub>	50.0	2.070	2.13
3	Th <sup>4+</sup>	DMSO	40.0	3.25	3.16
	Y <sup>3+</sup>	2.0 M HNO <sub>3</sub>	50.0	0.889	0.844
4	Th <sup>4+</sup>	DMSO	40.0	3.25	3.20
	Ce <sup>3+</sup>	2.0 M HNO <sub>3</sub>	130.0	2.66	2.80

### DISCUSSION

Ion-exchange studies in non-aqueous and mixed solvents offer attractive possibilities and often lead to important analytical separations which are not easily achieved in common solvents. The present studies in DMSO-formic acid media support this trend. To bring out clearly the role of formic acid and DMSO in cation-

exchange separations, the  $K_d$  values of 26 cations in formic acid, DMSO, and acetone media have been tabulated. In DMSO the  $K_d$  value of thorium is zero because it forms bulky complexes, e.g.,  $\text{ThCl}_4 \cdot 10 \text{ DMSO}$ <sup>9</sup>. In acetone, thorium is not solvated but it is not sufficiently ionized and the  $K_d$  value increases to 28. In 85% formic acid, the  $K_d$  value increases suddenly to 409, probably because thorium forms positively charged complexes in formic acid. Earlier studies<sup>6</sup> showed that all thorium complexes in 0.1 M–1.0 M formic acid are positively charged and thorium is totally adsorbed from these solutions on cation-exchange resins. The selectivity sequence for thorium in DMSO, acetone and formic acid media also holds good for all other cations studied except zinc and cadmium. It is therefore probable that similar explanations may be given for their behaviour. The  $K_d$  values of Y, La, Ce, Pr and Nd are very low in DMSO, which may be due to the low conductance of their complexes in DMSO<sup>10</sup>. The DMSO complexes of copper(II) and iron(III) have been studied<sup>11</sup>. Copper forms  $\text{Cu}(\text{Me}_2\text{SO})_4^{2+}$  while iron forms  $\text{Fe}(\text{Me}_2\text{SO})_6^{3+}$  complexes. The low  $K_d$  value of iron(III) may be due to the larger size of the iron complex compared to the copper one.

The high values of the distribution coefficient in acetone may be due to the low dielectric constant of the solvent ( $\epsilon=27$ ); metal ions are therefore less solvated and their uptake on the resin increases. However, in formic acid ( $\epsilon=58.5$ ) positively charged complexes are formed, as could be inferred from electrophoretic studies<sup>6</sup>, and therefore the high uptake must be due to another mechanism. Dimethyl sulphoxide, which has a dielectric constant of 47 and two donor electron pairs, should show a high degree of solvation of the counter ions which explains the low  $K_d$  values of most metal ions in DMSO.

Reference to Figs. 1–3 shows the effect of formic acid. There is a considerable change in  $K_d$  values even with a small increase in formic acid (%) thus indicating that the effect of formic acid overshadows that of DMSO. The frequent fluctuations in the plots may be due to solvent–solvent interactions<sup>2</sup>.

The separation of thorium from its congeners by ion exchange is still receiving considerable attention. Kuroda *et al.*<sup>12</sup> have reported Th–Y, La–Th, Th–U separations on the weakly basic anion-exchange resin Amberlyst CG4B in hydrochloric acid media. Korkisch *et al.*<sup>13,14</sup> have separated thorium from rare earths on a Dowex 1W-X8 column in 75% acetone–25% hydrochloric acid medium, and on a Dowex 50W-X8 column in methanol containing 0.1 M trioctylphosphine oxide and 5% of 12 M nitric acid. In the latter case, the  $K_d$  values of thorium and uranium are almost zero while those of Ce, Y, Sc, etc. are very high. Thus the separation of thorium from uranium is not possible in the solvent studied by Korkisch *et al.* As can easily be inferred from Table I, the  $K_d$  value of thorium in DMSO is zero while that of uranium and lanthanide elements varies from 71 to 18. The separation factor of these elements with respect to thorium is therefore very favourable and the separation of thorium from uranium and lanthanide elements becomes possible.

The separations achieved in these studies show the separation potential of DMSO. However, many other separations are possible in DMSO–formic acid systems. Thus in the DMSO–formic acid (9:1) system, iron and nickel ( $K_d$  values = 0) can be separated from numerous metal ions. Zinc can be separated from cadmium in the DMSO–formic acid (6:4) system. Zirconium can be separated from numerous metal ions in the 2:3 and 10:0 systems. It is therefore clear that systems containing only small amounts of DMSO or formic acid have high separation potentials. When

the DMSO or formic acid concentration exceeds 10%, the average  $\Delta K_d$  becomes very small and separations become either difficult or impossible. The most interesting case is probably that of zirconium(IV). Zirconium is not adsorbed either from pure DMSO or 85% formic acid (Fig. 3). However, in the (5:5) system its  $K_d$  value is maximal. This apparent anomaly may be explained in a very simple manner. Zirconium forms both positively and negatively charged complexes<sup>6</sup>. The initial addition of formic acid to DMSO leads to the formation of the positively charged complexes. However, once the (5:5) has been passed zirconium(IV) forms either neutral or negatively charged complexes. The  $K_d$  value therefore decreases and becomes zero in 85% formic acid.

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#### SUMMARY

Cation-exchange studies for 26 metal ions in dimethyl sulphoxide, acetone, and formic acid-DMSO-water systems on Dowex 50W-X8 are reported. Thorium can be separated from uranium, yttrium, lanthanum and cerium by elution first with DMSO and then with 2 M nitric acid.

#### RÉSUMÉ

Une étude est effectuée sur le comportement de 26 ions métalliques sur échangeur de cations, Dowex 50W-X8, en milieu diméthylsulfoxyde, acétone et acide formique-DMSO-eau. Le thorium peut être séparé d'avec uranium, yttrium, lanthane et cérium par élution, d'abord avec DMSO, puis avec acide nitrique 2 M.

#### ZUSAMMENFASSUNG

Es wurde der Kationenaustausch von 26 Metallionen in Dimethylsulfoxid, Aceton und Ameisensäure-DMSO-Wasser-Systemen an Dowex 50W-X8 untersucht. Thorium kann von Uran, Yttrium, Lanthan und Cer durch Elution mit DMSO und anschliessend mit 2 M Salpetersäure abgetrennt werden.

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## THE EXTRACTION OF SELENIUM(IV) WITH DITHIZONE

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Recently, there has been some controversy regarding the existence of selenium dithizonate in extraction processes<sup>1-6</sup>. It has been concluded<sup>1,2</sup> that selenium dithizonate is not extracted as such, and that the coloured species extracted into the organic phase is an oxidation product of dithizone whereas selenium still remains in the aqueous phase and can be coagulated and collected as a red solid. This conclusion was drawn almost entirely on the basis of absorption spectra, and the earlier radiochemical studies<sup>5</sup> were dismissed as being due to extraction of some elementary selenium.

However, a considerable amount of data now exists on the extraction of selenium as its dithizonate. Some of this evidence has already been presented<sup>3,4</sup> and further experimental data are offered in the present paper. Since the extraction of selenium with other thiol reagents, such as diethyldithiocarbamic acid, toluene-3,4-dithiol, diethyldithiophosphoric acid and dibutyldithiophosphoric acid, has frequently been described in the literature<sup>7</sup>, the evidence for the formation of selenium dithizonate may have a broader relevance.

### EXPERIMENTAL

#### *Apparatus*

Radiometer pH-Meter pHM-2 (Copenhagen) with glass electrode; Zeiss (Jena) Universal spectrophotometer VSU 2-P; recording spectrophotometer Unicam SP 800; scintillation counter with well-type NaI(Tl) crystal; radiochromatograph NOQ 611 (Tesla); mechanical shaker.

#### *Reagents*

All the reagents used were of A.R. purity. Radiochemical purity of carrier-free <sup>75</sup>Se (Amersham) was checked by  $\gamma$ -spectrometry.

Hydrochloric acid (6 M) was purified by shaking with dithizone solution in carbon tetrachloride followed by shaking with several portions of pure solvent.

Dithizone (H<sub>2</sub>Dz) solutions were purified in the usual way<sup>7</sup>. Their concentrations were determined spectrophotometrically at 620 nm.

A solution of elementary selenium in benzene was prepared by the reduction of selenium(IV) solution (labelled with <sup>75</sup>Se) in 1.5 M sulphuric acid with an excess of ascorbic acid. The red solid was extracted into benzene during 1 h of shaking<sup>8</sup>. The organic phase was separated and filtered.

Selenium dithizonate was prepared by the extraction of 10<sup>-3</sup> M selenous acid

(labelled with  $^{75}\text{Se}$ ) in 5 M sulphuric or hydrochloric acid with the same volume of  $10^{-3}$  M dithizone solution in carbon tetrachloride (1 min shaking). The yellow organic phase was separated and filtered.

The "iodine oxidation product of dithizone" was prepared as described by Ramakrishna and Irving<sup>2</sup>, from  $10^{-3}$  M dithizone solution in carbon tetrachloride.

Carbon tetrachloride and benzene were purified by double distillation.

All the above solutions were prepared freshly before each set of experiments.

Silica gel sheets for thin-layer chromatography (Service Laboratory, ČSAV, Prague) were purified by immersion in  $10^{-3}$  M dithizone solution in chloroform for 12 h. After the dithizone has been washed off by pure solvent, the sheets were air-dried and activated at  $110^\circ$  for 1 h.

#### *Solvent extraction*

Selenium(IV) solutions (labelled with  $^{75}\text{Se}$ ) in hydrochloric acid were shaken on a mechanical shaker with the same volume (usually 5 ml) of carbon tetrachloride or dithizone solution in this solvent. The organic and aqueous phases were separated and their activities were measured for the determination of distribution ratio  $D$  or percentage extraction  $E$ .

#### *Thin-layer chromatography*

The solutions of selenium dithizonate (0.1 ml), the "iodine oxidation product of dithizone" (0.05 ml) and elementary selenium (0.1 ml) were gradually pipetted on the start of the silica gel sheets. The spots obtained were air-dried, sheets were positioned in a chromatographic chamber and eluted by ascending chromatography at a  $45^\circ$  angle with a mixture of carbon tetrachloride-benzene (3 + 7). The chromatography was ended when the solvent front had travelled 12 cm from the start.  $R_F$  values of selenium dithizonate and the iodine oxidation product of dithizone were determined from the position of the colour zones, and those of selenium dithizonate and of elementary selenium from the position of maximum radioactivity peaks and from the black spots of autoradiograms.

## RESULTS

#### *Kinetics of the extraction*

From the results obtained (Table I) it can be seen that selenium can be partially extracted (in the form of elementary selenium and/or chlorocomplex) even in the absence of dithizone. The time needed to reach the extraction equilibrium strongly increases with decrease in the dithizone concentration. The rate of the extraction also increases with increase in the hydrochloric acid concentration. For example, equilibrium was not reached even after 50 h of shaking when selenium(IV) in 0.1 M hydrochloric acid was extracted with  $10^{-5}$  M dithizone solution in carbon tetrachloride. However, some minutes of shaking were sufficient for complete extraction of selenium from 5 M hydrochloric acid with dithizone concentration higher than  $10^{-4}$  M.

#### *The extraction of selenium with an excess of dithizone*

It was found that the distribution ratio  $D$  does not depend on the selenium(IV) concentration in the region from  $10^{-10}$  to  $5 \cdot 10^{-5}$  M; thus no polymeric complexes

TABLE I  
 PERCENTAGE OF SELENIUM(IV) EXTRACTED FROM HYDROCHLORIC ACID BY DITHIZONE SOLUTIONS IN CARBON TETRACHLORIDE  
 ( $[\text{Se}] < 10^{-7} \text{ M}$ )

$[\text{H}_2\text{Dz}]_{\text{org}}$	Time (h)						
	1	3	5	10	20	30	50
<i>From 0.1 M HCl</i>							
0			1	2	4	6	8
$5 \cdot 10^{-6} \text{ M}$		2		5	8	10	13
$10^{-5} \text{ M}$	2		5	7	11	15	25
$2.5 \cdot 10^{-5} \text{ M}$	3	6	10	15	30	41	
$5 \cdot 10^{-5} \text{ M}$	4	7	13	24			
<i>From 1.0 M HCl</i>							
0			3	5	7	9	12
$5 \cdot 10^{-6} \text{ M}$		12	14	26	32	40	45
$10^{-5} \text{ M}$	10	20	24	35	48	50	
$2.5 \cdot 10^{-5} \text{ M}$	40		72	84	93		
$5 \cdot 10^{-5} \text{ M}$	45	75	86	95			
<i>From 2.0 M HCl</i>							
0	6		14	17	26	35	
$5 \cdot 10^{-6} \text{ M}$		18	25	35	50	55	
$10^{-5} \text{ M}$	25		54	58	65	70	
$2.5 \cdot 10^{-5} \text{ M}$		45	75	94	95		
$5 \cdot 10^{-5} \text{ M}$		78	96				
<i>From 3.0 M HCl</i>							
0		7		20	40	50	
$5 \cdot 10^{-6} \text{ M}$		32	45	60	75	80	
$10^{-5} \text{ M}$	25	56	70	80	86		
$2.5 \cdot 10^{-5} \text{ M}$	75	93	94	96			
$5 \cdot 10^{-5} \text{ M}$	95	98					
<i>From 5.0 M HCl</i>							
0	8	25	40	65	90		
$5 \cdot 10^{-6} \text{ M}$	65	90	94	96			
$10^{-5} \text{ M}$	94	96	97	97			
$2.5 \cdot 10^{-5} \text{ M}$	95	98	98				
$5 \cdot 10^{-5} \text{ M}$	98	99					

are formed in the aqueous or in the organic phases.

The dependence of the extraction of selenium(IV) by dithizone solutions ( $5 \cdot 10^{-6}$ – $1.2 \cdot 10^{-3} \text{ M}$ ) in carbon tetrachloride on the hydrochloric acid concentration is shown in Fig. 1. From this Fig. it is evident that selenium(IV) is quantitatively extracted (in contrast to Ramakrishna and Irving's statement<sup>1,2</sup>) from 1–12 M hydrochloric acid when the dithizone concentration exceeds  $5 \cdot 10^{-5} \text{ M}$ . At higher pH values the extraction of selenium(IV) decreases because of the dissociation of selenous acid.

From the  $\log D$  values obtained (0.3, 0.6, 1.0 and 1.4 for  $\log [\text{H}_2\text{Dz}]_{\text{org}} - 4.8$ ,  $-4.7$ ,  $-4.6$  and  $-4.5$ , respectively, in 1 M hydrochloric acid), it follows that one mole of selenium(IV) reacts with four moles of dithizone.

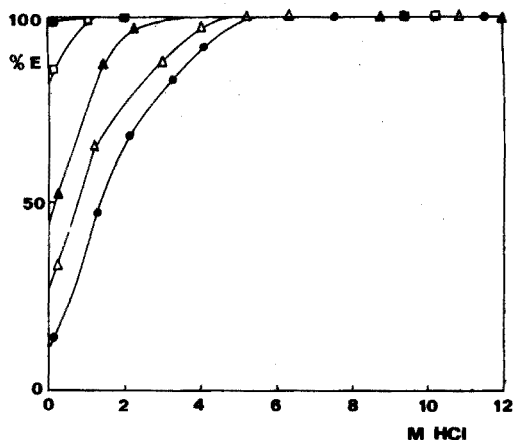


Fig. 1. The extraction of selenium(IV) by dithizone solution in carbon tetrachloride.  $(H_2Dz)_{org}$ : (●)  $5 \cdot 10^{-6} M$ ; ( $\Delta$ )  $10^{-5} M$ ; ( $\blacktriangle$ )  $2.5 \cdot 10^{-5} M$ ; ( $\square$ )  $5 \cdot 10^{-5} M$ ; ( $\blacksquare$ )  $10^{-4} M$ .  $[Se] < 10^{-7} M$

*Extraction of selenium with a substoichiometric amount of dithizone*

Selenium(IV) ( $0.5 \mu\text{mole}$ ) labelled with  $^{75}\text{Se}$  (total activity 119,488 c.p.m.) in 5 ml of 5 M hydrochloric acid was successively extracted with three  $0.5\text{-}\mu\text{mole}$  portions of dithizone in carbon tetrachloride (5 ml) for 3 min. From the activities of organic extracts isolated (28,614, 29,130 and 29,156 c.p.m.) it is evident that selenium(IV) reacts with dithizone in the ratio 1:4.2, 1:4.1 and 1:4.1, respectively.

Analogously, three  $0.5\text{-}\mu\text{mole}$  portions of selenium(IV) labelled with  $^{75}\text{Se}$  in 5 ml of 5 M hydrochloric acid were extracted with increasing amounts of dithizone in carbon tetrachloride (5 ml) for 30 min. From the amounts of selenium extracted (25, 48 and 69% for 0.5, 1.0 and 1.5  $\mu\text{mole}$  of dithizone, respectively) it follows that the ratio selenium(IV):dithizone in the reaction equals 1:4.0, 1:4.2 and 1:4.3.

All activities were corrected for the background and for the activity of selenium



Fig. 2. Silica gel thin-layer chromatography. A = photograph, B = autoradiogram. (1) Mixture of elementary  $^{75}\text{Se}$  and oxidation product of dithizone; (2) oxidation product of dithizone; (3)  $^{75}\text{Se}$  dithizonate; (4) mixture of elementary  $^{75}\text{Se}$ ,  $^{75}\text{Se}$  dithizonate and oxidation product of dithizone; (5) elementary  $^{75}\text{Se}$ .

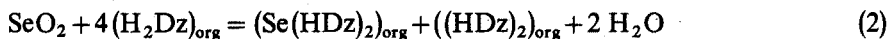
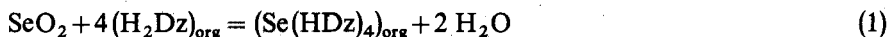
transferred into the organic phase in the absence of dithizone (1% and 2% of the total activity in the first and second series of experiments, respectively).

#### Thin-layer chromatography

A photograph of typical chromatograms and their autoradiograms is presented in Fig. 2, from which the  $R_F$  values were determined for elementary selenium (0.67), selenium dithizonate (0.45) and the iodine oxidation product of dithizone (0.37).

#### DISCUSSION

From the results obtained, it follows that selenium(IV) reacts with dithizone in the ratio 1:4. However, there are at least three possible reactions (neglecting the formation of mixed complexes) fulfilling the above condition:



The results of thin-layer chromatography showed quite evidently that selenium(IV) is not extracted according to eqn. (3) as postulated in Ramakrishna and Irving's work<sup>1,2</sup>. A mixture of elementary selenium and the iodine oxidation product of dithizone (see Fig. 2, A1 and B1) behaves quite differently from selenium dithizonate (Fig. 2, A3 and B3). The activity of <sup>75</sup>Se strictly follows the yellow spot of selenium dithizonate and no activity was found in the position corresponding to elementary selenium. Thus, Ramakrishna and Irving's "selenium oxidation product of dithizone" is in fact *selenium dithizonate* and it is *not identical* (despite the similarity of absorption spectra and chemical reaction) with the iodine oxidation product of dithizone which can be separated on silica gel sheets or column.

Two coloured spots appeared on the chromatogram (see Fig. 2, A3) which suggest that selenium(IV) can be extracted (at least partially) according to eqn. (2). An analogous reaction has been proposed for the extraction of tellurium(IV) with dithizone<sup>9</sup> or for the extraction of selenium(IV) with diethyldithiophosphoric acid or 2-mercaptobenzimidazole<sup>10</sup>. However, there exists the possibility that the initially formed  $\text{Se}(\text{HDz})_4$  can be destroyed on the silica gel forming  $\text{Se}(\text{HDz})_2$  and  $(\text{HDz})_2$ . Because of the similarity in the absorption spectra of selenium dithizonate and the iodine oxidation product of dithizone, as well as their low stability, the detailed investigation of their chemical behaviour is extremely difficult.

#### SUMMARY

The extraction of selenium(IV) with dithizone solution in carbon tetrachloride has been investigated in relation to the concentrations of selenium(IV), hydrochloric acid and dithizone, by means of <sup>75</sup>Se. It was found that selenium(IV) reacts with dithizone in the ratio 1:4, forming an extractable chelate which can be separated from the oxidation product of dithizone and elementary selenium by thin-layer chromatography.

## RÉSUMÉ

On examine l'extraction du sélénium(IV) au moyen d'une solution de dithizone dans le tétrachlorure de carbone, en fonction des concentrations de sélénium(IV), acide chlorhydrique et dithizone, au moyen de  $^{75}\text{Se}$ . On constate que le sélénium(IV) réagit avec la dithizone dans un rapport 1:4, formant un chélate pouvant être séparé d'avec le produit d'oxydation de la dithizone et d'avec le sélénium élémentaire, par chromatographie sur couche mince.

## ZUSAMMENFASSUNG

Die Extraktion von Selen(IV) mit Dithizon in Tetrachlorkohlenstoff wurde unter Verwendung von  $^{75}\text{Se}$  in Abhängigkeit von den Konzentrationen von Selen(IV), Salzsäure und Dithizon untersucht. Es wurde festgestellt, dass Selen(IV) mit Dithizon im Verhältnis 1:4 unter Bildung eines extrahierbaren Chelates reagiert, der vom Oxidationsprodukt des Dithizons und von elementarem Selen durch Dünnschichtchromatographie abgetrennt werden kann.

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## THE CHROMATOGRAPHIC BEHAVIOUR AND NATURE OF METAL CHELATES OF 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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Since the work of Hilliard and Freiser<sup>1</sup> on the separation of metal hydroxyquinolinates on a column of silica gel, the approach of combining the extraction of a group of metal chelates with their subsequent separation by adsorption chromatography, which offers a possibility for valuable multi-element analytical procedures, has attracted the attention of several authors. The coupling of extraction with thin-layer chromatography has been especially favoured<sup>2</sup>. Further development of the approach is hindered, however, by a lack of knowledge about the relationships between the nature of metal chelates and their chromatographic behaviour, so that solvent mixtures for the development of chromatograms are selected almost entirely empirically.

The present paper describes an attempt to harness, for a study of these relationships, a recent approach of Soczewiński<sup>3,4</sup> who applied the law of mass action to competitive adsorption of solute and solvent molecules, assuming a one-phase chromatographic system, the components of which are the surface hydroxyl groups, molecules of the solute and solvents, and the reversibly formed adsorption and solvation complexes. For the experimental part of the study, 1-(2-pyridylazo)-2-naphthol and its chelates were chosen, because of their excellent analytical properties<sup>5-8</sup>.

### THEORETICAL CONSIDERATIONS

As has been observed earlier, there is a definite relationship between the composition of a two-component developing solvent system and the  $R_F$  values of chelates<sup>8</sup>. In order to understand this relationship better, an attempt was made to derive it on the basis of a simplified model of chromatographic process. The chromatographic system assumed involves the solute Z (the chromatographed metal chelate), the adsorbent represented by silica gel, and the developing solvent consisting of polar solvent S diluted by a non-polar solvent N. Both the solute Z and the active solvent S are assumed to be adsorbed by the surface layer of silica gel by formation of adsorption complexes with free (not hydrogen-bonded) hydroxyl groups A of silica gel. The surface layer formed in this way obviously changes the properties of both the silica gel surface and the adsorbed species; it may therefore be considered as a new stationary phase.

If this view is accepted, Martin's equation may be applied; on rearrangement one obtains:

$$R_M = \log \alpha + \log Q \quad (1)$$

where  $\alpha$  is the distribution coefficient of the solute Z between the moving solvent and the above-defined stationary phase, and  $Q$  denotes the ratio of the cross-section of the stationary phase to that of the mobile one. The changes of  $Q$  along the chromatogram can be neglected, and the  $R_M$  values of the solute then depend only on the distribution coefficient  $\alpha$ . This value can be calculated by applying the law of mass action to the complexation phenomena involved in the system, if the solvent movement is slow enough for attainment of equilibrium.

For the formation of the adsorption complex of the solute Z with  $m$  active centres A of silica gel, an equilibrium constant  $K_{ZA}$  may be written as follows:

$$K_{ZA} = \frac{(X_{ZA_m})_a}{X_Z(X_A)_a^m} \quad (2)$$

where  $X_i$  denotes the molar fraction of the indexed species in either the mobile or the stationary phases, the latter being denoted by the suffix a.

For the sake of simplicity, the active solvent S is assumed to be capable of bonding only one active centre A of silica gel per molecule of S; thus the formation constant of adsorption complex SA can be written as:

$$K_{SA} = \frac{(X_{SA})_a}{X_S(X_A)_a} \quad (3)$$

Since the active centres of the molecule of solute Z are occupied by active centres of silica gel in the adsorption complex  $ZA_m$ , the solvation of this complex by molecules of solvent S is improbable; solvation cannot be neglected, however, for free molecules of the solute. Accordingly, the solvation constant  $K_{ZS}$  must also be taken in account:

$$K_{ZS} = \frac{X_{ZS_n}}{X_Z X_S^n} \quad (4)$$

In addition to the equilibrium constants  $K_{ZA}$ ,  $K_{SA}$  and  $K_{ZS}$ , the mass balances of all the species present in the mobile or the stationary phase must be involved in calculation of the distribution coefficient  $\alpha$ . In the mobile phase the sum of the molar fractions of solvents S and N, solute Z, and its solvate  $ZS_n$  must be equal to one. Since the latter two are usually much lower than the others, this can be approximated to:

$$X_S + X_N = 1 \quad (5)$$

The molar fraction of the adsorption complex  $ZA_m$  can be neglected in the stationary phase, but the molar fraction of the active centres of the silica gel which are bound by moisture,  $X_w$ , must be included. Thus, for the stationary phase:

$$(X_A)_a + (X_{SA})_a + (X_w)_a = 1 \quad (6)$$

Because the distribution coefficient,  $\alpha$ , involved in Martin's equation (1), represents the distribution of all the forms of the solute Z between the two phases, *i.e.*

$$\alpha = \frac{(X_{ZA_m})_a}{X_Z + X_{ZS_n}} \quad (7)$$

rearrangement of eqns. (2)–(5) and (6) and (7), and substitution of the results into eqn.



(1) gives the relationship:

$$R_M = \log Q + \log K_{ZA} + m \log (1 - (X_w)_a) - m \log (1 + K_{SA} X_S) - \log (1 + K_{ZS} X_S^2) \quad (8)$$

This relationship may be simplified by neglecting the solvation of the solute (the uncharged metal chelate), so that the last term on the right hand side of eqn. (8) can be omitted. Another simplification is possible because  $(X_{SA})_a$  is much higher than  $(X_A)_a$ , the active solvent S being strongly adsorbed. Then  $K_{SA} X_S \gg 1$  (cf. eqn. 3) and relationship (8) achieves its final form:

$$R_M = \log Q + \log K_{ZA}/K_{SA}^m - m \log (1 - (X_w)_a) - m \log X_S \quad (9)$$

The validity of eqn. (9) was verified by the results of Soczewiński<sup>3,4</sup>, with regard to the last term; it is also supported by the results of Geiss *et al.*<sup>9,10</sup> who found that  $R_F$  values of substances increase with increasing humidity (and hence with increasing moisture content  $(X_w)_a$  of the adsorbent), as is predicted by eqn. (9). The practical importance of eqn. (9) is emphasized by its versatility; it includes the effects of the composition of the developing solvent system and of humidity. Moreover, it explains why the effect of humidity varies for different solutes, as has been observed earlier<sup>10</sup>. There is also another possibility of using the equation: by plotting  $R_M$  values of the chelates obtained in solvent systems of varying composition *vs.*  $\log X_S$ , a straight line should be obtained at constant humidity, and the absolute value of its slope should indicate the composition of the adsorption complex  $ZA_m$ . Further, by comparing  $R_M$  values of two solutes, Z and Z', at constant humidity with the same solvent composition, the relative stability of the adsorption complexes may be compared:

$$\Delta R_M = \log K_{ZA} - \log K_{Z'A} \quad (10)$$

if the two solutes form adsorption complexes of the same stoichiometry. Since the last two applications of eqn. (9) were assumed to be related to the nature of the chelates investigated, their study became the main object of the present work.

## EXPERIMENTAL

### Solutes

1-(2-Pyridylazo)-2-naphthol ( $\beta$ -PAN) was obtained from Merck, and from the Research Institute for Pure Reagents, Brno, ČSSR. The purity and chromatographic behaviour of these samples were compared with those of a 4-(2-pyridylazo)-1-naphthol ( $p$ -PAN) sample<sup>11</sup>, and of two samples of 2-(2-pyridylazo)-1-naphthol ( $\alpha$ -PAN)<sup>11,12</sup>. About  $10^{-5}$  M solutions of the dyes in chloroform were applied on the chromatographic plates.

Solutions of the cobalt, nickel and iron chelates of  $\beta$ -PAN were prepared by adding a 2–5-fold molar excess of the solution of the dye in acetone to 20 ml of 0.02 M potassium bromide solution containing 100  $\mu$ g of the metal ions and, after colour development<sup>8</sup>, extracting with 3 ml of chloroform. Solutions of the copper chelate were prepared by extracting 20 ml of 0.02 M potassium bromide– $10^{-3}$  M copper sulphate solution, with 3 ml of chloroform immediately after addition of 0.5 ml of  $10^{-3}$  M  $\beta$ -PAN in acetone.

### Adsorbent

Silufol chromatographic plates (Kavalier, ČSSR), pre-coated with a 0.1-mm layer of Pearlsil (silica gel with round particles of uniform size and wide pores) were used.

Since the activation of the adsorbent by heating and subsequent changes of its activity were considered to be possible sources of irreproducible  $R_F$  values (cf. eqn. 9), and because silica gel functions well only when not too dry<sup>13</sup>, Silufol in equilibrium with laboratory humidity was used throughout. The relative humidity ranged from 50 to 85%; a hair hygrometer was used to check that humidity changes were negligible during a particular run of experiments.

### Solvent systems

As the polar components of solvent mixtures, acetone, cyclohexanone, methanol and ethanol were used; the first two represent electron-donor solvents, while the latter two can both yield and accept an electron pair. Benzene, chloroform, 1,1,1-trichloroethane and 1,2-dichloroethane served as comparatively inactive diluents. All the solvents were of analytical-reagent or similar grade except for chloroform, which was purified<sup>8,14</sup> and dehydrated with anhydrous sodium sulphate. Mixtures of the solvents were prepared immediately before use.

### Procedure

An aliquot (2–5  $\mu$ l) of the solute solution was placed on Silufol (5  $\times$  1.5 mm strip) 2.5 cm from the lower end of the chromatoplate. The plate was positioned in a Kavalier chromatographic chamber (18  $\times$  18  $\times$  6.5 cm inner dimensions) lined with filter paper, without the adsorbent being wetted by the solvent mixture (50 ml) in the chamber. The chamber was closed and its inner space and the adsorbent were saturating with solvent vapours for 1 h. Then the chamber was set upright so that the solvent wetted the bottom end of the Silufol. Chromatography was finished after the solvent had moved 10–12 cm from the start.  $R_F$  values were measured with respect to the visible solvent front.

When the dependence of  $R_F$  values on the varying composition of a solvent mixture was studied, the whole run was made with Silufol plates of the same batch. The solutes to be compared were chromatographed on the same plate. Evaluation of the results was performed by the least squares method.

## RESULTS AND DISCUSSION

### 1-(2-Pyridylazo)-2-naphthol and its isomers

Comparison of the chromatographic behaviour of  $\beta$ -PAN with that of its isomers,  $\alpha$ -PAN and  $p$ -PAN, was interesting for two reasons. First, a mixture of at least two of the isomers may be obtained by some methods of synthesis<sup>11</sup>. Thin-layer chromatography might then solve the problem of their identification and, perhaps, purification. Secondly, a better understanding of the relationship between the chromatographic behaviour of  $\beta$ -PAN and its structure was expected, which could help in understanding the behaviour of the chelates.

$\beta$ -PAN and  $\alpha$ -PAN solutions in chloroform, which were initially orange and red, turned red-orange and violet, respectively, when applied to the start of chromato-

gram, while yellow *p*-PAN remained unchanged. Pyridylazonaphthols were readily separated by development with acetone-benzene or methanol-benzene solvent mixtures containing up to several tens % (v/v) of the polar component. Over the whole range of content of the polar component, the order of elution of the dyes was unchanged:  $\alpha$ -PAN moved first, followed by  $\beta$ -PAN and then by *p*-PAN. For the purpose of identification, both the characteristic colours and the sequence of the elution could therefore be used. Optimal separation of the dyes was achieved by development with 1–4 % (v/v) methanol in benzene, in an arrangement for prolonged development consisting of a flat piece of cotton-wool held to the upper end of the chromatoplate by a clip.

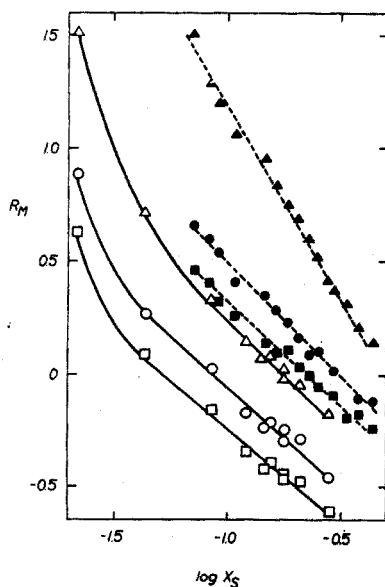


Fig. 1. Effect of solvent composition on  $R_M$  values of pyridylazonaphthols.  $\alpha$ -PAN ( $\square$ ,  $\blacksquare$ ),  $\beta$ -PAN ( $\circ$ ,  $\bullet$ ) and *p*-PAN ( $\triangle$ ,  $\blacktriangle$ ) developed by either methanol-benzene (—) or acetone-benzene (---) solvent mixtures. Relative humidity 77%.

TABLE I

SLOPES OF  $R_M$  vs.  $\log X_S$  PLOTS OF PYRIDYLZONAPHTHOLS

Solute	Solvent A <sup>a</sup>	Slope	n <sup>b</sup>	Solvent B <sup>a</sup>	Slope	n <sup>b</sup>
<i>p</i> -PAN	Acetone-C <sub>6</sub> H <sub>6</sub>	-1.63	15	Methanol-C <sub>6</sub> H <sub>6</sub>	-0.995	11
$\alpha$ -PAN	Acetone-C <sub>6</sub> H <sub>6</sub>	-0.86	15	Methanol-C <sub>6</sub> H <sub>6</sub>	-0.80	9
$\beta$ -PAN	Acetone-C <sub>6</sub> H <sub>6</sub>	-1.06	39	Methanol-C <sub>6</sub> H <sub>6</sub>	-1.22	17
	Acetone-CHCl <sub>3</sub>	-0.80	5	Ethanol-C <sub>6</sub> H <sub>6</sub>	-0.94	6
	Acetone-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	-0.93	4	Ethanol-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	-1.20	17
	Cyclohexanone-C <sub>6</sub> H <sub>6</sub>	-1.25	14			

<sup>a</sup> Solvent A contains a donor polar component, while solvent B has a component which can both give and accept (by hydrogen bonding) electron pairs.

<sup>b</sup> Number of chromatograms included in the calculation of the slope.

The experimental  $R_F$  values were transformed into  $R_M$  values and these were plotted vs.  $\log X_S$  (Fig. 1). It is obvious that at least for  $\log X_S$  higher than about  $-1.4$ , plots are linear, so confirming the validity of eqn. (9). The slopes of the linear parts of the plots are listed in Table I, together with the slopes of the  $R_M - \log X_S$  lines of  $\beta$ -PAN obtained during investigations of cobalt, nickel and iron chelates.

The above theory of adsorption thin-layer chromatography suggests that the change of  $R_M$  caused by the change of the type of solvent should be a constant for all the solutes which are bound to silica gel by the same number of bonds, assuming that solvation may be neglected. In order to prove this, it is sufficient to write eqn. (9) for two solvents, S and S', and for the same solute Z; subtraction of the two equations gives:

$$R_M - R'_M = m(\log K_{S'A} - \log K_{SA}) \quad (11)$$

for  $X_S = X_{S'}$ . Experimental data given in Fig. 1 yield  $\Delta R_M \approx 0.53$  with  $\alpha$ -PAN and  $\Delta R_M \approx 0.55$  with  $\beta$ -PAN (S = acetone, S' = methanol), i.e. almost identical values, so confirming the validity of eqn. (9) again. The anomalous slope of the  $R_M$  vs.  $\log X_S$  plot of  $p$ -PAN in acetone cannot be explained satisfactorily; even the assumption of solvation and its treatment by subtracting eqns. (8) and (9) from each other did not give quantitative agreement with the experimental data.

In addition to comparison of the effect of changing the solvent, a comparison of  $R_M$  values for the three pyridylazonaphthols is also possible within a single solvent system. According to eqn. (10), the relative strengths of the dye-adsorbent bond may be evaluated (at least in methanol-benzene systems, where the slopes of  $R_M$  vs.  $\log X_S$  plots are the same for all three dyes). It is interesting to compare these relative values with other properties of the dyes. Table II shows that  $\Delta R_M$  values correlate markedly with melting point and with the wavelength of maximum absorption of the neutral forms of the dyes, while there is no evidence of correlation with dissociation constants, perhaps because of the scatter of the published data. Since the sequence of melting points of the dyes may be reasonably explained by intramolecular hydrogen bonding

TABLE II

 $\Delta R_M$  VALUES AND OTHER PROPERTIES OF PYRIDYLAZONAPHTHOLS

Solute	$\Delta R_M =$ $(R_M)_I - (R_M)_{p\text{-PAN}}$	Melting point (°)	$\lambda_{\max}$ (nm)	$pK_{OH}$	$pK_{NH}$	Ref.
$\alpha$ -PAN	0.475	126-127		9.5	3.0	12, 15
		102-104	482	10.0	2.29	16
		123-125	490	11.7	1.05	11
		140-141		12.3	< 2	17
$\beta$ -PAN	0.273	140-141		12.2	1.9	18
		140-141		11.2	2.9	19
				11.5	2.9	20
		137	470	11.2	2.9	21, 22
			470	12.0	2.32	16
$p$ -PAN	0		472		2.35	23
		200	450	10.4	1.57	11

of the naphtholic group to the diazo group, the correlations observed suggest that the dyes attach to silica gel by a bond from the oxygen atom of the dyes. This opinion is confirmed by comparison of steric hindrances in the dye molecules: in *p*-PAN an oxygen atom is easily accessible, but in  $\beta$ -PAN it is shielded by the diazo group, as in  $\alpha$ -PAN, where a steric hindrance of the adjacent benzene ring must also be considered.

#### Metal chelates of $\alpha$ -PAN

With all the solvent mixtures investigated, the sequence of elution of  $\beta$ -PAN metal chelates was essentially unchanged, as has been observed earlier<sup>6-8</sup>. The  $R_F$  values decreased in the following order: Fe > Ni > PAN  $\gg$  Cu > Co. The  $R_M$  vs.  $\log X_S$  plots constructed from the present results showed linear parts, the slopes of which are summarized in Table III.

TABLE III

SLOPES OF  $R_M$  vs.  $\log X_S$  PLOTS OF  $\beta$ -PAN METAL CHELATES

Chelate of	Solvent A	Slope	n	Solvent B	Slope	n	Average slope <sup>a</sup>
Fe <sup>3+</sup>	Acetone-C <sub>6</sub> H <sub>6</sub>	-1.10	9	Methanol-C <sub>6</sub> H <sub>6</sub>	-1.11	8	-1.21
	Acetone-CHCl <sub>3</sub>	-1.37	5	Ethanol-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	-1.20	7	
	Acetone-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	-1.25	4				
Ni <sup>2+</sup>	Acetone-C <sub>6</sub> H <sub>6</sub>	-1.01	14	Ethanol-C <sub>6</sub> H <sub>6</sub>	-1.08	8	-1.09
	Cyclohexanone-C <sub>6</sub> H <sub>6</sub>	-1.30	10	Ethanol-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	-0.96	6	
Cu <sup>2+</sup>	Acetone-C <sub>6</sub> H <sub>6</sub>	-1.96	13	Ethanol-C <sub>6</sub> H <sub>6</sub>	-2.07	44	-2.04
	Acetone-CH <sub>3</sub> CCl <sub>3</sub>	-1.93	5				
Co <sup>3+</sup>	—	—	—	Methanol-C <sub>6</sub> H <sub>6</sub>	-4.14	11	-4.07
				Ethanol-C <sub>6</sub> H <sub>6</sub>	-4.01	11	

<sup>a</sup> Average slope =  $(\sum \text{slope}_i \cdot n_i) / \sum n_i$ ; for other signs, see Table I.

These data suggest that solvation of the chelates may be essentially neglected, since the slopes are the same in both types of solvents, which differ in their solvation ability. From the values of the slopes it may be concluded that the chelates of iron and of nickel are bound to silica gel by a single bond, while the copper chelate is held by two bonds, and that of cobalt by four bonds. Evidently the solutes capable of multiple bonding are held far better than those with a single bond. The former obviously form a sort of adsorption chelate with the surface hydroxyl groups of silica gel, while the latter form only a simple adsorption complex. The increase in the adsorptive strength may therefore be explained by a chelation entropy effect.

As for the centres of bonding of the chelates to silica gel, it seems reasonable to assume that the bonds come mainly from the ligand molecules, since the central metal

atom of the chelate is screened by the large organic ligands. An oxygen atom of the  $\beta$ -PAN ligand is probably the centre of bonding, because it possesses free electron pairs available for bonding with silica gel even in the chelate, while both the heterocyclic nitrogen and the diazo group lose almost all their electron pairs on chelation.

The differences in the number of bonds observed among the chelates investigated may be attributed to the differences in the composition and the structure of particular chelates. It is therefore reasonable to deal with each of the chelates separately.

**Copper.** In slightly acidic solution, copper forms a violet chelate with a 1:1 copper-PAN ratio<sup>14,15,18</sup>. The chelate is positively charged and therefore is not extracted by chloroform, unless a suitable monobasic anion L is present in the aqueous phase<sup>8,14</sup>. Obviously, either an ion-association pair or, because one  $\beta$ -PAN ligand cannot saturate the coordination ability of copper(II), a mixed (1-1) ligand complex  $\text{Cu}(\text{PAN})\text{L}$  is formed and extracted. Whichever is the case, at most one of the two bonds to silica gel suggested by the data of Table III may come from an oxygen atom of the  $\beta$ -PAN ligand. The other bond might be explained by an assumption that the ion-association pair is dissociated in the organic phase<sup>24</sup> or dissociates during chromatography, so that a  $\text{CuPAN}^+$  cation is adsorbed on silica gel via an ion-exchange mechanism<sup>25</sup>. Here, a change of the anion L in the extraction should not influence the  $R_F$  values of the copper chelate. The second bond could also arise from an atom of the ligand L, provided that the mixed ligand chelate does not dissociate when chromatographed. In this case, a change of ligand L should affect the electron density of the whole solute molecule, and so its hydrogen bonding with silica gel, and hence also its  $R_F$  value.

In order to distinguish the two possibilities, a series of chloroform solutions was prepared by extracting the copper chelate as described above but with potassium bromide being replaced by other salts. The solutes so prepared were then chromatographed simultaneously with the copper chelate extracted from a potassium bromide solution. The effects of sodium chloride, potassium iodide, sodium acetate, ammonium chloroacetate, ammonium phenylacetate, ammonium indolylacetate, methyl orange, tropaeoline-00 and -000, potassium hydrogenphthalate, ammonium thiocyanate, salicylic and acetylsalicylic acid were studied, since they all facilitate the extraction of  $\text{CuPAN}^+$ . Except for the last three, most of these salts caused either no change or a negligible change of  $R_F$  values. With the acid-base dyes, the indicator spots were separated from the copper chelate spot, which suggests that dissociation also occurs with other salts. Since the indicators are not extractable alone or in presence of copper(II) unless  $\text{CuPAN}^+$  is present, the appearance of their spots (identified by colour changes caused by ammonia or hydrochloric acid) on a chromatogram is evidence of coextraction of the indicators with the copper chelate.

A different picture was observed during chromatography of copper- $\beta$ -PAN chelate extracted from thiocyanate, acetylsalicylate or salicylate medium. The spots of these samples moved much faster than the copper chelate extracted from potassium bromide. Probably, the mixed ligand chelates involved did not dissociate during chromatography, so that they represent different solutes:  $[\text{Cu}(\text{PAN})]\text{SCN}$ ,  $[\text{Cu}(\text{PAN})]\text{AcSal}$  and  $[\text{Cu}(\text{PAN})]\text{Sal}$ , where Sal and AcSal denote salicylate and acetylsalicylate, respectively. In order to elucidate whether these solutes differ also in the number of bonds to silica gel, a  $R_M$  vs.  $\log X_S$  relationship was studied by chromatographing these solutes simultaneously with  $[\text{Cu}(\text{PAN})]\text{Br}$ . Figure 2 shows some of the

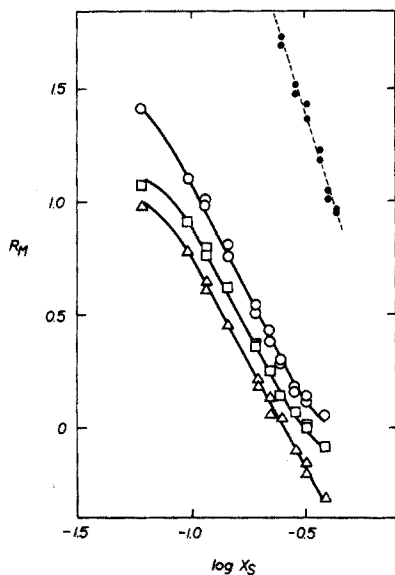


Fig. 2. Effect of solvent composition on  $R_M$  values of copper chelate extracted from KBr (○, ●),  $\text{NH}_4\text{SCN}$  (□) or ammonium salicylate (△) solution. Broken line denotes tropaeoline-000 spot. Developed by ethanol-benzene mixtures at relative humidity 50%.

results; from the slopes of the linear sections of the plots it may be concluded that the copper chelate is attached to silica gel by two bonds irrespective of the anion  $\text{L}^-$ .

The increase of the  $R_F$  values of the copper chelate by a suitable choice of anion  $\text{L}^-$  provides evidence of mixed ligand complex formation, and is also important analytically, because it makes a successive separation of all four chelates and of excess  $\beta$ -PAN possible by a single development instead of the double one used earlier<sup>8</sup>. Accordingly, it seemed useful to specify criteria for a suitable anion. For this purpose, the relative strengths of bonding of the  $\text{Cu}(\text{PAN})\text{L}$  species to silica gel (expressed by means of  $\Delta R_M$  obtained from the data of Fig. 2, cf. eqn. 10) and properties of ligand L and of the mixed ligand complexes were compared (Table IV). Some of the data are taken from the literature<sup>26,27</sup>, and others were provided experimentally in the present work. The equilibrium constant,  $K_{\text{mix}}$ , of the two-phase reaction



TABLE IV

$\Delta R_M$  AND PROPERTIES OF  $\text{Cu}(\text{PAN})\text{L}$  COMPLEXES

Ligand L	$\Delta R_M$	Mol. weight of ligand L	$\log K_{\text{CuL}}$	$\log K_{\text{mix}}$	$\lambda_{\text{max}}$ (nm)
$\text{Br}^-$	0	79.909	0.30	3.96	570
$\text{SCN}^-$	0.22	58.082	2.30	5.39	563
Salicyl <sup>-</sup>	0.30	137.116	10.6	5.61	560

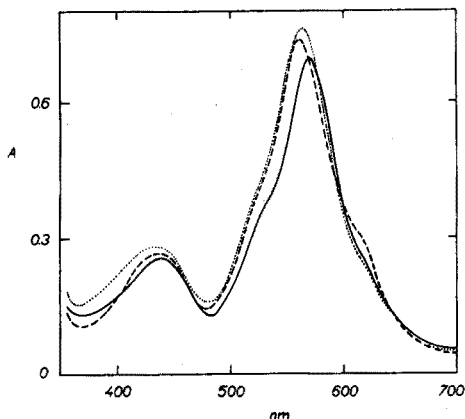
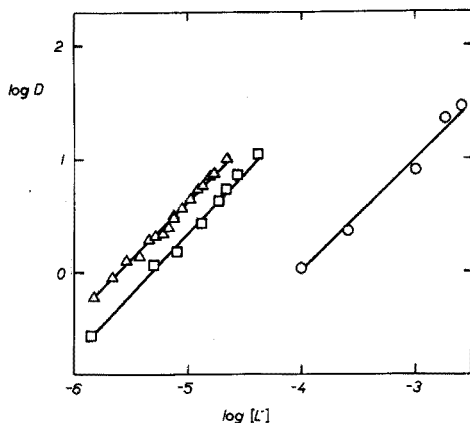


Fig. 3. Effect of the concentration of ligand L on extraction of copper chelate with  $\beta$ -PAN. Chelate extracted from either KBr (O) at pH 5.7, from  $\text{NH}_4\text{SCN}$  ( $\square$ ) at pH 6.0, or from ammonium salicylate ( $\Delta$ ) at pH 4.4.

Fig. 4. Absorbance spectra of  $\text{Cu}(\beta\text{-PAN})\text{L}$  complexes in chloroform. L = Br (—), L = SCN (.....), L = salicylate (-·-·-·-).

was calculated from the data given in Fig. 3, obtained as described earlier<sup>14</sup>. Wavelengths of maximum absorbance for equimolar solutions of mixed ligand complexes in chloroform were obtained from the spectra (Fig. 4); these solutions were prepared by extraction with 10 ml of chloroform of 20 ml of  $1.7 \cdot 10^{-4}$  M ammonium salicylate, 0.05 M potassium bromide or 0.01 M ammonium thiocyanate, each of which contained 200  $\mu\text{g}$  of copper(II) and 1 ml of  $1.4 \cdot 10^{-4}$  M  $\beta$ -PAN in acetone.

Table IV shows that  $\Delta R_M$  caused by ligand L increases with increasing strength of the ligand-copper bond, as indicated by correlation with the complexity constant  $K_{\text{CuL}}$ , and still better with the extraction constant  $K_{\text{mix}}$ . Since these constants are related only indirectly to the strength of the ligand-copper bond in the mixed complex, the correlation of  $\Delta R_M$  with a hypsochromic effect provides further necessary evidence of the validity of the relationship suggested, *viz.* that the higher the stability of the mixed ligand complex, the greater is the increase of  $R_F$ . There are, however, upper limits for the strength of the copper-ligand bond, for ligand L should not cause dissociation of the copper- $\beta$ -PAN chelate.

**Nickel.** The chelate of nickel with  $\beta$ -PAN contains two 1-(2-pyridylazo)-2-naphthol ligands for each nickel atom, when extracted into a polar organic solvents<sup>19,20</sup>, and is obviously uncharged. If  $\beta$ -PAN is a tridentate ligand and nickel has its usual coordination number of 6, the chelate should be coordinately saturated. When these properties of the chelate are compared with its number of bonds to silica gel (Table III), it is surprising at first sight that this chelate is attached to the adsorbent by a single bond. The chelate may change its initial composition when chromatographed, but this is unlikely, since there is no difference of  $R_F$  values for the nickel chelate extracted from excess of chelating agent, or under substoichiometric conditions, or from aqueous media containing diverse salts. Steric factors, *e.g.* shielding of an oxygen atom of the  $\beta$ -PAN ligands by adjacent naphthalene rings, may intervene, but current knowledge of the structure of the nickel chelate is insufficient for more than rough considerations.



**Cobalt.** When a solution of  $\beta$ -PAN is added to a neutral or acidic aqueous solution of cobalt(II) ions, a reddish brown chelate appears, which turns greyish green on standing. The latter chelate is easily extracted into chloroform and other more polar solvents, but floats in the interface with carbon tetrachloride<sup>19</sup>. Cobalt is oxidized to its tervalent state in the green chelate<sup>28,29</sup>, which contains two molecules of  $\beta$ -PAN for each atom of cobalt<sup>14,19,28</sup>, and so is positively charged as well as coordinately saturated. The chelate is extracted into chloroform via formation of an ion-association pair with a suitable anion, as is indicated indirectly by the fact that extraction is suppressed by ammonium thiocyanate<sup>3</sup> unless more polar 1,2-dichloroethane is used.

The chromatographic behaviour of the green cobalt chelate in ethanol-benzene and in methanol-benzene mixtures suggested that the chelate is attached to silica gel by four bonds (see Table III). At most two, more probably only one, of these bonds may be attributed to some atom of the  $\beta$ -PAN in the chelate, because the steric factors are obviously similar to those encountered with the nickel chelate. Some of the other bonds might be explained similarly to the case of the copper chelate, *i.e.* either by ion exchange or by assuming that the ion-association pair of the cobalt chelate with ligand L does not dissociate on silica gel and that these other bonds come from some atoms of ligand L. In the latter case, ligand L should affect the  $R_F$  values, and this was found to be true when potassium bromide in the initial aqueous phase was replaced by potassium hydrogenphthalate or salicylic acid (Fig. 5). The slopes of the  $R_M$  vs.  $\log X_S$  plots did not differ essentially, which suggests that the number of bonds to silica gel remained similar. For these ligands L the ion-association pairs obviously do not dissociate; with regard to the coordination sphere of cobalt being saturated with  $\beta$ -PAN molecules, ligands L may be supposed to be bound to the chelate in an external sphere, as in some other cobalt complexes.

However, not all the bonds of the cobalt chelate to silica gel can be explained

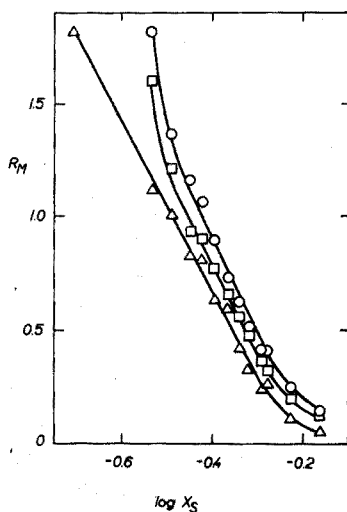


Fig. 5. Effect of solvent composition on  $R_M$  values of green cobalt chelate with  $\beta$ -PAN. Chelate was extracted from either KBr ( $\circ$ ), or potassium hydrogenphthalate ( $\square$ ), or from ammonium salicylate ( $\triangle$ ) solutions, respectively. Developed by methanol-benzene solvent mixtures at relative humidity of 55%.

in this way. The high value of the slope of the  $R_M$  vs.  $\log X_S$  plot may also be influenced by solvation. Unfortunately, it was not possible to obtain sufficiently high  $R_F$  values in acetone-benzene mixtures for proper comparison of solvation phenomena, if any.

*Iron.* The 1:2 metal-ligand composition of the iron(III)  $\beta$ -PAN chelate is well established<sup>8,30</sup>; a charged chelate  $\text{Fe}(\text{PAN})_2^+$  has been suggested<sup>30</sup>. In agreement with this assumption, diverse salts have a strong effect on the extraction of the chelate into chloroform<sup>8</sup>.

It was therefore expected that the iron chelate would behave similarly to the cobalt chelate during chromatography on silica gel. However, the  $R_M$  vs.  $\log X_S$  relationship yielded a line of unit slope, suggesting that only a single bond is involved in bonding to silica gel (Table III). The iron chelate thus resembles the uncharged nickel chelate. This behaviour of the iron chelate might be understood, if iron were in the divalent state, forming an uncharged species, which disagrees with earlier assumptions. However, previously there has been no direct experimental evidence for iron(III) being present in the chelate, and the fact that ascorbic acid facilitates the extraction of the iron chelate with  $\beta$ -PAN<sup>8,31</sup> suggests that iron(II) may be present rather than that the iron(III) chelate retains its charge even in ascorbic acid media<sup>32</sup>. In this work, it was observed that the iron chelate in chloroform dissociated when shaken with hydrogen peroxide or dilute permanganate solution; the 1-(2-pyridylazo)-2-naphthol released gave characteristic colour reactions with copper(II) or zinc ions. This tends to confirm that the chelate contains iron(II).

However, diverse salts markedly affect the extraction of the iron chelate, which indicates the formation of an ion-association pair with a charged chelate of iron(III). In order to elucidate the extraction mechanism, the influence of salts (potassium nitrate, bromide, iodide or bromate, ammonium thiocyanate and sodium sulphate) on the extraction of the iron chelate into chloroform was re-investigated. To 20 ml of solutions of these salts, which contained  $10 \mu\text{g}$  of iron(III), 1 ml of  $8 \cdot 10^{-4} M$   $\beta$ -PAN in acetone was added and the colour was developed for 1 h; the chelate formed was extracted into 10 ml of chloroform by shaking for 1 min, and the absorbance  $A_1$  of the extracts was measured at 725 and at 550 nm. Then 1 ml of 1 M potassium bromide was added to the aqueous phase and all the remaining iron chelate was extracted into a fresh 10-ml portion of chloroform by shaking for 3 min. The absorbance  $A_2$  of these second extracts was measured at the above wavelengths again. Since the sum of  $A_1$  and  $A_2$  remained constant over the whole range of salt concentrations investigated, it was possible to estimate the distribution coefficient of the chelate between the phases (in the first extraction) as a ratio  $A_1/A_2$ . The results are given in Fig. 6. The rather complicated picture observed indicates that the effect of salts cannot be explained simply by formation of  $[\text{Fe}(\text{PAN})_2^+, \text{L}^-]$  ion-association pairs. Especially remarkable is the resemblance of the curve found with sulphate to those of monobasic anions; the shape of the curve describing the effect of thiocyanate is also unexpected and may indicate stepwise equilibria as well as reduction-oxidation phenomena. Kinetic effects may also be involved.

The effect of salts was also studied by thin-layer chromatography. Iron chelate samples extracted into chloroform from the above solutions and also from potassium hydrogenphthalate, sodium acetate or chloride, or salicylic acid, were placed on the start of the same chromatogram and developed as described above. Essentially no differences were observed between the samples mentioned, except for that extracted

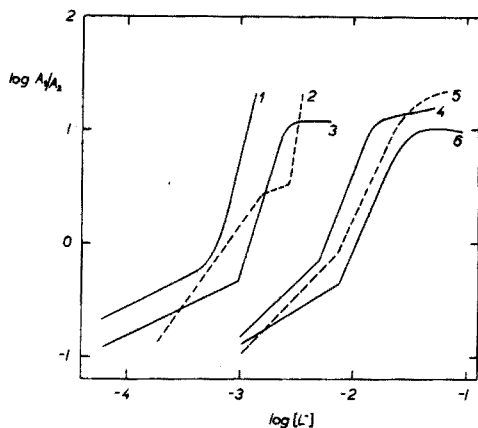


Fig. 6. Effect of inorganic salts on the extraction of the  $\beta$ -PAN chelate formed with iron(III). Chelate extracted from either KI (1),  $\text{NH}_4\text{SCN}$  (2),  $\text{Na}_2\text{SO}_4$  (3), KBr (4),  $\text{KNO}_3$  (5), or  $\text{KBrO}_3$  (6). Each curve was constructed on the basis of about thirty extraction experiments.

from bromate solution. While the iron chelate extracted from other media moved in front of  $\beta$ -PAN, the chelate extracted from bromate solution remained at the start forming a brownish spot, which evidently represents a new form of the iron chelate. It could not be moved even with 1:1 ethanol–benzene, so that its bonding to silica gel could not be established. Because of the probability of oxidation in bromate medium, the new iron spot may be attributed to some charged chelate of iron, possibly iron(III).

The results are not conclusive, but it may be suggested that the iron– $\beta$ -PAN system involves stepwise chelation, formation of ion-associate pairs and possibly simultaneous extraction of chelates containing bivalent and trivalent iron. Further investigation of the system is undoubtedly needed. The complex character of the chelation has, however, only a small effect on the analytical applicability of thin-layer chromatography of the chelates involved.

#### Effect of air humidity

The validity of the above conclusions on the relationships between the chromatographic behaviour of metal pyridylazonaphtholates and solvent composition is largely contingent on the adequacy of eqn. (9). The validity of the conclusions would be supported by experimentally checking the other part of this equation, *viz.* the effect of the water content of the adsorbent on  $R_M$  values, other variables being kept constant, *i.e.* the equation

$$R_M = \text{const} + m \log (1 - (X_w)_a) \quad (9a)$$

Since the molar fraction of water in the stationary layer,  $(X_w)_a$ , is not readily measurable, eqn. (9a) was tested indirectly, by measuring the  $R_F$  values of the solutes at various relative air humidity values, with a constant solvent mixture.

*Procedure.* The solutes were applied on  $2 \times 14$ -cm strips cut from the same  $15 \times 15$ -cm Silufol plate, with the start being placed 3.5 cm from the lower end of the strips. The chromatograms were hung on wire hooks through rubber stoppers. Measuring cylinders (5.3 cm dia., 22 cm high) were used as chromatographic chambers;

each cylinder contained a saturated inorganic salt solution in contact with its undissolved crystals, serving as a hygrostat. The salts used were<sup>26</sup>: KCl, NaCl,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (analytical-reagent grade). A 25-ml beaker containing 18 ml of the developing solvent mixture and a  $4 \times 15$ -cm strip of filter paper, to saturate the chamber with solvent vapours, was inserted into each cylinder. The cylinders were stoppered, without the chromatograms being wetted, so that they equilibrated both with the solvent vapours and air humidity. After 20 h the wire hooks were pushed down so that about 3 mm of the lower end of the chromatograms were immersed in the organic solvent. The chromatograms were removed after the solvent front had travelled 8 cm.

For verification of eqn. (9a), the results were recalculated.  $R_F$  values were converted into  $R_M$  values as usual. As for  $(X_w)_{\text{a}}$ , the results of Pitra<sup>13</sup> suggest that the water content of silica gel is a monotonous function of the relative air humidity  $P/P_0$ , where  $P$  is the actual water vapour pressure and  $P_0$  is the pressure of saturated water vapour at a given temperature. For simplicity  $P/P_0$  was equated to  $(X_w)_{\text{a}}$ , and  $R_M$  vs.  $(\log 1 - P/P_0)$  was plotted. As shown in Figs. 7 and 8, the resulting curves are not linear, but are better suited to discussion than simple  $R_F$  vs.  $P/P_0$  ones.

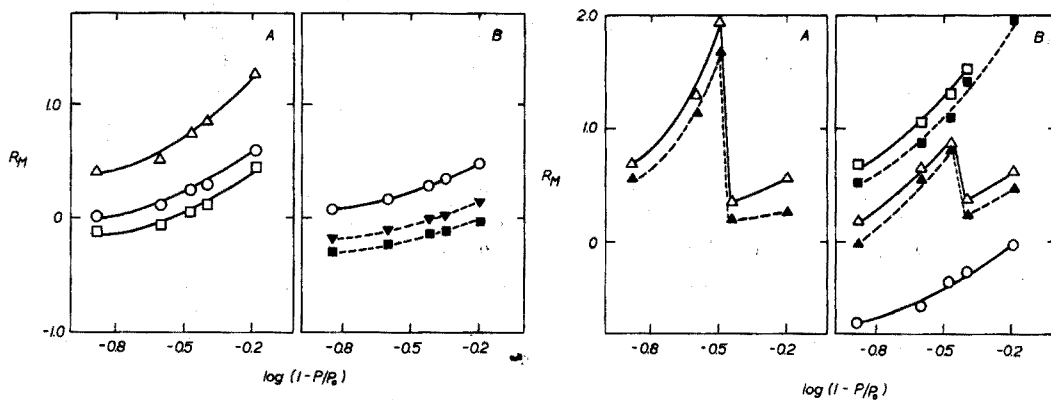


Fig. 7. Effect of air humidity. (A) Pyridylazonaphthols (for symbols see Fig. 1) developed by 4% (v/v) methanol in  $\text{C}_6\text{H}_6$ . (B)  $\beta$ -PAN (O) and its nickel ( $\blacktriangledown$ ) and iron ( $\blacksquare$ ) chelates developed by 1.8% (v/v) acetone in chloroform.

Fig. 8. Effect of air humidity. (A) Copper chelate developed by 15% (v/v) ethanol in  $\text{C}_6\text{H}_6$ . (B)  $\beta$ -PAN (O) developed beside its copper ( $\Delta$ ,  $\blacktriangle$ ) and cobalt ( $\square$ ,  $\blacksquare$ ) chelates by 28% (v/v) methanol in  $\text{C}_6\text{H}_6$ . In both A and B, broken lines denote chelates extracted from salicylate medium and full lines from KBr medium.

The shapes and slopes of the curves given in Fig. 7 are similar; these refer to solutes with single bonding to silica gel (as found by  $R_M$  vs.  $\log X_S$  experiments). This agrees with eqn. (9), which predicts that solutes with the same number of bonds to the adsorbent should be similarly sensitive to the effect of water content of adsorbent. The validity of eqn. (9) is further supported by the slope of the curve obtained for the cobalt chelate (Fig. 8, part B), which is higher than that of the  $\beta$ -PAN curve, as was expected from the higher number of bonds of the cobalt chelate.

As for the curve obtained with the copper chelate, an anomalous shape (as

given in Fig. 8) was observed in four separate runs when the chromatograms were developed by 7% methanol in chloroform, 20% acetone in chloroform, 15% ethanol in benzene or 28% methanol in benzene. Since this anomalous behaviour was also observed on chromatograms where  $\beta$ -PAN and the cobalt chelate behaved normally, the break observed on the copper curve cannot be caused by irregular solvent flow, and remains unexplained. The slope of the curve at higher  $P/P_0$  values seems, however, to indicate that eqn. (9) is fulfilled in these ranges, because the slope is higher than that observed with single-bonded solutes.

The author wishes to thank Dr. D Betteridge for a specimen of 2-(2-pyridylazo)-1-naphthol, and Professor S. I. Gusev for specimens of 2-(2-pyridylazo)-1-naphthol and 4-(2-pyridylazo)-1-naphthol. The interest of Professor Soczewiński in the present work is acknowledged.

#### SUMMARY

The relationships between the thin-layer chromatographic behaviour of solutes, the solvent composition and the water content of silica gel were derived on the basis of the mass action law applied to Martin's equation. The relationships were proved experimentally by studying 1-(2-pyridylazo)-2-naphthol, its isomers and its metal chelates with copper, nickel, cobalt and iron. The results suggest that an oxygen atom of the solutes is the centre of bonding to silica gel. Mixed ligand chelates of copper with PAN and diverse ligands were studied; an increase of  $R_F$  values was related to the affinity of the auxiliary ligand for the  $\text{CuPAN}^+$  species. The extraction mechanism of the iron chelate with PAN appears to be complex and involves at least partial reduction to iron(II) in the chelate.

#### RÉSUMÉ

Les relations entre le comportement des substances dissoutes, de la composition de la solution et de la teneur en eau du gel de silice chez la chromatographie en couche mince, furent déduites à raison de la loi d'action de masse, appliquée à l'équation de Martin. Les relations furent confirmées expérimentalement par l'étude du 1-(2-pyridylazo)-2-naphthol, de ses isomères et des noyaux chélatés avec du cuivre, du nickel, du cobalt et du fer. La discussion des résultats mène à la supposition, qu'un atome d'oxygène des substances dissoutes pourrait être le centre de la liaison au gel de silice. En cours de l'étude des noyaux chélatés mixtes de cuivre avec PAN et avec ses divers ligands on a pu déterminer une élévation de la valeur du  $R_F$ , qui fut mise en rapport à l'affinité de l'aide-ligand aux espèces du  $\text{CuPAN}^+$ . L'étude du noyau chélaté de fer avec PAN indique un caractère complexe du mécanisme de l'extraction, amenant une réduction partielle du fer en noyau chélaté à l'état divalent.

#### ZUSAMMENFASSUNG

Die Beziehungen zwischen dem Verhalten gelöster Stoffe, der Zusammensetzung der Lösung und dem Wassergehalt des Kieselgels bei der Dünnschicht-Chromatographie wurden auf Grund des auf die Gleichung von Martin angewandten

Massenwirkungsgesetzes abgeleitet. Die Beziehungen wurden experimentell durch Untersuchung 1-(2-Pyridylazo)-2-naphthol, seiner Isomeren und Metallchelaten mit Kupfer, Nickel, Kobalt und Eisen geprüft. Die Ergebnisse führt zur Annahme, dass ein Sauerstoffatom der gelösten Stoffe ein Zentrum für die Bindung an Kiesegel sein könnte. Während des Studiums der gemischten Liganden-Chelate von Kupfer mit PAN und verschiedenen Liganden wurde eine Erhöhung der  $R_F$ -Werte festgestellt und zur Affinität des Hilfs-Liganden zu  $\text{CuPAN}^+$ -Arten in Beziehung gesetzt. Das Studium des Eisenchelates mit PAN weist auf einen komplexen Charakter des Extraktionsmechanismus hin, wobei es zur teilweisen Reduktion des Eisens im Chelat zur divalenten Form kommt.

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## VOLATILE COMPLEXES OF SOME LANTHANIDES AND RELATED ELEMENTS WITH FLUORINATED $\beta$ -DIKETONES AND ORGANOPHOSPHORUS ADDUCTS\*

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Berg and Truemper<sup>1</sup> have measured the vapor pressures of the acetylacetonates of the transition metals. Berg and Acosta<sup>2</sup> have also published a comprehensive study on the sublimation of the chelates of the lanthanides, scandium, thorium and uranium(VI) with acetylacetone (HAA), trifluoroacetylacetone (HTFA), hexafluoroacetylacetone (HHFA) and 2,2,6,6-tetramethylheptane-3,5-dione (HTHD). Several separations of mixtures of the chelates of the lanthanides with HHFA were reported to be possible by fractional sublimation under reduced pressure. Bhaumik<sup>3</sup> found that tris(hexafluoroacetylacetonato)-europium(III) sublimes with partial decomposition. Vapor pressures, heats of sublimation and heats of vaporization of the chelates of the lanthanides with HTHD were measured by Sicre *et al.*<sup>4</sup>. They found these chelates to be completely volatile and thermally stable.

Lippard<sup>5</sup> discovered that an eight-coordinated  $\beta$ -diketone complex, CsY-(HFA)<sub>4</sub>, could easily be sublimed in air and *in vacuo* without apparent decomposition. This demonstration of the stability of an ion-association complex in the gas phase stimulated investigations by other workers. Belcher *et al.*<sup>6</sup> investigated a series of chelates of the lanthanides of the composition, L(R.E.)A<sub>4</sub>, where L represents the alkali metals, R.E. represents the lanthanides and A is the anion of the  $\beta$ -diketone, trifluoroacetylacetone, hexafluoroacetylacetone or 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione. Ismail *et al.*<sup>7</sup> also studied the chelates, L(R.E.)A<sub>4</sub> of 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione.

Thermal analysis has proven to be a convenient tool for the determination of the relative volatilities and the thermal stabilities of chelates prior to gas chromatographic studies. Eisentraut and Sievers<sup>8</sup> reported thermograms for the chelates of the lanthanides with HTHD. These anhydrous chelates were gas-chromatographed without decomposition<sup>9</sup>. Berg and Acosta<sup>2</sup> demonstrated that fluorine-containing  $\beta$ -diketones formed more volatile chelates than the corresponding hydrocarbon derivatives. Springer *et al.*<sup>10</sup> synthesized 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (HFOD), which was specifically designed to retain the desired shielding effect of the bulky ligand of HTHD and to possess the added advantage

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of increased volatility. The resuming chelates of the rare earths with HFOD were isolated as monohydrates which could easily be dehydrated *in vacuo* without significant hydrolysis. These chelates were chromatographed and were found to be more volatile than the corresponding chelates of HTHD.

Efforts have been continued in this Laboratory to obtain volatile chelates which possess improved thermal properties. Investigations of mixed complexes of the lanthanides with fluorinated  $\beta$ -diketones and organophosphorus compounds have resulted in new types of volatile chelates of these elements. The thermal behavior of these mixed complexes is reported in this paper.

## EXPERIMENTAL

### *Apparatus and reagents*

The DuPont 900 Differential Thermal Analyzer and 950 Thermogravimetric Analyzer were used to record thermograms. The Beckman Model GC4, equipped with a flame ionization detector, was used for gas-chromatographic studies.

Trifluoroacetylacetone and hexafluoroacetylacetone were obtained from Peninsular Chemresearch, Incorporated. Gas chromatograms of the freshly distilled reagents showed no detectable impurities. Tri-*n*-butylphosphate (TBP, Fisher Scientific Company) was purified by the procedure of Irving and Edgington<sup>11</sup>. Tri-(2,2,2-trifluoroethyl)-phosphate (TFEP) and tri-(3,3,3,2,2-pentafluoropropyl)-phosphate (PFPP) were prepared by procedures developed at the Ames Laboratory by John J. Richards. These compounds were distilled before use and gas chromatograms indicated highly pure reagents. Rare earth oxides of 99.9% purity were obtained from the Ames Laboratory. All other chemicals were of reagent-grade quality.

### *Preparation of chelates*

The method of Haszeldine *et al.*<sup>12</sup> was modified for the preparation of the chelates of uranium(IV) with HTFA and with HHFA. The pH of the green-colored aqueous solution containing uranium(IV) was adjusted between 2.0 and 3.0. The gelatinous uranium(IV)-HTFA chelate, which precipitated upon the addition of excess ligand, was dissolved by and extracted into benzene upon shaking. The organic phase containing the chelate was transferred to a container which allowed nitrogen to be bubbled through the solution. A nitrogen-filled polyethylene glove bag permitted all previous operations to be conducted in an inert atmosphere. The capped bubbler was removed from the glove bag and the solvent was evaporated by passing nitrogen through the solution which was heated by a water bath. The dissolution and evaporation procedures were repeated.

The chelate of uranium(IV) with HHFA was prepared by repeated extraction of an aqueous solution of the cation with excess HHFA in ether. The solid chelate was obtained by the previously mentioned evaporation technique. The chelates were stored in opaque vials under a nitrogen atmosphere. Analysis of the complexes showed 27.81 and 22.60% uranium for the U(IV)-HTFA and U(IV)-HHFA chelates, respectively (theoretical values, 28.00 and 22.32%).

The mixed complexes of the chelates of the lanthanides with either HTFA or HHFA with adducts, TBP, TFEP, or PFPP, were prepared by solvent extraction techniques. The pH of the aqueous phase containing the rare earth chloride was



adjusted to 5.27 with a buffer solution of sodium acetate and acetic acid. Aliquots of these solutions were equilibrated in separatory funnels with cyclohexane containing a sufficient amount of each ligand to establish a 3 : 1 ratio of  $\beta$ -diketone to rare earth and a 2 : 1 ratio of adduct to rare earth in the two-phase system. The mixed complexes were isolated as oils by evaporation of the organic solvent. Precipitation of the mixed complexes did not occur upon dissolution in ether and cooling in a dry ice-acetone bath. Corresponding mixed complexes of the uranyl ion were similarly prepared and isolated as oils or semi-solids.

The hydrated chelates of the lanthanides with HTFA or HHFA were prepared by standard methods<sup>6,13,14</sup> and recrystallized from benzene and *n*-hexane, respectively. Infrared spectra of the chelates showed the characteristic absorption bands reported by Richardson *et al.*<sup>14</sup> and Morris *et al.*<sup>15</sup>.

## RESULTS AND DISCUSSION

Several investigators<sup>16-18</sup> have proposed that the thermal instability of certain chelates of the  $\beta$ -diketones is related to the presence of hydrated water. The unsuccessful attempt to elute tris(trifluoroacetylacetonato)-neodymium(III) from a gas-chromatographic column was attributed to thermal degradation which in turn was postulated to be caused by hydrated water<sup>19</sup>. During the present investigation thermograms of the chelates of neodymium, europium and thulium with HTFA were recorded in a nitrogen atmosphere at a furnace heating rate of  $5^{\circ}\text{C min}^{-1}$ . The

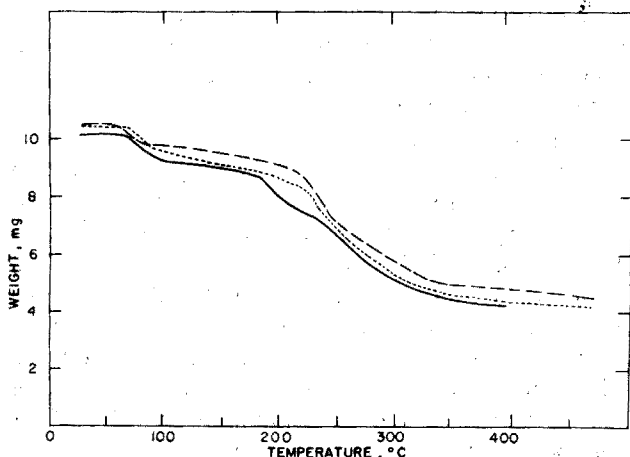


Fig. 1. Thermograms of hydrated chelates of some lanthanides with trifluoroacetylacetonate.  $\text{Nd}^{3+}$  ----,  $\text{Eu}^{3+}$  ·····,  $\text{Tm}^{3+}$  ———.

thermograms shown in Fig. 1 indicate that the trihydrated chelates undergo extensive decomposition. After an initial loss of water, the chelates decomposed leaving a residue corresponding to 40% of the initial weight. Thermograms of the trihydrated rare earth chelates of hexafluoroacetylacetonate are shown in Fig. 2. The highly fluorinated chelates are seen to be more volatile than the chelates of HTFA. However, sublimation of these complexes is accompanied by thermal degradation at tem-

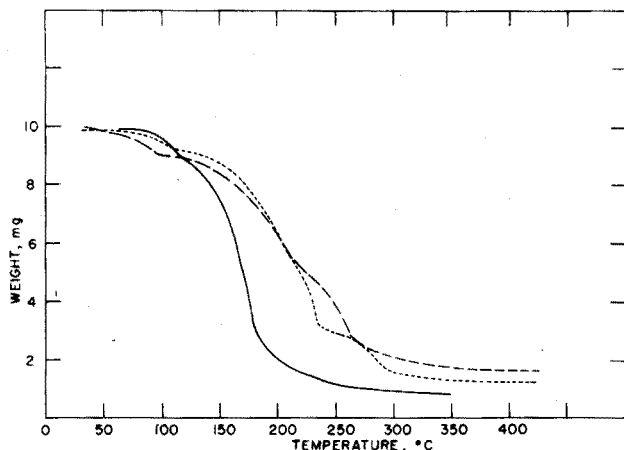


Fig. 2. Thermograms of hydrated chelates of some lanthanides with hexafluoroacetylacetone.  $\text{Nd}^{3+}$  ----,  $\text{Eu}^{3+}$  ·····,  $\text{Tm}^{3+}$  ———.

temperatures above  $200^\circ$ . The greater volatility of the thulium chelate is consistent with the known increase in volatility of the chelates of the lanthanide with increasing atomic number<sup>10</sup>.

Sievers *et al.*<sup>8,10</sup> have analyzed by thermogravimetric methods the chelates of the rare earths with HTHD and HFOD and reported that these chelates were volatilized without any apparent decomposition. Although it was reported that the former chelates were isolated as anhydrous tris-complexes, the latter contained one mole of weakly bonded water which was easily removed by drying over  $\text{P}_4\text{O}_{10}$ . Other investigators<sup>2,18</sup> have attempted to remove strongly bonded waters of hydration from the chelates of the rare earths. They reported that their efforts either resulted in decomposition with a loss of the  $\beta$ -diketone and the formation of basic, non-volatile polymerized species or produced highly hygroscopic anhydrous chelates which quickly reverted to the hydrated form upon exposure to the atmosphere.

The present authors took advantage of the well known synergic effect to prepare anhydrous chelates of the lanthanides with HTFA and HHFA. The waters of hydration of these chelates were displaced by adduct formation with neutral donors such as organophosphorus compounds. It was recently shown that species of composition,  $\text{M}(\text{A})_3 \cdot 2\text{TBP}$ , were transferred to the organic phase when an aqueous acetate-chloride medium of the lanthanides was equilibrated with cyclohexane solutions of aliphatic fluorinated  $\beta$ -diketones and tri-*n*-butylphosphate<sup>20</sup>; M represents any lanthanide element and A is the anion of the ligand ( $\beta$ -diketone).

Thermograms of the complexes of the lanthanides,  $\text{M}(\text{A})_3 \cdot 2\text{D}$ , where A is the anion of HTFA and D is TBP, are shown in Fig. 3. It is clearly evident that these complexes are anhydrous and considerably more volatile and thermally stable than the corresponding hydrated chelates. Thermograms of the mixed complexes of HHFA and TBP are recorded in Fig. 4. The improved volatility and thermal stabilities of these adduct complexes provide additional evidence to substantiate that water of hydration is instrumental in the thermal degradation of chelates of the rare earths with  $\beta$ -diketones.

In view of the known increase in the volatility of fluorinated ligands the com-

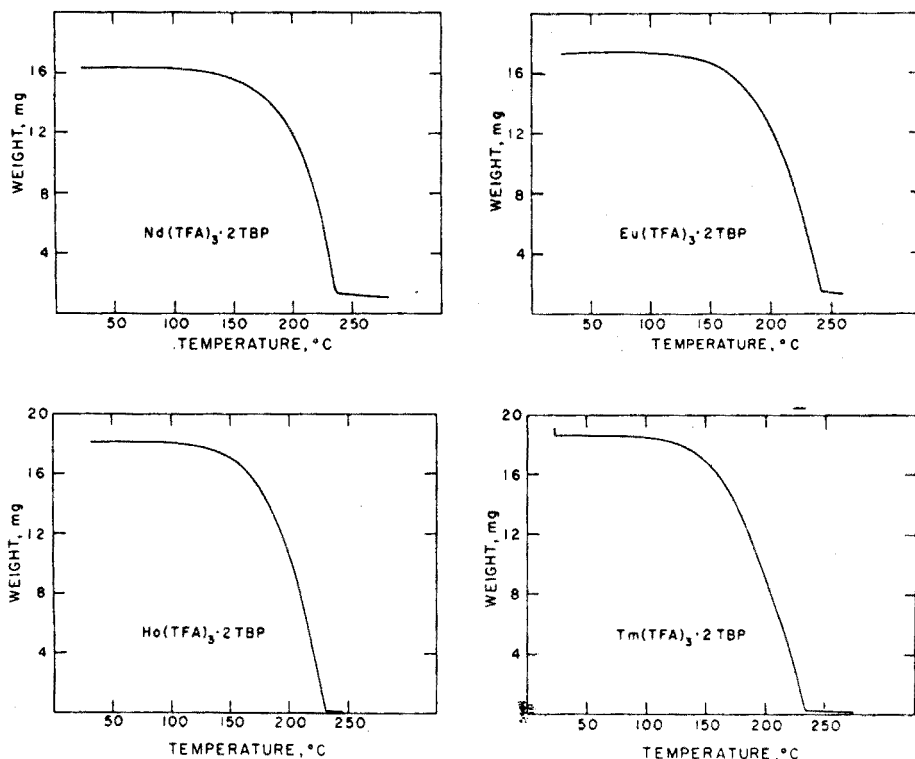


Fig. 3. Thermograms of ternary complexes of some lanthanides with trifluoroacetylacetone and TBP.

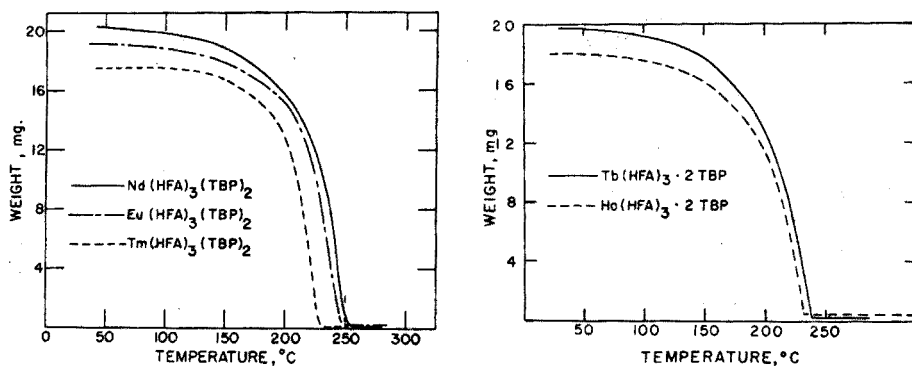


Fig. 4. Thermograms of ternary complexes of some lanthanides with hexafluoroacetylacetone and TBP.

pounds tri-(2,2,2-trifluoroethyl)-phosphate and tri-(3,3,3,2,2-pentafluoropropyl)-phosphate were employed in the preparation of mixed chelates. Results of thermogravimetric analysis of the mixed complexes of the rare earths with hexafluoroacetylacetone and either TFEP or PFPP are presented in Figs. 5 and 6. Comparison of these thermograms with those obtained from equal initial quantities of the corresponding mixed chelates containing HHFA and TBP indicated that mixed com-

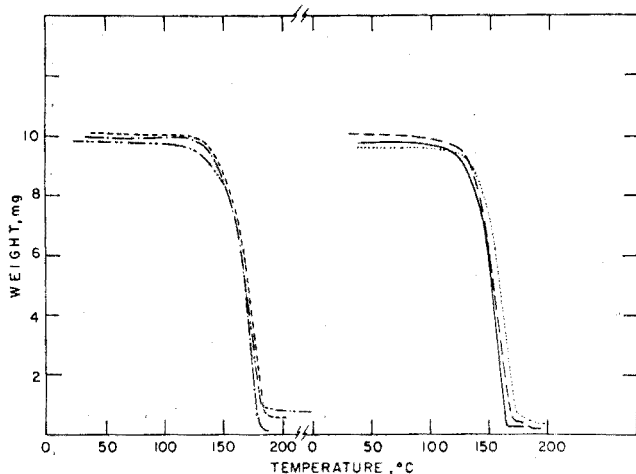


Fig. 5. Thermograms of ternary complexes of some lanthanides with hexafluoroacetylacetone and tri-(2,2,2-trifluoroethyl)-phosphate. R.E.  $(\text{HFA})_3(\text{TFEP})_2$ .  $\text{Pr}^{3+}$  —,  $\text{Nd}^{3+}$  - - - - ,  $\text{Eu}^{3+}$  - · - · - ,  $\text{Ho}^{3+}$  · · · · · ,  $\text{Er}^{3+}$  - - - - - ,  $\text{Tm}^{3+}$  - - - - - .

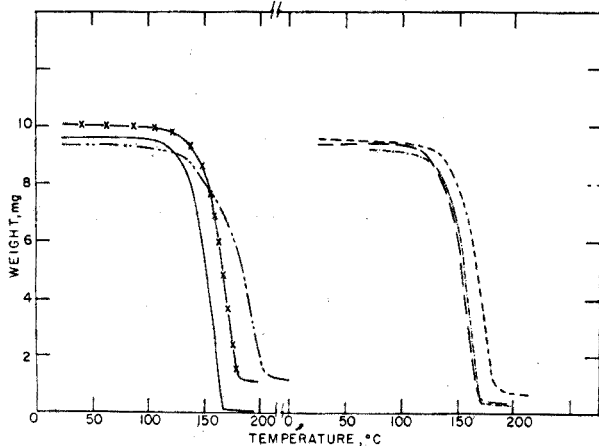


Fig. 6. Thermograms of ternary complexes of some lanthanides with hexafluoroacetylacetone and tri-(3,3,3,2,2-pentafluoropropyl)-phosphate. R.E.  $(\text{HFA})_3(\text{PFPP})_2$ .  $\text{Pr}^{3+}$  —,  $\text{Nd}^{3+}$  - - - - ,  $\text{Eu}^{3+}$  - x - ,  $\text{Ho}^{3+}$  - - - - - ,  $\text{Er}^{3+}$  - - - - - ,  $\text{Tm}^{3+}$  - · - · - .

plexes containing fluorinated phosphates were volatilized at lower temperatures. The mixed complexes containing TFEP are observed to be more stable than those containing PFPP.

Figure 7 shows thermograms of mixed complexes of uranium(VI),  $\text{UO}_2(\text{A})_2 \cdot \text{D}$ . Although the mixed chelate,  $\text{UO}_2(\text{HFA})_2 \cdot \text{TBP}$ , is reasonably volatile and thermally stable, the thermogram of the mixed chelate,  $\text{UO}_2(\text{TFA})_2 \cdot \text{TBP}$ , suggests that factors other than thermal degradation initiated by hydrated water must contribute to the thermal behavior of these particular mixed chelates. Thermograms of the anhydrous chelates of uranium(IV) with HTFA and with HHFA are shown in Fig. 8. The greater volatility and stability of  $\text{U}(\text{TFA})_4$  than was previously observed for  $\text{UO}_2(\text{TFA})_2 \cdot \text{TBP}$  indicates that the presence of the uranyl oxygen atoms could stimulate thermal de-

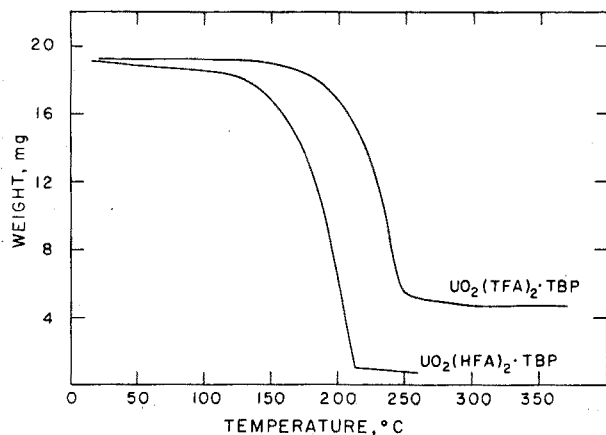


Fig. 7. Thermograms of ternary complexes of uranium(VI) with either HTFA or HHFA and TBP.

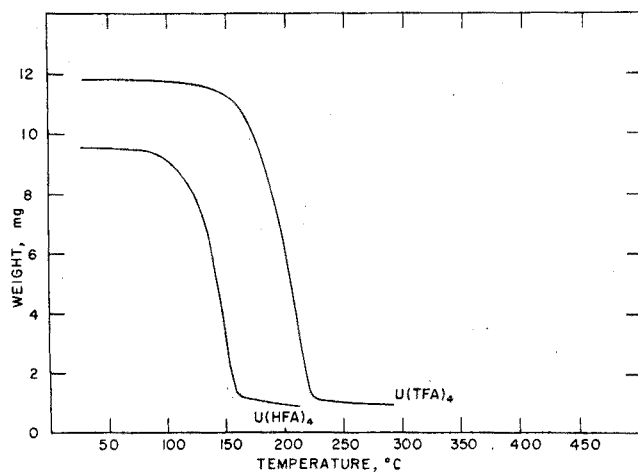


Fig. 8. Thermograms of chelates of uranium(IV) with either HHFA or HTFA.

composition by initiating the formation of stable non-stoichiometric uranium oxides.

Thermograms for  $\text{UO}_2(\text{HFA})_2 \cdot \text{PFPP}$ ,  $\text{UO}_2(\text{HFA})_2 \cdot \text{TFEP}$ ,  $\text{Th}(\text{HFA})_4 \cdot \text{PFPP}$  and  $\text{Th}(\text{HFA})_4 \cdot \text{TFEP}$  are presented in Fig. 9. The inferior extraction of these cations in synergic systems containing the fluoroorganophosphorus donors indicated that the extreme thermal instability of the uranyl complexes probably resulted from the poor thermodynamic stability of the mixed complexes.

Although the chelates of uranium(IV) were not completely volatilized under thermogravimetric conditions, no evidence indicative of thermal decomposition was observed by gas chromatography. Well defined peaks are shown for the  $\text{U}(\text{TFA})_4$  and  $\text{U}(\text{HFA})_4$  chelates in Fig. 10. The mixed chelate,  $\text{U}(\text{HFA})_4 \cdot 2\text{TBP}$  was eluted with a tailing effect while  $\text{U}(\text{TFA})_4 \cdot 2\text{TBP}$  was not successfully chromatographed. To the knowledge of the authors the gas chromatography of chelates of uranium(IV) has not been previously reported.

The importance of volatilization at low temperatures and thermal stability

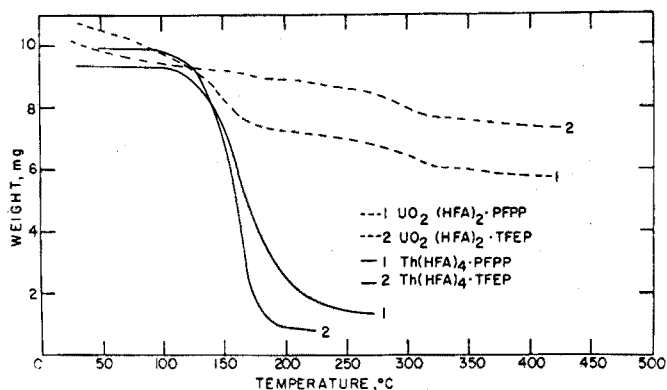


Fig. 9. Thermograms of ternary complexes of uranium(VI) and thorium(IV) with HHFA and either PFPP or TFEP, respectively.

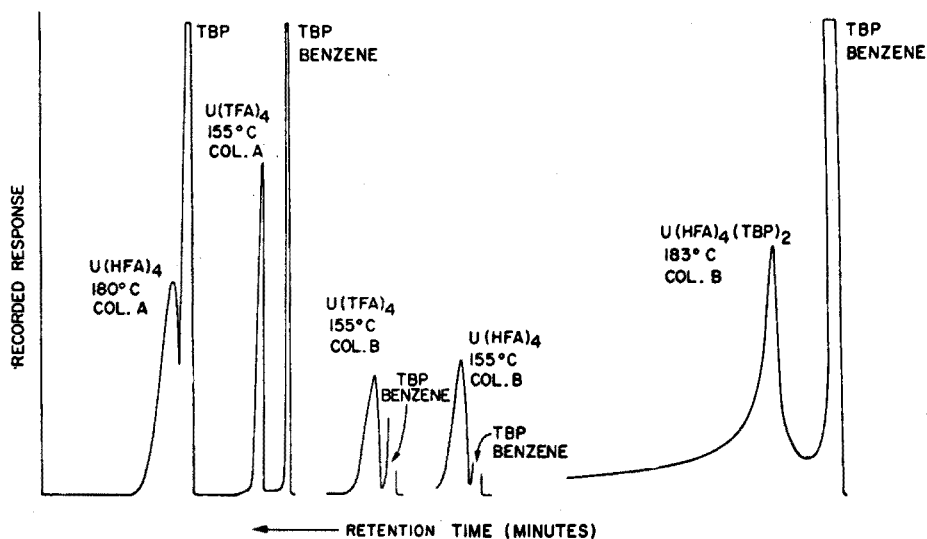


Fig. 10. Gas chromatograms of some chelates of uranium(IV) with and without the adduct TBP. Flow  $55 \text{ ml min}^{-1}$ .  $4' \times \frac{1}{4}'$ . Column A: 0.1% SE 30 on glass beads. Column B: 5% SE 30 on Chromosorb G.

with respect to fragmentation or decomposition is obvious in the gas chromatography of metal chelates. Although the temperatures at which volatilization occurred and the thermal stabilities of the mixed chelates of the lanthanides with either HTFA or HHFA along with TBP were similar under the conditions employed in thermogravimetry, only the mixed complexes containing HHFA have been successfully eluted intact during gas chromatography<sup>10</sup>. Investigations are presently being planned to determine the relative importance of the thermodynamic stability of mixed ligand-adduct chelate complexes on the possibilities of gas chromatography of these mixed chelates. Structural requirements and the effects of physical and chemical properties of the fluorinated  $\beta$ -diketone ligands and organophosphorus donors will also be studied.

## SUMMARY

The behavior of lanthanide trifluoroacetylacetonates and hexafluoroacetylacetonates of mixed complexes with tri-*n*-butylphosphate as the adduct has been studied by thermogravimetric methods. Thermal properties of mixed ligand-adduct complexes containing new fluoroorganophosphorus donors have also been examined. Substantial improvements in volatility and thermal stability of chelates of the lanthanides with either HTFA or HHFA were obtained by displacing the hydrated water with an organophosphorus donor. The thermal stability and volatility of chelates of uranium(IV), uranium(VI) and thorium(IV) were also determined.

## RÉSUMÉ

Une étude thermogravimétrique est effectuée sur le comportement des trifluoroacétylacétonates et hexafluoroacétylacétonates de lanthanides, de complexes mixtes avec tri-*n*-butylphosphate. On a examiné également les propriétés thermiques de nouveaux complexes fluoroorganophosphore. Une nette amélioration de la volatilité et de la stabilité thermique des chélates de lanthanides est obtenue avec HTFA ou HHFA, en déplaçant l'eau d'hydratation à l'aide d'un donneur organophosphore. On a également déterminé la stabilité thermique et la volatilité de chélates d'uranium(IV), d'uranium(VI) et de thorium(IV).

## ZUSAMMENFASSUNG

Das Verhalten der gemischten Komplexe von Trifluoracetylacetonaten und Hexafluoracetylacetonaten der Lanthaniden mit Tri-*n*-butylphosphat als Addukt wurde mit thermogravimetrischen Methoden untersucht. Ausserdem wurden die thermischen Eigenschaften von gemischten Ligand-Addukt-Komplexen untersucht, die als Elektronendonatoren neue Fluoroorganophosphor-Verbindungen enthalten. Es wurde wesentliche Verbesserungen in der Flüchtigkeit und thermischen Stabilität der Lanthanidenchelate mit sowohl HTFA als auch HHFA erzielt, wenn das Hydratwasser durch einen Organophosphor-Donator ersetzt wurde. Die thermische Stabilität und Flüchtigkeit der Chelate von Uran(IV), Uran(VI) und Thorium(IV) wurden ebenfalls bestimmt.

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## 1-(*o*-CARBOXYPHENYL)-3-HYDROXY-3-METHYLTRIAZENE FOR THE DIRECT GRAVIMETRIC DETERMINATION OF TITANIUM(IV) IN PRESENCE OF NIOBIUM AND TANTALUM

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N-Hydroxytriazenes<sup>1</sup> have been used successfully for the determination of a number of metal ions by spectrophotometric as well as by gravimetric methods. 3-Hydroxy-1-*p*-chlorophenyl-3-phenyltriazene has been recommended<sup>2</sup> as a reagent for the gravimetric determination of titanium but its precipitate, being of uncertain composition, needs ignition to the oxide and is subject to many interferences. 1-(*o*-Carboxyphenyl)-3-hydroxy-3-phenyltriazene, on the other hand, is highly suitable for the direct gravimetric determination of titanium(IV) in presence of all ions except niobium and tantalum<sup>3</sup> and for the spectrophotometric determination<sup>4</sup> of titanium(IV), vanadium(V) and iron(III) in the presence of each other. Since the reagent is not very soluble in water, its aqueous ammoniacal solution is preferred as a precipitant<sup>4</sup>.

In the present paper another triazene derivative is proposed; in this reagent, the phenyl group is replaced by a methyl group, so that there is less weighting effect and the precipitate is slightly more soluble. However, this new reagent permits direct determination of titanium even in the presence of niobium and tantalum besides other anions and cations. This is perhaps the only reagent which gives such a clear separation of titanium from niobium and tantalum by a single precipitation.

The orange titanium complex is highly stable and does not decompose or melt even upto 320°. It is slightly soluble in dimethylformamide, pyridine, chloroform or nitromethane, and almost insoluble in methanol, ethanol, carbon tetrachloride and benzene.

In this complex, the titanyl stretching frequency occurs at 883 cm<sup>-1</sup> and the asymmetric stretching frequency of the carboxyl group in the solid reagent as well as in the solid complex appears in the same region (1670 cm<sup>-1</sup>), suggesting thereby that it is a titanyl complex of the previous type<sup>3</sup> with an unreactive -COOH group.

Precipitation of the complex can be made at a pH value between 1.0 and 4.5 and the precipitate is weighed after drying at 120° as TiO(C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>N<sub>3</sub>)<sub>2</sub>. The few serious interferences can be readily overcome.

### EXPERIMENTAL

#### *Preparation of the reagent*

An ice-cold diazotized solution of anthranilic acid was added to a cold (0°) solution of methylhydroxylammonium chloride. The solution was then saturated with sodium acetate and kept at 0° for about an hour. Concentrated hydrochloric acid

was then added to adjust the pH to about 1 and the mixture was again kept at ice-cold temperature for 1 h. The yellow product was crystallized 2–3 times from ethanol in presence of activated charcoal.

The colourless crystalline product is highly stable (m.p. 186° decomp.). (Found, C 48.63%, H 4.68%, N 21.60%;  $C_8H_9O_3N_3$  requires C 49.23%, H 4.65%, N 21.53%.) The compound is fairly soluble in ethanol, methanol, nitrobenzene, acetone and dioxane and slightly soluble in chloroform, benzene, carbon tetrachloride and in hot water.

An alcoholic solution of the reagent was used for the precipitation of titanium.

### *Chemicals*

Standard solutions of titanium and other cations and anions were prepared in the same way as stated earlier<sup>3</sup>. EDTA (disodium salt) and tartaric acid, aqueous 5% (w/v) solutions of each, were used as the complexing agents.

### *Effect of pH*

The effect of pH on the precipitation and then direct weighing was examined for 11.70 mg of titanium(IV). Precipitation was found to be quantitative between pH 1.0 and 4.5. However, when the pH was below 2.0, a digestion period of 45 min was required, whereas only 15 min was necessary when the pH was above 4.0. For this reason, the pH of the solution was maintained between 2.0 and 4.5, and a digestion period of 25–30 min was chosen. The determination of titanium with ignition to the oxide was not possible since the complex exploded violently at its decomposition temperature.

### *General procedure*

An aliquot of titanium solution was diluted to 150–350 ml with water and then 0.20 g of the reagent in about 5 ml of hot ethanol was added. After the pH had been adjusted to 2.0–4.5, the mixture was heated on a boiling water bath for 25–30 min. The reddish orange precipitate which settled was filtered through a No. 3 Gooch crucible, and washed several times with hot water, the pH of which was adjusted to ca. 3.0 with hydrochloric acid, and finally with water. It was then dried at 120° and weighed.

The precipitation of different amounts of titanium from solutions containing 2.0 g of tartaric acid was carried out with 0.50 g of the reagent in 10 ml of hot ethanol, the other conditions remaining the same.

## RESULTS AND DISCUSSION

### *Composition of precipitate*

After the complex had been precipitated as described in the general procedure, the washed and dried precipitate was decomposed by a mixture of nitric, sulphuric and perchloric acids and its titanium content was determined as  $TiO_2$ . The nitrogen content was determined in the original sample by the Dumas method. The composition of the complex agreed with the formula  $TiO(C_8H_8O_3N_3)_2$ . (Found, Ti 10.58%, N 18.72%; calculated Ti 10.59%, N 18.59%.) The conversion factor for the titanium content is, therefore, 0.1059.

*Precipitation of titanium*

It was found that 1–40 mg of titanium could be determined under the recommended conditions.

*Separation from foreign ions*

A hot ethanolic solution (5 ml) of the reagent (0.20 g) was added to a solution containing known amounts of different foreign ions and titanium as sulphate, and the procedure followed was the same as suggested above. The results are shown in Table I. When complexing agents were used more reagent (0.5 g) was required, otherwise the results were a little low.

TABLE I

DIRECT DETERMINATION AND SEPARATION OF TITANIUM FROM OTHER IONS BETWEEN pH 2.0 AND 4.5  
(Ti taken = 11.70 mg in each case)

<i>Ions added</i>	<i>Amount (mg)</i>	<i>Weight of the dried complex (mg)</i>	<i>Titanium found (mg)</i>
Co <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup>	100 each	110.9	11.74
Zn <sup>2+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , Mg <sup>2+</sup>	100 each	110.0	11.65
Be <sup>2+</sup> , Al <sup>3+</sup>	200 each	110.2	11.67
Cr <sup>3+</sup>	200	110.4	11.69
Pd <sup>2+</sup>	100	110.8	11.73
AsO <sub>4</sub> <sup>3-</sup> , SeO <sub>3</sub> <sup>2-</sup> , TeO <sub>4</sub> <sup>2-</sup>	100 each	110.2	11.67
AsO <sub>3</sub> <sup>3-</sup>	100	110.4	11.69
MoO <sub>4</sub> <sup>2-</sup> , WO <sub>4</sub> <sup>2-</sup>	100 each	110.5	11.70
Ce <sup>4+</sup> , Th <sup>4+</sup>	100 each	110.0	11.65
La <sup>3+</sup> , Ce <sup>3+</sup>	100 each	110.8	11.73
Nb <sup>5+</sup>	100	110.6	11.70
Ta <sup>5+</sup>	60	110.8	11.73
Zr <sup>4+</sup>	200	110.6	11.70
Hf <sup>4+</sup>	50	110.5	11.70
UO <sub>2</sub> <sup>2+</sup>	200	110.9	11.74
VO <sub>3</sub> <sup>4-</sup>	100	110.6	11.70
H <sub>2</sub> O <sub>2</sub>	5 ml of 10 vol.	111.1	11.76
Oxalic acid, citric acid <sup>a</sup>	1000 each	110.2	11.67
F <sup>-</sup>	100	110.4	11.69
EDTA <sup>a</sup>	500	110.1	11.66
Tartaric acid <sup>a</sup>	2000	110.6	11.70
PO <sub>4</sub> <sup>3-</sup> <sup>a</sup>	100	110.7	11.71
Fe <sup>3+</sup> <sup>a</sup>	100	110.8	11.73

<sup>a</sup> Reagent used 40 times the amount of titanium present.

Iron(III) and vanadium(V) (100 mg of each) interfered, but this could be overcome by adding 1 g of EDTA. Interference of phosphate (100 mg) was prevented by addition of 1 g of tartaric acid. Fluoride interfered seriously but could be masked by the addition of excess of beryllium(II).

## SUMMARY

An improved direct gravimetric method for the determination of titanium in the presence of niobium and tantalum, as well as other cations and anions, with a new reagent, 1-(*o*-carboxyphenyl)-3-hydroxy-3-methyltriazene, is suggested. The titanium (1–40 mg) is quantitatively precipitated in the pH range 1.0–4.5 and can be weighed as  $\text{TiO}(\text{C}_8\text{H}_8\text{O}_3\text{N}_3)_2$  after drying at  $120^\circ$ . The few serious interferences can be avoided by the use of masking agents.

## RÉSUMÉ

On propose une meilleure méthode pour le dosage gravimétrique direct du titane, en présence de niobium et de tantale, ainsi qu'en présence d'autres cations et anions. On utilise comme réactif nouveau l'*o*-carboxyphényl-1-hydroxy-3-méthyl-3-triazène. Le titane (1–40 mg) est précipité quantitativement entre pH 1.0 et 4.5 et peut être pesé comme  $\text{TiO}(\text{C}_8\text{H}_8\text{O}_3\text{N}_3)_2$  après séchage à  $120^\circ$ . Les quelques interférences sérieuses peuvent être évitées en utilisant des réactifs de masquage.

## ZUSAMMENFASSUNG

Es wird eine verbesserte, direkte gravimetrische Methode für die Bestimmung von Titan in Gegenwart von Niob und Tantal sowie anderen Kationen und Anionen vorgeschlagen. Mit dem neuen Reagenz 1-(*o*-Carboxyphenyl)-3-hydroxy-3-methyltriazen wird das Titan (1–40 mg) im pH-Bereich 1.0–4.5 quantitativ gefällt und kann nach dem Trocknen bei  $120^\circ$  als  $\text{TiO}(\text{C}_8\text{H}_8\text{O}_3\text{N}_3)_2$  ausgewogen werden. Die wenigen ernsthaften Störungen können durch Verwendung von Maskierungsmitteln vermieden werden.

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*Anal. Chim. Acta*, 57 (1971) 425–428

## THE TITRATION OF ISONIAZID AND OTHER HYDRAZINE DERIVATIVES WITH CHLORAMINE-T

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Hydrazine and its derivatives find various applications in medicine, in rocket propulsion, as laboratory reagents, etc., hence their analytical determination is of importance. The antitubercular drug isoniazid (isonicotinic acid hydrazide) can be determined titrimetrically by bromine<sup>1</sup>, iodine<sup>2</sup> and iodate<sup>3</sup> methods as well as with sodium nitrite<sup>4</sup>. Quantitative oxidation of the hydrazine part of the molecule to nitrogen (with consumption of 4 equivalents of the oxidant per mole of the compound) is the basis of the first three methods. The nitrite method depends on a diazotisation reaction. Similar methods are available for other hydrazine derivatives such as phenylhydrazine<sup>5</sup>. Hydrazine itself has also been determined by a wide variety of oxidimetric titrations<sup>5</sup>. In the present paper, the results obtained for the oxidation of hydrazine and its derivatives with chloramine-T are reported.

Komarowsky *et al.*<sup>6</sup> noted as early as 1934 that hydrazine could be titrated with chloramine-T in a bicarbonate medium in the presence of a crystal of potassium iodide with starch as indicator; this is simply a variant of the iodine titration since the actual oxidant is iodine. Bishop and Jennings<sup>7</sup> later studied the potentiometric titration of hydrazine with chloramine-T under varying conditions of acidity, and concluded that the direct titration procedure cannot claim the high accuracy needed for a standard analytical method, although it may be of use in routine analysis. In the only other published application of chloramine-T for the determination of hydrazine derivatives, Singh *et al.*<sup>8</sup> used a type of Andrews' titration with iodine monochloride as intermediate in conjunction with chloramine-T; basically, this is a simple variation of the iodate titration.

In the work described here, it was established that hydrazine is quantitatively oxidized when an excess of chloramine-T is employed in an acidic medium; iodimetric titration of the excess is capable of giving results of high accuracy. The success of this method with hydrazine led to an examination of the chloramine-T oxidations of other hydrazine derivatives, such as phenylhydrazine, 2,4-dinitrophenylhydrazine, semicarbazide, *p*-nitrobenzhydrazide and isonicotinic acid hydrazide.

### EXPERIMENTAL

#### *Reagents*

Stock solutions of chloramine-T were prepared and standardized by the method of Bishop and Jennings<sup>9</sup>.

Samples of hydrazine sulphate, phenylhydrazine hydrochloride, 2,4-dinitro-

phenylhydrazine, semicarbazide hydrochloride, *p*-nitrobenzhydrazide and isonicotinic acid hydrazide (BDH AnalaR or Merck G.R.) were employed. Standard solutions of hydrazine sulphate, phenylhydrazine hydrochloride, semicarbazide hydrochloride and isonicotinic acid hydrazide were prepared in water and those of 2,4-dinitrophenylhydrazine and *p*-nitrobenzhydrazide were prepared in anhydrous acetic acid (A.R. grade). The strengths of all these solutions were checked by conventional indirect bromine or iodine methods. Other reagents employed were all of analytical reagent-grade purity.

#### *Preliminary study of pH*

The oxidation of hydrazine by chloramine-T was studied in solutions of pH value varying from 3 to 6 and also in strongly acidic and alkaline media. Oxidation was not quantitative in alkaline media. Variation of pH in the acidic range had little effect on the oxidation which was quantitative below pH 6. No pH control was therefore necessary provided that the medium was acidic. Since the redox potential of chloramine-T increases with decreasing pH it was considered desirable to effect the oxidation in strongly acidic media.

#### *Procedure*

Transfer an aliquot of chloramine-T (40 ml) to a 500-ml glass-stoppered conical flask and add 20 ml of 2.5 M sulphuric acid. Add a known volume of a solution of hydrazine (or its organic derivative) with shaking. Leave the solution at room temperature for about 15 min. Then add 20 ml of 10% potassium iodide solution and titrate the liberated iodine with standard thiosulphate solution. Determine blanks concurrently. No blank corrections were found necessary even for the maximum time of standing (60 min).

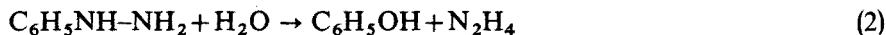
#### RESULTS AND DISCUSSION

Typical results for hydrazine and its derivatives are presented in Tables I–VI. It can be seen that four equivalents of the oxidant are consumed per mole of the reductant for all the compounds studied. This corresponds to the oxidation of the hydrazine part of each of these molecules to nitrogen according to the well-known reaction scheme



Reaction times varying from 5 to 60 min were examined. The reaction was found to be quantitative after a period of about 15 min in all cases. Longer standing times have no effect for hydrazine, semicarbazide, *p*-nitrobenzhydrazide and isonicotinic acid hydrazide. However, in the case of phenylhydrazine and 2,4-dinitrophenylhydrazine, the consumption of chloramine-T gradually increases on standing (Tables II and III). A tentative explanation for this phenomenon is suggested below.

It may be assumed that the following hydrolytic processes precede (or accompany) the oxidation.



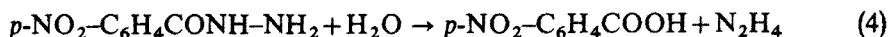


TABLE I

## OXIDATION OF HYDRAZINE SULPHATE WITH CHLORAMINE-T

Sample taken (mmol)	Time (min)	pH	Chloramine-T consumed (meq)	Equivalents of chloramine-T per mol of sample
0.2702	5	Acid medium <sup>a</sup>	1.081	4.000
0.2702	10	Acid medium <sup>a</sup>	1.081	4.000
0.2702	15	Acid medium <sup>a</sup>	1.081	4.000
0.2702	30	Acid medium <sup>a</sup>	1.081	4.000
0.2702	60	Acid medium <sup>a</sup>	1.081	4.000
0.3053	15	Acid medium <sup>a</sup>	1.221	3.999
0.3357	15	Acid medium <sup>a</sup>	1.340	3.992
0.3667	15	Acid medium <sup>a</sup>	1.468	4.004
0.3968	15	Acid medium <sup>a</sup>	1.586	3.997
0.4273	15	Acid medium <sup>a</sup>	1.704	3.987
0.3053	15	pH 3.00	1.221	3.999
0.3053	15	3.42	1.221	3.999
0.3053	15	3.72	1.221	3.999
0.3053	15	4.05	1.221	3.999
0.3053	15	4.45	1.221	3.999
0.3053	15	4.63	1.221	3.999
0.3053	15	4.99	1.221	3.999
0.3053	15	5.89	1.221	3.999
0.3053	15	Alkaline medium <sup>b</sup>	1.062	3.478

<sup>a</sup> Overall acidity was ca. 2 N.<sup>b</sup> Overall alkalinity was ca. 2 N.

TABLE II

OXIDATION OF PHENYLHYDRAZINE HYDROCHLORIDE WITH CHLORAMINE-T  
(Overall acidity ca. 2 N)

Sample taken (mmol)	Time (min)	Chloramine-T consumed (meq)	Equivalents of chloramine-T per mol of sample
0.5635	5	2.177	3.864
0.5635	10	2.228	3.954
0.5635	15	2.259	4.009
0.5635	30	2.357	4.181
0.5635	60	2.562	4.545
0.2320	15	0.9317	4.015
0.2784	15	1.110	3.987
0.3248	15	1.305	4.017
0.3711	15	1.491	4.018
0.4638	15	1.864	4.019
0.6534	15	2.615	4.001
0.8352	15	3.365	4.028

TABLE III

OXIDATION OF 2,4-DINITROPHENYLHYDRAZINE WITH CHLORAMINE-T  
(Overall acidity ca. 2 N)

Sample taken (mmol)	Time (min)	Chloramine-T consumed (meq)	Equivalents of chloramine-T per mol of sample
0.3178	5	1.170	3.681
0.3178	10	1.250	3.932
0.3178	15	1.260	3.965
0.3178	30	1.435	4.514
0.3178	60	1.566	4.927
0.3020	15	1.199	3.972
0.3178	15	1.260	3.965
0.3337	15	1.336	4.004
0.3496	15	1.386	3.965
0.4762	15	1.887	3.963

TABLE IV

OXIDATION OF SEMICARBAZIDE HYDROCHLORIDE WITH CHLORAMINE-T  
(Overall acidity ca. 2 N)

Sample taken (mmol)	Time (min)	Chloramine-T consumed (meq)	Equivalents of chloramine-T per mol of sample
0.4820	5	1.917	3.977
0.4820	10	1.917	3.977
0.4820	15	1.927	3.998
0.4820	30	1.927	3.998
0.4820	60	1.927	3.998
0.3195	15	1.277	3.987
0.3485	15	1.390	3.988
0.4065	15	1.626	4.000
0.4095	15	1.636	3.996
0.4356	15	1.743	4.000
0.4504	15	1.797	3.990
0.4646	15	1.861	4.005
0.4835	15	1.927	3.987

The hydrolytic product is a phenol in the case of phenylhydrazine and 2,4-dinitrophenylhydrazine (eqns. 2 and 3). Phenols are well-known to be susceptible to oxidative (here probably chlorination) processes. Such secondary oxidative processes are not likely to take place in the case of the other compounds, where the hydrolytic product is a carboxylic acid (eqns. 4-6), which would be expected to be resistant towards chloramine-T. Independent experiments confirmed that carboxylic acids like *p*-nitrobenzoic acid or benzoic acid are not affected by chloramine-T whereas phenol consumes the oxidant appreciably, under the present experimental conditions. The production of phenol during the oxidation of phenylhydrazine was verified by extracting the system with ether and testing for phenol qualitatively.

The chloramine-T method has the advantage over the usual iodimetric and bromimetric methods that no care is needed to prevent loss of the halogen by volatilization, and there is no necessity for inert atmospheres. The proposed method appears



TABLE V

OXIDATION OF *p*-NITROBENZHYDRAZIDE WITH CHLORAMINE-T  
(Overall acidity ca. 2 N)

Sample taken (mmol)	Time (min)	Chloramine-T consumed (meq)	Equivalents of chloramine-T per mol of sample
0.2351	5	0.9234	3.927
0.2351	10	0.9335	3.970
0.2351	15	0.9385	3.991
0.2351	30	0.9385	3.991
0.2351	60	0.9385	3.991
0.2468	15	0.9835	3.986
0.2586	15	1.034	3.998
0.2704	15	1.079	3.991
0.2821	15	1.124	3.984
0.3219	15	1.284	3.989

TABLE VI

OXIDATION OF ISONICOTINIC ACID HYDRAZIDE WITH CHLORAMINE-T  
(Overall acidity ca. 2 N)

Sample taken (mmol)	Time (min)	Chloramine-T consumed (meq)	Equivalents of chloramine-T per mol of sample
0.3629	5	1.442	3.974
0.3629	10	1.442	3.974
0.3629	15	1.452	4.001
0.3629	30	1.452	4.001
0.3629	60	1.452	4.001
0.3293	15	1.319	4.005
0.3443	15	1.382	4.014
0.3592	15	1.441	4.013
0.3742	15	1.494	3.993
0.3892	15	1.558	4.003

to be a simple and convenient alternative to the existing oxidimetric methods for the determination of hydrazine derivatives. Since prolonged reaction times are contra-indicated for the substituted hydrazines but not for hydrazides, the chloramine-T method seems to be ideally suited for hydrazides. With some caution, it could also be employed quite satisfactorily for substituted hydrazines.

We are grateful to the Council of Scientific & Industrial Research (India) for the award of a Junior Research Fellowship to one of us (V.R.N.).

#### SUMMARY

Back-titration procedures with chloramine-T as the oxidant in 2 N acidic medium are described for the following compounds: hydrazine, phenylhydrazine, 2,4-dinitrophenylhydrazine, semicarbazide, *p*-nitrobenzhydrazide and isoniazid. In

all cases, the oxidation, with consumption of 4 moles of chloramine-T per mole of sample, is quantitative in 15 min at room temperature.

#### RÉSUMÉ

On décrit des procédés de titrage en retour à l'aide de chloramine-T comme oxydant, en milieu acide 2 *N* pour les composés suivants: hydrazine, phénylhydrazine, dinitro-2,4-phénylhydrazine, semicarbazide, *p*-nitrobenzhydrazide et isoniazide. Dans chaque cas, l'oxydation avec consommation de 4 moles de chloramine-T par mole d'échantillon, est quantitative en 15 min à la température ordinaire.

#### ZUSAMMENFASSUNG

Es werden Rücktitrationsverfahren mit Chloramin-T als Oxidationsmittel in 2 *N* säurem Medium für die Bestimmung folgender Verbindungen beschrieben: Hydrazin, Phenylhydrazin, 2,4-Dinitrophenylhydrazin, Semicarbazid, *p*-Nitrobenzhydrazid und Isoniazid. In allen Fällen ist die Oxidation, die unter Verbrauch von 4 Mol Chloramin-T pro Mol Probe verläuft, bei Raumtemperatur innerhalb 15 min quantitativ.

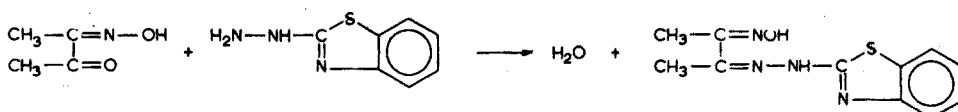
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## SHORT COMMUNICATIONS

### Spectrophotometric determination of palladium with diacetylmonoxime-2-benzothiazolyhydrazone

The proposed method uses a specific reagent for palladium recently described by Goldstein and Libergott<sup>1</sup>. The reagent, as claimed by the authors, is nearly an ideal one. Diacetylmonoxime-2-benzothiazolyhydrazone (DMBH) is a colorless compound, which is easily obtained by the condensation of diacetylmonoxime and 2-hydrazinobenzothiazole:



It reacts with palladium over a wide range of pH, from concentrated hydrochloric acid to concentrated ammonia solution. In acid solution the new reagent is specific for palladium<sup>1</sup>. The resulting complex is red-violet and can be extracted into chloroform. The absorption spectrum of the extracted complex shows a maximum at 560 nm (Fig. 1) and Beer's law is obeyed up to 15 p.p.m. of palladium. The method is extremely insensitive to interferences.

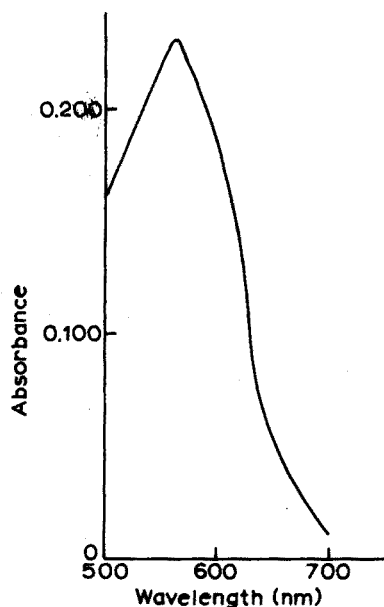


Fig. 1. Absorption spectrum. 100  $\mu\text{g}$  of palladium and excess of DMBH.

### Experimental

**Reagents.** A 0.01 M stock solution of palladium(II) chloride (Coleman and Bell Laboratories) in 2 M hydrochloric acid was prepared and standardized gravimetrically with dimethylglyoxime<sup>2</sup>. Palladium solutions of the required concentrations were prepared by suitable dilution of the stock solution.

DMBH, obtained by the above-mentioned condensation and recrystallized from ethanol, was used as an ethanolic 0.1% (w/v) solution.

**Apparatus.** Spectrophotometric measurements were made with a Beckman Spectrophotometer model B; matched pyrex cells of 1.00 cm optical path were used. The pH measurements were made with a Metronic pH meter Model 1.

**Procedure.** Into a 250-ml separatory funnel transfer not more than 10 ml of a 0.04 M hydrochloric (pH 1.8) palladium solution containing 10–150  $\mu\text{g}$  of palladium. Add 10 ml of the ethanolic DMBH solution. Shake vigorously for 1 min. Allow to stand for 20 min. Add 20 ml of chloroform, and shake vigorously for 1 min. Allow the phases to separate, and filter the chloroform extract through a small plug of glass wool. Measure the absorbance of the clear solution at 560 nm. Run a blank through the procedure.

### Results and discussion

To insure full color development a large excess of the reagent has to be used, over 10 moles of DMBH per g-atom of palladium being required.

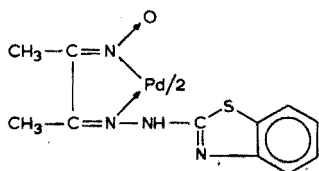
The red-violet color appears immediately after mixing the DMBH solution with palladium, but full color development is obtained only after standing for 20 min at room temperature. The complex is stable for several days.

The color obtained varies with the pH: at pH 1 the complex is red-violet, and at pH 9 it is red-orange. The method was developed for pH 1.8 (0.04 M HCl).

The DMBH–palladium complex conforms exactly to Beer's law for up to 15 p.p.m. of palladium in the original sample solution.

**Sensitivity and reproducibility.** In the study of the reproducibility of the method, 25 samples, each containing 10  $\mu\text{g}$  of palladium, were treated by the procedure described. The average deviation of a single measurement was found to be 0.0015 absorbance units. The standard deviation of a single measurement was 0.0019. None of the 25 determinations reached the rejection limit ( $3 \times$  standard deviation). The molar absorptivity of the DMBH–palladium complex is  $5.11 \cdot 10^3 \text{ l mole}^{-1} \text{ cm}^{-1}$ . The optimal concentration range for determining palladium is 1–15 p.p.m.

**Nature of the complex.** The absorption maximum for the DMBH–palladium complex is at 560 nm. The mole ratio method<sup>3,4</sup> was used to determine the structure of the complex. At pH 1.8 the DMBH–palladium ratio is 2:1, which is in accordance with the structure suggested by Goldstein and Libergott<sup>1</sup>.



At pH 1 more than one kind of complex seems to be present.

*Effect of foreign ions.* Varying amounts of the foreign ions were taken with a fixed amount of palladium and the color was developed in the described way. The tolerance for the foreign ion was taken as the largest amount that could be present and give an absorbance differing by no more than 0.01 from that produced by palladium alone. Tolerances for various foreign ions are shown in Table I.

TABLE I

TOLERANCE FOR FOREIGN IONS  
(Palladium concentration 1 p.p.m.)

Foreign ion	Tolerance (p.p.m.) at 560 nm
Ag(I), Al(III), As(III), Au(III), Ba(II), Be(II), Bi(III), Ca(II), Cd(II), Co(II), Cr(III), Cs(I), Cu(II) <sup>a</sup> , Fe(III), Ga(III), Ge(IV), Hg(II), In(I), Ir(III), K(I), La(III), Li(II), Mg(II), Mn(II), Mo(II), Na(I), Nb(V), Ni(II), Pb(II), Pt(II), Rh(III), Ru(III), Sb(III), Sr(II), Ta(V), Th(IV), Ti(III), U(IV), W(III), Zn(II), Zr(IV)	1.000 <sup>b</sup>
Ce(III), Sn(II)	100
V(V)	10

<sup>a</sup> This result was obtained when working in presence of ammonium oxalate (1.5 ml of a 10% (w/v) solution). Without this addition 2 p.p.m. of copper interfered in the determination.

<sup>b</sup> This was the largest amount tested.

It can be seen that one of the principal advantages of the process is the great tolerance for foreign ions, including metals of the platinum group, as expected from the specificity of the reagent.

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## Le fluorure de tétraphénylstibonium. Mesures dans l'ultra-violet

Une extraction des fluorures par le sulfate de tétraphénylstibonium et le tétrachlorure de carbone, est proposée en vue de leur dosage gravimétrique<sup>1</sup>. Elle s'applique également à la préparation du <sup>18</sup>F résultant de l'irradiation du carbonate de lithium<sup>2</sup> aux neutrons lents; elle se fait à un pH de 3.

Des essais ont été effectués pour appliquer cette méthode à la séparation de petites quantités de fluorures en vue de leur dosage, par mesure d'absorption du fluorure de tétraphénylstibonium dans l'ultra-violet. L'extrait dans le tétrachlorure de carbone présente un maximum d'absorption vers 264 nm; trois à quatre extractions successives sont nécessaires pour une séparation quantitative. Pour des raisons pratiques, il est préférable d'employer un solvant plus léger que l'eau: mélange hexane-chlorure de méthylène (1:1), ou mieux hexane-chloroforme (40:25); ce dernier doit être préalablement lavé à l'eau afin d'éliminer toute trace d'alcool. Dans les conditions indiquées ci-dessous une seule extraction suffit.

Les solutions de fluosilicate de sodium se comportent comme les solutions d'acide fluorhydrique.

### Partie expérimentale

Introduire dans un tube à centrifuger (bouchant à l'émeri): sulfate de tétraphénylstibonium ( $5 \cdot 10^{-3}$  M), solution de fluorure ( $2.5 \cdot 10^{-3}$  M en  $F^-$ ), eau et soude 0.2 M\*, agiter. Ajouter ensuite le solvant (hexane- $CHCl_3$ ). Agiter vivement. Centrifuger 4-5 min. Prélever la phase organique supérieure (à l'aide d'un tube à pointe effilée).

Faire les mesures à 240-245 nm (cuves de 5 mm). Cuve témoin: eau. L'absorption (par rapport au témoin, exempt de fluor) est de 1.5 environ à 240 nm, de 1.0 environ à 242 nm; celle du solvant par rapport à l'eau, de 0.9 et 0.7 respectivement. Les mesures sont faites de préférence en cuves couvertes, en raison de la volatilité du solvant.

### Résultats et discussion

L'absorption, en fonction des quantités de fluor est linéaire jusqu'à 50  $\mu g F^-$  au moins. La coefficient d'absorption moléculaire  $\epsilon$  est de  $3.2 \cdot 10^3$  environ. La variation de  $\log \epsilon$  en fonction de la longueur d'onde est indiquée sur la Fig. 1 (courbe 1).

La méthode à l'alizarine complexone, de Belcher et West<sup>3</sup>, a été comparée à celle établie ci-dessus. Ce réactif donne avec les fluorures une coloration bleue d'intensité directement proportionnelle à la concentration des ions fluorures. Le dosage se fait en milieu aqueux, en présence d'alcool isopropylique<sup>4</sup> ou d'acétone<sup>3,5</sup>, ou par extraction dans les alcools butyliques<sup>6</sup>. Il est possible d'arriver à un coefficient d'absorption moléculaire de  $20 \cdot 10^3$  environ au moyen d'une technique de sensibilité maximale, inspirée de celle de Hall<sup>6</sup>.

Les ions suivants:  $Mn(VII)$ ,  $ClO_4^-$ ,  $IO_4^-$ ,  $WO_4^{2-}$ , silico- et phosphotungstates, précipitent avec le tétraphénylstibonium préalablement amené à pH 3; ils ne sont

\* Le volume de soude nécessaire pour obtenir un pH de 3.0 à 3.2 est déterminé au préalable. La préparation de la solution de réactif est décrite dans le travail de Bowen et Rood<sup>2</sup>.

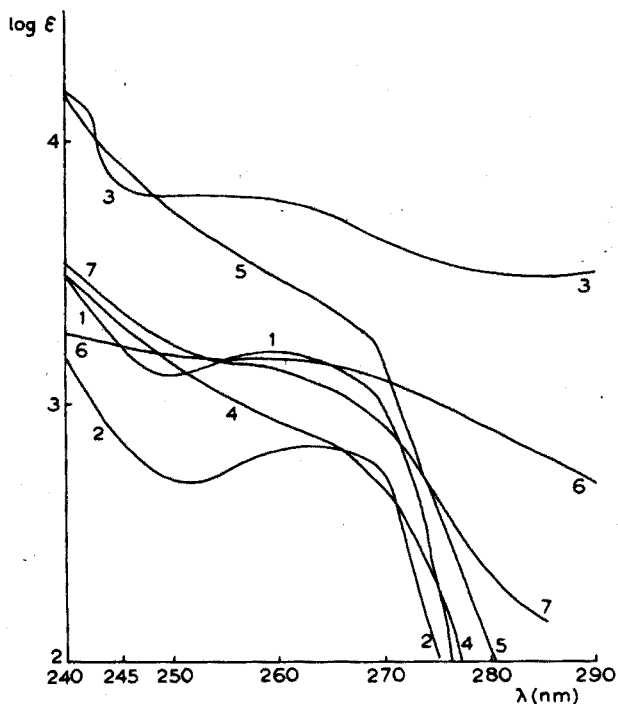


Fig. 1. Coefficient d'extinction moléculaire en fonction de la longueur d'onde. (1)  $F^-$ ; (2)  $Fe(CN)_6^{3-}$ ; (3)  $Fe(CN)_6^{4-}$ ; (4) Si et P—Mo; (5) Mo(VI); (6) V(V); (7)  $NO_2^-$ .

toutefois pas extraits par le solvant, selon la technique indiquée ci-dessus. Il en est de même des éléments métalliques précipitant, ou s'hydrolysant à pH 3 (Zr, Zn, etc.), ainsi que des ions  $BiI_4^-$  et  $Co(SCN)_4^{2-}$ <sup>8</sup>; enfin les sulfures précipitent l'antimoine du réactif. Par contre, les ions suivants: Cr(VI),  $VO_3^-$ ,  $MoO_4^{2-}$ ,  $NO_2^-$ , silico- et phosphomolybdates, ferro- et ferricyanures, précipitent avec le réactif à pH 3, et sont également extraits par le solvant même en appliquant la technique décrite ci-dessus. Les courbes (Fig. 1) indiquent les coefficients d'extinction moléculaire du milieu extrait, en fonction de la longueur d'onde; ces ions interfèrent donc totalement sur les fluorures.

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## Dosage de l'uranium dans l'ultra-violet

Parmi les méthodes d'absorption proposées pour le dosage de l'uranium(VI), dans différents milieux, on indique les mesures en solution perchlorique<sup>1,2</sup> à une longueur d'onde de 415 à 420 nm ; cependant la sensibilité est faible. L'absorption en milieu tributylphosphate, indiquée dans le visible par Woodhead<sup>3</sup>, permet un dosage à 250 nm avec  $\epsilon = 2600$  environ<sup>4</sup>. On signale également l'absorption, en milieu carbonaté, dans le visible et l'ultra-violet<sup>5</sup>.

Des essais ont été effectués pour l'uranium(VI), à pH 9 environ, en milieu carbonaté : (a) au moyen de l'uranylcarbonate de sodium ordinaire<sup>6</sup> ; (b) en formant le complexe au moyen d'une solution d'uranium(VI)  $10^{-3}$  M et d'une solution de carbonate de sodium à 25%, en ajustant le pH à 9.3 par addition d'acide sulfurique dilué ; (c) à l'aide d'une solution d'uranylcarbonate de sodium, additionnée de carbonate de sodium et d'acide sulfurique. Dans ces deux derniers cas, il a fallu tenir compte de l'absorption propre des sels alcalins. Les courbes (Fig. 1) indiquent l'absorption de

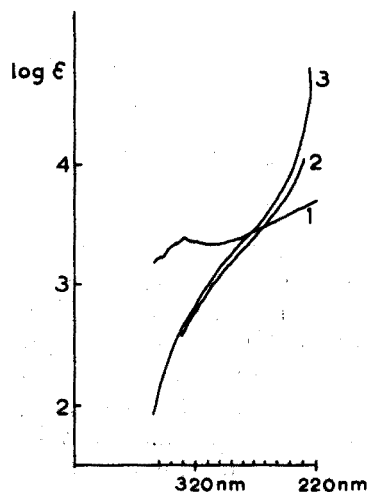


Fig. 1. Absorption de l'uranylcarbonate. (1)  $\text{UO}_2(\text{CO}_3)_3\text{Na}_4$ ; (2)  $\text{UO}_2(\text{CO}_3)_3\text{Na}_4$ , milieu carbonaté; (3) solution nitrique de U, milieu carbonaté.

l'uranium, sous forme de carbonate, à pH 9.3 environ. A noter que celle de l'uranylcarbonate seul se différencie quelque peu des valeurs obtenues pour les autres préparations.

L'uranium peut être dosé directement en milieu carbonaté par mesure de l'absorption à 240 nm ; le coefficient d'extinction moléculaire ( $\epsilon$ ) est égal à 7500 environ.

*Exemple d'application.* Des alliages de zirconium sont traités par un mélange d'acides sulfurique-perchlorique et nitrique ; une partie aliquote de la solution obtenue est additionnée de carbonate de sodium, les mesures étant effectuées en cuves de 10 mm, par rapport à l'eau. On peut ainsi doser jusqu'à 0.5 mg d'uranium au moins,



en présence de quantités de zirconium de l'ordre de 0.1 g. Le carbonate de zirconium est soluble dans un excès de carbonate alcalin<sup>7</sup>, à pH 9 environ, par formation d'un complexe, vraisemblablement de la forme  $[\text{Zr}(\text{CO}_3)_4]^{4-8}$ ; celui-ci présente une absorption assez notable à 200 nm, mais qui s'annule très rapidement dès 235 nm, permettant ainsi la mesure de l'uranium.

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*Anal. Chim. Acta*, 57 (1971) 440-441

### Enhancement of strontium absorption in the nitrous oxide-acetylene flame by potassium and sodium and the determination of strontium in biological material

When the alkaline earths are determined by atomic absorption, the absorption is reduced by several anions such as phosphate and sulfate. For strontium the suppressing effect of these anions has been studied by David<sup>1</sup> and in more detail by Trent and Slavin<sup>2</sup>. Phosphate forms refractory compounds with strontium at the temperature of the air-acetylene flame, and even small amounts affect the strontium absorption; for large amounts, as in biological material, the influence is disastrous, and preliminary chemical separations are essential. David<sup>1</sup> removed phosphate with the anion-exchange resin DcAcidite FF, measuring the effluent by the addition method. In this laboratory<sup>3</sup> strontium and calcium were separated from the sample solutions by precipitation as oxalate, the separation yield being determined with <sup>85</sup>Sr. Trent and Slavin<sup>2</sup> obtained good results by buffering both the sample and standard solutions with lanthanum. The chemical methods are highly time-consuming and the addition of lanthanum lowers the sensitivity of the method, because the samples require dilution to obtain a maximal 300-p.p.m. phosphate concentration.

When a nitrous oxide flame is used, however, the refractory compounds are broken down and more strontium atoms are liberated. The sensitivity of the method is, nevertheless, very low, because a considerable percentage of the free atoms are ionized at the high temperatures attained. Trent and Slavin<sup>2</sup> demonstrated that the presence of easily ionizing elements such as potassium and sodium improves the strontium absorption; alkali metals shift the equilibrium between strontium atoms and ions in favour of the atomic state. Using an air-acetylene flame, they proved that

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these elements of low ionization potential drive back the ionized strontium atoms. This was achieved by successive measurement of the ionic ground state line and the atomic ground state line of strontium.

With a nitrous oxide-acetylene flame these phenomena should appear much more strongly, and this was proved by Murdoch and Heaton<sup>4</sup> for calcium. In the present communication, the influence of sodium and potassium on the strontium absorption, and its consequences for the strontium determination in biological material are described.

#### *Interference of potassium and sodium on the strontium absorption in the nitrous oxide-acetylene flame*

Experiments were conducted with a Beckman 1301 atomic absorption spectrophotometer with laminar flow burner provided with the special burner head for the nitrous oxide flame. Aqueous strontium solutions (5 p.p.m.) were prepared from strontium carbonate with an equivalent amount of hydrochloric acid. To these solutions, increasing concentrations of potassium and sodium were added.

Figure 1 shows that the enhancement increases with rising concentrations of the alkali metals until a maximum is attained; further rise of the potassium and sodium concentrations has no effect. The plateau region begins at lower concentrations for potassium than for sodium. When both metals are present the maximum is attained at still lower concentrations and is the same as that produced by potassium alone.

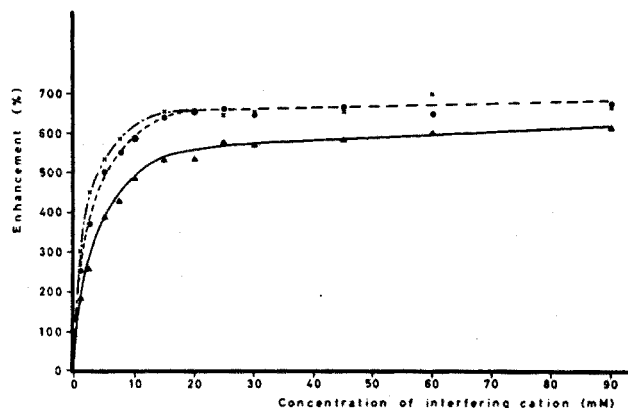


Fig. 1. Enhancement of strontium (5 p.p.m.) absorption by increasing concentrations of sodium and potassium. (▲) Na; (●) K; (×) Na + K (each at the concentration indicated on the abscissa).

The maximum enhancement differs for sodium and potassium, and with the flame conditions chosen here (support gas pressure 23 p.s.i.; fuel pressure 3.5 p.s.i.) amounted to 650 % for potassium and 550 % for sodium. This agrees with the observations of Trent and Slavin<sup>2</sup> who established that the highest increase is caused by the element with the lowest ionization potential. It contradicts, however, the statement of Murdoch and Heaton<sup>4</sup>, that potassium and sodium cause the same maximum increase on the calcium absorption. Further it was observed that the addition of phosphate to the solutions had no influence on the absorption.

The maximum enhancement depends strongly on the gas flow (Fig. 2). When

the fuel pressure is increased for a constant support gas pressure, the temperature increases to a maximum at the stoichiometric nitrous oxide–acetylene ratio (5:1), a maximum amount of fuel then being completely burned. Further increase of the fuel pressure results in a reducing flame of lower temperature.

To elucidate these results further, the gas flows obtained at the applied pressures were measured with a "Dynegal" flowmeter ("Air Liquide", Vitry sur Seine, France).

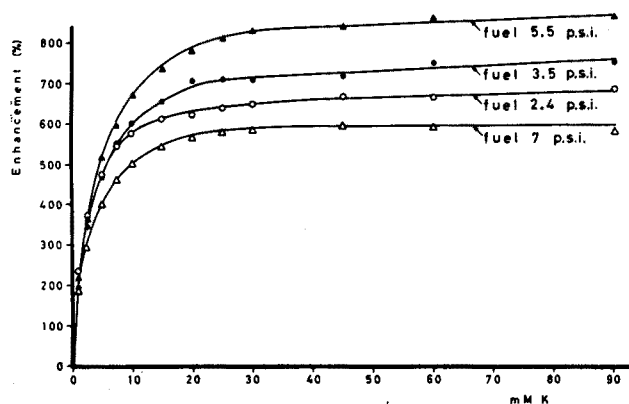


Fig. 2. Enhancement of strontium (5 p.p.m.) absorption by increasing concentrations of potassium and for increasing fuel pressures with constant support gas ( $N_2O$ ) pressure.

Corrections were made for the nature of the gas, the gas pressure and the temperature. The ratios between the nitrous oxide and the acetylene gas flows at fuel pressures of 2.4, 3.5, 5.5 and 7 p.s.i. were respectively 5.5, 4.0, 2.9 and 2.4. With the lowest fuel pressure, the flame was therefore practically stoichiometric; increasing the fuel pressure gave an excess of acetylene. In accordance with what happens in an air–acetylene flame, it would be supposed that in a reducing nitrous oxide–acetylene flame there should be more strontium atoms: there is less tendency to formation of strontium ions<sup>2</sup> because the temperature is lower, and less strontium oxide is formed because there is less oxidation. On increasing the fuel pressure from 2.4 to 5.5 p.s.i., more strontium atoms would be expected, and therefore higher absorption values for strontium and a lower percentage effect of adding potassium. The results obtained, however, indicated that these phenomena did not appear in a reducing nitrous oxide–acetylene flame as long as the ratio between the support gas and the fuel gas exceeded 3. When the fuel pressure was increased from 2.4 to 5.5 p.s.i. at constant support gas pressure, the absorptions measured on the strontium line with pure strontium remained the same, and the maximum enhancement caused by potassium increased (Figs. 3 and 4).

Thus, there are no more strontium atoms present in the flame at acetylene pressures of 3.5 and 5.5 p.s.i. than at 2.4 p.s.i., which indicates that lowering the temperature by changing the flame conditions does not, in fact, increase the amount of strontium atoms in the flame; the temperature seems to stay high enough to ionize most of the strontium atoms. Strontium oxide is probably present in the flame at an acetylene pressure of 2.4 p.s.i., but would not be formed in the reducing flames obtained with 3.5- and 5.5 p.s.i. fuel pressure. Thus more strontium atoms would be available in the

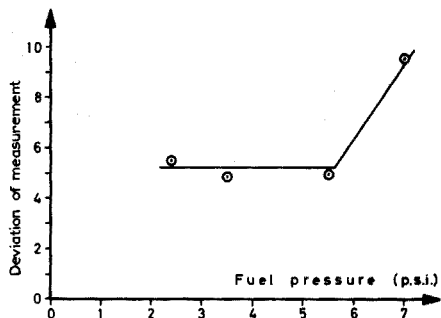


Fig. 3. Absorption measured with pure strontium (5 p.p.m.) in a nitrous oxide-acetylene flame at increasing fuel pressures and constant support gas pressure.

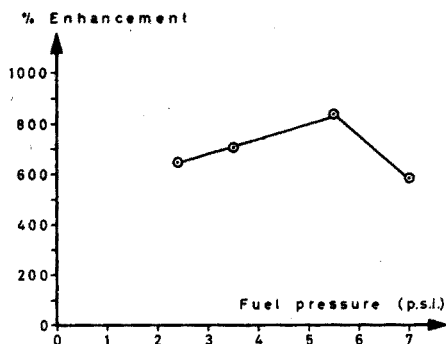


Fig. 4. Enhancement caused by 30 mM K on the strontium (5 p.p.m.) absorption at increasing fuel pressures and constant support gas pressure.

flame but are ionized in the absence of potassium. When potassium is added, more ionized strontium can form atoms. However, at a fuel pressure of 7 p.s.i., the absorption obtained with 5 p.p.m. strontium without potassium was doubled, and the percentage enhancement caused by adding potassium was lowered (Figs. 3 and 4). This sudden reversion may perhaps be explained by a drop in temperature, brought about by the fact that the fuel-support gas ratio is less than 3 so that insufficient oxidant remains to burn all the acetylene.

#### *The determination of strontium in biological material*

The above observations indicate that when strontium is determined in biological material with the nitrous oxide-acetylene flame, both unknown and standard solutions must contain sufficient potassium or sodium. The high temperature obtained with this gas mixture eliminates the phosphate interference even for the concentrations found in most biological samples. The addition of sodium or potassium is necessary because these elements are in general also abundant in such samples, and the sensitivity of the method is improved. The direct comparison of the unknown solutions with standard solutions with sufficient potassium and sodium, however, does not always give accurate results; this will be proved by the results obtained for three kinds of biological materials: human faeces, urine and food (a mixed diet).

*Procedure.* After incineration at 525°, the samples of food, faeces and urine were dissolved in 0.5 M nitric acid and diluted to 250 ml. An aliquot of the sample solutions was used to determine the strontium absorption in an air-acetylene flame after separation of the strontium and calcium by oxalate precipitation. The data obtained agreed very well with those obtained by activation analysis, for different kinds of biological samples, and this laborious and relatively insensitive method was used<sup>3</sup> as the safest to measure the true strontium content of the samples. Another smaller part of the samples served for the direct measurement of strontium by comparing the absorption with those produced by standard solutions containing a sufficient amount of potassium and sodium (1000 p.p.m. of each), in the nitrous oxide-acetylene flame. Calibration curves are shown in Fig. 5. All the samples, except some small faecal samples, con-

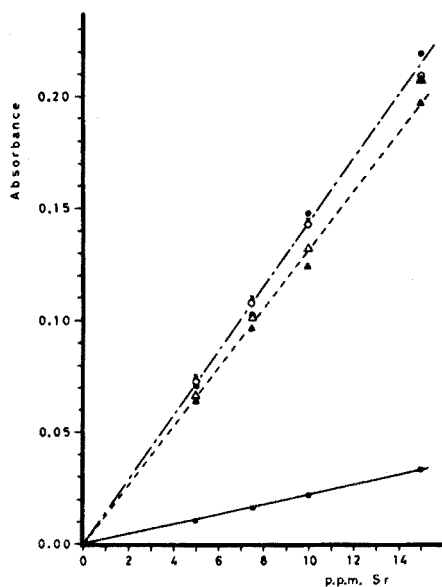


Fig. 5. Calibration curves for pure strontium and strontium with different sodium and potassium concentrations. (○) K, 25 mM; (●) K, 30 mM; (▲) Na, 30 mM; (△) Na, 45 mM; (×) Na + K, each 30 mM; (■) pure Sr.

TABLE I

STRONTIUM DETERMINATION IN HUMAN FOOD, URINE AND FAECES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY: COMPARISON OF DIFFERENT METHODS

	Mean strontium concentration of the samples		Comparison of the results	
	Method 1 Air-acetylene, after precipi- tation of Sr oxalate	Method 2 N <sub>2</sub> O-acetylene, direct measurement against standard solutions with Na and K	Mean ratio Results method 1 Results method 2	Mean ratio Results method 1 Results method 3 <sup>a</sup>
Food (mixed diet) daily intake	1.18 mg <i>n</i> = 19 <sup>b</sup> <i>s<sub>x</sub></i> = 0.16 <sup>c</sup>	1.15 mg <i>n</i> = 19 <i>s<sub>x</sub></i> = 0.18	1.07 <i>s<sub>x</sub></i> = 0.03 <i>n</i> = 19	
Human urine daily excretion	0.105 mg <i>n</i> = 18 <i>s<sub>x</sub></i> = 0.006	0.103 mg <i>n</i> = 18 <i>s<sub>x</sub></i> = 0.005	1.02 <i>s<sub>x</sub></i> = 0.04 <i>n</i> = 18	
Human faeces	1.58 mg <sup>d</sup> <i>n</i> = 21 <i>s<sub>x</sub></i> = 0.26	1.21 mg <sup>d</sup> <i>n</i> = 21 <i>s<sub>x</sub></i> = 0.21	1.39 <i>s<sub>x</sub></i> = 0.05 <i>n</i> = 33 — <sup>e</sup>	1.01 <i>s<sub>x</sub></i> = 0.02 <i>n</i> = 21 — <sup>e</sup>

<sup>a</sup> N<sub>2</sub>O-acetylene, addition method.

<sup>b</sup> Number of samples analysed.

<sup>c</sup> Standard deviation of the mean.

<sup>d</sup> Mean daily excretion.

<sup>e</sup> For food and urine daily samples were collected, but for faeces each defaecation was analysed separately and for the smallest samples there was no solution of the faecal ashes left to apply the addition method.

tained more than 20 mM K and Na, hence only these samples were treated with additional alkali metal.

*Discussion.* As shown in Table I, the "mixed diets" and urines yielded the same results by both methods, but the analysis of human faeces after strontium oxalate precipitation gave significantly higher (40%) concentrations than the analysis by direct comparison with standard solutions containing sufficient potassium and sodium. This was not due to the phosphate concentrations, for urine, diet and faeces contained respectively about 2600, 4000 and 1200 p.p.m. phosphorus, hence other depressing effects were involved. This was proved by an addition method: when 50  $\mu$ l and 100  $\mu$ l of a 200-p.p.m. strontium solution were added to two 10-ml aliquots of the faecal ash solutions, their strontium contents were respectively raised by 1 and 2 p.p.m., and the final results then agreed with those obtained after oxalate precipitation. This addition method was only applied on the largest faecal samples, because their alkali metal content was high enough to produce maximum enhancement, so that only strontium addition was needed.

It can be concluded, that a careful check for sufficient potassium and sodium in both sample and standard is necessary for these biological samples when atomic absorption with the nitrous oxide flame is used; the application of the addition method is recommended to compensate for remaining interferences in some (faecal) samples.

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## The gas chromatography of beryllium and zinc oxyacetates

The basic beryllium derivatives of organic acids (beryllium oxycarboxylates) have been widely investigated, but although their volatilities and thermal stabilities have been studied, there is no report of their gas chromatography.

Beryllium oxyacetate ( $\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_6$ ;  $\mu_4$ -oxohexa- $\mu$ -acetatotetraberyllium(II)) was prepared in 1901<sup>1</sup>, and homologues of this compound in 1902<sup>2</sup>. Parsons<sup>3</sup> suggested that the property of sublimation without decomposition might favour purification of the oxyacetate, and spectrographically pure beryllium has been prepared by the sublimation of this compound<sup>4</sup>. X-Ray crystallographic studies have shown that beryllium oxyacetate has a highly developed tetrahedral structure around the central oxygen atom<sup>5</sup>.

Mass spectrometric studies have been made<sup>6</sup>, but gas chromatography seems to have been used only by Hardt<sup>7</sup> who investigated the free acids produced from mixed acetate-propionate complexes.

In the present work beryllium oxyacetate was prepared by reacting freshly precipitated beryllium hydroxide with anhydrous acetic acid; beryllium oxypropionate ( $\mu_4$ -oxohexa- $\mu$ -propionatotetraberyllium(II)) and zinc oxyacetate ( $\mu_4$ -oxohexa- $\mu$ -acetatotetrazinc(II)) were prepared for comparison. The properties of these compounds were investigated by thermogravimetry and gas chromatography in order to establish their analytical potential in comparison to that exhibited by metal chelate complexes<sup>8</sup>.

### Preparation of beryllium oxycarboxylates

**Beryllium oxyacetate.** Beryllium sulphate tetrahydrate (10 g; A.R. grade) was dissolved in 100 ml of distilled water and aqueous 6 M ammonia solution was added slowly with stirring until precipitation of the hydroxide as a gelatinous mass was complete. The precipitate was filtered under suction, washed with water, and air-dried. The partially dried precipitate was dissolved in an excess of anhydrous acetic acid (20 ml; A.R. grade). The solution was heated under reflux for 2 h and then evaporated to give a white solid. Extraction of this residue with chloroform followed by crystallization yielded a white, microcrystalline product (34% yield). The dried product was sublimed (170° at 3 mm Hg) in a vacuum sublimation apparatus immersed in an oil bath. The sublimate was collected on a cold finger containing chloroform, and was characterized by its melting point, mass spectrum, infrared spectrum, and by elemental analysis.

The mass spectrum showed the fragments reported by Vogel and Hobrock<sup>6</sup>. The major features of the spectrum are summarized in Table I. The infrared spectra were recorded on a Perkin-Elmer 521 spectrometer over the range 4000–400  $\text{cm}^{-1}$ . The most important frequencies corresponded to those reported in the literature<sup>9</sup>. Analytical results for  $\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_6$ : theoretical 35.46% C, 4.47% H; found 35.7% C, 4.6% H; m.p. 280–281° (reported<sup>10</sup> 285–286°).

**Beryllium oxypropionate.** This was prepared in 65% yield by a similar procedure, and after sublimation (135° at 0.5 mm Hg) was characterized as described above. Analytical results for  $\text{Be}_4\text{O}(\text{OOC}\cdot\text{C}_2\text{H}_5)_6$ : theoretical 44.08% C, 6.12% H; found 44.2% C, 6.3% H; m.p. 130–131° (reported<sup>10</sup> 138°).

TABLE I

THE MAJOR FEATURES OF THE MASS SPECTRUM OF BERYLLIUM OXYACETATE

<i>m/e</i>	<i>Relative intensity</i>	<i>Ion</i>
347	100	$[\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_5]^+$
304	1	$[\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_4\text{O}]^+$
278	1.2	$[\text{Be}_3\text{O}(\text{OOC}\cdot\text{CH}_3)_3(\text{OOC}\cdot\text{CH}_2)]^+$
245	13	$[\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_3\text{O}]^+$
220	47	$[\text{Be}_3\text{O}(\text{OOC}\cdot\text{CH}_3)_3]^+$
178	4.5	$[\text{Be}_3\text{O}(\text{OOC}\cdot\text{CH}_3)_2\text{OH}]^+$
161	5	$[\text{Be}_3\text{O}(\text{OOC}\cdot\text{CH}_3)_2]^+$
118	2.5	$[\text{Be}_3\text{O}(\text{OOC}\cdot\text{CH}_3)\text{O}]^+$
101	2.5	$[\text{Be}_3\text{O}(\text{OOC}\cdot\text{CH}_2)]^+$

*Zinc oxyacetate.* In 1924, Auger and Robin<sup>11</sup> distilled zinc acetate and reported the preparation of zinc oxyacetate. The preparative procedure used in the present work employed a vacuum sublimation apparatus. A small quantity of zinc acetate dihydrate (A.R. grade) was placed in the sublimation vessel which was then heated in an oil bath. Initially the temperature was raised slowly to remove the water of hydration; subsequently, at 200–220° and 1.0 mm Hg pressure, a sublimate formed on the chloroform-filled cold finger which was characterized as the desired material by mass spectroscopy, infrared and elemental analysis. Analytical results for  $\text{Zn}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_6$ : theoretical 23.1% C, 2.9% H, 39.0% Zn; found 22.8% C, 2.8% H, 41.4% Zn; m.p.  $245 \pm 2^\circ$  (reported<sup>12</sup> 250°).

#### *Instrumental techniques*

The mass spectra were recorded on an A.E.I. MS9 double focusing mass spectrometer, operating at an ionizing voltage of 70 eV and an accelerating potential of 8 kV. The samples were evaporated into the source with the direct insertion probe.

Thermogravimetric analyses were carried out on a Perkin-Elmer TGS-1 thermobalance. The analyses were performed in a pure nitrogen atmosphere at a flow rate of 20 ml min<sup>-1</sup>. The temperature scan rate was 20° min<sup>-1</sup> with an upper temperature limit of 650°. Sample sizes were 1.5 mg.

A Pye 104 gas chromatograph with a heated flame ionization detector was used. Eluates were collected for characterization by means of a 100:1 stream splitter and the "Manual Preparative Unit" available for this instrument. Traps were cooled in liquid air.

Analytical gas chromatography was performed with Pyrex glass (or Teflon) columns (1 m × 0.4 cm) containing a liquid phase of Apiezon L (5% w/w) on 85–100 mesh "Universal B" support (a silanized flux-calcined diatomite; Phase Separations Ltd.). The column was conditioned for 12 h at 200° before use.

#### *Results and discussion*

*Thermal analysis.* Thermogravimetry has been used in studies of the complexes of beryllium oxyacetate with ammonia<sup>13</sup> and amines<sup>14</sup>. In the present work, thermogravimetric analyses were carried out on beryllium oxyacetate, beryllium oxypropionate and zinc oxyacetate, as well as on beryllium acetylacetonate,  $\text{Be}(\text{AA})_2$ , and



trifluoroacetylacetonate,  $\text{Be}(\text{TFA})_2$ , which are known to have good gas chromatographic characteristics<sup>15</sup>. The results are compared in Fig. 1.

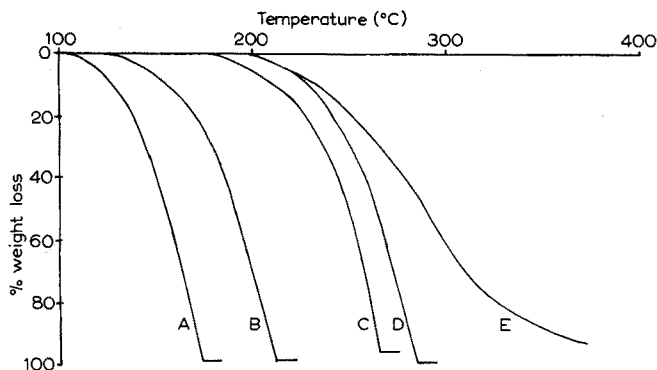


Fig. 1. Comparative thermograms for beryllium and zinc oxyacetates and beryllium  $\beta$ -diketonates. (A)  $\text{Be}(\text{TFA})_2$ ; (B)  $\text{Be}(\text{AA})_2$ ; (C)  $\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_2\text{CH}_3)_6$ ; (D)  $\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_6$ ; (E)  $\text{Zn}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_6$ .

Clearly the three metal oxycarboxylates are considerably less volatile than the beryllium  $\beta$ -diketonates, hence higher column temperatures are essential for gas chromatography. The shapes of the thermograms for all the beryllium samples are very similar and showed negligible thermal decomposition. Zinc oxyacetate, however, showed a less satisfactory thermogram with almost 10% of the sample remaining unsublimed.

This study indicated that the thermal stability and volatility of the beryllium oxycarboxylates should favour quantitative gas chromatography, whereas quantitative elution of zinc oxyacetate seemed improbable.

**Gas chromatography.** The gas-chromatographic behaviour of beryllium oxyacetate (as a 10% (w/v) solution in chloroform) was examined on a freshly prepared glass column of Apiezon L on "Universal B". The nitrogen flow rate was  $60 \text{ ml min}^{-1}$  and the temperatures of the injection port and detector oven were  $30^\circ$  above that of the column. The optimal column temperature for the elution of beryllium oxyacetate was  $150^\circ$ . A representative chromatogram (Fig. 2, curve A) shows good peak symmetry with little tailing; the initial minor peak (ca. 2%) could not be eliminated by changing conditions and is probably due to a little decomposition on the column. Thus while elemental analysis and mass spectrometry confirmed the identity of the eluted beryllium oxyacetate, thermogravimetry indicated the presence of a small quantity of material of greater volatility than the major portion of the eluate.

The variation of detector response with the size of the injected sample was investigated, and a rectilinear relationship with peak area was found over the range 2–60  $\mu\text{g}$  of beryllium oxyacetate. There was thus no indication of sample losses on the column.

The gas chromatography of beryllium oxypropionate and zinc oxyacetate was less satisfactory. Only broad poorly characterized peaks could be obtained for these complexes, although further investigations might result in improved elution characteristics for beryllium oxypropionate.

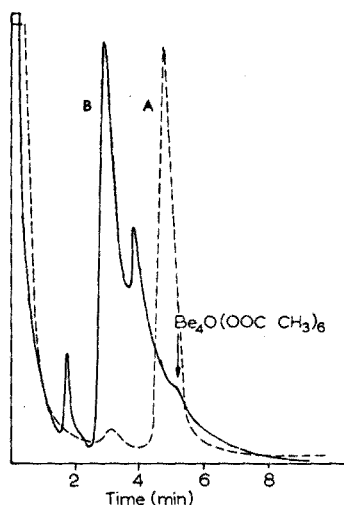


Fig. 2. Gas chromatogram of beryllium oxyacetate (25  $\mu\text{g}$ ). Conditions as in text. (---) On freshly prepared column (curve A); (—) on aged column (curve B).

The elution of beryllium oxycarboxylates was strongly dependent on the state of the column used. After some weeks of use, the Apiezon L column gave a chromatogram for beryllium oxyacetate with multiple peaks, most of which were of shorter retention time than the authentic beryllium oxyacetate peak (Fig. 2, curve B). For beryllium oxypropionate this effect was even more pronounced. Decomposition on the column probably resulted from activation of surface hydroxyl sites on the support. Successive injections of the same compound gave no improvement, but the original peak shape was regained after silanization of the column with injections of "Silyl 8" (Pierce Chemical Co., Rockford, Ill., U.S.A.), followed by conditioning the column for 12 h at 150°. It was thus evident that good chromatography of these compounds was particularly dependent on substrate deactivation.

These investigations indicate that beryllium oxyacetate can be useful in gas chromatography. Quantitative elution seems practicable, but the nature of the column is critical. Further studies on the elution characteristics of compounds of the beryllium oxycarboxylate series and on some analytical applications of the beryllium oxycarboxylates are planned.

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### Determination of phosphorus in silicate rocks by neutron activation and direct $\beta$ -counting

Instrumental activation analyses for minor and trace elements in silicate rocks have almost exclusively been carried out by  $\gamma$ -ray spectrometry. The only reported application of direct  $\beta$ -counting to neutron-irradiated rocks seems to be for the determination of potassium<sup>1</sup>, with aluminium absorbers to eliminate the contribution from <sup>24</sup>Na. Another element which is often present in relatively high concentration in silicate rocks, and which might be determined similarly, is phosphorus. Previously published methods<sup>2,3</sup> for the determination of phosphorus in rocks by neutron activation have included decomposition of the sample and radiochemical separation steps before counting of the <sup>32</sup>P  $\beta^-$ -activity. The present work was done in order to study whether phosphorus can be determined without the necessity of chemical separations, and, if so, to establish the interferences from other elements and proper counting conditions to reduce these interferences as far as possible.

#### *Preliminary experiments*

The events recorded by a simple  $\beta$ -detector such as an end-window proportional or Geiger-Mueller counter when exposed to an irradiated rock sample, represent a very complex mixture of nuclides and radiations. Although  $\beta^-$ -particles are mainly responsible, conversion electrons, X-rays,  $\gamma$ -rays and bremsstrahlung also contribute to the count-rate. Considering elemental abundances in common silicate rocks, and nuclear data of the radioisotopes induced by slow neutron bombardment, such as formation cross-section, half-life and characteristic radiation, it was estimated that isotopes of 26 elements might interfere with the determination of phosphorus by direct registration of the <sup>32</sup>P  $\beta^-$ -activity, even after the decay of <sup>24</sup>Na, <sup>42</sup>K and other nuclides with similar or shorter half-lives. The potential interfering elements and their radioisotopes are listed in Table I.

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TABLE I

"RELATIVE INTERFERENCE FACTORS" FOR ELEMENTS ESTIMATED TO INTERFERE WITH THE DETERMINATION OF PHOSPHORUS IN NEUTRON-ACTIVATED ROCKS BY  $\beta$ -COUNTING (IRRADIATION 1 h)

Element	Radioactive isotope (half-life)	Maximum $\beta$ -energy (MeV)	Other radiation types	(Specific activity) <sub>element</sub> / (Specific activity) <sub>P</sub>											
				10 d			17 d			25 d					
				A <sub>1</sub> -A <sub>3</sub>	A <sub>2</sub> -A <sub>3</sub>	A <sub>1</sub> -A <sub>3</sub>	A <sub>1</sub> -A <sub>3</sub>	A <sub>2</sub> -A <sub>3</sub>	A <sub>1</sub> -A <sub>3</sub>	A <sub>2</sub> -A <sub>3</sub>	A <sub>1</sub> -A <sub>3</sub>	A <sub>2</sub> -A <sub>3</sub>	A <sub>1</sub> -A <sub>3</sub>	A <sub>2</sub> -A <sub>3</sub>	
P	<sup>32</sup> P (14.3 d)	1.70	—	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ca	<sup>47</sup> Ca (4.7 d)- <sup>47</sup> Sc (3.4 d)	2.06 ( <sup>47</sup> Ca)	$\gamma$	0.00015	0.00015	0.00012	0.00012	0.00012	0.00012	0.00012	0.00012	0.00012	0.00012	0.00010	0.00010
Sc	<sup>46</sup> Sc (84 d)	0.36	$\gamma$	<0.03	<0.05	<0.05	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.10	<0.10
Cr	<sup>51</sup> Cr (28 d)	—	X, $\gamma$	<0.00002	<0.00002	<0.00002	<0.00003	<0.00003	<0.00003	<0.00003	<0.00003	<0.00003	<0.00003	<0.00004	<0.00004
Fe	<sup>59</sup> Fe (45 d)	0.46	$\gamma$	<0.00003	<0.00003	<0.00003	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004	<0.00005	<0.00005	<0.00005
Co	<sup>60</sup> Co (5.3 y)	0.31	$\gamma$	0.003	0.004	0.004	0.005	0.005	0.006	0.006	0.006	0.006	0.007	0.007	0.007
Zn	<sup>65</sup> Zn (245 d)	—	X, $\gamma$ ( $\beta^+$ )	<0.0001	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0003	<0.0003	<0.0003
Br	<sup>82</sup> Br (35 h)	0.47	$\gamma$	0.0047	0.0068	0.0068	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007
Rb	<sup>86</sup> Rb (19 d)	1.82	$\gamma$	1.14	1.30	1.30	1.25	1.25	1.38	1.38	1.38	1.36	1.52	1.52	1.52
Sr	<sup>87</sup> Sr (65 d) + <sup>89</sup> Sr (50 d)	1.46 ( <sup>89</sup> Sr)	$\gamma$ ,e <sup>-</sup>	0.0034	0.0029	0.0029	0.0043	0.0043	0.0037	0.0037	0.0037	0.0058	0.0048	0.0048	0.0048
Y	<sup>90</sup> Y (64 h)	2.18	—	1.95	2.41	2.41	0.47	0.47	0.56	0.56	0.10	0.10	0.12	0.12	0.12
Sb	<sup>122</sup> Sb (2.7 d) + <sup>124</sup> Sb (60 d)	—	$\gamma$	7.96	7.99	7.99	2.82	2.82	3.06	3.06	1.90	1.90	2.20	2.20	2.20
Ba	<sup>131</sup> Ba (11 d) + <sup>133</sup> Ba (11 y)	2.31 ( <sup>124</sup> Sb)	X, $\gamma$ ,e <sup>-</sup>	0.00006	0.00006	0.00007	0.00007	0.00007	0.00007	0.00007	0.00007	0.00007	0.00010	0.00010	0.00010
La	<sup>140</sup> La (40 h)	2.15	$\gamma$	1.60	1.32	1.32	0.11	0.11	0.087	0.087	0.003	0.003	0.003	0.003	0.003
Ce	<sup>141</sup> Ce (32 d) + <sup>143</sup> Pr (14 d)	0.93 ( <sup>143</sup> Pr)	X, $\gamma$ ,e <sup>-</sup>	0.033	0.015	0.015	0.026	0.026	0.012	0.012	0.024	0.024	0.011	0.011	0.011
Nd	<sup>147</sup> Nd (11 d)	0.83	X, $\gamma$ ,e <sup>-</sup>	0.061	0.022	0.022	0.027	0.027	0.0058	0.0058	0.018	0.018	0.0039	0.0039	0.0039
Sm	<sup>153</sup> Sm (47 h)	0.80	X, $\gamma$ ,e <sup>-</sup>	0.46	0.098	0.098	0.047	0.047	0.0097	0.0097	0.026	0.026	0.0007	0.0007	0.0007
Eu	<sup>152</sup> Eu (12 y) + <sup>154</sup> Eu (14 y)	1.88 ( <sup>152</sup> Eu)	X, $\gamma$	1.14	0.92	0.92	1.61	1.61	1.31	1.31	2.44	2.44	1.97	1.97	1.97
Tb	<sup>160</sup> Tb (72 d)	0.86	X, $\gamma$ ,e <sup>-</sup>	0.48	0.26	0.26	0.62	0.62	0.33	0.33	0.85	0.85	0.47	0.47	0.47
Tm	<sup>170</sup> Tm (130 d)	0.97	X, $\gamma$ ,e <sup>-</sup>	8.43	2.99	2.99	11.5	11.5	3.97	3.97	16.7	16.7	5.64	5.64	5.64
Yb	<sup>169</sup> Yb (32 d) + <sup>175</sup> Yb (4.2 d)	0.50 ( <sup>175</sup> Yb)	X, $\gamma$ ,e <sup>-</sup>	0.013	0.016	0.016	0.013	0.013	0.016	0.016	0.012	0.012	0.015	0.015	0.015
Lu	<sup>177</sup> Lu (6.7 d)	0.50	X, $\gamma$ ,e <sup>-</sup>	0.049	0.032	0.032	0.037	0.037	0.022	0.022	0.020	0.020	0.014	0.014	0.014
Hf	<sup>181</sup> Hf (42.5 d)	0.41	$\gamma$	0.0013	0.0017	0.0017	0.0015	0.0015	0.0021	0.0021	0.0021	0.0021	0.0028	0.0028	0.0028
Ta	<sup>182</sup> Ta (115 d)	0.51	X, $\gamma$ ,e <sup>-</sup>	0.083	0.099	0.099	0.115	0.115	0.133	0.133	0.165	0.165	0.192	0.192	0.192
Tl	<sup>204</sup> Tl (3.8 y)	0.77	$\gamma$	<0.002	<0.002	<0.002	<0.003	<0.003	<0.002	<0.002	<0.004	<0.004	<0.002	<0.002	<0.002
Th	<sup>233</sup> Pa (27 d)	0.25	X, $\gamma$ ,e <sup>-</sup>	0.0075	0.0081	0.0081	0.0083	0.0083	0.0092	0.0092	0.011	0.011	0.012	0.012	0.012
U	<sup>239</sup> Np (2.3 d)	0.44	X, $\gamma$ ,e <sup>-</sup>	0.32	0.29	0.29	0.29	0.29	0.24	0.24	0.31	0.31	0.28	0.28	0.28
	+ fission products	Various	Various												

TABLE II  
PHOSPHORUS CONTENT OF SOME STANDARD ROCKS (% P<sub>2</sub>O<sub>5</sub>)

Rock	Direct $\beta$ -counting			Radiochemical separation			Literature values	
	I	II	Mean	% of recorded activity due to <sup>32</sup> P	Previous results <sup>3</sup> Mean	New treatment of standard		
						Single values	Mean	
Andesite AGV-1	0.494	0.513	0.501	94.5	0.545	0.475	0.481	0.50 <sup>4</sup>
	0.490	0.508				0.479		0.49 <sup>5</sup>
Basalt BCR-1	0.357	0.359	0.361	93.1	0.401	0.355	0.347	0.34 <sup>4</sup>
	0.361	0.364				0.355		0.35 <sup>5</sup>
Granite G-2	0.130	0.130	0.132	69.6	0.141	0.133	0.133	0.13 <sup>4</sup>
	0.132	0.132				0.131		0.13 <sup>5</sup>
	0.136					0.134		
	0.136							
Granodiorite GSP-1	0.297	0.305	0.295	77.0	0.313	0.276	0.273	0.25 <sup>4</sup>
	0.285	0.292				0.271		0.28 <sup>5</sup>
Diabase W-1	0.130	0.133	0.132	92.9	0.145	0.131	0.130	0.119 <sup>2</sup>
	0.131	0.136				0.132		0.12 <sup>4</sup>
	0.133					0.127		
	0.133							
	0.130							
Peridotite PCC-1	0.0010	0.0009	0.0010	49	0.0016	—	—	0.0016 <sup>4</sup>
	0.0012	0.0010						
Dunite DTS-1	0.0013	0.0017	0.0016	76	0.0019	—	—	0.0017 <sup>4</sup>
	0.0014	0.0020						

If the activity of a nuclide like  $^{32}\text{P}$ , emitting high-energy  $\beta$ -rays, is to be shielded from interfering activities, a system of two absorbers may be advantageous. The thickness is so selected that one of the absorbers eliminates conversion electrons and low-energy  $\beta^-$ -particles, and the other is sufficiently thick to eliminate the  $\beta$ -rays from the high-energy  $\beta$ -emitter in question, thus transmitting only  $\gamma$ -rays and to some extent X-rays. The difference between the count-rates obtained with the two absorbers will mainly represent the contribution from high-energy  $\beta$ -emitters.

In order to study the feasibility of phosphorus determination by such a method, the following experiments were carried out.

Standard solutions of phosphorus and the 26 potential interfering elements were irradiated in sealed polyethylene tubes for 1 h in the JEEP II reactor (Kjeller, Norway) at a position with a thermal neutron flux of about  $1.5 \cdot 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$  and a cadmium ratio of gold of about 3. Aliquots (100  $\mu\text{l}$ ) of the irradiated solution were adsorbed on circular pieces of filter paper placed in small circular aluminium cups (20 mm diameter) for  $\beta$ -activity measurements. In some cases, where the standard solution contained significant amounts of chloride or sulphate, yielding  $^{32}\text{P}$  by fast-neutron induced reactions, or otherwise were expected to contain interfering radioactive impurities, radiochemical purification steps based on precipitation and filtering were employed. The samples were counted 10 d, 17 d and 25 d after the irradiation. A Geiger-Mueller counter with conventional shelf arrangement was used. The window thickness of the tube was  $10 \text{ mg cm}^{-2}$ , and the effective diameter was 28 mm. The samples were counted with three different aluminium absorbers, namely  $140 \text{ mg cm}^{-2}$  (activity  $A_1$ ),  $210 \text{ mg cm}^{-2}$  ( $A_2$ ) and  $650 \text{ mg cm}^{-2}$  ( $A_3$ ), and the differences  $A_1 - A_3$  and  $A_2 - A_3$  were calculated and divided by the weight of element present. These specific activity values were divided by the corresponding value for phosphorus, and the "relative interference factors" thus obtained are listed in Table I.

Although several elements show serious interference when present in the same concentration range as phosphorus, the possibility of obtaining useful data for phosphorus in rocks seemed to be good, since most of these elements are normally present in silicate rocks in concentrations far below that of phosphorus. It was decided to try this method on a series of U.S. Geological Survey standard rocks with well known contents of phosphorus. From the results of Table I, counting after about 3 weeks seemed to be advantageous for this purpose, and the  $210 \text{ mg cm}^{-2}$  absorber was preferred to the  $140 \text{ mg cm}^{-2}$  absorber because of less interference from several rare-earth nuclides. An aluminium absorber of  $210 \text{ mg cm}^{-2}$  thickness stops all  $\beta^-$ -particles with energies less than 0.6 MeV.

#### *Direct $\beta$ -counting*

Rock samples and phosphorus standards (about 50 mg of potassium dihydrogenphosphate) were irradiated for 5 days at the same conditions as in the preliminary experiments. After 20 days, 10-mg aliquots of the rock powder were weighed into the aluminium cups described before, spread evenly over an area of about  $1 \text{ cm}^2$  and covered with Scotch tape. The standards were dissolved in an appropriate volume of dilute nitric acid, and aliquots of 100  $\mu\text{l}$  were applied to small circular pieces of filter paper placed in the aluminium cups, dried under an infrared lamp and covered with Scotch tape. Counting was performed with the  $210 \text{ mg cm}^{-2}$  and  $650 \text{ mg cm}^{-2}$  absorbers. The differences in count-rate thus obtained were corrected for contribution

from activities other than  $^{32}\text{P}$  by applying the data available for the U.S.G.S. standard rocks<sup>6,7</sup> and the empirical correction factors of Table I adjusted to 5 days' irradiation. Values corresponding to 21 days' decay were estimated by interpolation. It appeared that rubidium and calcium, and antimony in the case of the ultrabasic rocks DTS-1 and PCC-1, were the only elements that caused interference exceeding 1%. The percentage of the recorded activity found to be due to  $^{32}\text{P}$  is given for each rock in Table II. The results for phosphorus corrected for interferences are also given in Table II.

#### *Radiochemical determination*

In order to assess the validity of the direct  $\beta$ -counting procedure, accurately known phosphorus data for the test samples were considered to be of vital importance. Previously a radiochemical neutron activation method for phosphorus in rocks had been developed<sup>3</sup> and data for the U.S.G.S. standard rocks had been obtained. Further experience indicated that the method used for chemical treatment of the standard did not bring about complete chemical exchange between active and carrier phosphorus, which would cause high results for the rock samples. Instead of heating aliquots of the standard with hydrochloric acid/hydrogen peroxide, a new method of standard treatment was therefore introduced, involving fusion with sodium hydroxide pellets in the same manner as for the samples. Three series of standards with six parallels of each treated in this way showed relative standard deviations of 2.1%, 2.4% and 2.2%, which was considerably better than the reproducibility observed with the previous standard treatment, thus indicating more complete chemical exchange. The rocks AGV-1, BCR-1, G-2, GSP-1 and W-1 were re-analyzed using the same procedure as before, except for the standard treatment. Three parallels of each rock were run, and the results are given in Table II. The mean values are 10% lower in average than the previous set of data, but are in good agreement with the neutron activation values of Greenland<sup>4</sup>, as well as the data obtained by conventional chemical analyses in the U.S.G.S. laboratories<sup>5</sup>. Interference from the  $^{32}\text{S}(n,p)^{32}\text{P}$  reaction was neglected<sup>3</sup>.

#### *Discussion*

The values from the direct  $\beta$ -counting experiments are in good agreement with the radiochemical values from this work as well as the literature values (Table II). The method is therefore considered to be well suited for use on a wide range of rocks with phosphorus contents exceeding 500 p.p.m. Even for rocks containing only 10 p.p.m. phosphorus, the method may yield the correct order of magnitude, as indicated by the results for DTS-1 and PCC-1.

Rubidium seems to be by far the most serious interference, and the accuracy of the results depends on a fairly good knowledge of the rubidium content. For calcium, an approximate knowledge of the content suffices in most cases. The rare-earth elements require special consideration. In the samples analyzed here, the total interference from this group appears to be 1% or less under the given conditions, but for many rocks, especially those which show a relative enrichment in the yttrium group, the interference would be appreciable. The nuclides  $^{90}\text{Y}$  and  $^{170}\text{Tm}$  are the most important contributors in this group.

The direct  $\beta$ -counting method should be especially useful in connection with multi-element analyses by neutron activation and Ge(Li)  $\gamma$ -spectrometry. In this case

Rb, Ca, Sb, as well as the rare earths, may be determined if present in concentrations high enough to interfere with the  $\beta$ -counting. Determination of phosphorus by the present method should represent a useful addition to such a scheme.

It must be emphasized that the correction factors given in Table I have been determined for a specific set of experimental conditions (energy distribution of neutron flux, irradiation time, decay time, performance of counting apparatus, absorber thickness, etc.) and cannot be applied directly to other experiments. The number of elements for which a correction factor needs to be determined, however, is small, as is evident from the preceding discussion.

Finally, it should be mentioned that the relative rubidium interference will be reduced if the activation is carried out in a more thermalized neutron flux, since  $^{85}\text{Rb}$  has a high resonance activation integral compared to its thermal neutron activation cross-section, while  $^{31}\text{P}$  follows the  $1/v$  law closely in the energy range to be considered<sup>8</sup>. When changing from a position with  $R_{\text{Ca}}^{\text{Au}} = 3.0$  to another with  $R_{\text{Ca}}^{\text{Au}} = 10$ , for example, the relative rubidium interference will be reduced by about 25%. Interference from antimony and thulium will also be appreciably reduced.

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## 5-Sulpho- $\beta$ -resorcylic acid as a new acid-base indicator

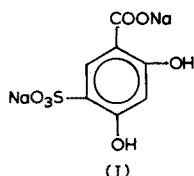
Simple visual titrimetric methods still play an important part in analytical chemistry and the selection of the best indicator for a particular titration is very important. In the present paper, the use of 5-sulpho- $\beta$ -resorcylic acid, which has previously been applied as a gravimetric reagent<sup>1</sup>, as an acid-base indicator is described. Accurate results can be achieved at quite high dilutions, the colour change being from yellow to red (with green fluorescence), as the medium changes from acid alkali; the pH range of the indicator is 7.0–8.5.

### Preparation of 5-sulpho- $\beta$ -resorcylic acid

Dissolve 6.40 g of  $\beta$ -resorcylic acid in the minimum quantity of ethanol in a 250-ml round-bottom flask. Add 15 ml of concentrated sulphuric acid (A.R.) dropwise with constant stirring, cooling so that the temperature does not rise above room temperature. Reflux the mixture on a water-bath for 6 h, cool, and remove the excess of sulphuric acid by adding 30% (w/v) sodium carbonate solution; avoid an excess of alkali. Reduce the volume of the solution to a minimum by evaporation at 80°. Add excess of pure ethanol to precipitate the sodium sulphate formed during neutralisation, filter and wash with alcohol until the filtrate is colourless. Distil the ethanol from the filtrate, transfer the contents of the flask to a wide-mouth porcelain dish and evaporate to dryness in an oven below 100°. The dark brown disodium salt of 5-sulpho- $\beta$ -resorcylic acid is obtained (yield 8.0 g).

### Composition and properties of the indicator

The determination of sodium by flame photometry showed that the compound contained two sodium atoms, which are most probably attached to the carboxylic and the sulphonic acid groups, respectively. Determination of sulphur confirmed the presence of one sulphonic group which is probably in the 5-position in the ring (I):



The reagent showed absorbance peaks at 345 nm and 430 nm in the acidic region, and 370 nm and 490 nm in the alkaline region.

In order to establish the pH range of the indicator, a series of solutions containing the same amount of 5-sulpho- $\beta$ -resorcylic acid was prepared and the pH was adjusted to different values in the range 5.0–10.0, with 0.1 M hydrochloric acid or 2 M ammonia solution. The absorbances of the solutions were measured at the wavelength of maximal absorption in the alkaline region, *i.e.* 490 nm. A plot of absorbance against pH showed a sharp inflection at pH 7.8 (Fig. 1).

### Acid-base titrations

**Reagents.** Stock solutions of potassium hydroxide, sodium hydroxide and

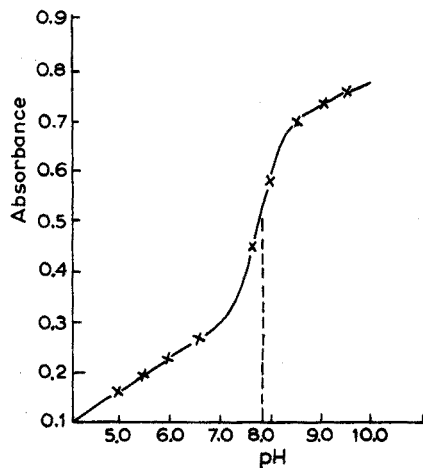


Fig. 1. pH range of the proposed indicator. Absorbance measured at 490 nm.

TABLE I

TITRATIONS WITH SODIUM HYDROXIDE

(10 ml of the particular acid were titrated in each test. In all cases, the alkali solution was of the same concentration as that of the acid being titrated)

Acid	0.1 N		0.01 N		0.002 N		0.005 N	
	Found (ml)	Error (%)	Found (ml)	Error (%)	Found (ml)	Error (%)	Found (ml)	Error (%)
HCl	10.00	0.0	10.02	+0.2	9.98	-0.2	10.98	-0.2
H <sub>2</sub> SO <sub>4</sub>	10.00	0.0	10.00	0.0	10.04	+0.4	9.98	-0.2
HNO <sub>3</sub>	10.00	0.0	10.00	0.0	10.02	+0.2	9.94	-0.6
(COOH) <sub>2</sub>	10.00	0.0	10.02	+0.2	9.96	-0.4	9.92	-0.8
Acetic acid	10.00	0.0	10.04	+0.4	10.06	+0.6	10.06	+0.6
Citric acid	10.00	0.0	10.00	0.0	10.02	+0.2	10.02	+0.2

TABLE II

TITRATIONS WITH SODIUM CARBONATE

(See Table I)

Acid	0.1 N		0.01 N		0.002 N		0.005 N	
	Found (ml)	Error (%)	Found (ml)	Error (%)	Found (ml)	Error (%)	Found (ml)	Error (%)
HCl	10.00	0.0	9.96	-0.4	10.06	+0.6	10.02	+0.2
H <sub>2</sub> SO <sub>4</sub>	10.00	0.0	10.00	0.0	10.06	+0.6	10.06	+0.6
HNO <sub>3</sub>	10.00	0.0	9.98	-0.2	9.98	-0.2	10.04	+0.4
(COOH) <sub>2</sub>	10.00	0.0	10.02	+0.2	10.02	+0.2	10.02	+0.2
Acetic acid	10.06	+0.6	— <sup>a</sup>	—	— <sup>a</sup>	—	— <sup>a</sup>	—
Citric acid	10.05	+0.5	— <sup>a</sup>	—	— <sup>a</sup>	—	— <sup>a</sup>	—

<sup>a</sup> Not titratable.

sodium carbonate were standardized against 0.1 *N* potassium hydrogenphthalate solution potentiometrically; more dilute solutions were prepared by suitable dilution as required. Solutions (0.1 *N*) of hydrochloric, sulphuric, nitric, oxalic, citric and acetic acids were standardized against the standard sodium hydroxide solution; more dilute solutions were prepared by dilution as required. An aqueous 1% solution of 5-sulpho- $\beta$ -resorcylic acid was used as indicator. All solutions were prepared in distilled water free from carbon dioxide.

*Method of titration.* To 10 ml of 0.1 *N* acid solution were added 1–2 drops of indicator solution. With more dilute acid solutions *e.g.* 0.01 *N*, 1–2 ml of indicator solution was required to give sharp end-points. The alkali solution was added dropwise from a micro-burette with vigorous shaking till the colour changed from yellow to reddish pink (with appearance of green fluorescence). In the reverse titration, the colour change was from reddish-pink to yellow. The results of direct and reverse titrations were compared and no differences were observed. The change of colour was distinct and clearly visible in both directions. There was no need to remove carbon dioxide when carbonates were titrated. No indicator blanks were required.

#### *Results and discussion*

Titrations of nitric, hydrochloric, sulphuric, oxalic, citric, and acetic acid solutions were carried out with solutions of sodium hydroxide, potassium hydroxide and sodium carbonate. The results of the titrations with sodium hydroxide and carbonate solutions are summarized in Tables I and II. The results obtained with 5-sulpho- $\beta$ -resorcylic acid indicator were compared with those obtained by potentiometric titrations and then the errors mentioned in Table I and II were calculated.

5-Sulpho- $\beta$ -resorcylic acid changes its colour from yellow to reddish pink (with the appearance of green fluorescence) as the medium changes from acid to alkali. The mechanism of the colour change is not well understood and is under study. 5-Sulpho- $\beta$ -resorcylic acid has an advantage over methyl orange and phenolphthalein which are the indicators most commonly used. Even with 0.002 *N* solutions of strong acids the colour changes are quite distinct. Further, the proposed indicator can be used for titrating relatively weak acids with weak bases, and it is easily prepared and dissolved in water.

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1 G. C. SHIVAHARE, S. MATHUR AND M. K. MATHUR, Paper presented at the 58th Session of Indian Science Congress, Bangalore, 1971.

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### Compleximetric determination of nickel with copper(II)-EDTA-TAR as indicator

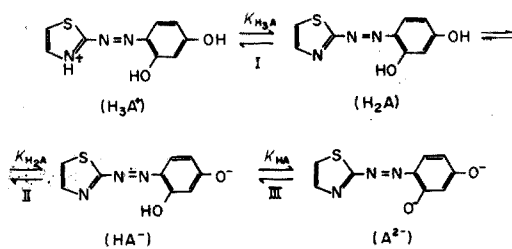
For the titration of nickel with EDTA, murexide<sup>1</sup>, pyrocatechol violet<sup>2</sup>, pyrogallol red<sup>3</sup>, bromopyrogallol red<sup>4</sup>, eriochrome red B<sup>5</sup> and the copper(II)-EDTA-PAN system<sup>6</sup> have been recommended as indicator. Few of these indicators are really satisfactory. More recently, various other pyridylazo and thiazolylazo dyes have been suggested<sup>7,8</sup>; of these, 1-(2-thiazolylazo)-2-hydroxy-3-naphthoic acid (TAHN)<sup>8</sup> appears to be the best indicator in the visual titration of nickel with EDTA, its color transition being fast and distinct except at high pH values.

The present communication describes the compleximetric titration of nickel with the copper(II)-EDTA-4-(2-thiazolylazo)resorcinol (TAR) system as indicator, similar to the titration of gallium with this indicator system<sup>9</sup>. The stability constants of the Ni-TAR and Cu-TAR complexes were determined in order to prove the system. The end-point is sharp and the method is simple and accurate.

#### Determination of equilibrium constants

It was necessary to determine the dissociation constants of TAR and the stability constants of the Ni-TAR and Cu-TAR complexes in order to test the relation between the fraction titrated ( $\alpha$ ) and the indicator transition ( $\phi$ ). These constants were determined in aqueous 2% (v/v) dioxan solution at an ionic strength of 0.10 M and at  $25 \pm 1^\circ$ .

*Dissociation constants of TAR.* The dissociation of TAR is considered to be similar to the dissociation process of TAN and PAR:

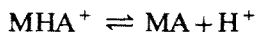


The dissociation constants of TAR for each step were established in the conventional manner, the values found being  $\text{p}K_{\text{H}_3\text{A}} = 0.98$  at 500 nm,  $\text{p}K_{\text{H}_2\text{A}} = 6.17$  at 500 nm,  $\text{p}K_{\text{HA}} = 9.49$  at 545 nm. These values are quite similar to the data previously reported<sup>10</sup>.

*Stability constants of Ni-TAR and Cu-TAR complexes.* If the concentration of copper or nickel ions is large compared with that of TAR, both metal ions form 1 : 1 complexes with TAR, i.e. normal complex MA and protonated complex MHA. The following equilibria:



and



are set up, the equilibrium constants being given by

$$K_{\text{MHA}}^{\text{H}_2\text{A}} = \frac{[\text{MHA}^+][\text{H}^+]}{[\text{M}^{2+}][\text{H}_2\text{A}]} \quad \text{and}$$

$$K_{\text{MHA}}^{\text{H}} = \frac{[\text{MHA}^+]}{[\text{MA}][\text{H}^+]}, \quad \text{respectively.}$$

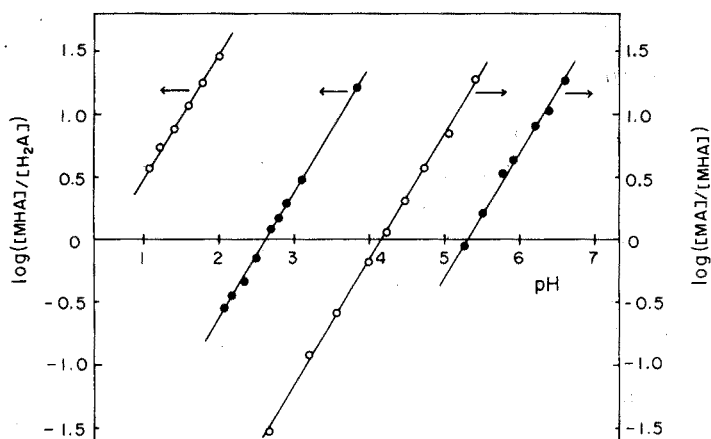


Fig. 1. Plots of  $\log ([\text{MHA}]/[\text{H}_2\text{A}])$  and  $\log ([\text{MA}]/[\text{MHA}])$  against pH for the TAR complexes of copper and nickel. (○) Copper; (●) nickel.

Plots of  $\log ([\text{MHA}^+]/[\text{H}_2\text{A}])$  and  $\log ([\text{MA}]/[\text{MHA}^+])$  against pH should give straight lines with slopes of unity and with intercepts of  $(\log K_{\text{MHA}}^{\text{H}_2\text{A}} + \log c_{\text{M}})$  and  $-\log K_{\text{MHA}}^{\text{H}}$ , respectively. These plots are shown in Fig. 1. From the values of the intercept of these plots, the stability constants  $\log K_{\text{MHA}}^{\text{H}_2\text{A}}$  and  $\log K_{\text{MHA}}^{\text{H}}$  were obtained. On the basis of these constants and of the dissociation constants of TAR, the stability constants of  $\text{MHA}^+$  and MA were calculated from the following equations:

$$K_{\text{MHA}}^{\text{HA}} = \frac{[\text{MHA}^+]}{[\text{M}^{2+}][\text{HA}^-]} = K_{\text{MHA}}^{\text{H}_2\text{A}}/K_{\text{H}_2\text{A}}$$

$$K_{\text{MA}} = \frac{[\text{MA}]}{[\text{M}^{2+}][\text{A}^{2-}]} = K_{\text{MHA}}^{\text{HA}}/K_{\text{HA}} \cdot K_{\text{MHA}}^{\text{H}}$$

The values found are given in Table I, along with the values previously reported for copper<sup>10</sup>.

TABLE I

STABILITY CONSTANTS OF NICKEL- AND COPPER-TAR COMPLEXES

	<i>This work</i>	<i>Ref. 10</i>
$\log K_{\text{NiHA}}^{\text{HA}}$	6.06 at 535 nm	—
$\log K_{\text{NiA}}^{\text{NIA}}$	10.23 at 520 nm	—
$\log K_{\text{CuHA}}^{\text{HA}}$	8.34 at 555 nm	8.41 at 550 nm
$\log K_{\text{CuA}}$	13.66 at 520 nm	13.92 at 520 nm

### Theoretical considerations

By an approach analogous to that outlined previously for the titration of gallium<sup>9</sup>, it is possible to develop the expression:

$$a = 1 - f_1 \frac{1 - \phi}{\phi} + f_2 \frac{\phi}{1 - \phi} - \frac{C_A}{C_{Ni}} (1 - \phi) \quad (1)$$

where  $a = (C_Y - C_{Cu})/C_{Ni}$ ,  $\phi = [A^-]/C_A$ ,

$$f_1 = (K_{CuY-Ni}^{-1} \frac{C_{Ni}}{C_{Cu}} + 1)(K_{Cu'A'(CuA)'} C_{Ni})^{-1} \text{ and } f_2 = K_{CuY-A} \frac{C_{Cu}}{C_{Ni}} \quad (2)$$

The lower  $f_1$  and  $f_2$ , the sharper the indicator transition in the vicinity of the equivalence point. As is evident from eqn. (2), both  $f_1$  and  $f_2$  depend on the concentrations of copper, nickel, and acetate ions as well as hydrogen ion concentration. Calculated values for  $K_{CuY-Ni}$  and  $K_{NiA-Cu}$  are given in Table II\*.

TABLE II

VALUES OF  $K_{CuY-Ni}$  AND  $K_{NiA-Cu}$ 

pH	log $K_{CuY-Ni}$	log $K_{NiA-Cu}$
3.0	-0.04	2.27
4.0	0.05	2.27
5.0	0.44	2.39
6.0	0.59	2.60
7.0	0.61	2.65

### Results and discussion

The  $f_1$  and  $f_2$  values calculated for various experimental conditions are tabulated in Table III, which indicates that indicator transitions should be sharp and distinct above pH 3.5 under the conditions given.

TABLE III

THE  $f_1$  AND  $f_2$  VALUES AT VARIOUS pH VALUES<sup>a</sup>

pH	$C_{Ni} = 1.93 \cdot 10^{-3} M$ $C_{Cu} = 1.00 \cdot 10^{-4} M$		$C_{Ni} = 1.65 \cdot 10^{-3} M$			
			$C_{Cu} = 1.00 \cdot 10^{-3} M$		$C_{Cu} = 3.00 \cdot 10^{-3} M$	
	log $f_1$	log $f_2$	log $f_1$	log $f_2$	log $f_1$	log $f_2$
3.0	-1.12	-4.59	-1.94	-3.55	-2.19	-3.04
4.0	-2.18	-5.30	-2.98	-4.23	-3.20	-3.75
5.0	-3.67	-5.60	-4.30	-4.53	-4.42	-4.05
6.0	-5.36	-5.65	-5.90	-4.58	-5.99	-4.10
7.0	-6.66	-5.64	-7.20	-4.57	-7.29	-4.09

<sup>a</sup>  $C_{OAc^-} = 0.10 M$  in all tests.

\* The values of the stability constants used for the calculations in the present paper were<sup>11,12</sup>:  $pK_{HOAc} = 4.76$ ;  $\log K_{NiOAc} = 0.67$ ;  $\log \beta_{Ni(OAc)_2} = 1.25$ ;  $\log K_{CuOAc} = 1.65$ ;  $\log \beta_{Cu(OAc)_2} = 2.65$ ;  $\log K_{CuY} = 18.79$ ;  $\log K_{CuHY}^H = 3.01$ ;  $\log K_{NiY} = 18.62$ ;  $\log K_{NiHY}^H = 3.62$ ;  $\log K_{H_4Y}^H = 1.99$ ;  $\log K_{H_3Y}^H = 2.67$ ;  $\log K_{H_2Y}^H = 6.16$ ;  $\log K_{HY}^H = 10.25$ .

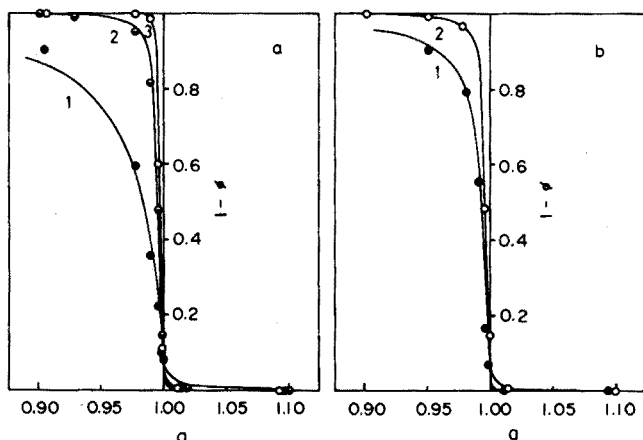
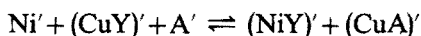


Fig. 2. (a) Effect of pH on the indicator transition.  $C_{Cu} = 10^{-3} M$ ;  $C_{Ni} = 1.65 \cdot 10^{-3} M$ ;  $C_A = 1.05 \cdot 10^{-5} M$ ;  $C_{OAc^-} = 0.10 M$ . (1) pH = 2.89; (2) pH = 4.18; (3) pH = 5.00. (b) Effect of CuY concentration on the indicator transition.  $C_A = 1.05 \cdot 10^{-5} M$ ;  $C_{OAc^-} = 0.10 M$ . (1) pH = 4.16,  $C_{Cu} = 10^{-4} M$ ,  $C_{Ni} = 1.93 \cdot 10^{-3} M$ ; (2) pH = 4.08,  $C_{Cu} = 3.00 \cdot 10^{-3} M$ ,  $C_{Ni} = 1.65 \cdot 10^{-3} M$ . a is the fraction titrated.

**Effect of pH.** Figure 2a shows the titration curves near the equivalence point at various pH values. Above pH 3.5, the indicator transition is very sharp, but it becomes less sharp as the pH decreases, in accordance with prediction from the  $f_1$  and  $f_2$  values. At high pH values where the third dissociation step of the TAR indicator occurs, the end-point becomes less sharp, owing to the reddish shade of the indicator anion. From these data, the range of pH available for titration of nickel is 3.5–7.0.

The concentration of acetate affects the value of  $K_{CuY-Ni}$  and  $K_{Cu'A'/(CuA)'}$ , but, as the nickel and copper acetate complexes are weak, varying concentrations of acetate do not alter the recommended pH range for titration.

**Effect of CuY concentration.** For the successful titration of nickel by the proposed method, the equilibrium



should move to the right. This is favored by high concentrations of CuY and low concentrations of hydrogen ion. However, a very high concentration of CuY makes end-point detection impossible owing to its deep color.

The present method is also applicable to the compleximetric determination of many other metals, e.g. Zn, Pb, In, Cd, etc.; back-titration techniques are possible for metals such as aluminum.

**Accuracy.** The results obtained by the proposed titration at pH 4.2 for amounts of nickel in the range 5.6–28.4 mg agreed (within 0.01 mg) with those obtained gravimetrically by the 8-hydroxyquinoline method and by the compleximetric titration with TAHN indicator. Results for ca. 6 mg of nickel were found to be reproducible (within  $\pm 0.01$  mg) over the pH range 3.0–6.8.

### Experimental

**Reagents.** Standard EDTA solution was prepared from the recrystallized di-

sodium salt and was standardized with zinc solution, with eriochrome black T as indicator. Nickel perchlorate<sup>13</sup> solutions were prepared in water and standardized gravimetrically as oxinate. Copper-EDTA solution was prepared by adding an equivalent amount of EDTA to recrystallized copper perchlorate<sup>14</sup>. 4-(2-Thiazolyl-azo)resorcinol (purity higher than 99%) was dissolved in dioxan. Acetate buffer solution was used to adjust the pH value. The total concentration of acetate was maintained at 0.10 M in the construction of titration curves.

*Recommended procedure.* To a sample solution containing 1–20 mg of nickel, add 5–10 ml of  $10^{-2}$  M Cu-EDTA solution. Adjust the pH value to 4.0–6.5 with acetate buffer solution. Add indicator amounts of TAR solution (*ca.*  $10^{-5}$  M), and titrate with standard  $10^{-2}$  M EDTA solution. Near the end-point, heat the solution to 80–100° for a few minutes and continue the titration dropwise. A distinct color change from lilac to light green is observed at the end-point. Titrate to a light green with no dark shade.

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## Microcoulometric argentimetric titrations\*

The determination of small amounts of material by coulometric titration is often limited by the technique used in detecting the equivalence point. Biamperometric end-point detection is frequently used in connection with coulometric titration, but with low ( $nM$ ) concentrations of materials, it is often not sensitive enough.

Another problem sometimes encountered is the need to have an excess of titrant present in order to ensure complete reaction. The excess is then determined by titration with another titrant or by addition of a known amount of a standardized substance that will react with the excess, and then continuation of the titration (back-titration). The most notable example is probably the iodine-thiosulfate system. Such titrations are usually suitable for microgram sample sizes.

The need for a sensitive method utilizing excess of titrant for determining protein sulphhydryl groups with silver(I) prompted us to investigate a method first described by Christian<sup>1</sup> for the titration of arsenic with electrogenerated bromine. This method was recently used by Champion *et al.*<sup>2</sup> for the titration of submicrogram amounts of chromium(VI) with electrogenerated iron(II). The purpose of this work is to describe the utility of the method in titrations with electrogenerated silver(I) and a simplification in calculations arising from the stability of the biamperometric indicator current with silver(I).

### Experimental

All coulometric measurements were made with the circuit and apparatus described previously<sup>3</sup>. The generating current was 0.0157 mA in all cases. The titration cell was similar to the one described previously except a piece of 2-mm glass tubing was inserted through the rubber stopper to facilitate the addition of the sample without lifting the stopper.

Biamperometric end-point detection was used for all titrations. The impressed voltage of 200 mV was supplied by a Sargent Polarograph, Model XXI. The current from the indicator electrodes was measured on this polarograph at a recorder sensitivity of  $0.003 \mu A \text{ mm}^{-1}$ .

The stirring of the contents of the titration vessel, cleaning of the electrodes, and measurement of pH were accomplished as described previously<sup>3</sup>.

All chemicals were reagent grade whenever possible. Deionized water was used for all solutions.

*Imidazole electrolyte.* 0.15 M imidazole, 0.01 M potassium chloride, 0.01% ethylenedinitrilotetraacetic acid, Na salt (EDTA), pH 6.2.

*2-Hydroxymethyl-2-amino-1,3-propanediol (TRIS) electrolyte.* 0.15 M TRIS, 0.01 M potassium chloride, 0.01% EDTA, pH 7.5.

*Ammoniacal electrolyte.* 0.05 M ammonia, 0.025 M ammonium nitrate, 0.01% EDTA.

### Coulometric titration by the direct method

Place 5 ml of the titration electrolyte (imidazole, TRIS, or ammoniacal) in the

\* Taken in part from the Ph.D. Dissertation of Dr. Jack H. Ladenson, University of Maryland, 1970.

titration cell and generate silver(I) at a current of 0.0157 mA until the indicator current (with a potential of 200 mV impressed across the indicator electrodes) rises 0.060  $\mu\text{A}$  above the lowest current level. This pretitration step ensures that impurities in the titration electrolyte do not interfere with the results. Reset the timer and add the sample. Perform the titration in the same manner as the pretitration. Calculate the amount of sample (in  $\mu\text{eq}$ ) by means of Faraday's law.

#### *Coulometric titration by the excess method*

Place 5 ml of titration electrolyte in the titration cell. Generate silver(I) at a current of 0.0157 mA for *ca.* 20 sec longer than was needed for the pretitration step of the direct method. Displace the recorder pen to the bottom of the chart paper and allow the indicator current to level off. After the indicator current becomes constant, reset the timer and generate silver(I) until the recorder pen travels approximately  $\frac{3}{4}$  of the distance across the chart. Stop the generation and again allow the indicator current to reach a constant value. Add the sample (5–100  $\mu\text{l}$ ) by means of an appropriate Hamilton syringe to the titration cell and allow the indicator current to reach a

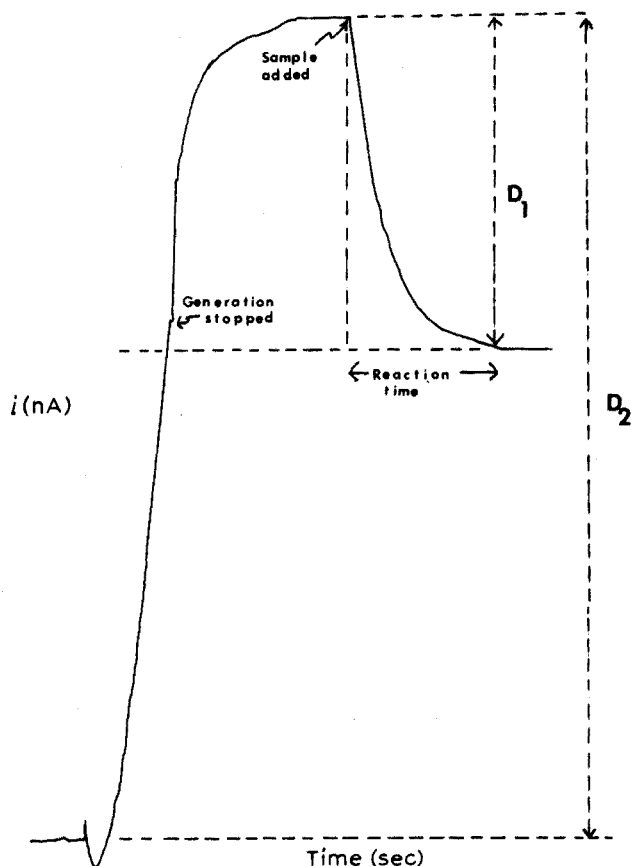


Fig. 1. Typical titration curve for the excess silver method.

constant value once again. A typical titration recording is shown in Fig. 1. It was found that lifting the stopper or disturbing the indicator electrodes caused a change in the current recorded. Also the recorder had to be slightly damped in order to reach stable current readings.

The titration time of the sample is calculated as follows:

$$\text{titration time (sec)} = \frac{D_1(\text{mm})}{D_2(\text{mm})} \cdot \text{generation time}$$

where  $D_1$  is equal to the distance (in mm) on the recorder chart between the current levels of the second generation of silver(I) and the sample addition and  $D_2$  is equal to the distance (in mm) on the recorder chart between the current levels of the initial and final generation of silver(I).

In addition to the titration time, the reaction time of the sample can be calculated by measuring the distance between the point of sample addition and the point at which the indicator current becomes constant. This distance is multiplied by the reciprocal of the chart speed ( $\text{sec mm}^{-1}$ ) to give the reaction time. Since the recorder was damped, the reaction times are treated in a relative manner and not used for kinetic calculations.

### Results and discussion

Table I shows the results of titrating reduced glutathione (GSH), cysteine

TABLE I

RECOVERY OF SUBSTANCES TITRATED BY THE MICROCOULOMETRIC METHOD

Substance titrated	Electrolyte	Method	$\mu\text{g}$ taken	<i>N</i>	$\mu\text{g}$ found	Recovery (%)	
GSH	Ammonia	Direct	15.4	6	$15.5 \pm 0.3$	100	
			5.69	4	$5.70 \pm 0.08$	100	
		Excess	0.584	3	0.600	102.7	
			0.284	1	0.284	100	
	TRIS	Direct		14.6	4	$14.9 \pm 0.2$	102.1
				5.84	6	$6.05 \pm 0.16$	103.6
Excess			1.38	4	$1.40 \pm 0.1$	101.4	
			1.46	3	$1.53 \pm 0.03$	104.8	
Cysteine	Ammonia	Direct	5.02	4	$6.92 \pm 0.07$	138	
		Excess	1.00	1	1.47	147	
	TRIS	Direct	5.02	3	$6.48 \pm 0.06$	129	
		Excess	2.51	1	3.37	134	
	Imidazole	Excess	1.22	4	$1.22 \pm 0.04$	100	
			0.488	7	$0.452 \pm 0.057$	92.6	
Iodide	Ammonia	Direct	45.4	3	33.7	74.2	
		Excess	11.4	1	8.12	71.2	
	TRIS	Direct	22.7	1	19.2	84.6	
		Excess	11.4	2	9.36	82.1	
	Imidazole		4.54	3	$3.68 \pm 0.05$	81.1	
		Direct	11.4	1	9.39	82.5	
Thiourea	Ammonia	Excess	4.54	6	$3.49 \pm 0.36$	77.0	
			2.05	3	$2.10 \pm 0.22$	102.4	
		Excess	0.820	4	$0.856 \pm 0.073$	104.4	

hydrochloride, iodide, and thiourea by both the direct and excess methods. No attempt was made to optimize conditions except for the GSH titration<sup>3</sup>. The ammonia and TRIS media yielded similar results for GSH. In agreement with Sluyterman<sup>4</sup>, correct results for cysteine were obtained only in imidazole medium. Thiourea gave correct results in ammoniacal medium. Table I shows that the procedure using excess silver(I) gave results essentially similar to those obtained by the direct-titration procedure. Titration times as short as 5 sec could be detected with a relative standard deviation ranging between 1 and 3 %.

The titration of thiourea with electrogenerated silver(I) has been performed by a back-titration method with silver bromide and then titrating the released bromide<sup>5</sup>. As shown, the excess method permits the determination of microgram amounts of thiourea without the need of back-titration.

In previous applications of this microcoulometric titration technique<sup>1,2</sup>, the biamperometric indicator current exhibited a slow decrease with time. With an excess of silver(I) present, the indicator current remained constant for at least 15 min. This stability allows the use of a direct proportion in calculating the results and makes the detection of the end-point easier. The reaction times for different samples can be compared easily. For example, in ammoniacal medium thiourea reacted 3–4 times more slowly than GSH and iodide reacted 5 times more slowly in ammoniacal medium than in TRIS medium.

The system of titration described should be applicable to any titration with silver(I). It provides a means of determining small amounts of materials and is suitable for titrating substances which require an excess of titrant, *e.g.*, thiourea, protein sulfhydryl groups.

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## Microdetermination of cadmium airborne particulates by means of the ring-oven technique

Cadmium and its compounds are toxic to humans and animals<sup>1,2</sup>. When inhaled, it can produce pulmonary emphysema and bronchitis<sup>3,4</sup>, kidney damage resulting in proteinuria<sup>4-6</sup>, and gastric and intestinal disorders<sup>7,8</sup>. Cadmium in the atmosphere has been related statistically to diseases of the heart<sup>3</sup>, and effects on liver and brain have also been observed. Animal experiments indicate that cadmium may be carcinogenic<sup>3,5</sup>.

The current methods used for the determination of cadmium in air pollution investigations are emission spectroscopy<sup>8,9</sup>, atomic absorption spectrometry<sup>9</sup>, polarography<sup>10,11</sup>, and colorimetry<sup>12</sup>. None of these methods are suitable for field applications because of the detailed sample preparation involved and the equipment required. A ring-oven method has been developed for the rapid estimation of cadmium in air pollution investigations which is very selective and is ideally suited for field applications. The sensitivity and reliability are comparable to those obtained by emission spectroscopy or atomic absorption spectrometry.

Stephen reported the estimation of cadmium by means of the ring oven in which he precipitated cadmium as the sulfide after necessary prior separations<sup>13</sup>. The separations are cumbersome and the method lacks sensitivity. Weisz *et al.* have used the universal standard scale<sup>14</sup> where, after necessary separations, cadmium is precipitated as the sulfide and subsequently converted to an equivalent amount of silver sulfide by immersion in a bath of silver nitrate. The intensity of silver sulfide is compared with silver sulfide standards. Because silver sulfide is darker than cadmium sulfide and easier to compare, the sensitivity is enhanced. Janjic has reported the use of copper(II) hexacyanoferrate(II) universal standards for estimation of cadmium by the ring oven<sup>15</sup> but the procedures lack simplicity. We have developed a new method for the estimation of cadmium by use of the ring oven and iron(II) bipyridine iodide as the reagent.

Feigl was the first to report the use of iron(II) bipyridine iodide as a spot test reagent for the detection of cadmium<sup>16,17</sup>. The organic base  $\alpha,\alpha'$ -bipyridine produces an intense red in acidic or neutral solutions of iron(II) salts, owing to the formation of the stable tris( $\alpha,\alpha'$ -bipyridine)iron(II) cation. This complex can combine with anions that have a large ionic volume, forming slightly soluble, red crystalline compounds. Partial precipitation occurs even from a very dilute solution. Accordingly, the complex serves as a general precipitant for anions, such as  $[\text{HgI}_4]^{2-}$ ,  $[\text{CdI}_4]^{2-}$ , and  $[\text{Ni}(\text{CN})_4]^{2-}$ .

The formation of red  $[\text{Fe}(\alpha,\alpha'\text{-bip})_3][\text{CdI}_4]$  can be used for the determination of cadmium if a saturated aqueous solution of tris( $\alpha,\alpha'$ -bipyridine)iron(II) iodide containing an excess of iodide ions is used as the reagent.

A red violet precipitate is obtained, which is characterized by the fact that both its cationic and anionic constituents are complexes. This unusual combination accounts for the remarkable sensitivity and selectivity of this test for cadmium. Interferences are inhibited by the use of suitable masking agents.

### Reagent and stock solutions

*Iron(II) bipyridine iodide.* Dissolve 0.25 g of  $\alpha,\alpha'$ -bipyridine (Fisher Scientific

Company, New Jersey) and 0.146 g of iron(II) sulfate heptahydrate in 50 ml of water. Add 10 g of potassium iodide and after shaking vigorously for 30 min, filter off the  $[\text{Fe}(\alpha, \alpha'\text{-bip})_3] \text{I}_2$ . The resulting saturated solution of  $[\text{Fe}(\alpha, \alpha'\text{-bip})_3] \text{I}_2$  contains excess iodide to accomplish the formation of the  $[\text{CdI}_4]^{2-}$  essential to the cadmium test. The solution is stable for one week; if it becomes turbid on long standing, it should be filtered before use.

*Standard stock cadmium solution.* A solution containing 10 mg Cd ml<sup>-1</sup> was prepared by dissolving 1.37 g of cadmium nitrate tetrahydrate, and making up to 50 ml with distilled water. This solution was diluted as necessary for preparing standard working solutions.

#### *Recommended procedure*

Place a Whatman no. 41 filter paper, the center of which has been previously marked with a pencil dot, on a Weisz ring oven (National Appliance Company, Oregon) maintained at 100–105° measured with a surface thermometer (Pacific Transducer Corporation, Model 311 F). Add an appropriate volume of the standard or unknown cadmium solution with a calibrated microliter pipet, followed by two 15- $\mu\text{l}$  portions of 0.5% (w/v) potassium cyanide solution. Wash the cadmium to the ring zone by 5 or 6 washings with 15- $\mu\text{l}$  portions of distilled water, taking care to avoid any diffusion of solutions beyond 1 mm from the heating block. Add 15  $\mu\text{l}$  of aqueous 5% (w/v) trisodium phosphate and wash it to the ring zone with water. Dry the paper on the ring oven and then expose it to ammonia fumes for about 2 min by holding it at the mouth of a bottle of concentrated ammonia liquor. Add the iron(II) bipyridine iodide reagent to the ring zone, either by spraying or by means of a capillary pipet. A red color develops almost immediately. After the color has developed fully (about 30 sec) wash the ring with a jet of distilled water for about 40 sec. Dry the filter paper in a stream of warm air and match against standards. The color intensity of the ring is stable for at least one month.

#### *Analysis of an unknown*

A standard scale is prepared following the above procedure by making rings with 1-, 3-, 5-, 7-, 9- and 10- $\mu\text{l}$  portions of a solution containing 0.1  $\mu\text{g}$  Cd  $\mu\text{l}^{-1}$ . For sampling, the usual methods of dust collection are applicable but the use of dust tapes is especially convenient because all operations can be performed directly on the sample spot. When the cadmium particulates are soluble in potassium cyanide, no previous treatment need be performed; and the tests can be run directly on dust tapes. If insoluble particulates (cadmium sulfide) are anticipated, a pretreatment is necessary before the analysis. The paper is exposed to bromine vapors for about 5 min or a dilute solution of bromine water is added to the spot and dried in a stream of warm air. The sulfide is thereby oxidized to the soluble sulfate and the analysis can be continued as first described.

Where sequential tape samplers are used, an instrument having an orifice of less than 22 mm should be selected so that the total sample can be centered on the ring without the spot extending to the ring area. Once the sample spot is properly positioned the cadmium can be dissolved by cautious treatment with dilute potassium cyanide solution, and the dissolved salts washed to the ring zone and the cadmium estimated as described above.

### Results and discussion

**Selection of paper.** Whatman 41 was selected because of its purity and good diffusion properties. Munktells No. 00 is also suitable. Whatman dust tapes are available and can be used on sequential tape samplers.

**Masking.** Trisodium phosphate is added to mask lead, which otherwise would precipitate as the iodide and react with the reagent to produce a pink color. The filter paper is exposed to ammonia fumes to mask copper, nickel, cobalt, and zinc. Cadmium and these ions form their respective ammine complexes but the  $[\text{Cd}(\text{NH}_3)_4]^{2+}$  equilibrates promptly to form the iodo complex whereas the other ammine complexes are inactive. Silver and thallium interfere but these are usually not of any significance in air pollution investigations.

### Interferences

The effect of interfering ions was investigated by preparing two rings for each ion. The first ring contained 20  $\mu\text{g}$  of the potential interfering ion and the second, 0.2  $\mu\text{g}$  of cadmium in the presence of 20  $\mu\text{g}$  of the interfering ion. The ion was established as non-interfering when the first ring was identical to the blank and the second matched with the 0.2- $\mu\text{g}$  cadmium ring of the standard scale.

The following ions do not interfere at 20- $\mu\text{g}$  levels:

- Group I  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$
- Group II  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$
- Group III  $\text{BO}_2^-$ ,  $\text{B}_4\text{O}_7^-$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Ce}^{3+}$
- Group IV  $\text{CO}_3^{2-}$ ,  $\text{Ac}^-$ ,  $\text{SiO}_3^{2-}$ ,  $\text{GeO}_3^{2-}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Th}^{4+}$
- Group V  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{VO}_2^+$ ,  $\text{VO}_3^-$ ,  $\text{HAsO}_3^{2-}$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sb}^{5+}$ ,  $\text{Bi}^{3+}$
- Group VI  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{TeO}_3^{2-}$ ,  $\text{TeO}_4^{2-}$ ,  $\text{Cr}^{3+}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{VO}_2^{2+}$
- Group VII  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Mn}^{2+}$ ,  $\text{MnO}_4^-$ ,  $\text{Br}^-$ ,  $\text{BrO}_3^-$ ,  $\text{I}^-$ ,  $\text{IO}_3^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$
- Group VIII  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$

Interference was observed from  $\text{Hg}^+$ ,  $\text{Pd}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{Au}^{3+}$ . However, these are of no practical significance in air pollution studies.

### Quantitative estimation

The accuracy and reproducibility of the method for the determination of cadmium were ascertained by the procedure of Weisz<sup>18</sup>. A standard scale and three rings from 1-, 2-, 3- and 4- $\mu\text{l}$  portions of unknown were prepared according to the recommended procedure. The rings were matched and the unknown concentration

TABLE I

DETERMINATION OF CADMIUM

Taken	Found <sup>a</sup>
0.200	0.204 $\pm$ 0.020 <sup>b</sup>
0.300	0.310 $\pm$ 0.016

<sup>a</sup> Based on averaging 5 values calculated from 3 rings, each according to the method of Weisz<sup>18</sup>.

<sup>b</sup> Calculated at 90% confidence level.

was given by the ratio of the sum of microliter portions of three rings, matching rings of the standard scale to the sum of microliter portions of three rings prepared from the unknown solution. Results are shown in Table I.

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## Triangular wave generator for cyclic voltammetry

In the practice of cyclic voltammetry, the source of the signal that is introduced to the potentiostat is usually a laboratory-built<sup>1</sup> or commercial function generator. Although these instruments are adequate for the purpose, some inconvenience is felt when it is desired to carry out a series of scans with varying rates and a fixed range, or *vice versa*, because these usually do not permit adjustments of the amplitude and the rate of scan, independently of each other. The instrument described here was evolved from one of the published circuits<sup>2</sup>, but gives triangular waves whose upper and lower potential limits can be separately set by two potentiometer controls, without affecting the pre-set scan rate. The positive limit of the scan may be set anywhere between  $E$  and  $E + 2.5$  V, where  $E$  is the potential of the built-in adjustable d.c. level, and the negative limit between  $E$  and  $E - 2.5$  V. The starting potential and also the direction of the first scan can be arbitrarily chosen if necessary. This instrument is rate-based, and the frequency of the generated wave is equal to  $v/2(E_1 - E_2)$  Hz, where  $v$  is the scan rate in  $V \text{ sec}^{-1}$ , and  $E_1$  and  $E_2$  are the potentials of the limits of the scan.

These features would make this instrument useful in some types of voltammetric experiments, especially in the assignment of the type of electrode reaction on the basis of the effect of the rate of scan on the potential and height of voltammetric peak<sup>3</sup>, and in the "potential clipping" technique which is frequently employed to distinguish a reaction peak which is an artefact of the reaction of another peak of the opposite polarity. The usable scan rates by this instrument extend from  $0.25 \text{ mV sec}^{-1}$  to several hundred  $V \text{ sec}^{-1}$ , so that it may be used as the signal generator for polarography as well as for cyclic voltammetry.

### Circuit

The instrument, which is shown diagrammatically in Fig. 1, uses three solid-state operational amplifiers in its main wave-generating part. OA 1 and OA 2 are used as Zener-bound switches with decoupling networks; the bound circuit of OA 1 helps to form a well-shaped square wave at the output of OA 2. OA 3 is an integrator. Another amplifier OA 4 is added to give an adjustable d.c. level to the generated triangular wave, and to superimpose another kind of signal on the output when necessary.

Two feedback paths are returned to the summing point of OA 1, one from the output of OA 2 and the other from that of OA 3. The first one carries a positive feedback current which maintains the output of OA 2 at one of the bound limits, which are  $+7.5$  and  $-7.5$  V. The magnitude of the positive feedback current is linearly adjustable by  $R_4$  when the output of OA 2 is negative, and by  $R_5$  when that is positive. The voltages at the ungrounded sides of  $R_4$  and  $R_5$  are  $-6.9$  and nearly zero volt, respectively, when the output is  $-7.5$  V, and they are zero and  $+6.9$  V, respectively, when the output is  $+7.5$  V.

With SW 2 closed and SW 3 open, the current from the output of OA 2 and through  $R_8$  causes the capacitor  $C_1$  to be charged, and the output voltage of OA 3 has to increase at a rate which is determined by  $R_7$ ,  $R_8$  and  $C_1$ . At the same time, a negative feedback current proportional to the output voltage of OA 3 flows through  $R_6$  and,

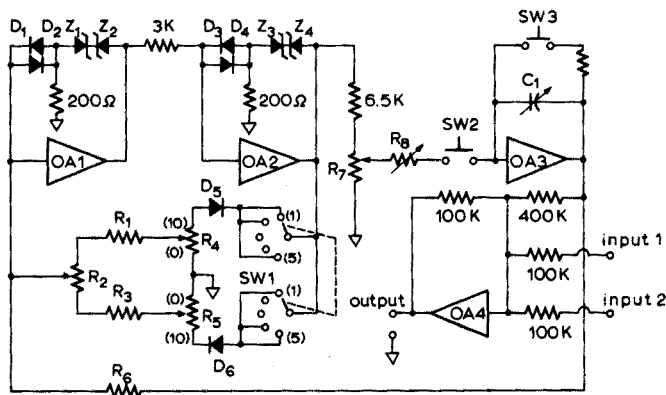


Fig. 1. Triangular wave generator. (OA 1, OA 2) Aiko H9F/5639 (Aiko Denki Inc., Narimasu, Tokyo, Japan). (OA 3) Aiko 4M/4229. (OA 4) Aiko 9F/4639. ( $D_1$  to  $D_6$ ) 1S 1585. ( $Z_1$  to  $Z_4$ ) 1S 53. ( $R_1, R_3$ ) 560 K. ( $R_2$ ) 10 K trimmer. ( $R_4, R_5$ ) Helical potentiometer, 10 turn, 5 K. ( $R_6$ ) 820 K plus trimmer (50 K). ( $R_7$ ) Helical potentiometer, 10 turn, 1 K. ( $R_8$ ) 100 K, 1 M and 10 M, 3 steps. ( $C_1$ ) Polyester film capacitor; 0.1, 1.0 and 10  $\mu$ F, 3 steps. (SW 1) Rotary switch, 2-pole, 5-position. (SW 2) "HOLD" at off and "RUN" at on position. (SW 3) "RUN" at off and "RESET" at on position. (INPUT 1) Connected to precision voltage source. (INPUT 2) Spare input. (Power supply and offset adjust circuits are not shown.)

after a time, becomes large enough to cancel out the positive feedback current. This makes OA 1 flip and reverses the polarity of the output of OA 2. Now the direction of the scan is reversed too, and the return scan can continue until the positive feedback current is cancelled out again. These processes are repeated automatically and result in the generation of a triangular wave at the output of OA 3. The upper and lower limits of this wave can be separately adjusted by  $R_4$  and  $R_5$ . With SW 1 in position 2 or 4, the scan range can extend only to one of the sides of the d.c. level, while it can extend to both sides with the switch in positions 1 and 5. The generation of the wave ceases with SW 1 in position 3, which may be utilized for checking the instrument.

In this circuit, the ratio of  $R_6$  to  $R_1$  (or  $R_3$ ) was selected to give maximum outputs of +10 and -10 V to OA 3. They are inverted and attenuated to  $\pm 2.5$  V at OA 4. It is to be noted that  $R_1$  (or  $R_3$ ) should be small enough to ensure accurate switching but, at the same time, cannot be so small that the proportionality of the limit control by  $R_4$  (or  $R_5$ ) could be impaired.

### Construction

Each of the amplifiers indicated in Fig. 1 may be replaced by any commercial product having similar or better characteristics. Aiko H9F/5639 is roughly equivalent to Philbrick-Nexus 1009 but has a larger output rating of  $\pm 20$  mA. Aiko 4M/4229 is a MOS-type amplifier with  $10^{14}\Omega$  input impedance and  $10^{-15}$  A offset current, suitable for slow integration. Aiko 9F/4639 is similar to P/N 1009.

Since the symmetry in regard to the forward and backward scan rates mainly depends on a well-balanced positive and negative output voltage of OA 2, each of the Zener pair and diode pair in its bound circuit have to be matched with care. It was our experience that two Zener diodes for use as  $Z_3$  and  $Z_4$  were easily selected from a stock of five, so that the selected pair, tied in series back to back, showed nearly identical ( $\pm 0.5\%$ ) voltage drops across it in both directions, against a current of 5.6

mA. Also, a diode pair matched for the forward drops at 2.6 mA was used as  $D_3$  and  $D_4$ .

The two diodes  $D_5$  and  $D_6$  must have very high reverse resistances. With the type of diode indicated in Fig. 1, the voltage drop across  $R_4$  was of the order of  $10^{-5}$  V when the output of OA 2 was +7.5 V.

Usual precautions concerning errors in integration<sup>4</sup> must be observed in the construction of the circuit around OA 3, because the input current can be rather small at the slower scan rate setting. It is advisable to keep this current not smaller than  $10^{-8}$  A in any case and, therefore, to avoid using the dial range of  $R_7$ , smaller than one turn.

After each of the amplifiers was trimmed for its offsets, especially for the bias current of OA 1, final adjustments are made as follows. Put SW 1 in position 1 or 5 and turn  $R_4$  and  $R_5$  so that their dials indicate 10.00 and their contacts are nearest to the diodes. Start a slow scan and observe on a fast recorder if the positive and negative limits of the triangular wave at the output of OA 3 are exactly equal to each other, with respect to zero. If not, make adjustment by  $R_2$ . Then adjust the limits of the wave at the output of OA 4 to exactly  $\pm 2.5$  V, by trimming  $R_6$  or the 400 k $\Omega$  resistor, with the d.c. level equal to zero.

### Operation

The mode of operation of this instrument in conjunction with a potentiostat is flexible, and the optimal mode may be selected for each case. Two possible examples are shown here.

When the scan should start at one of the extremes of the aimed scan range, put SW 2 to "RUN" and SW 3 to "RESET", and adjust the d.c. level to be equal to the starting potential, with the cell disconnected. Put SW 1 in one of the positions 2 and 4, depending on which direction the scan range should be with respect to the starting potential. The other limit is also set, by  $R_4$  or  $R_5$ . After the cell is connected, start the scan by SW 3.

If the scan should start at a potential between the extremes of the scan range, first adjust the limits of the scan range and start a slow scan with the cell disconnected. Observe the output voltage on the recorder and wait until it approaches the desired starting potential, travelling in the same direction as that required for the first scan. When that potential is reached, the scan is stopped by means of SW 2. The scan rate is then reset to the desired one, by means of only  $R_7$  and  $R_8$ , and the actual scan can be started after connection of the cell.

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### Ion-selective lead selenide and lead telluride membrane electrodes

Several investigations have been undertaken to prepare ion-selective solid-state membrane electrodes sensitive to lead ions. A lead sulfide-silver sulfide compacted membrane electrode has been developed by Orion Research Inc.<sup>1</sup>. Lead sulfide-silver sulfide-copper(I) sulfide sintered membrane electrode<sup>2</sup> and lead sulfide-impregnated silicone-rubber membrane electrode<sup>3</sup> have also been prepared and studied. All of these electrodes contained lead sulfide as the active material in the membranes.

The present communication describes preliminary studies of the analytical usefulness of membrane electrodes containing a mixture of lead selenide or telluride with silver sulfide as the membrane<sup>4</sup>, for the measurement of lead ion concentration.

#### Experimental

Lead selenide and lead telluride were prepared by the direct reaction of lead metal with selenium or tellurium in a sealed quartz tube under high vacuum. Silver sulfide was also made by the direct reaction of silver metal with sulfur in an inert gas stream. In the electrode membrane, either lead selenide or lead telluride was incorporated with silver sulfide. Both compacted pellets and sintered plates were tested as the electrode membrane. The sintering was run at a temperature of 100–600° in an inert gas stream.

These membranes were connected to a leading wire partly enveloped by a sealed wire and were mounted in a housing of epoxy resin, to eliminate the need for internal electrode and a filling solution. The potential measurements were made in a conventional manner.

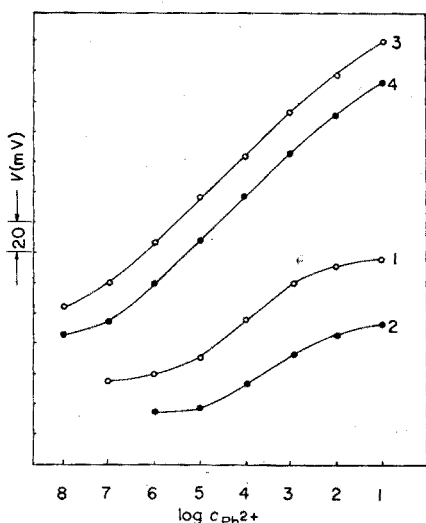


Fig. 1. Potential vs. concentration curves for lead ion-selective membrane electrodes. (1) Compacted lead selenide membrane; (2) compacted lead telluride membrane; (3) sintered lead selenide membrane; (4) sintered lead telluride membrane.

### Results

According to the conditions of preparation of the active materials, the ratio of lead selenide or telluride to silver sulfide, and the temperature and surrounding atmosphere for sintering, the sensitivity and the response rate of the membrane electrodes varied to a great extent, especially in lead nitrate solutions below  $10^{-5}$  M. Membranes prepared under the optimal conditions provided a linear response toward lead ions over the concentration range of  $10^{-1}$ – $10^{-7}$  M lead nitrate with an observed slope of 29.5 mV/pPb<sup>2+</sup>. The sensitivity obtained with the best membrane is rather better than that of a lead sulfide–silver sulfide sintered membrane. Typical potential *vs.* concentration curves for the various membranes are shown in Fig. 1; it is clear that compacted membranes, with both selenide and telluride, provided much poorer sensitivities than sintered ones. In other response characteristics, such as response rate and stability, the sintered membrane electrodes were also considerably superior to the compacted ones.

Among the common ions, silver, copper(II), mercury(II), iron(III), sulfide and chloride interfered seriously, but more than 1000-fold amounts of alkali metals, alkaline earth metals, aluminum, zinc, cadmium, cobalt, nickel, manganese(II) and nitrate were tolerated. Under identical conditions of ionic strength, the potentials did not change over a pH range from lower than zero to the pH at which lead hydroxide precipitated. Compared with a lead sulfide–silver sulfide sintered membrane, these new membranes are more stable to acidic solutions. The sintered membranes, selenide and telluride, were found to obey Nernst's law at temperatures from 0 to 95°.

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## A cesium-sensitive electrode

The development of ion-selective electrodes has made it possible to measure ion activities of a wide range of ions directly and selectively in aqueous as well as non-aqueous media. The analytical determination of cesium has always been a lengthy procedure. There are glasses that are suitable for the preparation of cesium-selective glass electrodes<sup>1</sup>. In this work an electrode sensitive to cesium ion was constructed employing a cesium-12-molybdophosphate precipitate in an inert support, enabling cesium activities to be measured directly.

### Experimental

*Chemicals.* All chemicals used were of A.R. grade except for the cesium nitrate and cesium 12-molybdophosphate. The cesium nitrate was prepared from cesium chloride by repeated evaporation to dryness with concentrated nitric acid, after which it was recrystallised from distilled water and dried at 120°. The cesium 12-molybdophosphate was prepared by precipitation of the salt with 12-molybdophosphoric acid and from a cesium nitrate solution containing excess of cesium. The precipitate was separated by centrifugation and dried at 260° for 24 h.

*Apparatus and preparation of the membrane.* The membrane was prepared by mixing equal masses (2.35 g) of cesium 12-molybdophosphate and G. E. Silicone XA 12 X 80. The mixture was partly dried under an infrared lamp for 2 h and then pressed to a circular disc about 3 mm thick and of 2.5 cm diameter at a pressure of 16000 p.s.i. The membrane was left in a 0.1 M cesium nitrate solution for equilibration for 24 h.

The membrane was mounted between two neoprene gaskets between two L-shaped flanged tubes held together by a clamp. Reference solution which was 0.1 M in cesium nitrate and test solution were placed in the arms of the cell. The arm containing the test solution was also fitted with a tap for easier change of solutions.

Two Beckman fibre-junction saturated calomel electrodes were inserted into the solutions and the potential measured with a Beckman Research model pH-meter. When not in use the calomel electrodes were stored in water. In the cell, when not in use, the test solution was replaced by a 0.1 M cesium nitrate solution.

### Results and discussion

*Response of electrode to cesium ion.* The response of the membrane electrode in pure cesium nitrate solutions is shown in Fig. 1. Activity coefficients were calculated from the extended Debye-Hückel equation,  $\log f = -0.51 Z^2 \mu^{\frac{1}{2}} (1 + \mu^{\frac{1}{2}})^{-1}$ . The slope of the calibration curve was 24.5 mV/pCs at 25°, which is very much smaller than the expected Nernstian value, but the electrode was usable to determine cesium concentrations as low as  $10^{-5}$  M. The membrane lasted for about 4 months.

*Effect of pH on the electrode potential.* The pH dependence of the electrode was studied for the pH range 1-6. The pH of test solutions was adjusted by addition of nitric acid; higher pH values could not be studied as the heteropoly compounds begin to depolymerize and dissolve. When 0.01 M cesium concentrations were used, the potential increased with pH in the range 1-4, and then remained constant. Other

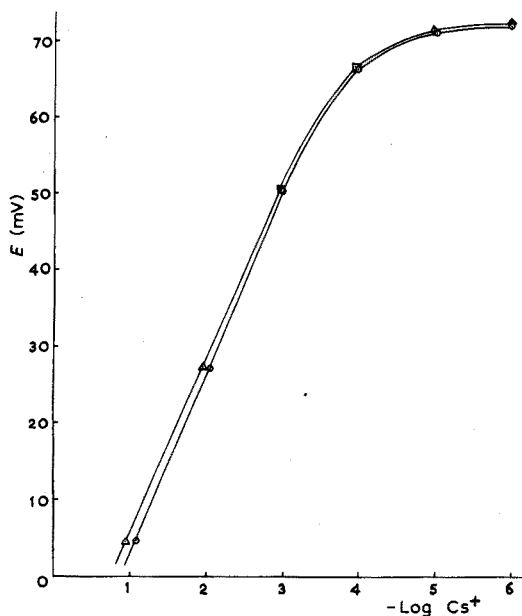


Fig. 1. Calibration curves for cesium electrode at 25°. (○) Activity; (△) concentration.

cesium concentrations gave similar curves. The "working" pH range of the electrode is between pH 4 and 6. All subsequent measurements were done at pH values between 4.5 and 5.5.

*Effect of temperature on electrode response.* The temperature coefficient of the cesium 12-molybdophosphate membrane electrode was determined by measuring the cell potential in  $10^{-2}$  M and  $10^{-3}$  M cesium nitrate solutions between 10 and 50°. A rectilinear relationship was obtained; the observed temperature coefficient for the measuring system was 0.33 mV/°.

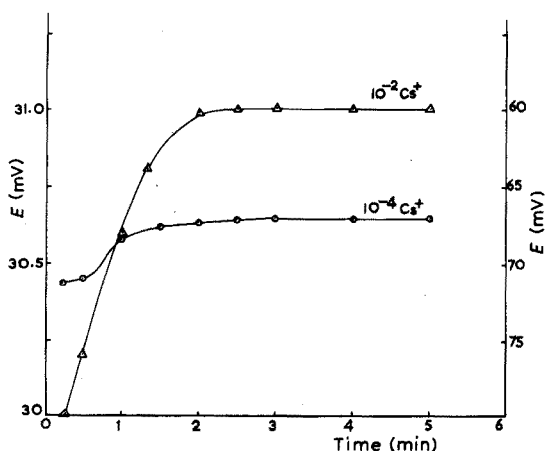


Fig. 2. Dynamic response of cesium electrode.

*Dynamic response characteristics.* The response characteristics were evaluated by exposing the membrane to a rapid change in cesium nitrate concentration and recording the resulting EMF vs. time function (Fig. 2). Although response times were longer than with the commercial available electrodes, a steady constant potential was reached after 2 min. All other measurements were taken 2 min after insertion of the electrode in sample solutions.

*Effect of cations on electrode response.* A systematic examination of the extent of interference of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{NH}_4^+$  and  $\text{Tl}^+$  ions on electrode response was undertaken. Electrode responses in solutions  $10^{-2} M$  in cesium and amounts of the interfering ion varying from  $10^{-1}$  to  $10^{-5} M$  were measured and the results used to evaluate selectivity ratios  $K$  as defined by

$$E = E_0 + \frac{RT}{F} \ln (a_{\text{Cs}} + Ka_i)$$

where  $a_{\text{Cs}}$  is the cesium activity and  $a_i$  that of the interfering cation.

The values expressed as  $\log K$  are the following: Li -0.92; Na -1.14; K -0.74; Rb 2.63;  $\text{NH}_4$  0.8 and Tl 2.75. The values show a dependence on the concentration of the interfering ion; the value of  $K$  increases slightly with increasing concentration and average values are listed. The same phenomenon was found during a previous investigation with ion-association systems<sup>2</sup>. The extent of interferences shows a qualitative relationship to results obtained in ion-exchange studies with the exchange of monovalent ions on ammonium 12-molybdophosphate<sup>3</sup>.

Although the electrode is not selective in presence of the heavier monovalent alkali cations and thallium, a wide range of useful measurements is possible. An analogous electrode has recently been used in the potentiometric titration of cesium<sup>4</sup>.

This work forms part of a doctoral thesis to be submitted by A. J. B. to the University of Stellenbosch and is published with the permission of his Promotor.

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## Potentialities of the voltammetric method for the determination of equilibrium constants

Recently Durand and Trémillon<sup>1</sup> have criticized the method of determination of equilibrium constants of perfectly mobile equilibria based on a quantitative examination of "reversible" voltammetric curves. This method, based on a theoretical treatment by Guidelli and Cozzi<sup>2</sup>, has been widely employed by us for the study of several disproportionation equilibria<sup>3-6</sup>. According to Durand and Trémillon, this method "must be accepted with reservations, since the theory neglects possible complications caused by several electro-kinetic phenomena, which may invalidate the method". This criticism is entirely without foundation, since in all applications of this method the use of the Nernst equation, as applied to the surface concentrations of the electro-active species along the whole rising portion of the voltammetric curves, was justified experimentally by comparing the theoretical current-potential characteristics with the experimental ones. In all cases, the polarographic reversibility of the curves was ascertained and the instantaneous currents were found to be diffusion-controlled in the time scale of polarographic measurements. It is clear that the very applicability of the Nernst equation at the electrode surface excludes kinetic complications as well as complications caused by possible adsorption phenomena. Whenever these latter complications affect the rate of the charge-transfer process to a sufficient extent in the time scale of polarographic measurements, appreciable deviations of the experimental voltammograms from the theoretical reversible current-potential characteristics are observed. Obviously, when this is the case, no equilibrium constants can be profitably derived from the voltammetric method. An example of such a situation is offered by the cathodic voltammograms of iodine to iodide in acetic acid and acetic anhydride, which exhibit deviations from the reversible behavior for iodine concentrations greater than  $10^{-4}$  M. Incidentally, these deviations have been accounted for semiquantitatively<sup>7</sup> by attributing them to the specific adsorption of iodine atoms and iodide ions. The anodic voltammograms of iodide to iodine in acetic acid and acetic anhydride are not distorted by adsorption phenomena for iodide ion concentrations less than  $2 \cdot 10^{-3}$  M, and consequently they can be profitably employed for the determination of the stability constant of  $I_3^-$ . In conclusion, it must be emphasized that deviations of experimental voltammograms from the reversible behavior may be easily detected. Hence, no *a priori* assumptions about the reversibility of experimental voltammograms are made when the voltammetric method is used for the determination of equilibrium constants.

Provided that the requirements for polarographic reversibility are fulfilled, our voltammetric method has several practical advantages over the potentiometric method, while retaining a precision which, although slightly less than that exhibited by the potentiometric method, is nevertheless satisfactory. Thus, in the study of disproportionation equilibria by our method<sup>3-6</sup>, the disproportionation constants are obtained from values of the differences between two potentials characteristic of a single voltammogram, with the consequence that the control of the reference electrode potential is less critical than in potentiometric measurements. Other advantages which are found in the application of our method to particular redox systems are as follows.

1. The reversible cathodic curves for manganese(IV) to manganese(II) in water-sulfuric acid mixtures on platinized platinum, which were employed for the determination of the constant for the disproportionation equilibrium  $2\text{Mn(III)} \rightleftharpoons \text{Mn(II)} + \text{Mn(IV)}$ , are quite close to solvent oxidation<sup>4</sup>. By the voltammetric technique it was possible to correct the voltammetric curves of manganese(IV) for solvent oxidation by subtracting from these curves the voltammetric curve given by the solvent alone. Clearly a similar correction was not possible in the potentiometric study of the same system<sup>8</sup>.

2. Accurate potentiometric measurements of the disproportionation equilibrium  $\text{I}_3^- \rightleftharpoons \text{I}^- + \text{I}_2$  in acetic anhydride and in acetonitrile are not feasible, since iodine solutions in these solvents are not sufficiently stable. Such a difficulty can easily be obviated by the voltammetric method<sup>3-6</sup> through the recording of the oxidation waves of iodide to iodine.

Durand and Trémillon<sup>1</sup> were induced to criticize our method by the discrepancy between their value, 5.24, for the logarithm of the stability constant  $\beta$  of  $\text{I}_3^-$  in acetic acid, as determined by the potentiometric method, and our value of about 4.45. This criticism was based on the "irreversibility" exhibited by the voltammetric curves of iodide to iodine recorded at a rotating platinum electrode<sup>1</sup>. As a matter of fact the above authors do not state explicitly that their voltammetric curves (Fig. 3<sup>1</sup>) are irreversible, but the slopes of the two portions of these curves compared to the slopes of the theoretical curves calculated by our procedure, shows that the experimental curves obtained by Durand and Trémillon are far from being reversible. This explains why such curves are sensitive to electrode pre-treatments. In comparing their irreversible voltammetric curves with the reversible ones obtained by us under similar experimental conditions, the above authors do not take into account that the "degree of reversibility" of a given electrode process depends on the particular electrochemical technique employed. Thus, for any given electrode process the contribution of diffusion overpotential to the total overpotential is less for a rotating electrode than for a dropping electrode. In this respect the platinum electrode with periodical renewal of the diffusion layer (DLPRE)<sup>9</sup>, which we have constantly employed in our measurements, is quite similar to a dropping electrode. (Incidentally, it must be noted that Durand and Trémillon erroneously attribute to us the use of a rotating electrode.) Hence the anodic curve of iodide to iodine in acetic acid may well be reversible at a DLPRE and irreversible at a rotating electrode.

Guidelli and Pezzatini<sup>7</sup> have also determined the value of the stability constant  $\beta$  of  $\text{I}_2^-$  in acetic acid by the potentiometric method. Their procedure for the elaboration of the experimental data is slightly different and more accurate than that followed by Durand and Trémillon. In fact, when the analytical concentration of  $\text{I}_2$ ,  $C_{\text{I}_2}$ , was greater than that of  $\text{I}^-$ ,  $C_{\text{I}^-}$ , then the actual concentration of  $\text{I}_3^-$ ,  $[\text{I}_3^-]^*$ , was set equal to  $C_{\text{I}^-}$ , whereas the actual concentration of  $\text{I}_2$ ,  $[\text{I}_2]^*$ , was set equal to  $C_{\text{I}_2} - C_{\text{I}^-}$ , and not to  $C_{\text{I}_2}$ , as in Ref. 1. By so doing, it was possible to utilize all experimental data for which  $C_{\text{I}_2} \geq 2.5 C_{\text{I}^-}$ . Analogously, upon setting  $[\text{I}_3^-]^* = C_{\text{I}_2}$  and  $[\text{I}^-]^* = C_{\text{I}^-} - C_{\text{I}_2}$  it was possible to utilize all experimental data for which  $C_{\text{I}^-} \geq 2.5 C_{\text{I}_2}$ . The value of  $\beta$  determined potentiometrically by Guidelli and Pezzatini is 4.7 and is therefore in satisfactory agreement with the value 4.45 determined from voltammetric curves, whereas it is at variance with the value 5.24 reported by Durand and Trémillon.

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### Commentaires sur l'article intitulé "Potentialités de la méthode voltampérométrique pour la détermination des constantes d'équilibre"\*

Dans un mémoire sur une étude électrochimique de l'iode en solution dans l'acide acétique anhydre<sup>1</sup>, nous avons, à propos de la détermination de la constante de formation de  $I_3^-$ , critiqué l'emploi de la méthode préconisée par Guidelli et Piccardi<sup>2</sup>—consistant à exploiter une courbe voltampérométrique correspondant au système  $I_2/I^-$ —par rapport à la méthode potentiométrique classique. A notre avis, la méthode voltampérométrique "doit, *a priori*, être accepté(e) avec circonspection"—c'est-à-dire avec réserve jusqu'à une confirmation éventuelle—, "la théorie (des vagues réversibles) négligeant l'intervention possible de divers phénomènes électro-cinétiques". Guidelli et Piccardi n'ayant pas admis cette critique, qu'ils réfutent dans l'article précédent en y ajoutant à leur tour une critique sur l'obtention d'un de nos résultats, ceci appelle, de notre part, les précisions et les commentaires qui suivent.

En ce qui concerne d'abord la comparaison entre la méthode voltampérométrique et la méthode potentiométrique, sur un plan général—qui était celui sur lequel nous nous étions placé dans notre introduction, ref. 1 ("*a priori*")—, nous convenons que la première peut, dans certains cas particuliers, présenter sur la seconde un avantage de *facilité de réalisation pratique*; parce que, par exemple, il n'est pas nécessaire de faire varier d'une façon contrôlée les activités au sein de la solution des espèces participant au système électrochimique; c'est un avantage que nous avons d'ailleurs l'habitude de largement exploiter dans notre laboratoire pour des études en milieux non aqueux et sels fondus. Néanmoins, la potentiométrie à courant nul conduit à des résultats qui, dans les conditions de réversibilité thermodynamique, sont fonction seulement d'activités, tandis que la voltampérométrie, même dans les conditions de réversibilité polarographique parfaitement réalisées, conduit à des résultats qui sont *en plus* fonction de caractéristiques non thermodynamiques (transport de matière à l'électrode, phénomènes de double couche, chute ohmique) et dont la théorie—en particulier, celle du transport de matière par diffusion plus ou moins convective—n'est établie

\* R. Guidelli et G. Piccardi, *Anal. Chim. Acta*, 57 (1971) 481.

qu'avec des approximations plus ou moins réalistes. Il nous paraît par conséquent de toute évidence que les résultats potentiométriques, dont l'analyse est plus aisée et donc plus sûre, sont *a priori plus fiables* que ceux tirés d'une courbe voltampérométrique.

Plus particulièrement maintenant en ce qui concerne l'étude de  $I_3^-$  dans l'acide acétique, nous avons relevé dans l'étude voltampérométrique de Guidelli et Piccardi<sup>2</sup> et dans étude potentiométrique<sup>1</sup> différents caractères comparatifs.

A l'encontre de leur affirmation de l'article précédent, premier paragraphe, Guidelli et Piccardi ont eux-mêmes relevé dans leur mémoire originel que, "contrairement à leur attente, sur les courbes voltampérométriques de  $I_2$  et  $I_3^-$  dans l'acide acétique et l'anhydride acétique, sur platine poli aussi bien que sur platine platiné, la portion de la vague totale relative à l'étape  $3I^- = I_3^- + 2e^-$  s'écarte de la caractéristique  $i-E$  théorique plus que prévu"; ce qu'ils attribuent, comme dans d'autres solvants et par d'autres auteurs également, à des phénomènes d'adsorption (réf. 2, p. 786-7). Il y a donc contradiction à affirmer ensuite, dans ce cas, "la parfaite applicabilité de l'équation de Nernst..." excluant "des complications cinétiques aussi bien que des complications dues à d'éventuels phénomènes d'adsorption". L'emploi d'une électrode produisant un régime de diffusion nettement plus lent que l'électrode rotative ne suffit pas à supprimer tout risque de complication.

Aux causes de désaccord entre la courbe voltampérométrique expérimentale et son équation théorique, nous ajouterons encore: les modifications d'état de surface du platine au cours du tracé par variations de potentiel et de courant; les approximations du calcul théorique du transport de matière, lequel ne tient pas compte de la convection non sphérique (et non stationnaire) produite par le système de renouvellement de la couche de diffusion; le caractère non idéal du compensateur de chute ohmique, certainement inférieur, dans le cas de l'acide acétique, à un montage à trois électrodes avec une disposition adéquate dans la cellule. Toutes ces causes n'interviennent pas dans les mesures potentiométriques.

Quant à la précision de la détermination de la constante d'équilibre, elle est à coup sûr supérieure par la méthode potentiométrique. En effet, Guidelli et Piccardi n'ont utilisé pour cette détermination que la différence entre les deux potentiels de demi-vague et une relation entre cette valeur et celle de la constante d'équilibre  $\beta$ . (Notons au passage qu'il est faux de considérer les potentiels de demi-vague égaux aux potentiels normaux des deux couples  $I^-/I_3^-$  et  $I_3^-/I_2$ , mais la relation (2)<sup>2</sup> est correcte, à l'approximation près de l'égalité, non prouvée, des coefficients de diffusion des trois espèces  $I^-$ ,  $I_2$  et  $I_3^-$ ). Ce faisant, ils n'obtiennent qu'une seule estimation de  $\beta$ , sans estimation de sa précision (en fait, sa reproductibilité, par un écart-type sur une valeur moyenne). Pour y arriver, il faut procéder à plusieurs déterminations similaires—disparaît alors l'avantage signalé de l'absence d'influence d'une irreproductibilité éventuelle de l'électrode de référence—; des sept valeurs expérimentales données Table I<sup>2</sup>, on tirerait ainsi un intervalle d'incertitude, à un taux de confiance de 95 %, de l'ordre de  $\pm 0.25$  sur la valeur de  $\log \beta$ . En revanche, les valeurs que nous avons tirées de nos expériences<sup>1</sup> résultent d'une analyse statistique de 82 mesures expérimentales; ces mesures, en même temps, vérifient statistiquement la formule de Nernst, ce qui est bien plus satisfaisant que l'appréciation visuelle de la superposition d'une courbe expérimentale et d'une courbe théorique formée de 7 à 13 points calculés (cf. Fig. 3<sup>2</sup>). L'intervalle d'incertitude est alors réduit à  $\pm 0.12$  pour le milieu basique, à  $\pm 0.02$  pour le milieu neutre (cf. Table I<sup>1</sup>).

Nous ajouterons enfin que le reproche exprimé par Guidelli et Piccardi dans le dernier paragraphe de leur article est sans fondement. En effet, si nous avons exposé le principe de la méthode du logarithme-limite en faisant, pour simplifier l'exposé, l'hypothèse que  $C_{1-}$  est négligeable devant  $C_{1_2}$  (lorsque  $C_{1_2} \gg C_{1-}$ ), les calculs réels ont été effectués, à partir des valeurs numériques rassemblées Table I<sup>1</sup>, *sans omettre les corrections indispensables*, comme on peut s'en rendre compte en reproduisant les calculs. L'oubli de cette correction n'eût d'ailleurs pas manqué de se répercuter sur les "droites" de régression.

En conclusion, si d'autres mesures potentiométriques ont conduit Guidelli et Pezzatini (réf. citée dans l'article précédent) à une valeur de  $\log \beta$  significativement différente de la nôtre (et presque autant de celle donnée réf. 2), il reste à en chercher la cause. Il est notamment difficile de savoir si la composition des solutions était identique dans les deux cas, en ce qui concerne la teneur en eau tout particulièrement. Guidelli et Piccardi ne font à ce sujet état d'aucune valeur; nous avons pour notre part mesuré moins de 10 mg d'eau par litre de solution (AcOH + électrolyte-support).

Nous pensons que chercher, par une sélection des conditions opératoires, à obtenir des valeurs concordantes dignes de la confiance des électroanalystes intéressés serait la meilleure voie de discussion.

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**ERRATA**

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E. AKATSU AND M. ASANO, Radiochemical studies on the solvent extraction of several elements in  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ - and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ -tri-*n*-butyl phosphate systems, *Anal. Chim. Acta*, 55 (1971) 333-340.

page 335, the equation under the figure should read:

$$K_d = (V_{1-2}/V_{0-2})[a_{0-2}/(a_{0-1} - a_{0-2})]$$

N. K. CHAUDHURI AND J. DAS, Cyclopentanone-2-carboxyanilide as a reagent for the gravimetric, titrimetric and spectrophotometric determination of beryllium, *Anal. Chim. Acta*, 57 (1971) 193-199.

page 197, Table IV, the heading "*Diverse ions (mg)*" should read "*Diverse ions ( $\mu\text{g}$ )*".

*Anal. Chim. Acta*, 57 (1971) 492

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