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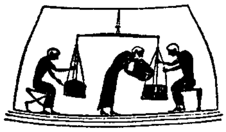

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Professor TAITIRO FUJINAGA was born in City Kobe, Japan. He graduated B.Sc. in 1941 and D.Sc in 1956 from the University of Kyoto. He has been working with the Department of Chemistry of the same University since 1941; first as assistant then lecturer (1946), assistant professor (1957) and professor (1959). He has numerous research publications mainly in the field of polarography and electrolytic method of analysis, those on current-controlled polarography and electrolytic chromatography being especially well known. He is a member of the Chemical Society of Japan, the Japan Society for Analytical Chemistry, the Polarographic Society of Japan and the American Chemical Society. Since 1967 he has been a titular member of the International Union of Pure and Applied Chemistry, Division of Analytical Chemistry. In 1963 he was awarded the 1st Analytical Chemistry Prize by the Japan Society for Analytical Chemistry.

Dr. W. F. PICKERING, Associate Professor of Chemistry, University of Newcastle, N.S.W., Australia. Dr. Pickering holds an Honours Diploma in Applied Chemistry as well as a B.Sc., M.Sc., and Ph.D. from the University of New South Wales. He is a Fellow and active member of the Royal Australian Chemical Institute. In 1952, after seven years in industrial laboratories, he took up the position of Lecturer in Analytical Chemistry at Newcastle University College (now the University of Newcastle, N.S.W.) and still retains responsibility for this branch of chemistry. Research experience includes two annual periods spent at The Queen's University of Belfast (1961) and The University of Strathclyde (1967). Published work includes papers on many aspects of analytical chemistry and a text "Fundamental Principles of Chemical Analysis".

JAMES E. REIN, B.S. 1944 and Ph.D. 1949; Chemistry, University of Illinois. Research chemist, Los Alamos Scientific Laboratory, 1949–1953. Since 1953, Section Leader of Analytical Chemistry Development, Idaho Nuclear Corporation, located at National Reactor Testing Station, Idaho Falls, Idaho, USA. Contributor to chapters in three books and author or co-author of over 30 technical journal papers. Major interest is analytical chemistry of nuclear fuel processing including separations techniques, radiochemistry, burnup analysis, and statistical quality control.

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TALANTA REVIEW*

A CRITICAL REVIEW OF ATOMIC ABSORPTION, SPECTROCHEMICAL, AND X-RAY FLUORESCENCE METHODS FOR THE DETERMINATION OF THE NOBLE METALS—II

F. E. BEAMISH, C. L. LEWIS† and J. C. VAN LOON‡
Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada

(*Received* 29 *November* 1967. *Accepted* 8 *June* 1968)

Summary—The review is a continuation of the initial reviews and covers the period of abstracting up to and including April, 1967. Work on the atomic-absorption determination of noble metals is also included.

ATOMIC ABSORPTION

ATOMIC-ABSORPTION methods were applied to the determination of noble metals almost immediately following inception of the technique some ten years ago. Hunt[1] stated "For a free milling ore, in which all the gold can be put into solution by hot cyanide solution in a short time the atomic absorption method is far superior" (to the usual wet or fire assay methods). "But if the ore is like most gold ores in Canada where the sample must be roasted first or *aqua regia* has to be used, the picture then is not so clear." It was stated that in such cases dissolution and filtration are necessary and for non-homogeneous ores 15-g samples are needed to obtain the required accuracy. However, even under these circumstances the method is promising. In the case of bullion assays or for ores which resist dissolution of gold by cyanide solution the fire assay seems to be more accurate. The meeting at which the report was presented provided many useful opinions on the value of various methods of gold determinations. It is often said that no spectral interferences occur in atomic-absorption methods, but Korityohann and Pickett[2] say that the background due to absorption by molecular species must be considered, and that it may occur with either hot or cool flames. Theoretical explanations for the bending of analytical curves were outlined by Rubeška and Svoboda,[3] including the effect of resonance broadening and shift of the absorption line. Firman stated[4] that exhaustive tests on the effect of small concentrations of interfering elements were needed, and especially on tests of combinations of elements which do not interfere separately—tests which could well be applied in all types of analysis. The depressant effects of dissolved impurities have been noted for many base metal determinations. Very little is known with certainty about the mechanism of interference or the mode of action of reagents which suppress the interference. Specific cases have been discussed by Adams and Passmore,[5] Mostyn and Cunningham,[6] Halls and Townshend.[7]

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* For reprints of this Review, see advertisement.

† Falconbridge Nickel Mines Limited, Metallurgical Laboratories, Thornhill, Ontario, Canada.

‡ Department of Geology, University of Toronto, Toronto 5, Ontario, Canada.

Aswathanarayna and Vishnoi[8] found that nickel, cobalt, lead and iron in up to 100-fold amounts did not interfere with determination of 10 ppm of gold.

Khalifa *et al.*[9] found that 40- and 100-fold amounts of foreign ions, including copper, nickel and iron, gave no appreciable interference in gold determination, except for oxalate which produces metallic gold. The precision for higher gold concentrations (50–500 ppm) was ~2%.

The factors which affect atomic-absorption sensitivity for noble metals and other elements have been outlined by Slavin *et al.*[10] who found "The primary limitation is that imposed by the absorption coefficient of the transition that gives rise to the particular line used analytically; this coefficient is also influenced by the temperature of the flame". The efficiency of the burner-atomizer influences the fraction of the sample vapourized in the flame, and the dissociation of the molecular species controls the fraction of the vapour which is available in the atomic state. The flame temperature influences the concentration of the atoms, the degree of molecular dissociation, and the fraction lost from the ground state because of excitation or ionization. Sensitivity is reduced if the emitted analytical line is not completely isolated. Varying the optical path-length through the flame also changes the sensitivity. The emission line of the hollow cathode source must be narrower than the absorption line of the constituent in the flame so that changes of peak absorption can be measured. Under conditions which broaden the emission line the sensitivity is reduced. For comparing analytical methods the detection limit is useful because it involves the factors which control sensitivity and the level of background fluctuations.

The relative detection limit has been defined as the concentration which produces an absorption equal to twice the fluctuation in the background. Apart from analytical sensitivity, the most important factor governing the relative detection limit is the available light energy. This is related to the brightness of the source at the analytical wavelength and to the nearness of the neighbouring emission lines in the source.

Slavin *et al.*[10] gave a list of the sensitivities and detection limits for a number of metals.

Gold

Determinations in aqua regia. Attempts have been made to aspirate *aqua regia* extracts of gold directly into the flame for determinations by atomic-absorption spectroscopy (AAS), in some cases through platinum–titanium nebulizers, but the metal was corroded, the gold values lacked precision and blanks were abnormally high. Peterson,[11] using a stainless-steel nebulizer, determined 1·5–15 ppm of gold in *aqua regia* samples, obtaining values which compared favourably with those from an unidentified chemical determination.

In aqueous media. The determination of gold in aqueous media and in urine has been described.[12,13]

In organic media. The advantages of extraction by an immiscible solvent were discussed by Allan.[14] Up to a 7-fold gain in sensitivity may be obtained, presumably in part because more solution reaches the flame.

In cyanide solution. Zeeman *et al.*[15] used organic extractants and a burner system modified to provide an extra air supply, thus producing a bright flame. Gold was extracted into ethyl acetate. For rhodium determination a 95% acetone solution was nebulized. The three gold samples were "precipitation tailings solutions" from the Rand mines, with reported gold contents 0·005, 0·015 and 0·2–0·3 ppm. The atomic-absorption results were 0·014, 0·02 and 0·18 ppm. The authors concluded, without confirmatory evidence, that their results for the two lower concentrations were correct.

In a method designed for automation Butler, Strasheim and Strelow[16] used palladium as an internal standard, by means of a palladium–gold hollow cathode lamp with equal intensities of the 2476 Å (Pd) and 2428 Å (Au) lines obtained from a 50:1 ratio of Pd:Au. The two lines were isolated with fixed 0·1-mm double exit slits appropriately spaced. A vibrating chopper behind the slits allowed the light from each slit to fall alternately on the cathode of a single multiplier tube; the output from this was amplified and the two signals were separated by a timed reed-switch in phase with the chopper, and after amplification could be read by difference or transfer to a ratio recorder. Gold chloride and added palladium dimethylglyoxinate were extracted together into a measured volume of isobutyl methyl ketone. With a concentration factor of 10, gold concentrations as low as 0·004 ppm could be determined. For lower concentrations of gold the volume of the ketone could be reduced. Because of lower sensitivity, the palladium concentration in solution was increased two or three times to obtain equal absorption signals. Change in air pressure had much less effect on ratio readings than on the absolute absorption values, and loss of metal to the aqueous phase was compensated for by using the internal standard method. For samples containing about 0·03 ppm of gold the standard deviation for the fire assay was ±0·0034 ppm; for the absorption method, ±0·0009 ppm.

The determination of 0·01–0·5 ppm of gold in cyanide waste solutions by solvent extraction and atomic absorption at 2428 Å was discussed by Strelow *et al.*[17] After suitable treatment[8] the solution was extracted with isobutyl methyl ketone. The organic phase was aspirated into the flame of a water-cooler burner. There were no interferences from the many constituents sometimes present in wastes; some of these were not co-extracted. The results gave good precision and accuracy, in comparison with fire assay results.

Skewes[18] determined gold in cyanide solutions, the best range being 5–50 ppm, and considered the method to be more rapid and simple than fire assay or polarography. Both chloride and cyanide solutions were examined. Optimum operating conditions were established. The effect of impurities common in gold cyanide mill solutions was examined; it was necessary only to add EDTA at pH 11·0 to complex calcium, to allow free atomization in the spray chamber. There was excellent agreement between atomic absorption and fire assay results. Recoveries from spiked solutions over the range 3–30 ppm were 100·5 ± 2·5%. The standard deviation was 1·3 ppm.

In limestone. Olson[19] considered four methods of preparing gold solutions for AAS: these were acid extraction, solvent extraction, cyanide extraction, and fusion, but none was a reasonable adaptation of known methods of dissolution for ore analysis. However, Simmons[20] later claimed that for soft sandy ore with a high gold content the error for 0·5 troy oz per ton was 1%; for 0·05–1 oz per ton it was 2%. He stated that for different ore types the method of extraction could be appropriately modified or *aqua regia* or an organic solvent used, and that "This result surely indicates that the atomic absorption method is more dependably accurate than fire assay". The conclusion might more properly read that with the kind of gold ore used and with the techniques used by a particular group of operators the values obtained by atomic-absorption were more precise. The question of accuracy cannot be decided from the results in the report.

Ores and concentrates. Tindall[21] applied AAS to samples of varying types found in the copper mining industry. Tails, concentrates and heads were assayed for gold and silver and the results compared with those obtained by fire assay. The atomic-absorption method for gold and silver gave closer agreement between assayed heads and calculated heads from flotation tests than did the fire assay. However, one test on a concentrate yielded 0·070 oz of gold per ton by fire assay and 0·206 by atomic absorption. In a second test the respective values were 0·580 and 0·553 oz per ton. *Aqua regia* dissolution was followed by extraction of the gold bromide complex into isobutyl methyl ketone. The extract was aspirated into the flame. The author found that the sensitivity was equal to that obtained by fire assay and the precision was somewhat superior. The method was later modified[22] to allow the determination of base metals; addition of hydrobromic acid for gold extraction was found unnecessary.

In high-purity gold. The relative efficiences of atomic absorption, spectrochemical and fire assay methods for determination of the fineness of gold were examined by Finkelstein and Lock.[23] They concluded that the indirect methods, atomic absorption and spectrochemical, by which the purity is determined by difference from the sum of impurities, are fundamentally sound and capable of determining fineness of 999·5–999·95. Both spectrochemical and atomic-absorption methods were considered capable of determining the full range of impurities which occur in South African refined gold, the former having great speed and the latter higher precision throughout the high-purity region. From the practical point of view the fire assay was not generally applicable for a gold fineness of 999 and for the 995 level the indirect techniques could prove to be serious competitors of the fire assay. On the other hand, consideration of relative accuracies of the methods yielded anomalous results and the authors concluded that "a good deal of further development work is necessary before the promise of the indirect assay may be realized and applied to the routine assay of high purity gold." It should be noted that the determination of the fineness of gold is a special problem. The atomic-absorption method will not recognize impurities beyond its sensitivity limits and the total of the unrecognized impurities may sometines be significant; this difficulty applies also, but with lesser force, to emission spectroscopy, and neutron activation methods may well find use in this problem.

In copper. An atomic-absorption technique which might well be applied profitably to the analysis of noble metal ores was described by Gatehouse and Walsh.[24] The flame was replaced by a sputtering chamber with a cylinder of sample fitted into its lid. The discharge current could be varied according to the sensitivity required and the identity of the metal. The sputtered vapour absorbs energy from a light-beam traversing the chamber. The method was used with acceptable precision on samples of copper containing small amounts of silver.

Palladium

The optimum conditions for the atomic-absorption determination of palladium were investigated by Erinc and Magee.[25] The wavelength 2448 Å was found to give a better response than the 2476 Å line used by Lockyer and Hames.[26] Several organic extractants were examined for their effect on the sensitivity and the best results were obtained with 50% v/v t-butanol. Hydrolysis of palladium in the solutions sprayed was prevented by addition of hydrochloric or nitric acid up to 5*M*. If sulphuric acid was used the absorbance decreased from 0.061 to 0.032 with increase in acid concentration from 0·1 to 5·0*M*. The effects of complexing the plalladium were examined. $Pd(py)_2Cl_2$ dissolved in 50% v/v aqueous ethanol gave results superior to those for aqueous solutions. Isobutyl methyl ketone extraction of $Pd(py)_2(SCN)_2$ gave an increased absorbance, and though this was offset by the higher background signal, acceptable results were obtained with amounts as low as 0·10 ppm, compared to 2 ppm as the limit for aqueous solutions. The authors' methods provided very acceptable results for Pd–Pt and Pd–Ag alloys. Samples were dissolved in *aqua regia* and the solutions converted into the chloride form.

Iridium

Manning and Fernandez[27] used the 2640 Å line from a lamp constructed from a copper cathode cup with an iridium lining. The 2089 Å line, though more sensitive, gave a poorer signal-to-noise ratio. The absorbance curve was almost linear up to 1000 μg/ml. An air–acetylene flame was used; with nitrous oxide–acetylene the absorption was about halved. Sensitivities were given for 15 resonance lines.

Mulford[28] found that air–acetylene could be used instead of the nitrous oxide–acetylene flame which had been considered necessary for the determination of iridium. Six suitable wavelengths together with the appropriate slit widths and resulting sensitivities were reported. The most sensitive wavelength was 2850 Å.

Rhodium

Heneage[29] has reported on 8 rhodium resonance lines free from adjacent interfering lines, and described the effect, of changing slitwidths and fuel-to-air ratios, on the absorbance. The detection limit was 0·03 ppm at 3435 Å.

Noble metal mixtures

One of the earliest researches on the atomic-absorption determination of silver, gold, platinum, rhodium and palladium was reported by Lockyer and Hames,[26] who claimed determinations down to 1 ppm with good precision and no interferences from associated metals. In order to prevent the formation of metallic gold the oxidation of iron was ensured and a water-jacket was fitted round the top of the burner. The drift noted in transmission readings and atrributed to thermal reduction to metallic gold[26] was not confirmed by Greaves[30] or Gatehouse and Willis,[31] whose findings indicated a sensitivity limit of 0.3 ppm for gold in aqueous solution or about $3 \times 10^{-5}\%$ of gold in an ore. A 5-fold concentration of gold was achieved by extraction with isobutyl methyl ketone. Because lead did not interfere in the absorbance measurements, the use of lead sulphide was proposed for the co-precipitation of gold and it was hoped to determine gold in metallurgical samples if a satisfactory method of dissolution could be found. This, of course, is usually the nub of the problem.

Strasheim and Wessels[32] also determined these four elements but used the 3405 Å line for palladium instead of the less satisfactory 2476 Å line. Contrary to Lockyer and Hames,[26] they found serious inter-element interferences for platinum and rhodium. The effects, and their elimination, of a wide variety of elements on the interference from noble metals and sodium were tested. Addition of copper sulphate caused an initial sharp decrease in sensitivity for platinum; concentrations of copper above 20000 ppm overcame the interference by other noble metals in the platinum determination. Interferences in the case of rhodium could not thus be eliminated, but because the working curve for rhodium up to 40 ppm is "for all practical purposes" linear, the addition method[33] was used. With palladium and gold in a constant concentration of hydrochloric acid there was no significant interference from other noble metals or sodium. The procedure involved initial removal of base metals and final dissolution of the noble metals by hydrochloric acid made up to 10% acid.

The experimental values were compared with those from an unstated chemical method. With about 300 ppm of platinum the difference varied from 1 to 4%; with about 200 ppm of palladium, 0–2·5%; with about 35 ppm of rhodium, +0·5 to −22%; with about 50 ppm of gold 2–10%. The base metals were removed by an unstated method, and the recoveries therefore do not indicate the errors arising from the separation.

A procedure for determination of silver, gold, platinum, palladium and rhodium in acidic solution without separation was described by Ginzburg *et al.*[34] Silver was dissolved in nitric acid, and rhodium was first sintered with barium peroxide. The sensitivity was taken as the lowest absorbance (0·01) which could be measured with a maximum error of 10%. A higher sensitivity for platinum could be attained by using the higher flame temperature of the acetylene–air flame instead of the propane–air flame generally used by the authors. An extensive examination was made of the effect of base metals and mineral acids. With gold, lead up to 5% had no deleterious effect but zinc up to 10% and copper up to 7·5% present simultaneously, depressed the sensitivity. With palladium the presence of sulphuric acid decreased the sensitivity as did copper and zinc when present together. With platinum and rhodium the sensitivity was decreased in the presence of 6·8N sulphuric acid, and the salts of many metals including zinc and copper complicated the determination. The authors assumed that a flame of higher temperature reduced these effects. In a 1·5% w/v solution of silver in nitric acid, the sensitivity for palladium was 1·5 ppm and for gold 0·5 ppm. These sensitivities were also found in the case of a copper assay button dissolved in *aqua regia* to form a 4% copper solution. There would be value in results from a chemical analysis of a silver assay bead compared to those from atomic absorption as well as a similar comparison made with a copper assay button.

Gold, rhodium, palladium and platinum were examined by Gatehouse and Willis.[31] The 10-cm burner was made of stainless steel and could be used for coal gas–air or acetylene–air flames. A simple single beam absorption spectrophotometer was used with the lamp fed by a stabilized supply. (The sensitivities were markedly dependent on lamp current, slitwidth and flame type.)

A general study of atomic-absorption spectroscopy was made by Menzies.[35] Along with a discussion of instruments, techniques, *etc.*, he dealt with the determination of gold, palladium, rhodium platinum in *aqua regia*, at the 1,2,2 and 10 ppm levels respectively. There was no mutual interference nor interference from lead or iron provided the precautions outlined by Lockyer and Hames[26] were observed. The lines used, 2428 Å for gold, 2476 Å for palladium, 2659 Å for platinum and 3035 Å for rhodium, were optimum for the instrument used but were not claimed as the most sensitive for general purposes.

Comparisons of the accuracy of the determination of noble metals in refinery products by atomic-absorption and spectrophotometric techniques were made by Ott and Macmillan.[36] The sample was dissolved by an adaptation of the fusion technique described by Schoeller and Powell.[37] In the case of precious metal concentrates, silver was removed and the solution was made up to known volume, suitable aliquots from which were acidified with hydrochloric acid, diluted and aspirated into the flame. Interference with rhodium was removed by addition of lanthanum chloride, and with platinum by addition of copper sulphate. For the analysis of materials in which the noble metal content was low, the sample solution was treated with lanthanum chloride, made up to volume with 0.5M hydrochloric acid and was used to determine gold, platinum, palladium and rhodium. Detailed directions were given for samples containing less as well as more than 0·05% of silver. Measurements were made on the Perkin–Elmer Atomic-Absorption Spectrophotometer, the high-solids burner head being used. The air and acetylene pressures were 28 and 8 psi respectively; the flow-meter settings were 8·5 for air and 7·5 for acetylene. The spectral lines used were 2670 Å for gold, 2659 Å for platinum, 2759 Å for palladium, 3435 Å for rhodium and 3280 Å, 3383 Å for silver. The results compared favourably with those obtained by spectrophotometric methods. Source lamps for ruthenium and iridium were not available.

The use of absorption tubes for the determination of noble metals by atomic-absorption spectroscopy was discussed by Rubeška and Štupar.[38] Preliminary experiments had shown that such tubes provided advantages in the determination of gold, palladium, rhodium and platinum. Silica and ceramic tubes were used and could be heated to 1200° in an electric furnace independently of the flame. The result indicated no systematic variation of sensitivity with tube diameter and in general there was no effect on sensitivity as a result of heating the tube. However, heating did provide relative freedom from scattering of the silver radiation in determining palladium in silver beads. The authors state that "Direct determination of noble metals after enrichment by cupellation is thus made possible by simply dissolving the silver beads in nitric acid." It may be noted that of the noble metals only palladium and to some degree platinum in colloidal form are dissolved from a silver bead by nitric acid. Iridium is not made at all soluble and rhodium and ruthenium are only slightly attacked, if at all. Osmium is not collected quantitatively by silver.* The relative sensitivities for gold, palladium, platinum and rhodium, determined in heated tubes without the addition of silver, were discussed. The authors present some interesting results but make no claim regarding the general validity of their conclusions.

The operating conditions for AAS of the platinum metals are summarized in Table I.

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* There is no published evidence that the collection is quantitative and in any case osmium is lost from a hot silver bead, probably by oxidation by the oxygen content of the bead.

TABLE I—OPERATING PARAMETERS FOR AAS OF NOBLE METALS

Metal	λ *mμ*	Flame (pressures, *psi*)	Lamp current *mA*	Range *ppm*	Sensitivity *ppm*/99%*T*	Detection limit, *ppm*/99%*T*	Medium	Ref.
Au	242·8	C_3H_8/C_4H_{10}–air (100)	30	1–50	—	—	water	8
		coal gas–air	40	—	—	—	water	9
		C_2H_2–air	14*	—	0·3	0·1	water	10
		—	—	1·5–15	—	—	*aqua regia*	11
		C_2H_2(8)–air	14*, 5†	2–20	0·5	0·1	water, urine	12, 13
		—	55	0·25–0·5	—	0·01	ethyl acetate	15
		—	10	—	—	0·004	IBMK	16
		C_2H_2(2·9)–air (15)	6‡(CN^-), 12(Cl^-)	5–50	—	—	CN^- or Cl^-	18
		C_2H_2(15)–air (20)	20	—	—	—	—	20
		coal gas–air (15)	10	1–50	—	—	—	26
		—	10	1–80	—	0·5	—	32
		C_3H_8–air	—	—	—	0·5	—	34
		coal gas–air	6	—	0·3	—	—	31
	267·6	coal gas–air	6	—	1·3	—	—	31
Ir	264·0	C_2H_2–air	45*, 15†	0–1000	13	2	acid	27
	285·0	—	40*	—	34	4	acid	28
Pd	247·6	C_2H_2–air	20*	—	2	0·5	water	10
		coal gas–air (15)	50	2–100	—	—	—	26
		—	40	2–400	—	1·2	—	32
		C_3H_8–air	—	—	—	0·7	—	34
		coal gas–air	6	—	—	—	—	31
	265·9	—	55	—	—	0·5	—	15
	244·8	C_3H_8(2·5)–air (24)	44·5¶	—	—	—	—	25
Rh	343·5	C_2H_2–air	20*	—	0·3	0·3	water	10
		—	55	—	—	0·1	acetone	15
		coal gas–air (15)	20	2–100	—	—	—	26
		—	20	0·5–100	—	0·2	—	32
		C_3H_8–air	—	—	—	2·0	—	34
		C_2H_2–air	4	—	0·3	—	—	31
Pt	265·9	C_2H_2–air	25*	—	2	0·5	water	10
		—	—	—	—	0·5	—	15
		coal gas–air (15)	36	10–100	—	—	—	26
		—	35	10–350	—	5	—	32
		C_3H_8–air	—	—	—	10	—	34
		C_2H_2–air	7	—	5	—	—	31
Ru	349·9	C_2H_2–air	—	—	0·25	—	water	10
Ag	328·1	C_3H_8–air	—	—	0·25	—	—	34

* P.E. 303
† P.E. 290
‡ Hilger H700/307
¶ Hilger H1100.

FLAME SPECTROPHOTOMETRY

Among the few papers on the determination of the noble metals by emission flame spectrophotometry is that by Eshelman *et al.*[39] on the determination of palladium and rhodium. The presentation leaves the inference that the large choice of methods, available especially for palladium, was unknown to the authors: their claim of superior speed and applicable concentration range and simplicity of operation seems untenable. The optimum conditions were established and the effects of organic solvents examined. There was little interference from mineral acids in concentrations of 0·1–0·5*M*; for rhodium it was a little greater than for palladium. Hydrochloric acid was the only acid entirely without interference. The cations tested include those of associated base metals, excluding copper. With 10 μg of rhodium or palladium per ml, the change in emission intensity was −6% for each with 500 ppm of iridium present, +2% and +3% respectively for 5000 ppm of platinum, and −6% and −2·5% for 1000 ppm of nickel. Anomalous results were obtained for iron and ruthenium.

Bellod,[40,41] using an oxygen–hydrogen flame, determined 50 ppm of palladium in 50% aqueous acetone medium with an error of 5%. With up to 1000 ppm of cobalt and 100 ppm of nickel and ammonium ion present the 365·5 mμ line was recommended. The 340·5 mμ line was used in the presence of 1000 ppm of gold, cadmium, copper, iron, manganese and magnesium. Both lines could be used for up to 1000 ppm of aluminium, boron, barium, bismuth, calcium, potassium, sodium, lead, uranium and zinc. There was no interference from sulphate, nitrate, chloride, chlorate and phosphate ions up to 1000 ppm.

SPECTROCHEMICAL METHODS

In a previous review[42] it was stated that "no spectrographic method has been recorded for the direct determination of platinum metals in ores or concentrates" and later[43] that "For the direct analysis of gold alloys no spectrographic procedure was found which gave adequate attention to homogeneity." However, success has been achieved in obtaining homogeneity in gold alloys and in particular gold–silver assay beads. Strasheim[45] devised a method of achieving homogeneity in gold ores containing from 2 to 12 dwt/ton. The method is a good approach to a direct spectrochemical determination and involves an acid treatment with a subsequent evaporation to yield a mixture of the residual ore and the salts produced from the acid solution; this mixture is then ground to a suitable fineness. It is not unlikely that this method could be applied to a large variety of ores provided the gold concentration was within the useful sensitivity of the spectrographic method.

Lewis[45] stated that "although thousands of troy ounces of precious metals are produced in Canada each year, the concentrations of these metals in ores are usually so low that direct spectrochemical detection is not possible." This remains the situation at the present time. Considerable research has been concerned with adequate preparations of spectrochemical standards and particularly those used for the noble metals in solid form. Successful preparations have been made both through fusions and powder metallurgy.

In the case of X-ray fluorescence determinations it has become clear that for many noble metals the sensitivity is about equal to that of the optical spectrochemical methods. In particular successful methods have been developed for osmium and ruthenium in microgram ranges. These involved the use of impregnated or ion-exchange papers.

Gold in ores, concentrates, rocks, solutions, etc.

A spectrochemical method for geological samples was described by Savichev and Shugurov.[46] The technique involves some novel features which could find wide applications. The *aqua regia* solution of a 5–20 g sample was made up to 200·0 ml and after the pale residue had settled, an aliquot containing 0·3–10 μg of gold was passed through a layer of activated carbon packed into the recess of a carbon rod with a hole drilled to allow filtration under suction. Lewis [47] found that passage through the cup was facilitated by the addition of a drop of nitric acid. The carbon rod and the absorbed gold were dried at 105° and used as the lower electrode. The upper electrode was a conical carbon rod. Exposure time was 6–8 min, the slitwidth 0·01 mm, and the lines used were gold 2675·95 Å/platinum 2659·45 Å. Calibration curves were made from artificial standards containing 0·03–1 ppm of gold. Standard specimens were analysed by wet methods. The method was applicable to a large variety of minerals and the results for silicate rocks were in good agreement with those obtained by an unstated wet method. The relative standard deviation was about 4·4% It may be noted that there is the need for proof that charcoal is an efficient absorbant for gold and that comparison of values with a wet method can scarcely be considered convincing when the accuracy of so few wet methods for gold in rocks, ores *etc.* has been proven, especially as the identity of the wet method is not stated. However, the proposed technique is worthy of extended investigation to determine its range of application and its accuracy.

An interesting and useful method was described by Strasheim and Van Wamelen.[44] The unusual features of the method include a method for ensuring homogeneity (at least for the ores used by the authors) and an enhancement in sensitivity by the use of four superimposed spectra. The authors incorrectly consider the method to be a direct spectrochemical determination of gold in ores. The sample requires a treatment with *aqua regia* but avoids the necessity of a filtration. In our opinion, the ore pretreatment used by Strasheim, in which the acid-insoluble material remains incorporated in the sample, is preferable to the many procedures which use a filtered and evaporated *aqua regia* extract. However, results of additional significance might have been forthcoming had the authors compared results obtained by the latter separational method. An assay ton of 200-mesh sample was treated with *aqua regia* and a solution of copper (as internal standard). The mixture was boiled dry and the residue heated in a silica crucible for 2 hr at 800° in a current of air. The solid was then ground, and 4 g of it were mixed with 3 % of sodium chloride as carrier and used to fill 12 electrodes (capacity 300 mg) by means of the "Elpack".[48] The arc gap was 4 mm and a 1:1 mixture of oxygen and argon gave the best line/background ratio at 15 A d.c. Four 40-sec exposures were superimposed, a stepped sector of 100%–50% transmission being used. The analytical lines were gold 2675·95 Å and copper 2618·37 Å. The high silica content made the gold line at 2427·95 Å unsuitable. A copper concentration above 0·05% adversely affected the line-background ratio of gold at 2676·95 Å. Use of sodium chloride as carrier removed all but 33 % of the gold from the electrode; however, "even with the use of sodium chloride as a carrier, only a fraction of the gold was evaporated on arcing:" and the authors therefore used an analysis curve prepared from normal gold ore samples assayed by standard methods. The results indicated good agreement between spectrochemical and fire assay methods, with good precision indicating that sufficient homogeneity had been achieved. This report is one of the more satisfactory comparisons of spectrochemical and classical determinations of gold in ores. However, it must not be concluded that the technique used will always achieve homogeneity irrespective of the type of gold ore used.

An experimental investigation of the relationship between the intensity of spectral lines and the particle-size of powdered geological samples containing gold *etc.* and introduced into the arc-discharge gap by air jet was made by Raikhbaum and Luzhnova.[49] The sample particles had to be crushed to a size at which they were completely evaporated in the arc. This introduced mechanical difficulty and required using special atomizers and feeding the samples into the air jet by a pneumatic method. The size of gold particles calculated to be completely evaporated inside an arc gap at 15 A and with an air-jet velocity of 2 m/sec was 0·04 mm.

Macher[50] treated 100 g of biotite with hydrofluoric and sulphuric acids in a graphite crucible. To the silica-free residue water and hydrochloric acid were added and the liquid was decanted. Iron was complexed with boric acid and gold was co-precipitated with lead sulphide, which was separated by centrifuge and then reduced to lead. The gold content was determined spectrochemically by measuring the intensity of the lines gold 2676·95 Å/copper 2723·95 Å. The surprising sensitivity of $1·58 \times 10^{-9}$% of gold was claimed by the author.

The spectrochemical determination of gold in silicate rocks was examined for precision and accuracy by Voskresenskaya, Zvereva and Rivhina.[51] In a rather sketchy introduction the authors deal with some of the chemical methods proposed for amounts of gold of the order of 10^{-6}% or greater. They rejected a method which involved preparation of a lead alloy and cupellation to a silver bead which was then used spectrographically, stating that "considerable skill on the part of the analyst" is required and furthermore that the gold impurity in the litharge was in excess of the amounts present in an ore containing 0·1 ppm. They wished to develop a method comparable in sensitivity to neutron-activation methods, *e.g.*, for ores containing 10^{-7}% of gold or less. Among the methods examined, co-precipitation by tellurium was considered to be the most promising. Initial work indicated difficulties from excessive silica in the tellurium concentrate and contamination from glassware and chemicals. The results were compared with those from a neutron-activation method and the relative mean standard deviation of the two methods was 41 %. From subsequent experiments and calculations the authors state that the high error "can be explained by sample non-uniformity rather than experimental errors in spectrochemical and radioactivation methods." In the light of this conclusion, which in our opinion is probably correct, it is surprising that no description of the method of sampling was included and that presumably no special effort was made to secure homogeneity. The reliability and precision of the spectrochemical method were determined by "carrying out a statistical comparison of the results obtained with those of the radioactivation method", although the latter "cannot be regarded as a referee method." The authors concluded that the sensitivity of their spectrochemical method was 10^{-7}% of gold for a 10-g sample; the experimental error was 12·5% and the precision 28%, which they thought made the method "reasonably reliable".

A spectrochemical determination of gold in solutions of rocks, wastes containing noble metals, zinc sulphide ores and zinc concentrates was described by Erdey *et al.*[52] Samples were treated with *aqua regia* and then silicon was removed by the Berzelius method. Tellurium(IV) was added to the hydrochloric acid solution of the evaporated residue then tellurium and gold were precipitated with zinc and filtered off. The *aqua regia* solution of the precipitate was evaporated in the presence of sodium chloride and a solution of the residue in dilute *aqua regia* was sprayed into the high voltage spark gap by the hollow electrode method. A medium quartz spectrograph was used, the applied voltage was 20 kV at 2·5 A, slitwidth 0·015 mm, exposure time 4·5 or 2 min, air-pressure 2 bar. The analytical lines (Å) were gold 2427·95 Å/tellurium 2385·76 Å and gold 2675·95 Å/tellurium 2659·45 Å. The sensitivity of the method was 0·8 ppm of gold, and 0·56 g of gold per ton could be determined on a 5-g sample. The maximum concentration allowed was 30 ppm. The results compared favourably with those obtained by fire assay, relative errors ranging from 3·3 to 3·8%.

For the determination of microgram amounts of gold and some 14 base metal constituents in the concentration range 10^{-4}–10^{-6}%, Grigor'eva and Kvyatkovskii[53] preferred the double arc method because of the relative simpler sample preparation; 100–120 samples could be analysed with one set of apparatus during each work shift. With a good selection of fluxes ten or more elements could be determined simultaneously from one sample. The lower arc was used for preheating and the upper for excitation. The apparatus and technique were described initially by Shaw, Joensuu and Ahrens.[54] There would be considerable interest in an experimentally determined comparison of sensitivity obtained from the conventional and double-arc methods for gold in a variety of ores and alloys, *etc.*

For the determination of gold in copper concentrates Salcheva *et al.*[55] recommended initial treatment with *aqua regia*, filtration, adjustment of acidity and adsorption of gold on activated carbon. The latter was burned and the ash mixed with a buffer of carbon, sodium chloride and a 0·06% solution of cobalt as the internal standard, and transferred to the electrode. The sample was arced at 12 A. For gold contents of 2×10^{-3}% the relative error was 8·5% and 12·5% for 2×10^{-3}%. For a 1-g sample the sensitivity was 3×10^{-6}%.

For the rapid spectrographic determination of gold during a metal survey, Koyal'chuk and Stepanov[56] used a fire assay, concentrating the gold in lead and silver. The lead was separated by cupellation and continued heating at 850–900° for 15 min. The silver–gold bead was analysed spectrographically with an a.c. arc at 7 V. The bead was placed in the crater of a carbon electrode and burned off completely.

For the determination of gold in solution Degtyareva and Ostrovskaya[57] used the approach developed by Zil'bershtein,[58] which involved an optimum location of the dry powder on the carbon electrode of an a.c. arc and the use of sodium to increase the intensity of the line by decreasing the temparature of the arc. This use of sodium chloride would normally be expected to decrease the sensitivity of the line. The sensitivity for palladium was 1×10^{-8}g. The samples were evaporated and the solid residue was used.

Dobzhaeva[59] used preliminary electrochemical separation of gold. By direct determination 0·001% could be determined and by a prior chemical treatment 3×10^{-6}%. The 5–10 g sample was treated with *aqua regia* and then mixed mechanically for 1 hr. The mixture was filtered and the solution electrolysed at 40–60°, 4–5 V and 600 mA. The electrodes were polished spectrally pure carbon and immersed to 5–6 mm depth. Only about 50% of the gold was deposited on the electrode; the author relied on the questionable assumption that the results could be reliably interpreted through the use of standards similarly treated. The accuracy, precision and sensitivity of the proposed method were considered to be comparable to the chemical sorption spectrographic method and about twice as rapid.

A comparison of the spectrographic and spectrophotometric methods of determining gold in silver assay beads was made by Chow *et al.*[60] The spectrographic results were obtained from two experienced laboratories, each using a different technique. The spectrophotometric analyses were made in the chemical laboratories of the University of Toronto, from which standard gold solutions were distributed as "unknowns". To avoid errors arising from the fusion process of a fire assay, the standard gold solution was evaporated in sheet-lead boats, silver powder was added, and the boat was shaped to form a button weighing 20–23 g. A detailed description was given of the cupellation, parting and spectrophotometric determination as bromaurate.

In the first spectrochemical method, 100-mg silver beads mounted on pointed copper rods were used as the lower electrode and were arced against a conical-tipped graphite electrode at 2·2 A and 5 kV a.c. A grating spectrograph was used and the film calibrated by an iron line group method.[61] The internal standard was the silver background adjacent to the copper line at 3273·96 Å. The gold line was 2675·95 Å.

In the second method, the lead buttons were cupelled to 50 mg attached to copper electrodes, which were used as cathodes for sparking against a graphite anode with a peak voltage of 20 kV and a radiofrequency current of 5 A. The lead line 3118·92 Å was used as the internal standard. The gold lines were 2675·95, 2427·95 and 3122·78 Å. Several sets of the four different gold concentrations (0,20,41,62 ppm) were determined by all three methods, which were found to be of equal accuracy.

Noble metals in ores, rocks, concentrates, solvents

Hahn-Weinheimer[62] concentrated the noble metals by fusing 3-g samples, removing silica, adding hydroxylamine chloride to the solution and adjusting the pH to 5. Nitrogen was passed through the solution, which was heated till colourless. Hydrochloric acid and 2-quinolineselenol were added to precipitate ruthenium(III), rhodium(III), palladium(III), osmium(IV), iridium(III), platinum(IV) and gold(III) as well as 10 base metals. The precipitate was extracted into chloroform, which was then distilled off. The residue was mixed in a porcelain dish with magnesium nitrate solution and nitric acid, and then washed at 500°. The ash was mixed with 2 parts of carbon. The author believed that the smallest traces were best determined by an a.c. arc with a current of 1·5 A and 250 discharges per min. The greater part of this report is concerned with the preparation of the reagent and the optimum precipitation conditions. By far the most important aspect of the work as indicated by the title, concerned the efficiency of the method for the determination of trace noble metals in the rock, but relatively little attention was given to it. This is another instance of the failure to provide proof for the limits of detection and determination for each noble metal. The limits (ppm) claimed by the author are osmium 2·0, iridium, rhodium and ruthenium 0·05, platinum and palladium 0·01. The statement that as little as 0·009 ppm of platinum is precipitated by the reagent, while interesting and useful in itself, gives little indication of the success with which platinum can be determined in rocks by spectrochemical methods.

Preconcentration of noble metals in silicate rocks by ion-exchange was used by Brooks and Ahrens.[63] The separational techniques were discussed in a previous review[64] and in general depended on the fact that under appropriate conditions noble metals form anionic chloro-complexes whereas the associated base metals form cationic species. It was possible to obtain enrichment factors up to 20,000. The authors believed that the method provided the possibility of determining noble metals in silicate rocks. In the present authors' opinion the combination of ion-exchange separational methods with determinative methods offers some very attractive possibilities for the determination of noble metals in complex materials such as ores, concentrates *etc.*

For determination in rocks, ores and minerals, Tomisky[65] preconcentrated gold, palladium and platinum by precipitation with magnesium from hydrochloric acid solution at pH 1–1·5. The collecting reagent was activated carbon. The mixed precipitate was ashed and mixed with graphite powder containing molydenum as internal standard. With a 10-g sample the enrichment factor was 250 and the sensitivity limits for palladium and platinum were about 0·03 g/ton, and for gold 0·004 g/ton. The error was about 10%, and for smaller proportions of noble metals the results were only semiquantitative.

Miyamoto[66] concentrated platinum and palladium by adding 2 mg of gold and 10 mg of silver (as standard solutions) to 10–100 g of sulphide or silicate ore, and fire assaying to produce a gold–silver bead. This was excited on a graphite electrode by a d.c. arc at 120 V and 8 A with an arc-gap of 5 mm. Measurements were made with the line pairs, platinum 2659·454 Å/gold 2688·71 Å, and palladium 2763·092 Å/gold 2688·71 Å. The coefficients of variation for 1 ppm of platinum and 1·5 ppm of palladium were 7·2 and 5·6% respectively, and 0·01 ppm of the metals could be determined.

Barnard and Zeeman[67] dissolved rock samples in hydrochloric acid, oxidized with manganese dioxide, heated, filtered off and washed the residue. The noble metals were collected by treatment of the solution with mercury and tin(II) chloride in a separatory funnel. Iron was extracted with hydrochloric acid and mercury was volatilized at 210°. The residue was added to a graphite electrode. The spectral range of 2480–3600 Å was used with beryllium and molybdenum as internal standards. The present authors have no data available which indicate the degree of recovery of platinum metals by mercury. If the recovery is comparable to that for gold the method used by Barnard and Zeeman could have wide applications.

Lewis[45] stated that in general the concentrations of noble metals in Canadian ores were "so low that direct spectrochemical detection is not possible" and that in general, of the methods available the most practical seemed to be concentration by fire assay and optical spectrochemical analysis of the fire assay bead; X-ray spectrochemical methods were not yet suitable for low concentrations of precious metals.

The direct and the enrichment spectrochemical methods of determining platinum metals in rocks and ores were discussed by Ginzburg,[68] who concluded that the direct method failed to reveal the full value of an ore and was of no practical value. For the enrichment method 50–100 g of rock were used for a fire assay. The collectors which were considered were lead, silver, copper and copper–nickel alloys. Silver should be used for gold, platinum, palladium and rhodium. For iridium the silver bead could be converted into the copper–silver alloy. The author considered ion-exchange, solvent extraction and co-precipitation as promising methods of enrichment and a flow sheet was included for the collection of the noble metals. Liquid and solid concentrates may be obtained by subjecting the copper–noble metal alloy to the various separational processes; atomic-absorption is applied to the liquids and emission spectrography to the solids.

For 50-g samples of ores and materials having a low concentration of platinum metals, Anisimov *et al.*[69] used the fire assay to produce lead buttons which were scorified and then cupelled to form silver assay beads. These were finished at a high temperature to remove traces of lead, and platinum, palladium, gold and rhodium were determined spectrochemically.

Pastukhova and Belouova[70] also used fire assay preconcentration. Two 50-g, 150-mesh samples were fire assayed to form silver beads. Metal sulphide ores were first roasted at 700°, then leached with dilute sulphuric acid, and the insoluble material was filtered off and mixed with the assay charge. The charges were fused at 1200° for 1·5 hr, held for 15 min and poured to produce two 35-g lead buttons. These were cupelled at 900–1100° to form two silver beads which were cleaned with dilute hydrochloric acid and water, and combined by heating in a graphite crucible, each bead being cleaned again as before. The authors checked the purity of the bead by examination with a magnifying glass; the efficiency of this process may be questioned. Finally the bead was analysed spectrographically with standards of platinum, palladium and gold.

To determine palladium and platinum in copper ores or concentrates Kalinin *et al.*[71] assayed to form a 1·24-mg silver bead and used a d.c. arc at 15 A. The grating spectra were enlarged to 1 Å/mm. Intermittent exposures of film for 50 sec allowed determination of intensity and order of appearance of lines. At about 0·2 ppm of palladium the line 3404·58 Å appeared, at 0·5 ppm the line 3242·703 Å. In the case of platinum with its relatively poor sensitivity 1 ppm was indicated by the 3064·712 Å line and 5 ppm at 2997·967 Å. With insufficient evidence, the authors recommended the method for the determination of the platinum group in other copper ores.

Rubinovich *et al.*[72] made a preliminary concentration by selective ion-exchange with AN-18 anion-exchanger under dynamic conditions, and with activated carbon under static conditions. The anion-exchanger accomplished a 95% separation of gold, palladium and platinum. Irrespective of the kind of amount of mineral acid or acid mixture about 0·05 g of activated carbon extracted completely 0·1 μg of gold from 100 ml of solution. To extract 95% of palladium and platinum from sulphuric acid solutions at least 0·5 g of carbon was required, with a contact time of 20–30 min. Nitric and hydrochloric acids were less effective than sulphuric acid at similar concentrations. The exchange procedure involved ignition of the sample, treatment first with *aqua regia*, then with hydrochloric acid and potassium chlorate with intermittent evaporations, dissolution in water, filtration, adjustment of the filtrate to 1*M* hydrochloric acid concentration, and anion-exchange. The resin was washed and then transferred to a filter paper, and burned at 700–800°. In the carbon separation, after *aqua regia* treatment, fuming with sulphuric acid, dilution and filtration, the filtrate was treated with carbon, which was then filtered off and ashed at 700–800°. In both cases the residue was treated with nitric and hydrochloric acids, then carbon powder containing sodium chloride and cobalt was added and the mixture was evaporated to dryness. The residue was transferred to a carbon electrode and arced at 13–15 A. The exposure time, equivalent to the burning period, was 2·5–3 min. The analytical lines were gold 2676·0 Å/cobalt 2648·6 Å for both separations, palladium 3421·2 Å/cobalt 3409·2 Å for carbon separation and 3242·7 Å/3409·2 Å for ion-exchange, platinum 2659·5 Å/cobalt 2698·6 Å for both methods. For palladium, the area of the plate including the two analytical lines was overlapped by a cassette 25 sec after starting the exposure; this reduced the background intensity from the cyanide bands and this increased the sensitivty. For 10-g samples the sensitivities for platinum, palladium and gold were 10^{-6}, 5×10^{-7} and 2×10^{-7} respectively for anion-exchange, and 5×10^{-6}, 5×10^{-6} and $1{\cdot}5 \times 10^{-6}$% for carbon separation.

Various authors have used chemical precipitation as a method of enrichment for spectrochemical purposes. P'yankov[73] dissolved 5–10 g of ore, treated it with *aqua regia*, fumed it with sulphuric acid, added hydrochloric acid and potassium chlorate, and finally heated to remove chlorine. The noble metals were precipitated in the presence of added copper sulphate by sodium thiosulphate. The sulphide precipitate was filtered off, burned reduced in hydrogen and melted in a graphite crucible to form a copper bead, which was arced at 4 A a.c. for 30 sec. The exposure was 30–60 sec. The analytical line pairs (Å) were platinum 2659·45/copper 2645·4; palladium 2447·91/copper 2645·4; gold 2675·95/copper 2645·4; and rhodium 3434·89/copper 3375·67. For very low noble metal content a silver bead was prepared by fire assay of about 50 g of the sample. The a.c. arc was again used and the analytical line pairs (Å) were platinum 2997·96/silver 3130; rhodium 3323·09/silver 3130; gold 2675·96/silver 2721·70; palladium 3114·04/silver 3130.

Other related chemical methods of concentrating the noble metals have been proposed. Sin'kov[74] used samples containing 0·2–2 mg of platinum metals, added copper sulphate solution and heated to 80°. Zinc dust was then added and the mixture was filtered with a Buchner funnel. Base metals were selectively removed by hydrochloric acid. It should be noted here that this treatment may result in losses of platinum, iridium, *etc.*, small amounts of which may pass into solution in the presence of copper and hydrochloric acid. The residue was dried and melted with copper to form a 2-g button which was cut in half and used as electrodes in the a.c. arc, slitwidth 0·01 mm, arc gap 2.5 mm, current 6 A. Copper was used as internal standard. For 0·005–0·1% of the noble metals the error was 10–15%. Solutions of samples containing larger amounts of the noble metals were added to a hollow porous graphite electrode with a bottom thickness of 1 mm. This was sparked (2-mm gap) with a lower graphite electrode having a 45° conical tip, exposure 30 sec. For platinum, palladium and rhodium the error was 2·5–9·2%.

Copper–noble metal alloys have been used by a number of Russian researchers for the spectrochemical determination of platinum metals. For rich products Nedler *et al.*[75] added 80–120 mg of silver to samples containing 0·2–2·0 mg of platinum metals. The mixture was melted with 2 g of copper in a graphite crucible at 1300–1400°. The copper button was pressed into a plate 1·5–2·0 mm thick, which was cut into two parts, each used as an electrode held in a water-cooled clamp and arced at 6 A. Samples containing only 0·04–2 mg/l of platinum metals were fire assayed and the noble metals collected in 30 mg of silver and 400 mg of copper. The copper–silver button was divided into two parts each of which was melted to form spherical buttons which were used as electrodes for an a.c. arc. The authors make the interesting observation that rhodium in the presence of platinum and palladium is readily dissolved by silver, the assay beads which contain these metals, along with gold, forming homogeneous alloys. Lewis *et al.*[76] have indicated that gold is superior to silver as a solvent for rhodium. Nedler *et al.* found the arc between the silver alloys extremely unstable and homologous pairs of lines were therefore recommended.

Preconcentration of noble metals was discussed by Livshits.[77] To determine platinum, palladium, gold and rhodium in spent solutions he added copper(II) and co-precipitated the metals by adding sodium thiosulphate to their sulphuric acid solution. The sulphide precipitate was isolated and treated with hydrogen. The metallic sponge was fused to form a 0·1-g copper–noble metal button which was placed in the hollow of a carbon electrode and burned in an a.c. arc for 30 sec at 4 A and an arc gap of 3 mm. Standards were prepared by admixture with copper as the base element. The emission lines (Å) used were, platinum 2659·4, palladium 2447·9, gold 2675·9, iridium 2664·4, rhodium 3434·9, copper 3375·7 and 2645. For low concentrations of iridium co-precipitation was made with thiourea. Standards were made by fusion of pure iridium and copper.

Noble metals in alloys

In silver. Lincoln and Kohler[78] converted 1 g of silver sample into the nitrate, which was then melted, cooled and ground to a powder, and 180 mg were applied to a graphite anode inserted in a Stallwood jet supplied with pure argon at 4 l./min. The graphite upper electrode had a flat end; the gap was 3 mm. Samples and standards were excited for 30 sec in a d.c. arc at 12 A and 300 V. Standards were prepared from high-purity silver nitrate, iridium, gold platinum and ruthenium chlorides, and rhodium sulphate. The range of concentration of impurities was 0·1–100 ppm. The lines (Å) used with silver 3099·1 as internal standard were gold 2675·9 (50–100 ppm), iridium 3220·4 (10–100), palladium 3421·5 (10–100), platinum 3064·7 (10–100), rhodium 3434·9 (1·0–50), ruthenium 3436·7 (10–100).

The success of this method depends on the solubility of these noble metals in the silver nitrate–nitric acid medium, or on the extent to which they form a homogeneous mixture with the powdered silver nitrate, but the authors make no comment other than "The overall precision in terms of coefficient of variation was found to be 17%." Nitric acid will dissolve palladium from a silver alloy or assay bead after repeated treatments, and yield the platinum largely as a colloidal solution. The other noble metals remain as a residue. The concentration ranges claimed by the authors, calculated on the basis of a 10-mg silver bead, an assay ton of sample, and expressed as oz/ton, would be for gold 0·005–0·001, for iridium, palladium, platinum, and ruthenium 0·0001–0·001 and rhodium 0·00001–0·0005. Despite the fact that these quantities are much below the range used for fire assay one cannot assume that even fractions of micrograms of such metals as iridium are soluble in a nitric acid medium. However, it may well be that in all cases homogeneity may be achieved within the precision of 17% claimed by the authors. In any case the application of a method such as the authors cannot be extended directly to the noble metals assay bead. The authors give no reason for assigning the upper limits for which the method is applicable; however, their interest was largely confined to the lower limits of impurities. The authors' preliminary data indicate that the use of argon in an igloo quartz dome will increase the sensitivity of their method by at least one order of magnitude.

For the determination of palladium, platinum, gold, lead, bismuth, antimony, copper and iron in pure silver Kuranov and Sviridova[79] used the standard addition method with samples in the form of rods 6 mm in diameter, with oval ends. An a.c. arc at 12 A and 6000–8000 V, a gap of 2 mm, an exposure of 120 sec, and a slitwidth of 0·03 mm were used. The error was 10–20%.

For the spectrochemical determination of 0·01–1·5% of platinum palladium, *etc.* in gold alloys in which silver is the basic element, Khrapai[80] found that with 10% copper and 20% gold present the absolute intensities of the palladium, platinum and silver lines increased with increasing copper and gold concentrations. The working curves for palladium and platinum undergo a parallel shift, greater for palladium than for platinum. The spectra were excited with an a.c. arc or for very low concentrations with a condensed spark. The standards were accurately prepared routine refinery alloys. The average relative errors for platinum and palladium were 5·2 and 5·5% respectively. The present authors suggest that the method requires the use of one analytical system for each matrix or the use of a family of analytical curves which take into account the changing matrix.

Fissium alloys. Several spectrochemical methods have been proposed for the analysis of "fissium alloys." Goleb[81] determined rhodium, ruthenium, palladium, molybdenum and zirconium at the levels of 0·3, 2, 0·2, 2·5 and 2·5% respectively. The corresponding precisions were 1·7, 1·8, 2·1, 1·0 and 2·2%. The relative standard deviations, obtained by comparison with chemical methods were respectively 7·2, 4·3, 6·6, 3·9 and 7·5%. Unfortunately the author did not identify the chemical methods. Standards were prepared from a 15% fissium alloy mixed with unalloyed uranium metal, melted *in vacuo* in a magnesia crucible at 1450° for 30–45 min and cast in thoria-coated precision bore Vycor tubing at 1450–1500°. Four standards were made, containing 3·8–15% of the five elements sought, and were analysed chemically. A minimum of 5 g of freshly-machined sample were used as upper electrode in the point-to-plane technique with a high voltage condensed spark. The carbon counter-electrode was machined to a cone and the gap was 4 mm. The sample was presparked for 5 sec and exposed for 18 sec. Excitation conditions were selected with a view to avoiding oxidation or burning of the alloy. A large Littrow quartz spectrograph was used and an aluminized quartz plate giving a transmittance of about 20% was used next to the slit. Tests were made to ensure that the line pairs listed had proper excitation characteristics and that no differential heating effects or violatilization occurred with either sample or standard. Checks were also made to ascertain any heterogeneity or segregation.

Although point-to-plane techniques produced satisfactory results, Goleb and Brody[82] believed that the irradiated alloys would be too radioactive for the application of this method. An examination of the Sckuler–Gollnow hollow cathode tube, used for plutonium, revealed that the radioactivity was confined to the anode-cathode interface; negligible activity was found on the outside walls of the cathode and none on the metal surfaces except at the interface. This cathode tube, water-cooled, was then used for the analysis of un-irradiated uranium alloys containing 2·0% ruthenium, 0·3% rhodium, 0·2% palladium and 2·5% molybdenum. The authors believed that synthesized fission alloys and highly irradiated refined alloys had similar chemical and metallurgical properties. The standards and samples were prepared and processed as described above.[81]

The line-pairs of the four constituents with uranium as the internal standard avoided interferences, and showed optimum intensities and nearly similar background for each line-pair. Six uranium alloys were analysed by both the hollow cathode and the point-to-plane methods and gave the following relative standard deviations: ruthenium 5·9%, rhodium 5·4%, palladium 9·1% and molybdenum 7·8%. Calibration curves were linear for 0·7–4% ruthenium, 0·07–0·4% palladium, 0·1–0·5% rhodium and 1–5% molybdenum.

The vacuum-cup technique was studied by Yokoyama and Faris[83] with a view to the analysis of uranium–plutonium alloys containing ruthenium, rhodium, palladium and molybdenum. Nickel was used as internal standard. Spectral intensities were correlated with consumption of sample solution but were influenced to a large extent by the deposition of solutes on the electrode surface and to some degree by concentration of the sample solution by heat. The results may also be influenced by factors such as viscosity and density of solution, variation in electrodes such as the axial canal diameter and the presence of solvents, additives *etc.* The authors concluded that the vacuum cup method offered no outstanding advantages over other solution techniques.

Impurities in noble metals. For the spectrographic determination of 26 base and noble metal impurities in high-purity gold Lincoln and Kohler[84] used their technique for trace impurities in platinum.[85] The impurities included iridium, palladium, platinum, rhodium and ruthenium. The concentration ranges and analytical lines are shown in Table II.

For each metal the lower limit of detection was taken as the lower limit of the concentration range. Sensitivity was improved if the gold-on-graphite preparation was pelleted and burnt in a friction-fitting platform-type crater. Standards were prepared in much the same way as for platinum[85] and because of possible line interference the high-concentration standards contained only one of two groups of impurities; the low-concentration standards contained the full 26 impurities. Corrections for impurities in reagents and graphite powder were assumed to be constant for both standards and samples but corrections were made for residual impurities known to be present in the gold used for standards. The working curves were reasonably linear for the ranges covered. The overall coefficient of variation for a mean total of 28 ppm of impurities was about 5%.

A spectrographic method for the determination of traces of palladium, silver, copper, iron, lead and zinc in high-purity gold was described by Strasheim *et al.*,[86] who prepared four master standards from which working standards were prepared by dilution with pure gold. The range of palladium concentration varied from 4·8 to 5·7 ppm. A set of four samples was also analysed by atomic absorption with closely agreeing results. The result for palladium obtained by the authors for commericial sponge was 2·7 ppm which is at variance with a calculated limit of 4·1 ppm. This was explained by "the somewhat conservative formula used for calculation of the detection limit" as well as by the assumption that the palladium concentration found was below the detection limit of the visual method of estimation used by the commercial firm. It may be noted that several colorimetric methods of higher sensitivities have been recorded.

For the spectrochemical determination of 0·01–0·0001% of platinum, palladium, silver and associated base metal impurities in gold, Zelle *et al.*[87] used a wet method of concentration which involved the usual treatments with *aqua regia* and hydrochloric acid followed by an ether extraction of gold at pH 2·1–2·6, the impurities being collected in the aqueous layer. The latter was evaporated to 0·5–1 ml and analysed with a medium dispersion spectrograph.

Khrapai[88] described spectrochemical procedures for the determination of six base metal impurities in gold and eight metal impurities in silver, including platinum, palladium and gold. The concentration range was 2×10^{-4}–1×10^{-2}%. The average error was 3·5–7%.

Spectrochemical methods of determining impurities in gold, silver and their alloys standards were discussed by Kuranov *et al.*[89] The impurities in the case of silver were palladium, platinum, gold, copper, iron, bismuth, antimony and lead, and the errors were 10–20%. The spectrograph used had a dispersion sufficient for the separation of the lines for antimony at 2598·06 Å and iron at 2598·36 Å. In a second paper Kuranov[90] discussed the preparation of metal standards. In the case of silver alloys the concentrations of platinum, palladium, gold, copper, lead, bismuth, antimony and iron ranged from 10^{-5} to 10^{-2}%. The difficulty of arriving at homogeneity in the case of iron with silver was solved by the addition of palladium or iron–palladium alloy which encouraged the dissolution of iron. Standards were smelted in a high-frequency induction furnace in carbon-lined graphite crucibles. Analogous standards were prepared for extra high-purity gold, platinum, *etc.* The author discussed methods of preparing standards by mixing metallic powders in the required ratios and heating them to the smelting temperature of the base. The composition of each standard was confirmed by chemical analysis, and homogeneity was tested by use of radioisotopes and by spectrochemical examination. The method proved successful for silver and for platinum–rhodium alloys, each containing some fifteen constituents. The method was also efficient when applied to metal and carbon powder, and alloys of rhodium and iridium; when smelting was inapplicable, powder metallurgy was used. Methods of preparing dissolved standards were also described. Solutions of the acid-insoluble consistituents iridium, rhodium and ruthenium were obtained electrolytically in 20% hydrochloric acid, at a current density of 0·5–5 A/cm². The resulting solution of the standard was evaporated and the residue was pulverized, roasted at 900° in hydrogen, and again pulverized. There was good agreement in the iridium content of samples prepared from standard solutions and powder metallurgy.

TABLE II

Element	Concentration, *ppm*	Analytical lines, *Å*
Ir	5–50; 10–100	Ir 3220·8 Au 3105·3
Pd	0·1–5; 1–10	Pd 3404·6 Au 3105·3
	10–100	Pd 2447·9 Au 3105·3
Pt	5–50	Pt 2659·4 Au 3105·3
	10–100	Pt 2930·8 Au 3105·3
	100–500	Pt 2659·4 Au 3147·6
Rh	0·5–10	Rh 3434·9 Au 3105·3
	5–50; 25–100	Rh 3396·8 Au 3105·3
Ru	1–25 10–50	Ru 3436·7 Au 3105·3

A spectrochemical method for determining some ten metal constituents in alkaline electroplating solutions of gold, nickel, and chromium was described by Luppino,[91] who considered the porous cup electrode, graphite spark, conversion to oxide powder, and the rotating platform techniques. The last was chosen because of the greater discharge area; a larger volume could be used and better precision was obtained. Furthermore, a wide range of impurity concentration could be determined without modification. Molybdenum was added as the internal standard. Precision data were recorded for each impurity and accuracy was determined by comparison with gravimetric, colorimetric and electrolytic methods of determination.

To determine impurities in platinum, Kuranov and Ruksha[92] used oxide powders of 10–30 μm particle-size, mixed and briquetted at 2500 kg/cm², and then annealed at 300°. These briquettes were subjected to pressures of 400 and 5000 kg/cm^2 after a prior annealing at 300–900 kg/cm^2, then annealed again at 1200°. The impurities ranged from 10^{-3} to 10^{-2}%, with the total not exceeding 0·5%.

A spectrographic method for the determination of 27 impurities in platinum over the range 0·1–800 ppm was recorded by Lincoln and Kohler.[85] The standards were prepared by a method somewhat similar to that used by Kuranov *et al.*[93] The impurities were added in solution to pure ammonium hexachloroplatinate made from 99·999+ % pure metal. At a concentration level of 10 ppm the standards contained the 27 impurities; above 10 ppm two standards were prepared, one containing 13 and the other 14 impurities. Selected analytical lines were attenuated by filter to a readable level. Table III contains the analytical lines for each noble metal and the internal standard, the % transmissions, the concentration ranges and the interfering lines.

The limit of detection for each element was taken as the lowest value given in Table III. In the case of palladium and rhodium the level of detection was limited by the residual impurities as indicated in the last column. The overall relative standard deviation was 10%.

A spectrochemical method of determination of 2–5% of palladium and rhodium in platinum was described by Kuranov.[94] The precision was about 2%.

TABLE III

Element	Line, Å	Transmission, %	Internal Pt std. line, Å	Transmission, %	Range, *ppm*	Interference line, Å	Interference Concn., *ppm*
Au	2676·0	10	2578·4	20	0·5–20	Ru 2676·2	400
	3122·8		3110·1	10	10–100		
Ir	3220·8	10	3110·1	10	10–160		
	2924·8		2814·0		80–800		
Os	2909·1	10	2814·0	10	80–800	Cr 2909·1	1000
Pd	3404·6	10	3110·1	10	1–10	Fe 3404·3	1000
	2447·9	20	2578·4	20	10–400	Ag 2447·9	
Rh	3434·9	10	3110·1	10	0·6–10		
	3396·9	2	3110·1		10–80		
Ru	3498·9	10	3110·1	10	5–40		
	2678·8		2578·4	20	40–800	Cr 2678·8	40

Procedures for the spectrochemical analysis of iridium and ruthenium were described by Pankratova and Gut'ko.[95,96] The sample, in powdered form mixed with graphite powder in 1:2 ratio, was transferred to the cavity of the lower graphite electrode and vapourized completely. Homologous line pairs were recorded for platinum, palladium, gold and iron. The concentrations of the impurities ranged from 0·002 to 0·2%. The results compared satisfactorily with these from chemical determinations.

For the determination of some nineteen impurities in platinum and platinum–rhodium alloys Narasimham[97] used graphite electrodes, a d.c. arc and a zinc oxide buffer. The impurities determined included palladium and gold. Rhodium was separated from platinum by adsorption of platinum on the anion-exchanger IRA-400.

The spectrochemical determination of impurities in iridium and rhodium was discussed by Kuranov *et al.*[98] The impurities were those associated with the two metals in ores or after refining. The objective was comparison of two methods of preparing standards. The first involved the use of standard solutions, proposed earlier by Lewis, Ott and Hawley.[76] The second, rejected by the latter authors because of the difficulty of achieving homogeneity, involved the use of powdered metals. For the preparation of standard solutions Kuranov dissolved the base metals in mineral acids and platinum, palladium and gold in *aqua regia* and used ammonium hexachloroiridate for iridium; rhodium and ruthenium were dissolved electrolytically in 20% hydrochloric acid with an a.c. current density of 0·5–5 A/cm^2. The total amount of the 12 impurities varied from 0·024% to 0·630% in the various standards. The solutions were evaporated to dryness and the residues were ground and then heated at 900° in hydrogen. The spongy metal was mixed mechanically for 12 hr with carbon in the proportion of 2:1 (metal:carbon). In the powder metallurgy method, aluminium oxide and barium oxide powders (particle-size 15–20; mesh, prepared by elutriation) were mixed mechanically for 15–18 hr with iridium, rhodium, the 12 impurities and carbon powder (total weight of sample 20 g), briquetted under a pressure of about 1600 kg/cm^2, annealed at 1000° in hydrogen for 5–8 hr, and ground in a mortar. Samples of 0·15 g were used for the analysis. A check was made to ensure homogeneity. A comparison of the calibration curves showed that both series of standards were identical. It was noted that the presence of sodium in the standards resulted in a significant increase in the absolute sensitivity of the determination of the elements. Third element effects could be disregarded provided that the total of all the impurities or of any one did not exceed 0·6%. The authors described an internal electrolysis method (aluminium anode, gold cathode) which increased the sensitivity for the determination of iridium in rhodium several times.

Kuranov *et al.*[98] also reported that with a similar procedure the sensitivity for rhodium impurity in iridium was 0·01% and for the remaining impurities >0·001% but <0·01%. In rhodium the sensitivity for most elements was 0·001% but iridium and ruthenium could not be detected below 0·1%.

For the spectrochemical determination of platinum, palladium, rhodium and iron in porous refined iridium, Chentsova[99] used briquetted 100-mg samples collected in an assay button which was placed in an a.c. arc between carbon electrodes. A low voltage spark was used and the concentrations recommended were between 0·03 and 0·3%. In the case of refined platinum or palladium, silver was used to produce alloys containing 75% of the platinum metal. For rhodium, palladium was added to produce a 91% rhodium alloy. With these alloys as electrodes, impurities of platinum metals (excepting osmium) and gold, copper, iron and nickel could be determined in one process with satisfactory accuracy and precision. Six standard alloys were prepared for the determination of impurities in the refined platinum, palladium and rhodium. In the case of platinum or palladium master alloys of each metal with the impurities were melted with weighted samples of spectrally pure platinum or palladium containing silver. In the case of rhodium, a master alloy of impurities with spectrally pure palladium was prepared and wieghed amounts of it were added to the 91% rhodium standard. The error ranged from 6 to 12%.

To determine impurities in refined platinum, palladium and rhodium, Zolotukhin *et al.*[100] converted these metals into alloys, thus stabilizing the arc and producing a high rate of disintegration, which reduced fractionation. A similar method for spectral analysis of refined metals and products containing the noble metals was recorded by Gut'ko,[101] but with a 33% silver–platinum or palladium electrode, and for rhodium a 10% palladium–rhodium alloy. In the case of platinum metals and gold in solutions, zinc dust was added to precipitate the noble metals at 80–90°, and base metal salts and excess of zinc were leached with acid from the precipitated metal, which was then melted in an arc furnace to form a copper button. It may be noted that most acid leaching processes may result in simultaneous loss of certain noble metals. Solutions with very small proportions of noble metals were assayed to form a silver alloy which was analysed directly or melted to form a copper button.

An interesting method of considerably increasing the sensitivity of spectrochemical methods for the detection of the noble metals was described by Gut'ko and Shchurova.[102] The method depended on introduction of the impurities into the discharge at a constant rate, a change in the ratio of the impurity concentration at the beginning and end of the vapourization, the complete vapourization of the sample, and making equal-time exposures during maximum vapourization of each impurity. Sensitivity could be increased from 5 to 1000 times that for the normal technique, *e.g.*, with complete vapourization of a palladium sample, copper and silver are first vapourized, then platinum, rhodium, iridium, iron, and nickel. This fractional vapourization and concentration of impurities was observed in the case of refined rhodium, iridium, ruthenium, palladium and platinum. Difficulties in the application of prepared standards may be expected when this technique is used.

The principle of fractional distillation had been used earlier by Peters.[103] A carbon electrode was used at 10–13 A and 220 V. Seven successive 20-sec exposures were made with 5-sec intervals between them. The method as presented by Peters would be difficult to apply quantitatively.

Gut'ko *et al.*[104] also applied the method to high-purity platinum, palladium and ruthenium. The sensitivities for tellurium, gold, zinc, magnanese, silicon, iron, aluminium, copper, silver, nickel, palladium and platinum in refined platinum or palladium were increased. The low-boiling impurities were first enriched, allowing an increase in concentration of the residue of rhodium, ruthenium, iridium, and other high-boiling impurities. The authors obtained sensitivities of about 10^{-4}% with a precision of 10–30%. Removal of ruthenium from the substrate by oxidation to the tetroxide allowed a further increase in sensitivity by an order of magnitude. It would be interesting to learn the evidence for the formation of the tetroxide by direct oxidation.

For the determination of rhodium in platinum–rhodium alloys, Plsko[105] subjected 0·1-mg samples directly to a high-voltage condensed a.c. spark. The rhodium lines at 2461·04, 2458·90, 2455·71, 2456·18 and 2466·15 Å were used, with the 2450·97 Å platinum line as an internal standard. The method was applicable over the range 2·75–37% rhodium and the average relative deviation was ±7%.

It has been stated that classical methods are effective only in detecting more than 100 ppm of impurities in noble metals. In the 1–100 ppm range, spectrochemical methods may be applied. Diehl[106] used solutions of appropriate salts for standardization and mixed the residues with carbon to form powder pellets which were then a.c. arced.

Determination of noble metals in base metal products

For the determination of platinum metals in "lean plant solutions" Anismov *et al.*[107] compared the efficiency of chemical concentration followed by spectrochemical determination with that of a fire assay and cupellation. They recommended the chemical method for fast control analysis and the assaying method for more exact work. We regret our inability to secure the original manuscript since such a recommendation must depend on the character of the chemical and assay techniques used.

In catalysts. A method for the determination of 0·005–0·1% of palladium and ruthenium in aluminium oxide catalysts was recorded by Talalaev.[108] The ground samples were mixed with carbon powder 1:1 w/w and ground with ethanol in an agate mortar and dried at 100–120°. Standards were similarly prepared and were analysed chemically. Samples and standards (~10 mg) were excited in a 15-A a.c. arc between carbon electrodes. With aluminium as the internal standard the line pairs used were 3114·04/3054·70 Å for 0·05–0·5% of palladium and 3242·73/3054.70 for 0·005–0·05%; for ruthenium the line pairs were 2988·95/3654·70 Å. The aluminium line at 3059·9 Å could also be used. The precision was ±10%, and the deviation from chemical results did not exceed the random diviation of both methods.

Later, Talalaev[109] recorded a similar procedure for the spectrographic determination of residual palladium (0·0005–0·005%) and ruthenium (0·0025–0·01%) in aluminium oxide catalysts. The line pairs for palladium were 3404·58/3059·93 Å and for ruthenium 3498·94/3059·93 Å. The errors were 12% for palladium and 9% for ruthenium.

Platinum in aluminium oxide was determined spectrochemically by Tang *et al.*[110] Initial spattering in the carbon crater was avoided by drilling a cavity of 2 mm diameter and 5 mm depth in the lower electrode and adding the sample covered with carbon powder. Molybdenum(VI) oxide was used as the internal standard. The spectral lines used were platinum 2998 Å/molybdenum 3132 Å. The average error was 5% and the deviation from chemical determinations was 3% for 0·33% platinium and 15% for 0·56%.

Various reports deal with the spectrochemical determination of noble and other metal impurities in high-purity metals such as silver, gold, gallium, tellurium and uranium-fission alloy. Bianchini and Zanaroli[111] described methods for determining gold, copper, lead and bismuth in electrolytic silver, and for determining platinum, silver, bismuth, lead, iron and copper in gold. Lysenko and Kim[112] used a preliminary extraction with butyl acetate in determining platinum and 15 additional base metal elements in gallium. The solution was treated with carbon and sodium chloride solution and evaporated at 110°. The residue was transferred to the crater in the carbon anode and subjected to a 10-A d.c. arc.

A study of the principles involved in the determination of noble metals in tellurium was made by Ginzburg.[113] Evaporation from the arc resulted in early evaporation of tellurium and thus in fractional evaporation of the noble metals. The author was primarily concerned with the optimum conditions for the spectrochemical determination of noble metals and in particular the advantages provided by addition to the mixture of constituents such as carbon, sulphur *etc.*

Naka and Naka[114] studied the spectrographic determination of platinum in fluor-phlogopite prepared in a platinum vessel. They mixed the sample with an equal amount of carbon powder and added 200 ppm of ruthenium as internal standard. A d.c. arc was used for the excitation at 300 V and 5 A, with a gap of 3 mm. The exposure time was 60 sec with a 60 sec preliminary discharge. Standard samples were prepared by adding platinum to fluor-phlogopite free from platinum. The line pairs were platinum 3064·7 Å/ruthenium 2988·9 Å and each line intensity was corrected for background effect. The working curves covered the range 5–500 ppm. The relative standard deviation was 10–15%.

To determine traces of some 30 metal elements in electrolytically pure copper Publicover[115] used a globule arc procedure. For 2–20 ppm of gold the lines gold 2675·95 Å/copper 2871·44 Å were used. It was noted that the gold content of electrolytically refined copper rarely exceeded 0·3 ppm and thus the sensitivity was generally inadequate. In the range 0·02–0·30 ppm, gold is usually determined spectrochemically after fire assay and concentration in a silver bead. Platinum and palladium in the range of 0·001–0·01 ppm are also determined after concentration by fire assay.

A unique spectrographic method for the determination of osmium was described by Fain,[116] who used a special electric furnace consisting of a non-chromous spiral mounted on a ceramic frame and suitably insulated. Samples or standards (12–15 g) were mixed with equal weights of bismuth subnitrate and lead peroxide in 1:5 ratio and transferred to the chamber of the furnace. The upper lid of the furnace was constructed to allow the projection of a hollow carbon electrode, 2 mm in diameter.

The chamber contents were heated to 700–800° and the volatilized osmium compound passed through the hollow electrode into the arc area between the lower and upper carbon electrode. The osmium lines were more intense near the cathode, and the spectrum from this part of the arc was used. The exposure time was 5 min, the first min of which was used to heat the furnace contents. The spectral lines were 3058·66 and 2909·061 Å; in the presence of molybdenum the line at 2909·116 Å interfered. The author claimed a sensitivity of about $2 \times 10^{-5}\%$ for osmium, which indicates 3 μg of osmium or 0·2 ppm for a 15-g sample. The technique is ingenious and should give acceptable osmium values provided that the osmium in the ore sample can be volatilized, preferably quantitatively. No data were included concerning this necessity. It is a fact that certain osmium minerals will fail to release osmium even at high temperatures and for these at least it is most improbable that the oxidants used would prove effective. Furthermore, the author's method of preparing standards is unacceptable in that there is the assumption that the decomposition characteristics of the osmium mineral approximate to those of a hexachloro-osmate. In any case, the method invites a more complete examination than that provided by the author. It would be interesting to learn why the author considered the method acceptable merely because "the curves of osmium evaporation, obtained for standards and natural samples are nearly the same."

In order to increase the sensitivity of spectrochemical methods for traces of impurities, Tymchuk, Russell and Berman[117] used a carrier distillation technique. The halides of copper, particularly the chloride and fluorides, provided sensitivity enhancement factors of up to 20-fold for some impurities in copper. With copper fluoride the sensitivities achieved were at least equivalent to, and in many cases an order of magnitude greater than those obtained by the globule method. The authors found indications that these carriers could be used effectively for determining impurities in silver and the noble metals.

For the preparation of standards for noble metals Vorsatz[118] used pieces of filter paper impregnated with known amounts of impurities and the burned these in the arc in contact with a globule of the pure noble metal. This method obviously will have very restricted applications.

Visual spectral analysis with the steeloscope was applied by Pomylov[119] to determine palladium, platinum, rhodium, iridium and gold over the range 0·025–0·1%. An error of ±15% was claimed and the time required was less than 2–3 min. The accuracy was evaluated from synthetic samples and by a spectrochemical method. Unfortunately the original article was not available to us.

X-RAY FLUORESCENCE

In a discussion on the uses of X-ray fluorescence in mining operations, Zimmerman[120] stated "the main advantage of the X-ray method that appeals most to industry is the speed of getting results. It is not uncommon to have results within half an hour of receiving the sample. . . ". Other advantages include the provision of both qualitative and quantitative analysis, and the non-destructive nature of the method. It would seem that while atomic-absorption and polarographic methods for noble metals in ores *etc.* are competing techniques, the relative cost and maintenance place the X-ray fluorescence method in a distinct category. The area of application for noble metals indicates close competition with optical spectrochemical methods but for some determinations, narrower scope and sensitivity.

Gold

In ores. From time to time efforts have been made to develop methods for the determination of gold in ores which would compete with or prove superior to the classical assay methods. Mitchell, Saum and Hiltrop[121] were interested in this problem because of the time expended by Alaskan assayers in providing gold values for amateur prospectors who were given this service free of charge. Their approach to the problem involved the usual dissolution of gold in *aqua regia* and evaporation. The value of a gold assay bead as a standard is of course questionable. Working solutions contained 0·1687–6·748 mg of gold. The gold solution was treated with sodium carbonate and cyanide, heated, then electrolysed for 150 min at 3·0–3·5 V with a platinum anode and a copper sheet cathode cut to fit the sample holder. The copper with its deposit of gold was dried in air and the intensity of the $L\beta_1$ line at $2\theta = 31{\cdot}19°$ was determined along with the background. The authors state that the "method has not as yet been applied to the determination of gold in a naturally occurring rock or mineral." While the proposed method has a good deal of merit and its applications ought to be extended, it will not, in general, prove to be a serious competitor to fire assay.

X-ray spectrometry was used by Pietzner and Werner[122] to determine gold in sulphide ores in the range 0·05–5 ppm. Gold was precipitated by the addition of tin(II) chloride and potassium tellurite to the filtrate from an *aqua regia* solution of a 20-g sample, and heating, the tellurium serving as collector. Selenium as sodium selenite was added as internal standard. The precipitate was collected on a membrane filter, and washing it needed care. To avoid drying out, which disrupts the layer, the filter and residue were placed in a closed container along with a filter paper moistened with perhydrol. The resulting oxidized state provided a background sufficiently low to allow the detection of 0.05 ppm of gold. The filter and residue were placed in the container between two mylar sheets. Interfering K_β radiation from the molybdenum target was avoided by the use of a zirconium filter, and background interference was further reduced by using a discriminator. Calibration covered the range 0·05–5·0 ppm and the count-rates for gold L and selenium K_α radiation were plotted. The coefficient of variation varied from ±54% for 0·05 ppm to ±19% for 5·0 ppm. The larger amounts of precipitate did not adhere properly to the filter. At concentrations below 1 ppm the accuracy was considered to be satisfactory for geochemical purposes. The authors provided gold values obtained from various types of ore samples but results such as these lose much of their significance in the absence of a comparison with some acceptable analytical procedure. The authors believe that "the procedures described in the literature do not afford a direct determination of gold." Very little ingenuity is required for the development of a similar acid extraction and the application of one or more of the sensitive spectrophotometric methods. The authors' method is worthy of extended examination and application to appropriate gold ores, and it is not unlikely that the precision could be greatly improved.

X-Ray fluorescence methods for the determination of gold alone, in the presence of platinum metals in hydrochloric acid solutions, and in silver assay beads were recorded by Chow and Beamish.[123] Applied to solutions the method proved to be a rapid and accurate alternative to spectrophotometric and titrimetric methods with the advantage that platinum metals did not interfere appreciably. The gold L_{β_1} line at $2\theta = 31{\cdot}19°$ was used. The blank was obtained from a solution containing the same constituents as the sample, except gold. About 10 ml of sample solution was found to correspond to infinite layer thickness. Because gold solutions are decomposed by ultraviolet light a fixed irradiation time of 10·0 sec was maintained. At least five aliquots were counted and the average deviation was always less than 1%. The counting rate was affected by large variations in hydrochloric acid concentration; an increase from 0·25 to 0·50*M* decreased the counting rate by 7%. The results showed good consistency for the range 40–1000 ppm. Equal amounts of platinum metals gave results 0–5% low. The high background was reduced by about 7% with a pulse-height analyser. The same instrumental conditions could be used for silver beads. The use of a blank eliminated changing the goniometer settings for a set of samples as well as adjustment errors and interference from reagent impurities. The homogeneity of several beads was checked, and the average deviation was not more than 1%. Repeated counting of the same area showed a deviation of less than 0·5%. Pulse-height analysis eliminated some of the interference from silver. No significant gain in precision was achieved by counting for longer than 100 sec. The useful concentration range was 0·2–5% or 20–500 μg of gold in a 10-mg silver bead. Some beads were dissolved and the gold determined by X-ray fluorescence and by the spectrophotometric bromoaurate method; the results agreed reasonably well with the direct determination. There was no interference from platinum, palladium and iridium.

In molybdenum wire. For the determination of gold deposited on a molybdenum wire, Lassner[124] dissolved the wire in *aqua regia* and added mercury as an internal standard. No internal standard was required for the determination of gold from a plating solution.

Platinum

In assay alloys. To determine platinum by an X-ray method Losev[125] dissolved the assay regulus in dilute nitric acid, added tantalum as a comparison element, evaporated the solution, ignited the residue and then ground it. The analytical lines used were the platinum L_{α_1}, tantalum L_{β_1} and L_{β_2}. For concentrations less than 0·5% the regulus was first treated with dilute sulphuric acid to dissolve the silver.

In aluminium catalysts. A method for the determination of platinum in alumina base reforming catalysts by X-ray spectroscopy was described by Lincoln and Davis.[126] The work was conducted in two laboratories with identical equipment except that one laboratory used a molybdenum tube and the other a tungsten tube. With the molybdenum tube the L_{β_1} line at $2\theta = 32{\cdot}29°$, was chosen because the background was smooth and flat. With the tungsten tube the background was complicated by the large number of target lines and there was little to choose between the L_{β_1} and L_{α_1} line except that the latter gave higher intensity and a better slope to the calibration curve.

With the molybdenum tube a 99% aluminium–1% platinum alloy was used as external standard; this method proved to be self-compensating and the calibration curve was used for 2 years. With the tungsten tube the external standard method did not compensate for daily variations in instrumental sensitivity and a calibration curve had to be prepared daily, after a 2-hr warming-up of the instrument. The standard deviation was about 0·0025% at the 0·6% platinum level. The elapsed time between receipt of the sample and the result was about 3 hr, with about 30 min attention being required. The accuracy of the two methods was comparable.

It is of interest that Lincoln and co-workers[127] used X-ray diffraction methods for the direct determination of the amount and the crystal size of metallic platinum in alumina-based catalysts containing about 0·5% total platinum. This work is of analytical significance in that the efficiency of the method of production and application of the catalyst is affected by the dispersion of the platinum and by factors causing agglomeration and redispersion.

Osmium

An X-ray fluorimetric determination of osmium was described by Neeb.[128] In principle the method involved the precipitation of an osmium complex on a filtering medium prepared by soaking in ethanolic solutions of tetraphenylarsonium chloride, tetraphenylphosphonium bromide or benzyltriphenylphosphonium chloride and drying. A 40 × 40 mm filter-tablet absorbed 0·5–1 ml of the sample solution. With 50 μg of osmium as chloride or 20 μg as bromide a sharp stain a few mm in diameter was formed. The technique must be applied with precision. After drying, the tablets were cut into 15 × 20 mm pieces for X-ray examination. The optimum counting time was predetermined by calculation. With a lithium fluoride crystal the $L_{\beta 1}$ line was used; the background was obtained by measuring the impulse frequency at an angle 20′ from the line maximum. Instrumental errors were checked by using a 50-μg osmium standard. The optimum acidity had to be found experimentally for each type of reagent paper. The osmium concentration was 2·6–90 μg/ml. For amounts of osmium less than 0·5 μg/ml the benzyltriphenylphosphonium chloride reagent was unsuitable. The other two papers could be used for 0·3 μg of osmium in hydrobromic acid solution. For quantities up to 5 μg the relative standard deviation was about 5% and higher for smaller amounts of osmium. The method was used to determine osmium in the presence of ruthenium, iridium, palladium, rhodium and neutral salts. In hydrochloric acid media there was no interference from traces of palladium, platinum and iridium(IV), but large quantities altered the precipitation characteristics and also produced matrix effects. Rhodium and ruthenium were without effect. In hydrobromic acid media large amounts of these metals also interfered and ruthenium in more than traces produced low osmium values. Potassium bromide in hydrobromic acid interfered when present in large amounts; sodium chloride was without effect. No evidence was given for complete recovery other than the standard deviation.

Ruthenium

A method has been developed for the anion-exchange paper isolation of ruthenium and its subsequent determination by X-ray fluorescence. Taylor[129] used solutions containing 10–150 μg of ruthenium, evaporated to dryness in the presence of sodium chloride. The residue was dissolved, diluted to 20–25 ml and adjusted to pH 1–3. The solution was filtered twice through anion-exchange paper and washed with hydrochloric acid at pH 1–3. Uniform distribution on the paper was achieved by using a modification of the filtering apparatus described by Campbell *et al.*[130] The paper was removed, pressed flat between two filter papers, then allowed to dry completely. For the X-ray work the $K_{\alpha 1}$ line ($2\theta = 18·37°$, LiF crystal) was used in preference to others because of its high intensity and the relatively low interference. Readings from both sides of the paper were averaged. Instead of a background correction, blanks were carried through the procedure; there was no significant difference in counts for rather wide variation in sodium chloride concentration. The ruthenium values agreed closely with those obtained by treating the disks used for the X-ray determination with sodium hydroxide solution and chlorine gas, collecting the tetroxide in cold hydrogen peroxide and determining ruthenium with thiourea. This anion-exchange collection and X-ray fluorescence method can also be applied to osmium.[131]

In uranium. A method of direct assay of molybdenum and ruthenium in uranium by X-ray emission spectrometry was described by Flikkema and Schablaska.[132] The flat surface of the sliced and polished ingot was examined for the *K* emission of ruthenium and molybdenum with counting times of 1–8 min. The results were obtained from plots of intensities *vs.* chemically determined content.

Noble metal alloys

In dental alloys. An X-ray spectrometric method for the analysis of dental alloys was recorded by Mulligan *et al.*[133] The alloys contained about 70% gold, 10% copper and silver, and 2% platinum, palladium and zinc. Samples were prepared for analysis by investment casting with crystobalite and gypsum in a wax dish, then cast into a 0·8-mm thick dish which was mounted in methyl methacrylate resin, polished and then subjected to X-ray analysis. The optimum conditions were listed for each of the six metal constituents, a lithium fluoride crystal and molybdenum target being used. The lines used were $L_{\beta 1}$ for gold, L_{α} for platinum and K_{α} for silver, copper, palladium and zinc. The coefficients of variation were: gold 0·34%, silver 0·44%, copper 2·2%, platinum 1·0%, palladium 1·2% and zinc 0·72%. Each alloy was also analysed chemically. Losses of constituents during the sample preparation were found to be negligible.

In a progress report Eick *et al.*[134] also described an X-ray fluorescence method for the analysis of dental alloys. Determinations of palladium, platinum, gold, copper and zinc could be completed in about a tenth the time required for conventional wet chemical methods. The authors applied their method to dental gold casting alloys and gold binaries, cast into flat disks 0·8 mm thick and 32 mm in diameter. Discrepancies in the concentration of gold amounted to as much as 8%. The non-linear calibration curves for both gold and silver were attributed to complex interelement absorption and enhancement effects and were corrected by applying the Lucas-Tooth and Price equation.[135] In the case of alloys of copper, palladium, platinum and zinc, no correction was required, the maximum composition discrepancy amounting to 0·2%. Excellent agreement was obtained between values from chemical and X-ray procedures. The X-ray lines were: gold $L_{\beta1}$ 1·083 Å, palladium K_α 0·585 Å and platinum $K_{\alpha1}$ 1·313 Å.

In fissium alloys. X-ray fluorescence determinations of ruthenium, rhodium, palladium, zirconium and molybdenum in solutions of uranium-base fission alloys were made by Karttunen[136] with a tungsten tube, and lithium chloride crystal. Because of the complex composition of the fission alloys, containing 5–25% of "non-fertile material," the author used a series of separations rather than internal standards or a suitable calibration technique. Removal of uranium alone failed to remove all of the direct X-ray line interference and negative absorption. With low palladium content, 5–10% fissium alloy, the palladium was extracted as the dimethylglyoximate with chloroform. The chloroform was evaporated and the palladium converted into the chloride and the content adjusted to 0·3–1·5 mg/ml. The K_α line, $2\theta = 16{\cdot}70°$, was used and the time required for 10^5 counts was determined and compared with that from standard palladium solutions. Passage of the aqueous phase through Dowex 1 anion-exchanger gave an eluate containing rhodium(III) and zirconium, which were determined on separate aliquots, the rhodium after extraction of zirconium with TBP. The absorbed uranium was eluted with 0·03*M* hydrochloric acid and discarded. Ruthenium(IV) and molybdenum(VI) were then eluted from the exchanger with 8*M* nitric acid, and after further treatment were determined simultaneously. A faster alternative procedure was also proposed. The greatest source of error was said to arise from the chemical separations. The greatest loss of palladium was thought to occur by incomplete dissolution of the palladium salt after the chloroform was evaporated, a conclusion with which we do not concur, but which could have been easily verified. Recovery was 91% for ruthenium and 95% for rhodium. It would be of interest to learn the reasons behind the author's suggestion for improving the rhodium recovery.

In matte. Procedures for the X-ray determination of platinum, gold and iridium in matte solutions were described by Strasheim and Wybenga.[137] Because of overlapping lines, the authors preferred a molybdenum target to tungsten. A pulse-height analyser was used to avoid interference from molybdenum lines, Compton scattering and second-order lines of associated elements. For platinum a lithium fluoride crystal was used and a topaz crystal was found satisfactory for 200–600 ppm of gold and iridium in the presence of 0·7–1·0% of platinum. The hydrochloric acid solutions of the matte containing nickel, iron, 0·5% copper and 0·7–1·0% platinum were diluted with 10% hydrochloric acid to eliminate interference from the copper K_β line. For gold and iridium the matte solutions were used directly. To determine the stability of the apparatus the authors used a 300-ppm platinum solution and the time required for 256000 impluses was measured from the platinum $L_{\alpha1}$ peak, with zinc as a reference metal. It was concluded that (1) the relative standard deviations were $<0{\cdot}4\%$ for platinum and zinc intensities and $<0{\cdot}5\%$ for platinum–zinc intensity ratios after a warm-up period of 30–40 min; (2) the maximum deviation for individual counts within 4 days was less than 2%; (3) changes in room or sample temperature were without effect and evacuation of the crystal chamber showed a 10% increase in sensitivity but no change in stability; (4) the platinum concentration decreased after about 5 days, because of either photochemical reduction or adsoprtion on the wall of the holder. Changes in the matrix composition resulted in changes of peak-to-background ratios and both intensities were considerably lowered by an increase in matrix density.

To correct for the matrix effects the ratios of background intensities for a standard solution and a second matrix, were plotted against the ratios of the corresponding intensities of the platinum L_α line for the same solutions and produced a straight line with a slope which was the correction factor for each of the different matrices. In effect the correction could be interpreted as the intensity for the unknown platinum solution determined in the absence of the matrix. The graph also allowed direct determination of the platinum.

Samples were first examined to find the approximate platinum concentration and if necessary diluted to give a level of about 300 ppm of platinum. Two standards were measured at the same time, one with higher and one with lower platinum concentration than the unknown. Peak and background intensities were measured; the angle at which the background was determined affected the result.

Measurements must be made at a safe distance from interfering peaks, this distance being influenced by the concentration of the interfering element.

An internal standard method was also used, with the zinc $K\alpha$ line at 1·437 Å, which was close to the platinum $L_{\alpha 1}$ line at 1·313 Å. Gold and iridium were determined from their intensity ratios to the platinum at the $L_{\alpha 1}$ peaks, both calibration and a standard addition method being used. For platinum the detection limit was about 1 ppm, corresponding to 5 counts above the background, with a total of 256000 counts for both measurements.

The precision of the correction factor method was slightly better than that of the internal standard method and the results from both were in good agreement with those from a chemical and an atomic-absorption method. The coefficients of variation were 0·6–1 % for platinum and 1·3–3·0 for gold and iridium. For iridium, though the X-ray results agreed well, those from the chemical method were quite low and it is unfortunate that the method was not identified, particularly in view of the authors' acknowledgement that the cause of the low values was not known.

Wybenga and Strasheim[138] also used X-ray fluorescence to determine palladium, rhodium, and ruthenium in solutions of matte in an extension of their application of X-ray fluorescence to determine platinum, gold and iridium in similar matte solutions. The use of an internal standard method for palladium was investigated, and molybdenum, the only suitable element not present in the matte solutions, was tested but without success. They therefore used the background correction made in the vicinity of the analytical method[137] just described. Palladium was used as a variable internal standard for the determination of rhodium and ruthenium. The background value adjacent to the palladium $K\alpha$ peak showed a slight increase with higher palladium concentrations but the rhodium–ruthenium ratio remained fairly constant. The results for palladium agreed well enough with those obtained by atomic absorption and an unidentified chemical method. The rhodium results were comparable to those obtained by an unidentified chemical method but with ruthenium the agreement was only approximate. It is unfortunate that the chemical methods were not identified.

Rhodium and platinum alloy. Brief directions for the X-ray fluorescence determination of various elements including rhodium, and alloys of rhodium and platinum, were described by Rabillon and Griffoul.[139] They used the tungsten cathode tube, the $K\alpha$ line of rhodium and a lithium fluoride crystal. The sensitivity limit was about 500 ppm of rhodium.

In noble metal solutions. An X-ray spectrographic determination of platinum, palladium, rhodium and iridium was described by Hakkila.[140] Samples (1 ml) were adsorbed on Eaton-Dekeman No. 652 chromatographic paper and dried. Intensity measurements were made at the platinum $L_{\alpha 1}$, palladium $K\alpha$, rhodium $K\alpha$, and iridium $L_{\alpha 1}$ lines. Interferences from adjacent lines were corrected for from calibration curves. No enhancement or absorption interferences were found in the concentration ranges studied. Palladium was used as internal standard for rhodium determination in the range 0·01–0·10 mg/ml. The method was accurate to 7 μg/ml in the presence of a large excess of iridium. Three different methods of separating rhodium and iridium in the presence of chloride and EDTA were discussed.

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Zusammenfassung—Diese Übersicht setzt frühere Übersichtsartikel fort und umfaßt den Zeitraum der Abstracts bis einschließlich April 1967. Arbeiten über Atomabsorptions-Bestimmung von Edelmetallen sind auch aufgenommen.

Résumé—Cette revue est une suite des revues initiales et couvre la. période d'analyse jusqu'à et y compris Avril 1967. Le travail sur la détermination des métaux nobles par absorption atomique est également inclus.

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SEMIPERMEABLE ION-EXCHANGE MEMBRANES AS A PRECONCENTRATION MATRIX FOR TRACE ANALYSIS BY ELECTROCHEMICAL AND NEUTRON-ACTIVATION TECHNIQUES*

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Summary—Ion-exchange membranes were used in conjunction with neutron-activation analysis and anodic stripping voltammetry for the determination of certain trace metal ions. The various parameters which govern the applicability, limitations and sensitivity of the methods were investigated. A new membrane "barrier" electrode assembly was introduced and found to be useful for the anodic stripping determination of trace metal ions in the presence of surface active materials.

THE application of the mercury-membrane electrode for voltammetry was introduced by Bowers and Wilson[1] and was discussed in detail by Bowers and Murray.[2] The membrane in this case was cellophane and acted as a fixed diffusion layer for the electroactive species to the electrode. These studies discussed in detail the diffusion model of the electrode process and its possible application to direct voltammetric analysis.

In a preliminary communication,[3] a new electrode assembly for the anodic stripping technique was introduced in which the electrode material was pyrolytic graphite and a cellophane membrane acted as a diffusion layer. The use of membranes was also extended to ion-exchange membranes. These membranes, recently introduced commercially, are produced as sheets which are homogeneous in composition with respect to the ion-exchange sites and their polymeric skeleton is polyethylene which is stable towards most acids, bases, and oxidants. The ion-exchange capacity of a particular membrane (Type C-103 manufactured by the American Machine and Foundry Co., Springdale, Conn.) was similar to that of regular ion-exchange resins and was 1·3 meq/g. (The usual application of these ion-exchange membranes is in electrodialysis, and a summary of the theoretical and experimental application of these membranes is given by Helfferich.[4])

Ion-exchange membrane electrodes have also been used in potentiometric precipitation[5] and acid-base[6] titrations. A recent paper described the application of ion-exchange membranes for enrichment of trace amounts of cations from large volumes of dilute electrolyte solution into a small volume of highly concentrated electrolyte solution.[7] The membrane separated the two electrolyte solutions.

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The high affinity of the ion-exchange membranes for trace metal ions makes them suitable for use as a preconcentration matrix. After equilibration in the test solution they can be mounted in front of an electrode (as described in Ref. 3) for use in an anodic stripping technique. The membrane then acts as a reservoir of ions to be deposited on the electrode. This technique is most useful when direct anodic stripping is not possible because of inhibition of the electrochemical process by certain species such as surface active agents in the solution. The electrode itself can be either pyrolytic graphite or a mercury plated graphite electrode. Thus a wide range of potentials is covered which allows for the determination of most metal ions. Provided that the concentration of ions in the membrane is linearly related to their bulk concentration in the solution, the latter can be calculated. The pre-equilibrated membrane can also be analysed by neutron activation. This permits determination of species which are not suitable for electrochemical measurements and of species which are especially suited for trace analysis by neutron activation. The two techniques have special conditions under which one is favoured over the other, as explained below.

The emphasis in this paper will be on the determination of the various parameters which govern the applicability of the ion-exchange membranes as a preconcentration matrix.

EXPERIMENTAL

Reagents and apparatus

All reagents were analytical grade and were used with no further purification. Demineralized water, which was then distilled twice (with potassium permanganate in the first stage of distillation) was used for preparing all stock solutions and for further dilutions.

Standard stock solutions of $0{\cdot}1M$ concentrations were made for each of the ions; silver, copper, cobalt and indium used in this study. Working solutions were prepared daily by dilution of the stock solutions.

The zinc tracer solutions were prepared by irradiating 2 mg of zinc metal, encapsulated in quartz, for 24 hr in the reactor. The irradiated metal was than dissolved in nitric acid and the solution diluted to 10 ml. The activity of the final solution ($3{\cdot}28 \times 10^{-3}M$ in zinc) was about 30000 cpm/ml.

Before use, the ion-exchange membranes were washed in $1M$ potassium hydroxide to remove oil and surface contaminants and then washed in $1M$ nitric acid and twice-distilled water. The washed membranes were stored in water until use.

The construction and operation of the membrane "barrier" electrode assembly has been described previously.[3]

The electrodeposition and anodic stripping voltammetry were carried out with a three-electrode unit, constructed from the basic operational amplifier circuits of DeFord,[8] and were recorded by a Mosley Autograph model 2D-2M X–Y recorder. The scan rates used throughout this work were 5–30 mV/sec.

All irradiations were carried out in the Ford Nuclear Reactor of the Michigan Memorial Phoenix Project, which has a thermal neutron flux (in the pneumatic tubes) of 5×10^{10} n.mm^{-2} . sec^{-1}. The gamma counting and spectroscopy of the irradiated samples were accomplished with an RIDL 400-channel analyser and a 75 × 75 mm NaI(Tl) scintillation crystal.

Preconcentration of the metal ion in the membrane

The cation-exchange membranes were equilibrated with the solution to be analysed, at a constant stirring rate. They were then removed and washed with water. The trace metal ion was determined either by neutron activation analysis or by anodic stripping voltammetry as described below.

Neutron-activation analysis. The equilibrated membranes were encapsulated in a polyethylene vial. The size of the membrane disc (diameter 10 mm) matched the inside diameter of the vial, so that there was no free movement within it. The pneumatic polyethylene rabbit was also milled so that this vial fitted it without free movement. Thus, a constant geometry for irradiation was maintained through the experiments, the neutron flux in the membrane being kept as constant as possible.[9]

After irradiation, the membrane was removed from the vial, enclosed in a new vial, and placed in the counting chamber. The process of removing and re-encapsulating took less than a minute, which permits the use of short-lived isotopes, with half-lives as short as 30 sec.

Anodic stripping voltammetry. The membranes were pre-equilibrated and washed, as described above, for the anodic stripping voltammetry determinations. The membrane electrode was assembled and electrolysis carried out with a solution of the supporting electrolyte alone. As the only ions that are available for deposition on the electrode are those initially attached in the membranes as counter-ions, stirring has no effect on the deposition step and the electrolyses were thus carried out in a quiescent solution. The dissolution step in the analysis was carried out in the same solution after removal of the membrane.

RESULTS AND DISCUSSION

The ions Ag^+, Cu^{2+}, Zn^{2+}, Co^{2+}, and In^{3+} were used to demonstrate the methods described in this paper. As these ions can be detected easily by radioactivation analysis, the different parameters to be considered in the exchange processes were investigated by this method. The effect of variation of these parameters is described below.

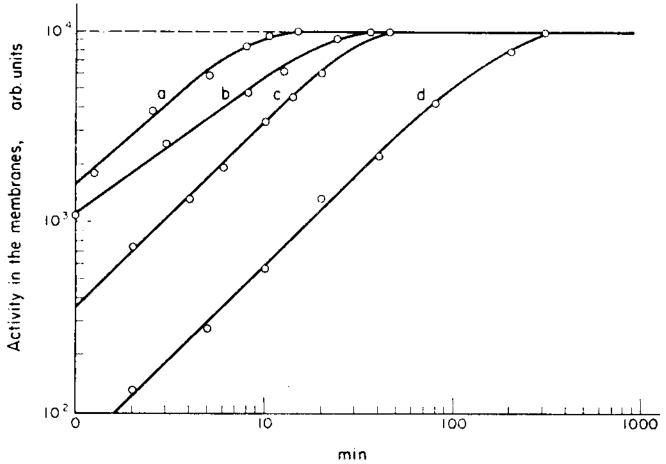

FIG. 1.—Equilibration time for membranes in various solutions.
(*a*) 3 × $10^{-4}M$ Co^{2+}, 0·1*M* KNO_3; (*b*) 2 × $10^{-4}M$ Ag^+, 0·1*M* KNO_3; (*c*) 2 × $10^{-4}M$ $Cu_2{}^+$, 0·1*M* KNO_3; (*d*) 2 × $10^{-5}M$ Zn^{2+}, 0·01*M* KNO_3.

Equilibration time of the membrane

The membranes were equilibrated in stirred solutions at 25°. As the concentration of the ion of interest is at trace level and the concentration of the counter-ion in the membrane is quite high (~1 meq/g), the exchange process can be described by the equations used for isotopic exchange governed by film diffusion. The rate of exchange is then proportional to the concentration of the trace ion diffusing to the membrane.[4]

The equilibration time for a trace metal concentration of 1 × $10^{-4}M$ was found to be about 30 min, for 2 × $10^{-5}M$ zinc it was 200 min (Fig. 1) and for $10^{-6}M$ indium 24 hr. (The zinc equilibration studies were carried out with the long-lived (235-day) ^{65}Zn nuclide as tracer, and for the other metal ions neutron activation was used to determine their concentration in the membranes.) The equilibration times for the trace metal ions were found to be essentially independent of the concentration of the alkali metal ions in the supporting electrolytes.

Determination of the distribution factor, D_i, *of the metal ion between solution and membrane*

The degree of enrichment of the metal ion of interest in the membrane is related to the ion undergoing exchange. The exchange is a dynamic process and the enrichment proceeds until the ion in the membrane reaches a certain equilibrium concentration. A useful way to define the extent of enrichment is the distribution factor, D_i:

$$D_i = \frac{\text{mg of metal in membrane/g of membrane}}{\text{mg of metal in solution/g of solution}}\,.$$

The D_i values are determined by several chemical characteristics of the various ions such as oxidation state, charge density, and size. The experimental values of D_i for the particular ions under investigation (in $0{\cdot}1M$ potassium nitrate) are shown in Table I.

TABLE I.—DISTRIBUTION FACTORS FOR VARIOUS IONS IN $0{\cdot}1M$ KNO_3

Ion	D_i
Ag^+	30
Co^{2+}	240
Zn^{2+}	250
Cu^{2+}	400
In^{3+}	13000

It is essential that the volume of the equilibrated solution be sufficiently large for the ion concentration in solution to remain virtually constant during the course of the equilibration experiment.

In contrast to the equilibrium time, the D_i values were found to vary with the concentration of the gross components (base electrolyte) in solution. In the case of ion-exchange resins, it is known that D_i is inversely proportional to the electrolyte concentration:[10]

$$D_i = \frac{\text{constant}}{A^{i/a}} \tag{1}$$

where A is the concentration of the electrolyte, i is the ionic charge on the trace element and a is the charge on the bulk ion.

A study was made to determine whether this relationship was valid for the ion-exchange membranes with potassium nitrate as the base electrolyte and Ag^+, Co^{2+}, Cu^{2+} and In^{3+} as the trace elements. While the plots of log D_i *vs.* log A were linear as expected, the slopes were $-0{\cdot}86$, $-1{\cdot}20$, $-1{\cdot}15$ and $-1{\cdot}25$ respectively (Fig. 2), considerably different from the predicted slopes[10] of $-1{\cdot}0$, $-2{\cdot}0$, $-2{\cdot}0$ and $-3{\cdot}0$. The reason for this disagreement is not yet understood but it is possible that the conditions imposed in deriving equation (1) may not be met in this case.[10]

Application of pre-equilibrated membranes as a preconcentration matrix for neutron-activation analysis

Analytical calibration curves in $0{\cdot}1M$ potassium nitrate were found to be linear over the concentration ranges 10^{-4}–$10^{-5}M$ for Cu^{2+} and Ag^+, 10^{-6}–$10^{-7}M$ for In^{3+} and 5–10 × $10^{-5}M$ for Co^{2+}. The factors which determine the sensitivity attainable by this preconcentration step are D_i and the usual parameters encountered in neutron activation. The parameters of importance for the ions Ag^+, Co^{2+}, Cu^{2+} and In^{3+} are summarized in Table II.

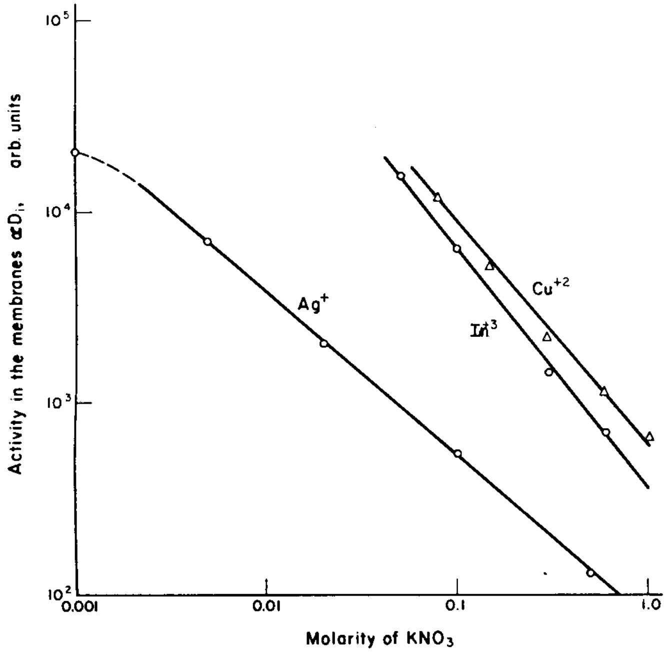

FIG. 2.—Dependence of the distribution factor of the trace ion on the concentration of supporting electrolyte.

TABLE II.—PARAMETERS AFFECTING SENSITIVITY OF ION-EXCHANGE MEMBRANES AS A PRECONCENTRATION MATRIX FOR NEUTRON-ACTIVATION ANALYSIS

Parameter	^{108}Ag	^{60m}Co	^{66}Cu	^{116m}In
D_i	30	240	400	13,000
σ (cross-section), *barns*	35	18	2·3	154
Abundance of parent, %	51·8	100	30·9	95·7
$t_{1/2}$, *min*	2·4	10·5	5·1	54
γ-Ray, *MeV*	0·63	1·33	1·04	1·27
Number of disintegrations per 100 atoms activated	2·0	0·28	9	83

These membranes can be used as a preconcentration matrix because they are essentially organic in nature and therefore do not themselves undergo any appreciable activation, as shown in Fig. 3, so the background from the matrix is very low.

For irradiation times of less than 5 min the lower limits of determination in $0{\cdot}01M$ potassium nitrate are $\sim 1 \times 10^{-6}M$ Ag^+, $5 \times 10^{-6}M$ Co^{2+}, $5 \times 10^{-7}M$ Cu^{2+} and $2 \times 10^{-10}M$ In^{3+}.

As several days are needed for equilibration of concentrations less than $10^{-6}M$, such determinations under equilibrium conditions are impractical.

However, as the rate of enrichment in the membrane is essentially linear with time up to approximately half the equilibrium concentration limit, the membranes could be left in contact with the sample solution for a fixed time interval, but considerable sensitivity would then be lost.

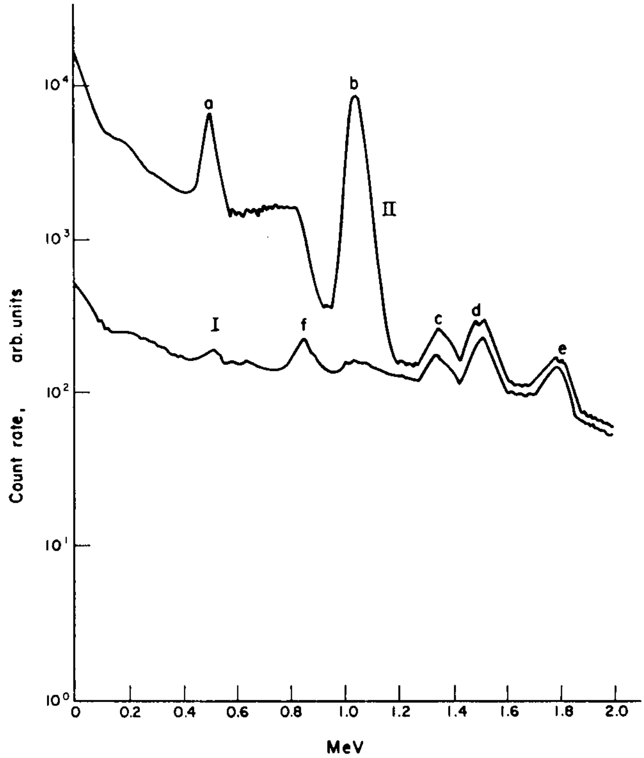

FIG. 3.—Gamma spectra of neutron-activated cation-exchange membranes. I. Equilibrated in 0·1*M* KNO_3; II. equilibrated in 0·1*M* KNO_3, $1 \times 10^{-4}M$ Cu^{2+}. (*a*) ^{64}Cu 0·51-MeV positron annihilation photopeak; (*b*) ^{66}Cu 1·04-MeV; (*c*) ^{27}Na 1·37-MeV; (*d*) ^{42}K 1·52-MeV; (*e*) ^{56}Mn 1·81-MeV; (*f*) ^{56}Mn 0·84-MeV.

The determination of trace elements in the presence of surface active materials by anodic stripping voltammetry

In the analysis of biological materials in waste water the problem of surface active agents arises. These agents tend to adsorb on the electrode surface and, in many cases, suppress electrodeposition and the anodic dissolution peak. As already mentioned the use of membranes can circumvent this problem.

It was previously suggested that the ion-exchange membranes could act as a simple diffusion barrier with respect to the organic surface active agents while allowing the metal ions of interest to diffuse unhindered to the electrode.[3,9] It was found, however, that the times for the deposition step of anodic stripping were extremely long. This is a result of the complex mode of transport of the metal ions through a medium containing ion-exchange sites. The rate of transport of the ions through the membrane increases to a maximum as the loading reaches equilibrium. However, this maximum rate of transport is still considerably less (about half) than that observed without the membrane. Even with thin cellophane membranes (which have far fewer exchange sites) the deposition times were excessive. Thus it was decided to place the membranes in the stirred sample solutions before mounting in the electrode assembly. In this way equilibration was reached faster. The equilibrated membranes were then mounted in the electrode assembly for stripping analysis.

A model system (silver ion in a supporting electrolyte of 0·1*M* potassium nitrate and 1*M* ammonia saturated with the surface active agent n-octanol) was investigated. The n-octanol adsorbs strongly on the electrode in the potential range from —0·1 to —0·9 V *vs*. S.C.E.[11] so that the silver peak is suppressed and distorted when normal anodic stripping voltammetry techniques are used.

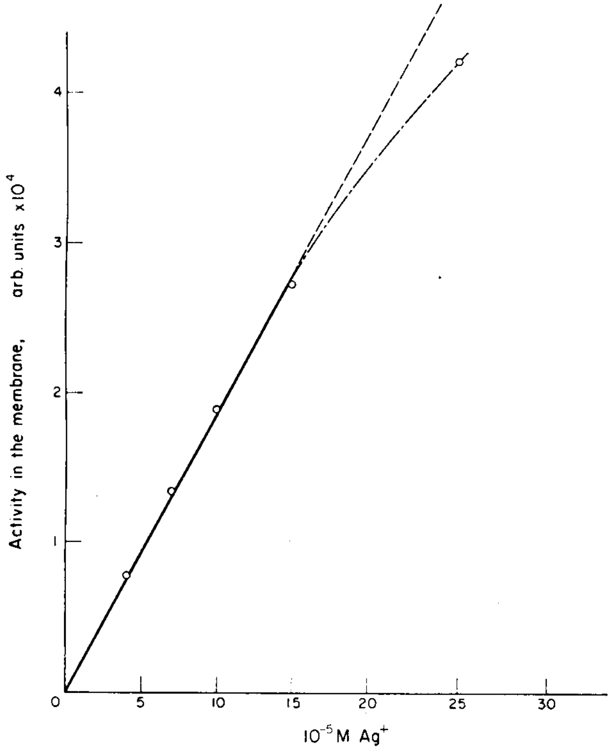

FIG. 4.—Calibration curve for silver in a solution saturated with n-octanol; supporting electrolyte 0·1*M* KNO_3.

Membranes were equilibrated in the octanol solution and in another solution which contained the same concentrations of all species except the n-octanol. Activation analysis showed that both sets of membranes took up the same amount of silver. Thus, the octanol itself does not cause any appreciable disturbance in the ion-exchange process and the equilibration time.

A calibration curve for equilibrated membranes in silver solution in the presence of n-octanol was found to be linear in the range 4–15 × $10^{-5}M$ (Fig. 4). Silver ion concentrations in this range were then determined by anodic stripping voltammetry with the membrane electrode assembly. An error of ±5% was obtained. The procedure was as follows: three membranes were equilibrated in the solution and after equilibration were removed and washed with ethyl alcohol followed by water to remove any octanol adhering to the membrane. The membranes were then mounted in the electrode assembly and electrolysis was carried out in a solution of the base electrolyte alone (0·1*M* potassium nitrate, 0·5*M* ammonia without octanol). The dissolution step was then carried out in the same solution after removal of the membrane.

This method cannot be automatically applied for the analysis of any solution containing surface active materials, as it must be ascertained whether the surface active agent undergoes a reaction with the ion under consideration. This can be illustrated by the following experiment: a solution containing $5 \times 10^{-5}M$ Cu^{2+} and 0·02% egg albumin showed no peak when a normal anodic stripping analysis was attempted. Equilibration of membranes in solutions containing various concentrations of copper ion showed a non-linear relationship between concentration of copper in the membranes and its concentration in the solution (Fig. 5 curve A). This indicates that the copper undergoes reaction with the albumin to form a complex.

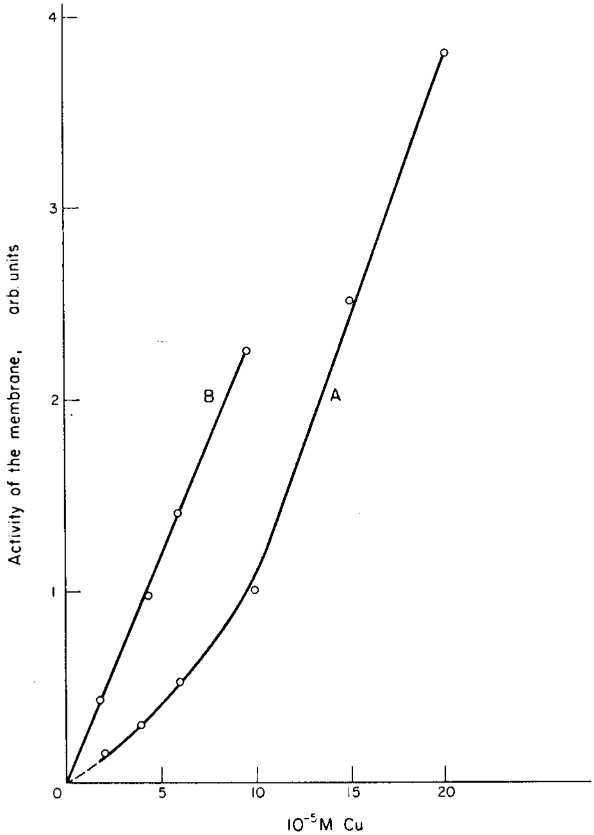

FIG. 5.—A. Calibration curve of copper in the presence of 0·02% albumin, supporting electrolyte 0·1M KNO_3 (a few drops of concentrated ammonia solution added to dissolve the albumin; for the two highest concentrations, the ammonia concentration was 0·1M).

B. Calibration curve of copper in the presence of 0·02% albumin, supporting electrolyte 0·1M KNO_3 and 0·1M ethylenediamine.

The complexation of copper ions by albumin has been discussed by Gurd and Wilcox.[12] Kolthoff and Willeford[13] found a stoichiometric reaction of copper with bovine serum albumin in an ammonia–ammonium nitrate buffer (pH 9·2). On the other hand there was no reaction between copper and human serum albumin under the same conditions.

In our case, the presence of $0{\cdot}1M$ ethylenediamine in the solution yielded a linear relationship between the concentration of copper in solution and its concentration in the membranes (curve B, Fig. 5). Equilibration of membranes in solutions containing $1 \times 10^{-4}M$ Cu^{2+}, $0{\cdot}1M$ potassium nitrate and $0{\cdot}1M$ ethylenediamine, showed the same uptake of copper in the presence and absence of egg albumin, indicating that the copper ions were complexed only with the ethylenediamine. When ammonia was used instead of ethylenediamine, it was found that even with $1M$ ammonia the concentration of copper in the membranes was 25% lower than in the presence of 0·02% albumin. The large difference in the formation constants of the two complexing agents accounts for this (log K_1 for Cu–NH_3 is 4·27 and for Cu–ethylenediamine 10·72).[14]

Zusammenfassung—Zur Bestimmung verschiedener Metallionen in Spurenmengen wurden Ionenaustauschmembranen in Verbindung mit Neutronenaktivierungsanalyse und anodischer stripping-Voltammetrie verwendet. Die verschiedenen Parameter wurden untersucht, die Anwendbarkeit, Grenzen und Empfindlichkeit der Methoden beeinflussen. Eine neue Membran-"Schranken"-Elektrode wurde eingeführt und zur Bestimmung von Metallionen in Spurenmengen durch "anodic stripping" in Gegenwart oberflächenaktiver Substanzen für nützlich befunden.

Résumé—On a utilisé des membranes échangeuses d'ions en liaison avec l'analyse par activation de neutrons et la voltammétrie de dissolution anodique pour le dosage de certains ions métalliques à l'état de traces. On a étudié les divers paramètres qui régissent les possibilités d'application, les limitations et la sensibilité des méthodes. On a introduit un nouveau montage d'électrode à "barrière" membrane et l'a trouvé utile pour le dosage par dissolution anodique d'ions métalliques à l'état de traces en la présence de substances tensio-actives.

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DETERMINATION OF RHENIUM IN MOLYBDENITE BY X-RAY FLUORESCENCE

A COMBINED CHEMICAL-SPECTROMETRIC TECHNIQUE*

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Summary—Rhenium in molybdenite is separated from molybdenum by distillation of rhenium heptoxide from a perchloric–sulphuric acid mixture. It is concentrated by precipitation of the sulphide and then determined by X-ray fluorescence. From 3 to 1000 μg of rhenium can be measured with a precision generally within 2%. The procedure tolerates larger amounts of molybdenum than the usual colorimetric methods.

RHENIUM occurs largely in molybdenite and in concentrations ranging from a few to more than 3000 ppm.[1,2] The predominance of molybdenum over the rhenium complicates the chemistry of the rhenium determination especially in colorimetric methods.[3–7] The separation of rhenium from molybdenum thus becomes essential, and is achieved by solvent extraction,[3,4,8,9] distillation from acid solution,[8,10–12] or both.[5,6] We chose distillation as being more convenient for our purposes.

Before exposure to the X-ray beam, the rhenium is concentrated by precipitation of rhenium heptasulphide on an arsenic carrier, by use of thioacetamide[13–15] instead of hydrogen sulphide.[16,17] A sulphide precipitate of improved quality and filterability is obtained by precipitation from homogeneous medium, and collected on a Millipore filter for the X-ray analysis.

The determination of rhenium by X-ray spectrometry compares favourably with the thiocyanate procedure of Geilman.[3,4,9] The X-ray method tolerates larger amounts of molybdenum, hence the need for complete removal of molybdenum is obviated. The method should be adaptable to the analysis of other rhenium-bearing minerals,[18] but so far has been applied only to determinations of rhenium in molybdenite and a few samples of wulfenite.

EXPERIMENTAL

Apparatus and reagents

Round-bottomed distillation flask, 500-ml Pyrex, standard taper ground joint (with stopper, wash-bottle type —see Fig. 1).

Culture tube, screw-cap type, 25 × 200 mm (or equivalent).
Fluorocarbon plastic tubing (Teflon or equivalent), 6-mm bore.
Glass tubing, Pyrex, 6-mm outside diameter.
Gas burner, Fisher type.
X-ray sample assembly (cap plug† with rings—see Fig. 1).
Mylar film, 0·00625 mm.
Filter funnel and strainer (or equivalent).
Microfilter (Millipore or equivalent), 45-μm pore size, 25-mm diameter.
Glass wash-bottle top to fit round-bottomed distillation flask.

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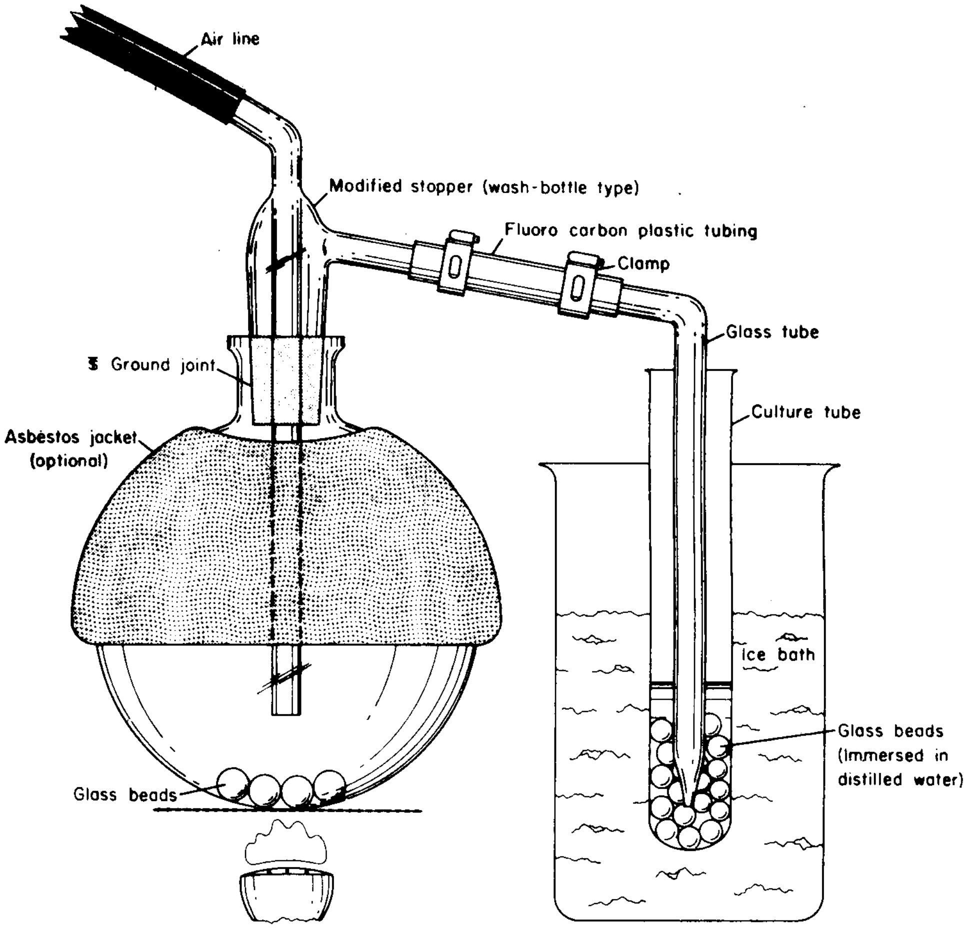
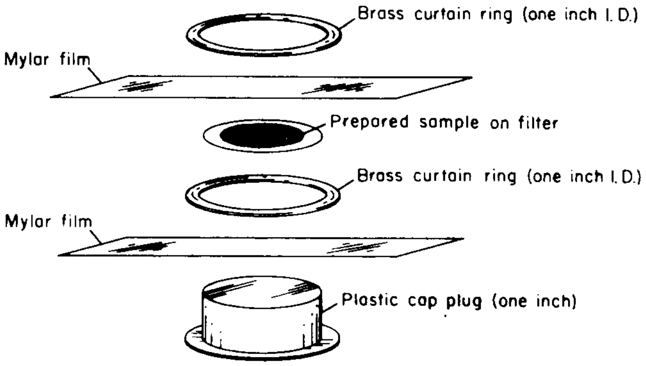
* Publication authorized by the Director, U.S. Geological Survey.

† *Caplugs* (No. EC-16) available from Protective Closures Co., Buffalo, N.Y.



DISTILLATION APPARATUS



X-RAY SAMPLE ASSEMBLY

NOTE: A third brass ring may be used, if required, as a spacer in X-ray sample holder

FIG. 1.—Sketch of distillation apparatus and sample holder assembly.

Potassium perrhenate (standard solution) 100 μg Re per ml. Dissolve 15·50 mg of pure (99·99%) $KReO_4$ and dilute to 100 ml.

Ammonium molybdate (standard solution) 100 μg Mo per ml. Dissolve 18·40 mg of pure ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and dilute to 100 ml.

Sodium arsenite solution, ~1 mg As/ml. Dissolve 0·132 g of As_2O_3 in approximately 1 ml of distilled water. Add one pellet (approx. 0·2 g) of sodium hydroxide and dilute to 100 ml.

Thioacetamide solution, 5% w/v.

Ammonium chloride–ethanol solution. Dissolve approximately 1 g of ammonium chloride in 100 ml of distilled water and dilute 3 parts of this solution with one part of ethanol.

Procedure

Weigh a sample of molybdenite (50-mesh or finer, washed free from flotation oil, and dried; should contain 30–50 μg of rhenium) and transfer it to a 500-ml distillation flask. Add 10 ml of concentrated sulphuric acid, 5 ml of concentrated perchloric acid, and a few glass beads. Attach the flask to the apparatus (Fig. 1), taking care to seat the condenser section carefully into the neck of the flask. A snug fit is required to minimize vapour loss during heating.

CAUTION. Steps 2–5 should be carried out in a fume hood equipped with a protective shield.

2. Heat the flask and contents gently until the molybdenite is completely decomposed, maintaining a positive pressure in the system (air-flow of 1 or 2 bubbles per sec). After the molybdenite has decomposed, increase the heat, and also the air-flow to 2 or 3 bubbles per sec, to distil the perchloric acid fraction.
3. Increase the heat to distil the rhenium heptoxide and sulphuric acid fraction, but increase the temperature gradually to prevent vapour leakage at the tapered glass joint. Again, adjust the air-flow and maintain it at a rate of 2 or 3 bubbles per sec.
4. Continue the distillation until only a few drops of acid remain in the flask (approx. 15 min).
5. Gradually reduce the heat to a low level and allow the system to reach pressure equilibrium during several minutes. Lower the receiver and collect all washings in the receiver.
6. Transfer the distillate to a 150-ml beaker and add all washings to the distillate. A filter funnel with a strainer (or equivalent) is used to facilitate this transfer and to recover the glass beads.
7. Add approximately 1 ml of sodium arsenite reagent and 2·5 ml of thioacetamide solution. Total volume of solution should then be approximately 100 ml. Stir thoroughly and allow to stand at room temperature (25°) for at least 16 hr, or overnight.
8. Disperse the sulphide precipitate into a fine suspension by vigorous stirring; collect this precipitate on a microfilter disk. Stir the suspension during filtration to ensure uniformity and a more homogeneous distribution of the precipitate.
9. Wash down the sides of the beaker with a few ml of the ammonium chloride–alcohol solution and pour all washings through the filter. Then wash the upper part of the microfilter and the precipitate carefully with 10–15 ml of the ammonium chloride–alcohol solution.

NOTE. Careful washing of the precipitate and entire filter disk after removal of the upper part of the microfilter is mandatory for precision and sample stability.

10. Allow the sulphide precipitate to dry on the filter disk for approximately 30 min (cover to minimize curling) and immediately mount the precipitate on the X-ray sample assembly (Fig. 1) between two sheets of Mylar film.
11. Analyse the prepared sample in the X-ray spectrometer. Reproducibility of the count rate is improved if the sample is allowed to stand for several hours, or overnight, before the count is taken.

Instrumental conditions

Generator power—20 kV at 20 mA.
X-Ray tube—Machlett type, FAQ 60 tungsten target, Be window (0·76 mm).
Optical path—air.
Detector-scintillation counter—operated at approximately 0·9 kV.
Analyser crystal—LiF.
Spectral line—Re L_{α_1} ($2\theta = 41{\cdot}69°$).
Pulse-height selection—optional, to suppress background.

Preparation of standards

Standards are prepared from a solution of pure (99·99%) potassium perrhenate. The required volume of rhenium standard solution is transferred into a 150-ml beaker containing 100 ml of 10% v/v sulphuric and 5% v/v perchloric acid solution. To each standard are added 100 μg of molybdenum (1 ml of ammonium molybdate standard solution), 1 ml of sodium arsenite reagent, and 2·5 ml of 5% thioacetamide solution. The solutions are thoroughly stirred and the beaker is set aside until precipitation is complete (at least 16 hr). The precipitate is then filtered off, mounted on the X-ray sample assembly as directed in *Procedure*, and counted.

A convenient set of standards contains rhenium levels ranging from 5 to 100 μg, in 5- and 10-μg increments. Standards containing higher levels of rhenium should be prepared if samples (distillates) containing more than 100 μg of rhenium are to be analysed.

A typical curve is shown in Fig. 2. Because of variations in instrumental counting-efficiency, it is generally necessary to prepare a new standard curve each day, or even more frequently, using the same standards.

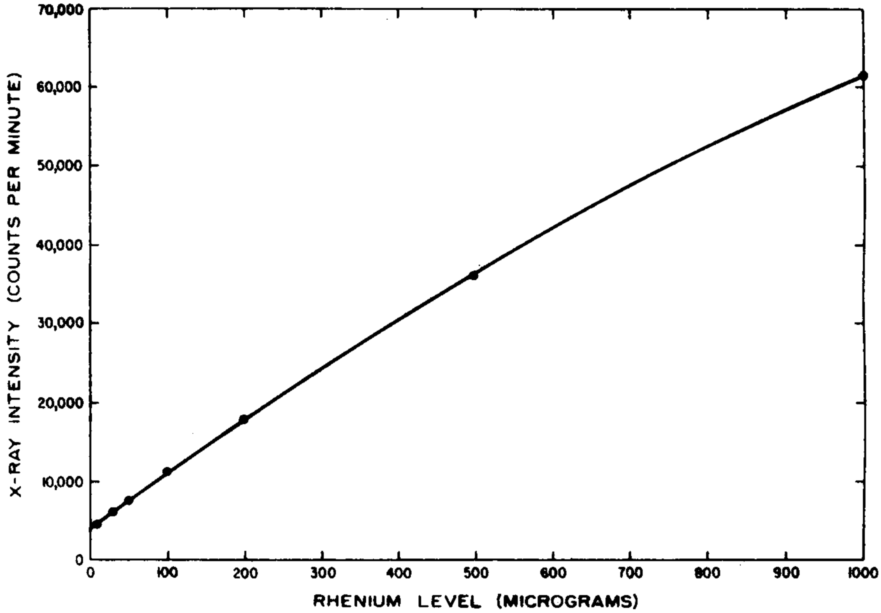


FIG. 2.—Typical calibration curve.

RESULTS AND DISCUSSION

The plot of X-ray intensity *vs.* rhenium level is linear from 3 μg to about 200 μg; the relative counting rate then decreases, this decrease becoming appreciable above 500 μg of rhenium (Fig. 2).

This decrease in the counting rate probably results from incomplete precipitation of rhenium, but there may also be absorption of the secondary X-radiation by the matrix. Tests on two 1000-μg standards to evaluate the recovery of rhenium showed that approximately 150 μg of rhenium remained in each of the filtrates after overnight precipitation. The standard curve used must therefore be extended if the rhenium levels exceed 200 μg.

The maximum amount of sample taken for analysis should not exceed 5 g. A larger sample usually results in lower rhenium recovery and in excessive spattering of accumulated salts, which may obstruct the air-line inside the flask. Of less importance is the increased molybdenum contamination which usually accompanies this spattering.

Table I lists the results of replicate determinations of rhenium on undistilled standards ranging from 3 to 1000 μg. Each determination is the average of 15 1-min counts. The statistical variations inherent in the X-ray method are generally minimized by this large number of counts, and the error caused by instrumental conditions

TABLE I.—DETERMINATION OF RHENIUM IN UNDISTILLED STANDARDS

Re added, μg*	Re found, μg	Std. dev. μg
3	3·5	1·3
	4·5	
	1·5	
5	5·4	1·0
	5·2	
	3·3	
10	10·4	0·8
	10·7	
	11·1	
15	15·0	0·7
	13·8	
	14·8	
30	30·0	0·4
	29·4	
	30·1	
50	50·0	0·6
	49·4	
	50·8	
100	100·3	1·9
	102·7	
200	201	1·2
	199	
500	491	7·0
	496	
1000	1010	8·6
	993	

* 100 μg of molybdenum added to each standard.

TABLE II.—RECOVERY OF RHENIUM FROM DISTILLED STANDARDS

Re added, μg	Re intensity, *cpm*		Recovery,* %
	Undistilled	Distilled	
30	2380	2400	100
50	3770	3600	95
100	7330	7210	98
			Mean 98

* Count rate of distilled samples relative to that of undistilled samples.

TABLE III.—EFFECT OF MOLYBDENUM ON DETERMINATION OF RHENIUM

Re added, μg	Mo added, μg	Re found, μg*	
		Count 1	Count 2
10	100	10·2	9·9
	1000	10·0	9·9
30	100	30·3	31·2
	1000	31·8	32·4
50	100	49·9	49·1
	1000	51·5	51·5

* Based on Re standard containing no molybdenum.

TABLE IV.—DETERMINATION OF RHENIUM IN MOLYBDENITE CONCENTRATES

Sample No.	Re content, *ppm*		
	X-ray	Colorimetric*	Other†
K-10-6‡	200, 220, 220	200, 240, 240	200, 200
P-9-10‡	400, 390	360, 390, 430	330, 370, 400
A-6‡	650, 650	580, 540, 660	530, 560, 580
35456 (1947)§	10, 12, 9	10, 9, 7	—
35458 (1955)§	11, 12	11, 10	—
CD 91¶	1200, 1000	1100, 1100	—

* Determined by acid distillation–thiocyanate colorimetric method (this laboratory).
† Determined by α-furildioxime colorimetric or equivalent method by other laboratories.
‡ Obtained from S. W. Shattuck Co., Denver, Colorado.
§ Obtained from American Metal Climax, Inc.
¶ Obtained from U.S. Geological Survey.

becomes less significant than that from the precipitation of the rhenium sulphide. The standard deviation is 2 μg in the 3–200 μg range.

Table II is a comparison of the counting intensities of distilled and undistilled standards after precipitation and indicates that about 95% (or more) of the rhenium added may be recovered from the distillate. This high recovery permits use of undistilled standards if required, as for example when time for a determination is limited. Distilled standards are preferable for greater accuracy and are mandatory for determination of rhenium levels much below 30 μg. The stability of the samples also permits the preparation of a set of standards which may be used for many determinations.

The effect of small amounts of molybdenum on the X-ray intensity of rhenium is shown in Table III. One mg of molybdenum in the distillate causes only a slight increase in the counting rate for rhenium. Lesser amounts of molybdenum cause almost no interference. It should be noted that the value shown in Table III is the molybdenum added to, rather than the molybdenum present in the precipitate, since molybdenum does not precipitate quantitatively under the conditions of this method. Further isolation of rhenium from molybdenum is not essential, and a small amount of molybdenum may be added to standards to simulate that usually found in the distillate of a molybdenite.

Rhenium determinations on molybdenite concentrates from various sources are reported in Table IV. Results obtained in this laboratory by both X-ray and colorimetric methods can be compared with results reported by other laboratories.

The rhenium content of molybdenite is easily determined by this X-ray procedure, results being generally equivalent to those obtained by the tin(II) chloride–thiocyanate colorimetric method. The X-ray procedure is more direct than the colorimetric method and has the added advantage that it can be adapted to the analysis of other rhenium-bearing minerals.

Rhenium levels as high as 1000 μg can be determined without modification of the procedure or use of aliquots. The standard deviation is 2 μg for 3–200 μg of rhenium, and the limit of detection is approximately 3 μg of rhenium in the distillate.

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Zusammenfassung—Rhenium in Molybdänit wird durch Abdestillieren von Rheniumheptoxid aus einem Überchlorsäure-Schwefelsäure-Gemisch von Molybdän getrennt. Es wird durch Fällung des Sulfids angereichert und durch Röntgenfluoreszenz bestimmt. 3 bis 1000 μg Rhenium können mit einer Genauigkeit gemessen werden, die im allgemeinen innerhalb von 2% liegt. Die Vorschrift verträgt größere Molybdänmengen als die üblichen kolorimetrischen Methoden.

Résumé—On sépare le rhénium dans la molybdénite du molybdène par distillation de l'heptoxyde de rhénium d'un mélange acide perchlorique-sulfurique. On le concentre par précipitation du sulfure puis le dose par fluorescence de rayöns X. On peut mesurer de 3 à 1000 μg de rhénium avec une précision généralement à 2% près. La technique tolère des quantités de molybdène plus grandes que les méthodes colorimétriques habituelles.

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CATION-EXCHANGE SEPARATION OF HAFNIUM AND ZIRCONIUM FROM ACCOMPANYING IONS*

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Summary—Hafnium and zirconium are not retained on the strongly acidic cation-exchange resin Dowex 50 from a mixture consisting of methanol and $12M$ nitric acid (19:1) which is $0{\cdot}1M$ in trioctylphosphine oxide. On the other hand most other elements investigated are strongly adsorbed on the resin from this medium so that they are readily separated from hafnium and zirconium. These elements include titanium, rare earths, alkali metals, alkaline earth metals, iron, cobalt, manganese and zinc. This separation technique has been found to be suitable for the separation of tracer and milligram amounts of hafnium and zirconium from accompanying metal ions. If in place of methanol other organic solvents such as acetone, tetrahydrofuran and methyl glycol are used the selectivity of the separation of zirconium and hafnium from the other elements is decreased. The same effect is observed when hydrochloric acid is used in the mixtures instead of nitric acid.

FROM pure aqueous $0{\cdot}1$–$1M$ nitric acid solutions zirconium and hafnium are strongly retained by strongly acidic cation-exchangers (*e.g.*, Dowex 50). The distribution coefficients that have been measured in these systems have values of $>10^3$–10^5.[1,2] At higher nitric acid concentrations the distribution coefficients decrease considerably and values of $>10^2$ and >10 have been measured in the acidity range from 2 to $4M$ nitric acid.[1,2] A very similar behaviour in nitric acid media is shown by many other elements, including the rare earths, chromium(III), heavy alkali metals and alkaline earth metals. Because of the very low selectivity, such systems can only be used to separate zirconium and hafnium from a very limited number of elements, *e.g.*, from beryllium.[3]

Similar conditions exist if nitric acid solutions are used which contain water-miscible organic solvents. From such media zirconium and hafnium are as a rule more strongly adsorbed on Dowex 50 than from pure aqueous solutions of comparable acidity.[4] However, as in the pure aqueous systems, only a very few elements can be separated from hafnium and zirconium.

It has been shown that zirconium and hafnium are much more highly extracted than many other elements from nitric, hydrochloric and sulphuric acid media into extractants such as trioctylphosphine oxide (TOPO)[5–7] or tri-n-butylphosphine oxide[12] dissolved in cyclohexane, carbon tetrachloride or other water-immiscible organic solvents. Because these extractants are also readily soluble in water-miscible organic solvents in the presence of a small amount of aqueous nitric acid, these systems can

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also be used as eluents in ion-exchange, making use of the principle of combined ion exchange–solvent extraction (CIESE) described earlier.[13]

In the present work the applicability of such organic solvent–TOPO–nitric acid systems for separating zirconium and hafnium on Dowex 50 from many other metal ions was investigated. As a result a highly effective and selective method for their separation has been developed.

EXPERIMENTAL

Reagents

Ion-exchange resin. Air-dried Dowex 50W-X8 (100–200 mesh; hydrogen form) was used for the column separations and for the batch experiments.

Trioctylphosphine oxide (TOPO). The pure reagent was obtained from Organic Chemicals, Rochester 3, New York; m.w. 386·65.

Organic solvents. The following reagent grade solvents were used: methanol (MeOH), acetone (Ac), tetrahydrofuran (THF), methyl glycol (monomethylether of ethylene glycol, MG) and glacial acetic acid (HAc).

Eluent solution, 0·1*M* TOPO in methanol–12*M* nitric acid (19:1).

Tracers. Nitric acid solutions of the following tracers were used: ^{181}Hf(IV), ^{95}Zr(IV)–^{95}Nb(V), ^{46}Sc(III), ^{169}Yb(III), ^{144}Ce(III), ^{241}Am(III), ^{54}Mn(II) ^{59}Fe(III), ^{60}Co(II), ^{22}Na(I), ^{137}Cs(I), ^{45}Ca(II), ^{85}Sr(II), ^{44}Ti(IV) and ^{65}Zn(II).

The radioactive measurements were made by standard counting techniques.

Determination of distribution coefficients

The batch distribution coefficients (K_d values) of hafnium, zirconium and other elements were determined by using the technique described earlier.[14]

Procedure

Pretreatment of resin bed. Resin (1 g) is soaked for about 5 min in a few ml of the eluent and the slurry is transferred to the ion-exchange column (250 mm long, 5 mm bore). The resulting resin bed is supported by a pad of glass or quartz wool and is washed with 5–10 ml of the eluent.

Sorption and elution. A mixture of 0·5 ml of 12*M* nitric acid containing up to 5 mg of hafnium and/or zirconium (plus ^{181}Hf and ^{95}Zr tracers) and other metal ions, with 9·5 ml of methanol containing 386 mg of TOPO, is cooled to room temperature and passed through the pretreated resin bed at a flow-rate corresponding to the back-pressure of the resin column (about 0·3 ml/min). Under these conditions many elements *e.g.*, rare earths, alkaline earth metals, alkali metals, iron, cobalt and titanium are strongly retained by the resin while hafnium and zirconium pass into the effluent. Elution of hafnium and zirconium is completed by passage (at the same flow-rate) of 10 ml of the eluent.

RESULTS AND DISCUSSION

Determinations of the batch distribution coefficients on Dowex 50 of zirconium and hafnium in organic solvent media containing 5% v/v of 12*M* nitric acid gave the results recorded in Table I. For comparison the results for pure aqueous nitric acid are included. It can be seen that in all cases both hafnium and zirconium are very strongly retained on Dowex 50. The extent of the adsorption of hafnium increases in the order W < MG < MeOH < THF < HAc < Ac. For zirconium-95 exact distribution values could not be obtained because of interference from its daughter niobium-95. Nevertheless it has been established that zirconium shows virtually the same adsorption behaviour as hafnium.

If, however, these media are made 0·1*M* in TOPO, the distribution coefficients of hafnium and zirconium drop to <1. These results are shown in Table II with the distribution data for 13 other metal ions. For effective separation of hafnium and zirconium from the other elements listed the methanolic medium is the most suitable.

TABLE I.—DISTRIBUTION COEFFICIENTS OF HAFNIUM AND ZIRCONIUM ON DOWEX 50 IN ORGANIC SOLVENT–12*M* NITRIC ACID (19:1)

Organic solvent	Distribution coefficients	
	^{181}Hf	^{95}Zr
Methanol (MeOH)	3×10^{4}	$>10^{3}$–10^{4}
Acetone (Ac)	$1\cdot1 \times 10^{5}$	$>10^{3}$–10^{4}
Tetrahydrofuran (THF)	$3\cdot5 \times 10^{4}$	$>10^{3}$–10^{4}
Methyl glycol (MG)	$1\cdot3 \times 10^{4}$	$>10^{3}$–10^{4}
Acetic acid (HAc)	$5\cdot2 \times 10^{4}$	$>10^{3}$–10^{4}
Water (W)	$7\cdot8 \times 10^{3}$	$>10^{3}$

TABLE II.—DISTRIBUTION COEFFICIENTS OF SEVERAL METAL IONS ON DOWEX 50 IN ORGANIC SOLVENT–12*M* NITRIC ACID (19:1) 0·1*M* IN TOPO

Metal ion	Organic solvent				
	MeOH	Ac	THF	MG	HAc
^{181}Hf	<1	<1	<1	<1	<1
^{95}Zr	<1	<1	<1	<1	<1
^{46}Sc	731	204	445	241	$2\cdot15 \times 10^{3}$
^{169}Yb	420	$3\cdot4 \times 10^{3}$	$5\cdot2 \times 10^{3}$	$1\cdot6 \times 10^{3}$	$>10^{4}$
^{144}Ce	$1\cdot64 \times 10^{4}$	$>10^{4}$	$1\cdot66 \times 10^{4}$	$8\cdot3 \times 10^{3}$	$2\cdot9 \times 10^{4}$
^{241}Am	$1\cdot27 \times 10^{4}$	$2\cdot76 \times 10^{4}$	$2\cdot17 \times 10^{3}$	$5\cdot56 \times 10^{4}$	$1\cdot1 \times 10^{5}$
^{54}Mn	$7\cdot3 \times 10^{3}$	9×10^{4}	$2\cdot35 \times 10^{3}$	$>10^{4}$	$6\cdot8 \times 10^{4}$
^{59}Fe	$2\cdot6 \times 10^{3}$	<1	<1	467	$>10^{2}$
^{60}Co	$4\cdot0 \times 10^{3}$	$2\cdot1 \times 10^{4}$	$1\cdot6 \times 10^{4}$	$1\cdot6 \times 10^{4}$	$7\cdot2 \times 10^{4}$
^{22}Na	167	$1\cdot85 \times 10^{3}$	$1\cdot42 \times 10^{4}$	210	$1\cdot28 \times 10^{3}$
^{137}Cs	$1\cdot1 \times 10^{3}$	$4\cdot8 \times 10^{3}$	$>10^{4}$	$>10^{4}$	$1\cdot45 \times 10^{3}$
^{45}Ca	426	441	460	490	470
^{85}Sr	$2\cdot4 \times 10^{4}$	$>10^{4}$	$>10^{4}$	$>10^{4}$	$>10^{4}$
^{44}Ti	330	20	<1	2·5	71
^{65}Zn	811	<1	<1	15	$>10^{2}$

TABLE III.—DISTRIBUTION COEFFICIENTS OF Hf, Zr, Ti, Fe AND Co ON DOWEX 50 IN 0·1*M* TOPO–METHANOL SYSTEMS CONTAINING 5% OF HYDROCHLORIC ACID OF VARIED MOLARITY

[HCl], *M*	Distribution coefficients				
	^{181}Hf	^{95}Zr	^{44}Ti	^{59}Fe	^{60}Co
12	<1	<1	46	<1	161
6	6	3·5	164	11	$1\cdot32 \times 10^{3}$
3	40	16	371	225	$5\cdot45 \times 10^{3}$
1	103	65	$1\cdot11 \times 10^{3}$	$6\cdot37 \times 10^{3}$	$7\cdot6 \times 10^{4}$

Other elements that are also strongly retained on Dowex 50 from this TOPO–methanol medium include magnesium, aluminium, chromium(III), nickel, copper, cadmium and lead, and these can also be separated from zirconium and hafnium.

Behaviour similar to that of hafnium and zirconium is shown by thorium(IV), uranium(VI) and niobium(V).

If in the TOPO–methanol system hydrochloric acid is used in place of nitric acid, zirconium and hafnium cannot be separated from iron or several other elements, *e.g.*, zinc, cadmium and scandium. Tables III and IV show that decrease in the acid concentration invariably increases the distribution coefficients. From Table IV it is seen that 6*M* nitric acid would be as suitable as 12*M* in the eluent used.

The effect of varying the concentration of TOPO was studied (Table V) and the distribution coefficients of zirconium and hafnium were found to increase with decrease in TOPO concentration, especially when the 6*M* nitric acid medium was used. The adsorption of hafnium and zirconium is also increased if methanol–3*M* nitric acid (9:1) 0·1*M* in TOPO is used, the distribution coefficients being 4·9 and 5 respectively. If the concentration of methanol is decreased below 90% v/v, TOPO is precipitated.

Table IV.—Distribution coefficients of hafnium and zirconium on Dowex 50 in 0·1*M* TOPO–methanol systems containing 5% of nitric acid of varied molarity

[HNO$_3$], M	*Distribution coefficients*	
	^{95}Zr	*^{181}Hf*
12	*<1*	*<1*
6	*<1*	*<1*
3	*20*	*19*
1	*250*	*214*

Table V.—Distribution coefficients of hafnium and zirconium on Dowex 50 in methanol–nitric acid (19:1) media containing varying concentrations of TOPO

[TOPO], *M*	Distribution coefficients			
	12*M* HNO$_3$		6*M* HNO$_3$	
	^{181}Hf	^{95}Zr	^{181}Hf	^{95}Zr
0·1*	<1	<1	<1	<1
0·05	<1	<1	8·3	<10
0·01	100	~100	728	$>10^2$
0·001	$6·7 \times 10^3$	$>10^3$	$2·5 \times 10^4$	$>10^4$
0·000	$3·0 \times 10^4$	$>10^4$	$>10^4$	$>10^4$

* At concentrations higher than 0·1*M* the distribution coefficients of hafnium and zirconium are also <1.

Investigation of the effect of metal ion concentration showed that the distribution coefficients do not change when the amount of hafnium or zirconium is varied from tracer quantities up to 10 mg. In all cases complete separations of hafnium and zirconium from the adsorbable elements (see Table II) were obtained. However, exceptional behaviour is shown by scandium which despite its high distribution coefficient is partially coeluted (about 1·4%) with hafnium and zirconium. Efficient separations of hafnium and zirconium can also be obtained with acetic acid in place of methanol in the eluent.

Zusammenfassung—Aus einer Mischung von Methanol und 12*M* Salpetersäure (19:1), die 0,1*M* Trioctylphosphinoxid enthält, werden Zirkonium und Hafnium an dem stark sauren Kationenaustauschharz Dowex 50 nicht zurückgehalten. Andererseits werden die meisten anderen untersuchten Elemente aus diesem Medium stark am Harz adsorbiert, sodaß sie gut von Zirkonium und Hafnium getrennt werden. Unter diesen Elementen sind Titan, die seltenen Erden, Alkali- und Erdalkalimetalle, Eisen, Kobalt, Mangan und Zink. Dieses Abtrennverfahren wurde zur Abtrennung von Tracer- und Milligrammengen Hafnium und Zirkonium von begleitenden Metallionen als geeignet befunden. Werden statt Methanol andere organische Lösungsmittel wie Aceton, Tetrahydrofuran und Methylglycol verwendet, so sinkt die Selektivität der Abtrennung von Zirkonium und Hafnium von den anderen Elementen. Dasselbe beobachtet man, wenn Salzsäure in den Gemischen statt Salpetersäure verwendet wird.

Résumé—Le hafnium et le zirconium ne sont pas retenus sur la résine échangeuse de cations fortement acide Dowex 50 à partir d'un mélange de méthanol et d'acide nitrique $12M$ (19:1) qui est $0{,}1M$ en oxyde de trioctylphosphine. D'autre part, la majeure partie des autres éléments étudiés est fortement adsorbée sur la résine à partir de ce milieu de sorte qu'ils sont aisément séparés du hafnium et du zirconium. Ces éléments comprennent le titane, les terres rares, les métaux alcalins, les métaux alcalino-terreux, le fer, le cobalt, le manganèse et le zinc. On a trouvé que cette technique de séparation est convenable pour la séparation de quantités de hafnium et de zirconium à l'état de traceur et à l'échelle du milligramme des ions métalliques qui les accompagnent. Si, à la place du méthanol, on utilise d'autres solvants organiques comme l'acétone, le tétrahydrofuran et la méthylglycol, la sélectivité de la séparation du zirconium et du hafnium des autres éléments décroît. Le même effet est observé lorsqu'on utilise l'acide chlorhydrique dans les mélanges au lieu de l'acide nitrique.

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SUBSTITUTED HYDROXYLAMINES AS ANALYTICAL REAGENTS

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Summary—The review deals with analytical applications of hydroxylamine derivatives. The defects of cupferron and versatility of *N*-benzoyl-*N*-phenylhydroxylamine in reaction with various metal ions is discussed. The application of the latter in chemical analysis is summarized and separation factors for some pairs of elements included. Suggestions for further use of this compound and other hydroxylamines are given.

THE substituted hydroxylamines include many reagents for analytical work, but so far only two seem to have been used much. These are the ammonium salt of nitrosophenylhydroxylamine (cupferron) and *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA). Reports describing the use of others are scanty although some are known to be sensitive and versatile. Two reviews[1] have been written describing some hydroxylamines considered to be potential reagents. Since 1961, applications in analytical procedures have increased enormously. Table I lists some hydroxylamine derivatives together with their relevant properties.

Cupferron as an analytical reagent

Cupferron has been known for a long time as a versatile reagent. It was first proposed as an analytical reagent by Baudisch.[2] The applications of this compound in chemical analysis have been described by Welcher[3] and others.[4–7] The use of cupferron in solvent extraction techniques goes as far back as 1896 when Bamberger and Ekecrantz[8] noted the solubility of cupferron-metal compounds in many water-immiscible solvents. However, it was Meunier[9] in 1934 who first used this substance for the extraction and separation of similar elements and since then it has often been used in analytical procedures.[10,11] Although cupferron is not as selective as might be desired, it has nevertheless proved to be of great value in chemical analysis, and some useful separations have been noted.[12–15] The conditions of pH required for the extraction of cupferron complexes with various metal ions are summarized in Table II. Furman *et al.*[4] have reviewed the use of this compound in precipitation reactions.

Defects and limitations of cupferron

While the versatility of cupferron has been amply verified, it is not without defects.

1. The reagent is unstable to visible and ultraviolet light and to air. To minimize this defect, it is usual to store it in a brown bottle with a few lumps of ammonium carbonate to act as preservative.[3]

2. Solutions of cupferron are unstable and decompose on heating. Addition of 50 mg of acetophenetide to each 150 ml of solution has been suggested as a stabilizer.[16]

3. Cupferron metal complexes are non-stoichiometric in nature,[3,4] hence ignition to the metal oxide is essential.

TABLE I.—HYDROXYLAMINE DERIVATIVES AND THEIR PROPERTIES

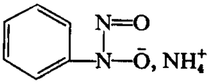
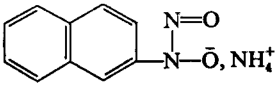
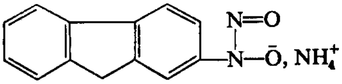
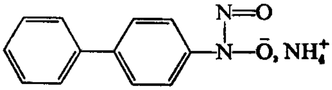
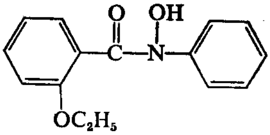
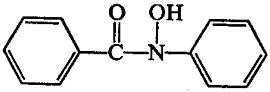
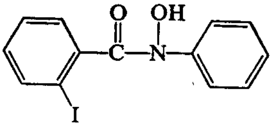
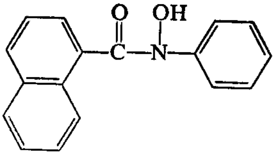
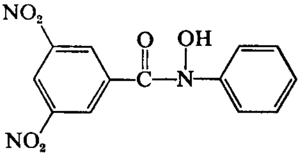
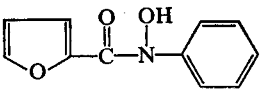
Compound	Structural formula	m.p., °C	Solubility in water g/100 ml (25°C)
Cupferron		—	12
Neocupferron		—	6·0
Fluorenyl analogue of cupferron		—	—
p-Phenylcupferron		—	—
N-(*o*-Ethoxybenzoyl)-phenylhydroxylamine		103	0·001
N-Benzoyl-*N*-phenyl-hydroxylamine		120–121	0·04
N-(*o*-Iodobenzoyl)-phenylhydroxylamine		128	0·01
N-(1-Naphthoyl) phenyl-hydroxylamine		129	0·003
N-(3,5-Dinitrobenzoyl)-phenylhydroxylamine		133	0·007
N-(2-Furoyl)phenylhydroxyl-amine		134	0·013

TABLE I. (*Contd.*)

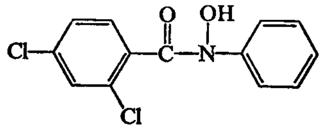
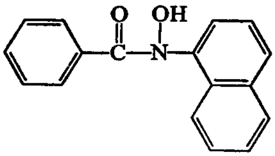
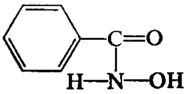
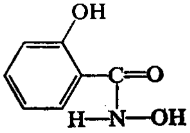
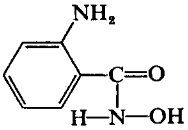
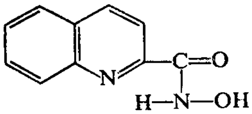
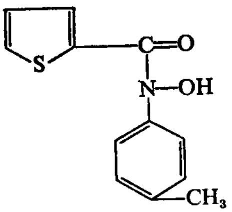
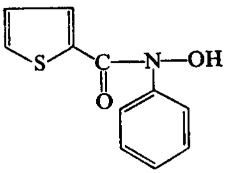
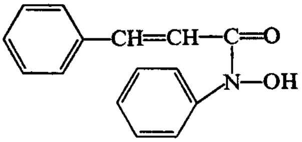
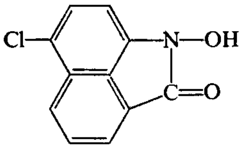
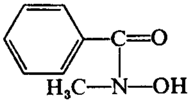
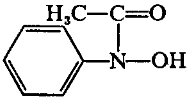
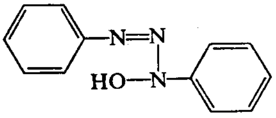
Compound	Structural formula	m.p., °*C*	Solubility in water *g*/100 *ml* (25°*C*)
N-(2,4-Dichlorobenzoyl)-phenylhydroxylamine		137	0·006
N-Benzoyl-1-naphthylhydroxylamine		164	0·013
Benzoylhydroxamic acid		131–132	2·25
Salicylhydroxamic acid		168–170	0·5
Anthranilohydroxamic acid		149	4·0
Quinaldinohydroxamic acid		205–206	0·5
N-2-Thenoyl-*N*-*p*-tolylhydroxylamine		123	—
N-2-Thenoyl-*N*-phenylhydroxylamine		98	—

TABLE I. (*Contd.*)

Compound	Structural formula	m.p., °*C*	Solubility in water *g*/100 *ml* (25°*C*)
N-Cinnamoyl-*N*-phenylhydroxylamine		162–163	—
N-Benzoyl-*p*-chlorophenylhydroxylamine		155	—
N-Benzoyl-*N*-methyl hydroxylamine		not sharp	40·5
N-Phenyl-*N*-acetylhydroxylamine		—	—
3-Hydroxy-1,3-diphenyltriazene		119·5–120	—

4. The reagent is unstable to mineral acids, and decomposes quickly. This limits its analytical applications.[13] Recently Lyle and Shendrikar[17] investigated the acid decomposition products of cupferron. Using a vapour phase chromatographic technique, they observed that from solutions 1–8*M* in hydrochloric acid, the decomposition product was nitrosobenzene and the amount of it increased with increase in acidity.

Because of the above-mentioned defects of cupferron, related substances have been examined in the hope of finding alternatives which would retain the advantages, but be free from the defects of cupferron. The benzene ring has been replaced by the naphthalene[18] and fluorene[19] ring systems, but the products only show a marginal superiority over cupferron.[20] Most of the substances included in Table I have been recommended as analytical reagents. They are all soluble in common organic solvents, but with the exception of a few are only slightly soluble in water. The melting points are usually accompanied by decomposition, the melt first appearing red and then turning black as decomposition proceeds. Most of these derivatives can be stored for a considerable period of time without preservative.

TABLE II.—EXTRACTION DATA FOR METAL DERIVATIVES OF CUPFERRON*

H																	He
Li	Be(II) 3·8											B	C	N	O	F	Ne
Na	Mg											Al(III) 3·5	Si	P	S	Cl	Ar
K	Ca	Sc(III) 3	Ti(IV) 4	V(IV),(V) 0–1, 2·5	Cr(III) 3	Mn(II)† 7	Fe(III) 0	Co(II) 4·5	Ni(II) 9	Cu(II) 2	Zn(II) 9	Ga(III) 4·5	Ge	As	Se	Br	Kr
Rb	Sr	Y(III) 5	Zr(IV) 3	Nb(V) 3·5	Mo(VI) 1·5	Tc	Ru	Rh	Pd(II) 0	Ag(I) 3·5	Cd(II) 4·5	In(III) 3	Sn(II), (IV) 0–1, 0–1	Sb(III) 0–1	Te	I	Xe
Cs	Ba	La(III) 4	Hf(IV) 0–1	Ta(V) 3	W(VI)† 0·3	Re	Os	Ir	Pt	Au	Hg(II) 5	Tl(III)† 1·5	Pb(II) 3	Bi(III) 2	Po	At	Rn
Fa	Ra	Ac															

Ce(III), (IV) 5, 0–1	Pr	Nd	Pm(III) 5	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th(IV) 2·5	Pa(V) 0–1	U(IV), (VI)† 0–1, 3	Np	Pu(IV) 2	Am	Cm	Bk	Cf	E	Fm	Mv	102	103

* The number under each element shows the pH required for complete extraction. Where two numbers occur they refer to the two oxidation states of the element taken in the same order.

† Partial extraction.

Phenylhydroxylamines

Lutwick and Ryan[21] have prepared *o*-ethoxybenzoyl, *o*-iodobenzoyl, 2,4-dichlorobenzoyl, α-naphthoyl, 3,5-dinitrobenzoyl and benzenesulphonyl derivatives of phenylhydroxylamine, as well as *N*-benzoylnaphthylhydroxylamine. With the exception of the benzenesulphonyl derivative, all these reagents precipitate manganese(II), lead(II), aluminium(III), uranium(VI), copper(II), and iron(III) in neutral solutions and tin(IV), tin(II), titanium(IV), zirconium(IV) and hafnium(IV) from 1*M* hydrochloric acid solution. Lutwick and Ryan[21] studied copper and tin reactions in detail. For copper, the lower pH limit of complete precipitation increases with the acidic nature of the reagent, thus *N*-benzoyl and *o*-iodobenzoyl derivatives precipitate copper completely at pH 3 whereas the benzoylnaphthyl derivative requires a pH of 5·5. Naphthoyl, 2,4-dichlorobenzoyl and benzoylnaphthylhydroxylamine precipitate tin completely from a 1% hydrochloric acid solution.

In a later paper Armour and Ryan[22] examined a further series of phenylhydroxylamine derivatives; hexanoyl, heptanoyl, cyclohexanoyl, nicotinoyl, thenoyl and furoyl, but none of these were promising as reagents. However *N*-furoylphenylhydroxylamine seems to be the most interesting,[1] as it forms an ammonium salt, a property which is advantageous in aqueous media. It precipitates copper at pH 3, but so far only titanium[23] and vanadium[24] have been studied.

Various hydroxylamine derivatives such as NBPHA,[25] *N*-cinnamoyl-*N*-phenylhydroxylamine,[26] *N*-2-thenoyl-*N*-*p*-tolylhydroxylamine and *N*-2-thenoyl-*N*-phenylhydroxylamine[27] are valuable as colorimetric reagents for the determination of small amounts of vanadium, and some of these are quite sensitive, but are of no use in the presence of zirconium, titanium, molybdenum and tungsten. It has been reported[28] that *N*-benzoyl-*N*-*p*-chloro-phenylhydroxylamine is one of the most sensitive reagents used for the determination of vanadium and that it can withstand the influence of titanium and zirconium, but not that of tungsten and molybdenum. *N*-benzoyl-*N*-*o*-tolylhydroxylamine[29] is sensitive for vanadium, and common elements like molybdenum, titanium and tungsten do not interfere. Recently vanadium has been determined in silicate rocks[30] with this compound.

Niobium and tantalum are incompletely precipitated by *N*-phenylacetyl-*N*-phenylhydroxylamine;[30] *N*-cinnamoyl-*N*-phenylhydroxylamine[31] precipitates these two elements, but both precipitates have to be ignited to the oxide before weighing; NBPHA was later preferred as reagent.[32] *N*-Cinnamoyl-*N*-phenylhydroxylamine also reacts with vanadium(V) in 2·7–7·5*M* hydrochloric acid to give a violet complex which can be extracted into chloroform.[26] Vanadium(V) also forms an intensely violet chelate with *N*-2-thenoyl-*N*-phenylhydroxylamine, which can be extracted into chloroform from 2·8–5·0*M* hydrochloric acid.[27]

Hydroxytriazenes

The hydroxytriazenes include some interesting compounds for analytical work. A recent review by Purohit[33] gives a survey of the chemical applications of this class of organic reagents. 3-Hydroxy-1,3-diphenyltriazene was first suggested for the gravimetric determination of palladium(II). Sogani and Bhattacharya[34] extended the use of this compound, which is prepared at little cost, for the determination of copper, nickel and titanium. The reagent has been reported[34] to be superior to all gravimetric reagents previously described for copper. Although 3-hydroxy-1,3-diphenyltriazene precipitates titanium quantitatively, the complex is fairly soluble in alcohol and thermally unstable above 55°. This substance forms only one complex with vanadium irrespective of the oxidation state of vanadium in the aqueous phase. According to Dutta *et al.*[35] vanadium(V), if present in the aqueous phase, is first reduced to vanadium(IV) by the reagent and then complex formation takes place. Reports of the use of other hydroxytriazenes in chemical analysis exist but no compound described shows any superiority over the substituted phenylhydroxylamines. 3-Hydroxy-1-(*p*-sulphophenyl, sodium salt)-3-phenyltriazene and *p*-(3-hydroxy-3-phenyltriazeno)phenyltrimethylammonium chloride both form water-soluble complexes and the former substance has been used as an indicator for direct complexometric determination of iron in solids, cement, ores and dolomite.[33]

Uses of hydroxamic acids

Many hydroxamic acids react with transition elements to give highly coloured solutions. Oxalohydroxamic acid[36] has been used for the colorimetric determination of uranium(VI). Salicylhydroxamic acid reacts with uranium(VI) and molybdenum(VI), producing colours suitable for absorptiometric measurements, within the pH ranges 8·5–9·5 and 6·3–6·5 respectively.[37] This reagent forms with vanadium(V) a blue to intense violet substance that can be quantitatively extracted into organic solvents such as ethyl acetate, butyl acetate and butyl alcohol.[38] The optimum pH for the extraction of vanadium(V) lies between pH 3·0 and 3·5.[39] The extraction of titanium, into acetylacetone, as a complex with salicylhydroxamic acid has been recommended for the determination of titanium in presence of aluminium.[40] Salicylhydroxamic acid reacts with iron, producing a violet chelate, which is sensitive to pH changes and is of doubtful composition. This reagent can also be used for gravimetric determination of cadmium, uranium and vanadium but does not seem attractive. Benzohydroxamic acid has been suggested for the colorimetric determination of vanadium(V) with which a red colour is obtained in dilute acid and blue in concentrated acid.[41] The reaction of iron with benzohydroxamic acid has been examined by spectrophotometric methods.[42] Poluektova and Nazarenko[43] have used this compound as an extractive reagent for determination of tungsten(VI)[44] and its separation from vanadium. It also forms a soluble complex with uranium(VI) that can be extracted into 1-hexanol.[45] This solvent has also been used for colorimetric determination of vanadium in uranium materials[46] and in steel and oils.[47] The other derivatives of hydroxamic acids such as nicotino,[48] and isonicotino[49] hydroxamic acids are useful for the determination of vanadium either in aqueous or non-aqueous solutions, but these reagents suffer from defects in that they need removal of numerous interfering elements including iron, uranium, titanium, aluminium, thorium, tin, molybdenum, zirconium and tungsten. Anthranilohydroxamic[50] and quinaldinohydroxamic[51] acid both react with iron(II) and iron(III). The former produces a red complex with manganese(II) while the latter forms a purple complex with vanadium(V).

NBPHA, its uses and advantages

It would appear that very few of the organic reagents mentioned above have advantages over the earlier reagents they were intended to supersede. Only NBPHA shows promise of becoming generally accepted.

TABLE III.—OPTIMUM CONDITIONS FOR THE PRECIPITATION OF VARIOUS ELEMENTS WITH NBPHA

Element	Optimum Conditions	Remarks*	References
Aluminium	pH 3·6–6·4	D.D.	63
Antimony	0·1–1·5*M* HCl	D.D.	17
Beryllium	pH 5·5–6·5	I.O.	54
Bismuth	pH 6·0–6·8	D.D.	72
Cerium	pH 6·5–7·5	I.O.	55
Cobalt	pH 5·5–6·5	D.D.	64
Copper	pH 3·6–6·4	D.D.	63
Gallium	pH 2·5–3·0	D.D.	57, 65
Indium	pH 4·8–5·3	D.D.	57
Iron	pH 3·0–8·5	D.D.	63
Lanthanum	pH 6·4–7·2	D.D.	56
Molybdenum	0·1–2·5*M* HCl	D.D. or I.O.	60
Nickel	pH 5·5–6·5	D.D.	64
Niobium	pH 3·5–6·5	D.D. or I.O.	66, 67
Tantalum	pH 0·0–1·0	D.D. or I.O.	66, 67
Thorium	pH 4·5–5·5	I.O.	55
Tin	0·1–0·5*M* HCl	D.D.	68
Titanium	0·1–0·4*M* HCl	I.O.	63
Tungsten	0·5–1·0*M* HCl	D.D.	58
Uranium	pH 5·2–5·6	D.D. or I.O.	69
Zirconium	0·15–2·5*M* HCl	D.D.	70, 71

* D.D. = Direct determination I.O. = Ignition to oxide

NBPHA was first synthesized by Bamberger[52] who noted that it gave coloured precipitates with certain transition-group elements such as copper, iron and nickel. However, Shome[53] was the first to demonstrate that this reagent has definite advantages over cupferron in gravimetry, and extended his knowledge of its behaviour to many metal ions in precipitation reactions.[54–60]

NBPHA has the following general characteristics:

1. It is moderately stable in air and light, and at moderate temperatures.
2. It is stable in hydrochloric, perchloric and sulphuric acids. Only nitric acid in concentrations above 3*M* attacks the reagent.
3. Although only slightly soluble in water (0·04% w/v at 25°), it is readily soluble in organic solvents.
4. The precipitates formed with many metal ions have a granular form, facilitating filtration or centrifugation.
5. The precipitates are not usually contaminated with the reagent when formed from hot solutions, and therefore, being stoichiometric, they can be weighed directly.
6. The solubility of the metal derivatives in organic solvents opens up possibilities for separation of metal ions by solvent extraction methods.

NBPHA is a white crystalline solid, m.p. 120–121°. The low solubility in water necessitates close control of the use of excess of NBPHA, while the weakness of its acidic functional group ($pK = 8{\cdot}15$)[61] prevents the effective use of its salts. Shome[62] in 1951 used this compound for the colorimetric determination of vanadium, and it has since been used extensively, particularly in gravimetric determinations (see Table III).

From the table it may be seen that many elements can be determined gravimetrically with NBPHA. Meyer *et al.*[73] have determined the thermal stability of some metal chelates of NBPHA with elements such as aluminium(III), cadmium(II), copper(II), cobalt(II), chromium(II), iron(III), manganese(II), nickel(II) and zinc(II). Vanadium yields a mahogany-red precipitate with NBPHA but it is not possible to determine this element gravimetrically since the complex is colloidal in nature. The oxidation state of tin in the tin–NBPHA complex has been in doubt for some time.[68] Recently, however, the work of Blakeley and Ryan[74] and Lyle and Shendrikar[17] proved this to be tin(IV) rather than tin(II).

Although NBPHA was synthesized in 1919 and the solubilities of its metal derivatives in organic solvents were noted as early as 1944,[53] its application as an extractant was limited until 1960 to a few elements only.[1] Today about two-thirds of all elements are known to be extracted (see Table IV) under suitable conditions, and some novel separations have been reported.[75–78] Separation factors[17,79–82] for some pairs of elements are given in Table V.

CONCLUSIONS

From Tables II and IV it may be seen that cupferron and NBPHA react under similar conditions with many elements. Apart from the established stoichiometric nature of metal derivatives of NBPHA, its stability to mineral acids offers a definite advantage over cupferron.[83] NBPHA precipitates antimony,[17] giving a white precipitate from 1*M* hydrochloric acid solution. The existing literature on antimony indicates a lack of reliable and quick precipitation methods[84] and therefore this reaction of NBPHA merits further investigation. Reaction of magnesium, scandium, chromium manganese, silver, zinc, cadmium and mercury with NBPHA has not so far been studied in detail, and such a study might lead to some useful separations. The process of precipitation could be facilitated by a study involving homogeneous precipitation from solution. Only niobium has been studied in this way with NBPHA.[85] For that matter not much relevant work has been done with cupferron. So far only a few elements have been studied by this technique of precipitation from homogeneous solution[86–88] which has definite advantages over the direct precipitation methods. Further substitution of the NBPHA molecule has been examined by Ellefsen *et al.*,[89] but only copper has been determined.

The application of NBPHA as a colorimetric reagent is limited to a few elements.[62,90–93] Attempts to use the reagent as an indicator have been recorded[94,95] but more work is required in this field. Using paper impregnated with a solution of NBPHA in 2-octanone, Fritz and Sherma[96] have achieved a number of selective separations by the paper chromatographic technique. NBPHA has been used in the polarographic determination of tin and antimony.[97] These two elements can be determined simultaneously in 1*M* hydrochloric acid solution in the presence of NBPHA. The advantage over cupferron lies in its stability to acid and also in the greater range of cathode potentials over which it is stable to reduction.[97] The use of cupferron in polarographic determinations is limited[98] because the reagent itself is reduced polarographically relatively easily ($E_{1/2}$ about $-0{\cdot}4$ V). Solvent extraction studies of lanthanide and actinide group elements with NBPHA are described[61,99] and might give some useful results.

It is therefore concluded that there is still considerable scope for development of new methods of analysis with NBPHA and for further investigation of other hydroxylamine derivatives. The furoyl derivative has some interesting properties[1] which might repay further investigation. The *N*-methyl derivative[100] is highly soluble in water, but not much work has been done with it. Similarly some hydroxytriazenes show

TABLE IV.—ELEMENTS EXTRACTED BY *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE*

H																	He
Li	Be(II) 6·5											B	C	N	O	F	Ne
Na	Mg											Al(III) 3·6	Si	P	S	Cl	Ar
K	Ca	Sc(III) 5·2	Ti(IV) 0–1	V(V) 6·5	Cr(III) 3	Mn(II) 10	Fe(II), (III) 5, 0–1	Co(II) 10	Ni(II) 9	Cu(II) 3·6	Zn(II) 9	Ga(III) 3·1	Ge	As	Se	Br	Kr
Rb	Sr	Y(III) 6	Zr(IV) 0–1	Nb(V) 3·5	Mo(VI) 1	Tc	Ru	Rh	Pd(II) 3	Ag(I) 1	Cd(II) 10	In(III) 5·3	Sn(II), (IV) 0–1	Sb(III), (V)† 0–1	Te	I	Xe
Cs	Ba	La(III) 8	Hf(IV)†	Ta(V) 0	W(VI) 3	Re	Cs	Ir	Pt	Au	Hg(II) 8	Tl(I) 10·5	Pb(II) 9	Bi(III) 4	Po	At	Rn
Fa	Ra	Ac															

Ce(III), (IV) 7, 0–1	Pr(III) 6	Nd(III) 6	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th(IV) 4·5	Pa(V)†	U(VI) 3·5	Np	Pu(IV)†	Am	Cm	Bk	Cf	E	Fm	Mv	102	103

* The number under each element indicates the pH at which the element can be extracted quantitatively. Where two numbers occur they refer to the two oxidation states of the element taken in the same order.

† Extracted almost completely from high acid concentrations.

Table V.—Separation factors for various pairs of elements

Separation	Method	Phases*	Separation factor†
Sn(IV) from Sb(V)	Radioactive Sb	0·8*M* HCl/1% B	1×10^2
Sn(IV) from Bi(III) or (V)	Radioactive Bi	4·0*M* $HClO_4$/1% B	9×10^3
Sb(V) from Bi(III) or (V)	Radioactive Bi	9·0*M* $HClO_4$/1% B	7×10^2
Sn(IV) and Sb(V) from Bi(III) or (V)	Radioactive Bi	9·0*M* $HClO_4$/1% B	7×10^2
Ga from In	Radioactive In	pH 3·1/1% B	10^4
In from Pb	Benzidine test	pH 5·3/1% B	10^4
Ga from Pb	Benzidine test	pH 3·1/1% B	10^4
Ga from Ge	^{68}Ge decay	pH 3·1/1% B	10^3
In from Sn	^{113m}In	pH 5·3/1% B	10^3
Sn from Ga	Radioactive Ga	0·8*M* HCl or 4·0*M* $HClO_4$/1% B	10^3
Sn from In	Radioactive In	0·8*M* HCl or 4·0*M* $HClO_4$/1% B	10^3
Sn from Pb	Benzidine test	0·8*M* HCl or 4·0*M* $HClO_4$/1% B	10^4
Pb from Tl	Radioactive Tl	pH 9·0/0·7% B	6×10^2
Nb from Ta	Radioactive Ta	1*M* HCl + 0·05*M* HF/0·2% B	10^2
Nb from Pa	Radioactive Pa	1*M* HCl + 0·05*M* HF/0·2% B	10^3
Ta from Pa	Radioactive Pa	1*M* HCl + 0·4*M* HF/0·5% B	10^3
Nb from Zr	Radioactive Zr	1*M* HCl 0·05*M* HF/0·2% B	10^4
Pa from Sb	Radioactive Sb	conc. HCl + 0·025*M* HF/1% B	2×10^2
Pa from Sn	Radioactive Sn	conc. HCl + 0·025*M* HF/1% B	7×10^2
Pa from U	^{238}U, spectrophotometric	conc. HCl + 0·025*M* HF/1% B	$>4 \times 10^3$
Pa from Th	Uranium-X	conc. HCl + 0·025*M* HF/1% B	3×10^4

* B = NBPHA dissolved in chloroform.

† The ratio of the initial and final amounts of impurity (the second component of the mixture). The aqueous phase was extracted twice with equal volumes (except in the separation of niobium from zirconium where one batch extraction was found to be sufficient) of the chloroform phase and then washed with two successive portions of chloroform alone.

promise of becoming useful organic reagents. Further work with 3-hydroxy-1,3-diphenyltriazene with the platinum group of metals may give some useful separations. The solubility of 3-hydroxy-1-(*p*-sulphophenyl, sodium salt)-3-phenyltriazene and *p*-(3-hydroxy-3-phenyltriazeno)phenyltrimethylammonium chloride in water could be utilized in developing some colorimetric methods for determinations of various metal ions, particularly transition elements. Recent work by Bass and Yoe[101] with 33 hydroxamic acids as possible colorimetric reagents needs following up. They have tested some 78 metal ions for colorimetric determination under varying conditions of acidity and basicity. Further work with some of these hydroxamic acids may provide some novel separations, since a number of them offer promise of being useful reagents, particularly in colorimetric determinations.[102] Possibly the substitution of chromophoric groups into the basic reagents would give better reagents, but lack of specificity will always be a drawback.

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Résumé—La revue traite des applications analytiques des dérivés d'hydroxylamine. Les défauts du cupferron et la versatilité de *N*-benzoyle-*N*-phénylhydroxylamine dans leurs réactions avec différents ions métalliques sont discutés. L'application de ce dernier dans les analyses chimiques est résumée et des facteurs de séparation pour quelques paires d'éléments sont compris. Des suggestions sont faites au sujet d'une utilisation ultérieure de ce composé et d'autres hydroxylamines.

Zusammenfassung—Die Übersicht befaßt sich mit analytischen Anwendungen von Hydroxylaminderivaten. Die Nachteile von Kupferron und die vielfältige Anwendbarkeit von *N*-Benzoyl-*N*-phenylhydroxylamin bei der Reaktion mit verschiedenen Metallionen werden diskutiert. Die Anwendung des letzteren in der chemischen Analyse wird zusammenfassend dargestellt und Trennfaktoren für einige Paare von Elementen beigefügt. Es werden Vorschläge zur weiteren Verwendung dieser Verbindung und anderer Hydroxylamine gemacht.

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FLUORESCENCE CHARACTERISTICS OF INORGANIC COMPLEXES IN HYDROCHLORIC ACID MEDIUM AT LIQUID-NITROGEN TEMPERATURE

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Summary—A study of the low-temperature fluorescence characteristics of the ions of 55 elements in concentrated hydrochloric acid is reported. The spectral characteristics, effects of hydrochloric acid concentration and time, calibration linearity and sensitivity for Sb(III), Bi, Ce(III), Pb, Te(IV), Tl(I) and Sn(IV) have been investigated. Uranium(VI), copper(I) and antimony(V) also exhibit fluorescence under these conditions. The detection limits using a commercial spectrofluorimeter with modified sample cells are Sb(III), $10^{-6}M$; Bi(III), $10^{-8}M$; Ce(III), $10^{-7}M$; Pb, $10^{-8}M$; Te(IV), $10^{-7}M$; Tl(I), $10^{-6}M$; Sn(IV), $10^{-4}M$. The suitability of some inorganic acid solvents for clear glass formation at −196° is also investigated.

Several workers have demonstrated that certain metal chelate complexes may show an increased fluorescence intensity at low temperatures compared to that obtained at room temperature.[1,2] Bozhevol'nov and Solov'ev[3] have studied organic chelate complexes of elements such as magnesium, niobium and gallium and shown, for example, that a 100-fold increase in the fluorescence intensity at room temperature of the niobium complex of 2,2′,4′-trihydroxy-5-chloro-(1-azo-1′)-benzene-3-sulphonic acid is obtained at −196°. These workers have also described the increase in fluorescence intensity which is obtained for lead and thallium in hydrochloric acid medium at −70° and −196° respectively, compared to that at room temperature,[4,5] and also report that the fluorescence of tin in concentrated sulphuric acid at −70° may be used for its determination.[6] The available optical geometries for fluorimetric analysis have been reviewed by Parker.[7] Much previous work[6] in low temperature fluorimetry of inorganic materials has employed the technique of "frontal illumination", in which the fluorescent radiation from the surface of the sample is viewed at an acute angle to the incident radiation. This technique is adopted because clear, rigid glasses suitable for use with the conventional fluorimetric "right angle" optical geometry are difficult to produce in conventional sample cells for aqueous samples.

Although many solvents which form suitable glasses at low temperature have been described,[8,9] these are almost all organic liquids at room temperature. This paper describes some inorganic acid solvents which form clear glasses at liquid-nitrogen temperatures, and their use in a simple sample cell which may be used with the conventional fluorimetric "right angle" geometry with the low-temperature attachment of a commercial spectrofluorimeter. In this paper are described the fluorescence emission characteristics of the ions of 55 elements in hydrochloric acid medium at −196°, under which conditions antimony(III), antimony(V), bismuth, cerium(III), copper(I), lead, tellurium(IV), thallium(I), tin(IV) and uranium(VI) exhibit characteristic fluorescence. The spectral characteristics, effect of hydrochloric acid concentration, stability of fluorescence emission and limits of detection for seven of these elements have been studied.

EXPERIMENTAL

Apparatus

Fluorescence measurements were made with an Aminco spectrofluorimeter (American Instrument Co.) fitted with a 150-W xenon arc lamp and RCA 1P28 photomultiplier tube, and equipped with a Bryan X–Y recorder. The Aminco low-temperature housing and Dewar flask with fused silica base supplied for spectrophosphorimetry were used to hold the sample tubes. Precision-bore transparent silica sample tubes (Jencons Ltd., Hemel Hempstead, England) of length 200 mm, bore 3 mm and 1-mm wall thickness were used. A sample volume of 0·5 ml is enough to fill these tubes sufficiently for work in the Aminco spectrofluorimeter. Sample solutions in hydrochloric acid in these thick-walled tubes may be placed directly into liquid nitrogen in the Dewar flask, and may subsequently be brought back to room temperature after measurement, without fracture of the tubes.

In order to obtain maximum sensitivity compatible with good definition of maxima, 3-mm slits (Aminco-Bowman slit arrangement No. 3, corresponding to a 30-nm band-pass) were used in the excitation and analysing monochromators.

Reagents

For the semi-quantitative survey of the low-temperature characteristics of the 55 elements examined, analytical-reagent grade salts and hydrochloric acid (Hopkins and Williams Ltd.) were used.

For quantitative measurements of the fluorescence emission characteristics of the ten elements which show intense emission analytical-reagent grade salts [antimony potassium tartrate, bismuth nitrate, cerium(III) nitrate, lead nitrate, thallium(I) sulphate, uranyl nitrate] were used to prepare stock $10^{-2}M$ solutions. Tellurium metal (Johnson and Matthey, Specpure), tin(IV) chloride (general purpose reagent grade, Hopkin and Williams Ltd.) antimony(V) chloride (technical grade, B.D.H.) and copper sulphate (Analar, Hopkin and Williams) were used as starting materials for the preparation of stock $10^{-2}M$ solutions of Te(IV), Sn(IV), Sb(V) and Cu(I). For these quantitative studies extra-pure analytical-reagent grade hydrochloric acid ("Aristar" grade, B.D.H.) was employed.

RESULTS AND DISCUSSION

Low-temperature glass formation

The application of spectrofluorimetric analysis at low temperatures to inorganic trace analysis has been restricted by the lack of solvents which form rigid, clear glasses rather than "snows" or extensively cracked glasses under these conditions. Thus while some complexes which may be extracted into organic solvents from aqueous media may be examined in one of the wide range of organic solvent mixtures available, there is a need for aqueous solvents in which other inorganic complexes may be examined at low temperature. We have examined the properties of a range of acids for this purpose. Concentrated hydrochloric, hydrobromic, sulphuric, nitric, phosphoric and perchloric acids were found to produce good clear glasses reproducibly at −196° in the thick-walled sample tubes used in this study. Concentrated acetic, formic, boric and oxalic acid solutions invariably formed opaque "snows" on rapid cooling in liquid nitrogen. Hydriodic acid, which always contains traces of free iodine, usually produced a yellow, extensively cracked glass. We have also found that transparent glasses are also given by less concentrated solutions of the mineral acids which form good, clear glasses. Thus on rapid cooling of the thick-walled sample tubes containing aqueous hydrochloric acid solutions, transparent glasses are formed reproducibly at all concentrations higher than $6M$, whereas below $5M$ a snow is invariably formed.

General study of elements in hydrochloric acid

A $2 \times 10^{-3}M$ solution of the purest available salt of each element in $6M$ hydrochloric acid was used. A portion of each solution (0·5 ml) was transferred to a silica sample tube and placed in the spectrofluorimeter Dewar flask containing liquid nitrogen. The glass produced was examined visually through the silica walls of the low temperature Dewar flask under a mercury vapour lamp. The quality of the glass and any fluorescence emission was noted, and the Dewar was then transferred to the spectrofluorimeter and the fluorescence specifically sought instrumentally.

No fluorescence emission was observed under these conditions for the following 45 ions: aluminium, arsenic(III), arsenic(V), beryllium, cadmium, cerium(IV), chromium(III), cobalt, copper(II), dysprosium, erbium, europium, gadolinium, gallium, holmium, indium, lanthanum, magnesium, manganese(II), mercury(II), molybdenum(VI), neodymium, nickel, niobium(V), palladium, platinum(II), platinum(IV), praseodymium, ruthenium, samarium, scandium, selenium(IV), silver, strontium, tantalum, terbium, thorium, thulium, tin(II), titanium(IV), vanadium(V), ytterbium, yttrium, zinc and zirconium. Under the same conditions the following 10 ions were found to exhibit fluorescence: antimony(III), antimony(V), bismuth(III), cerium(III), copper(I), lead, tellurium(IV), thallium(I), tin(IV) and uranium(VI). Table 1 gives the colour of the fluorescence observed visually for these ions and the wavelengths of maximum excitation and emission.

TABLE I.—IONS FOUND TO FLUORESCE IN $6M$ HYDROCHLORIC ACID AT −196°C

Ion	Colour of fluorescence	Excitation maximum, *nm*	Emission maximum, *nm*
Sb(III)	red	306	582
Sb(V)	faint red	390	580
Bi(III)	blue	330	410
Ce(III)	—	252	348
Cu(I)	green-blue	284	440
Pb	—	276	390
Te(IV)*	red*	326	550
	red	380	586
Tl(I)	—	256	380
Sn(IV)	—	272	390
U(VI)	green	302	494 strong 514 strong 540 weak 565 weak

* Tellurium(IV) shows two different characteristic excitation and emission spectra depending on the concentration of hydrochloric acid used. In $6M$ HCl excitation 326 *nm*/emission 550 *nm*, and in HCl $> 8M$ excitation 380 *nm*/emission 586 *nm*.

The fluorescence emission of uranium(VI) in solution and boric acid glasses at room-temperature is well characterized in the literature and we have not examined here the emission which we have observed in concentrated hydrochloric acid at −196°. The emission observed from antimony(V) and copper(I) (in the presence of ascorbic acid as reductant) was not very intense. The investigation of the analytical utility of low temperature spectrofluorimetric measurements at −196° in hydrochloric acid was therefore restricted to the ions Sb(III), Bi(III), Ce(III), Pb, Te(IV), Tl(I) and Sn(IV).

Spectral characteristics

Figure 1 shows the excitation and emission spectra for the 7 most intensely fluorescent ions in $6M$ hydrochloric acid at −196°. These spectra are uncorrected

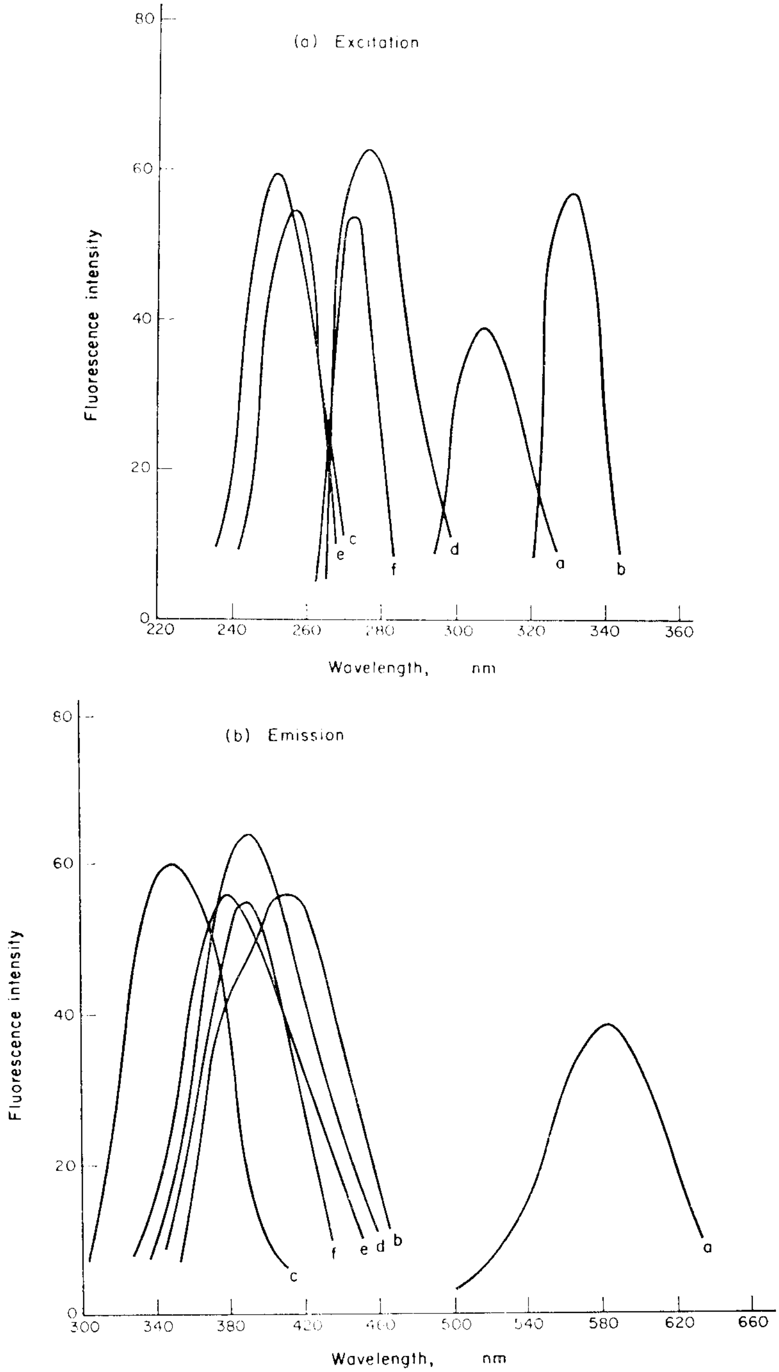

Fig. 1.—Excitation and Emission Spectra in 6*M* HCl.

a 2 × 10^{-3}*M* antimony(III); sensitivity scale: ×0·03
b 2 × 10^{-4}*M* bismuth(III); sensitivity scale; ×1
c 2 × 10^{-3}*M* cerium(III); sensitivity scale: ×0·3
d 2 × 10^{-4}*M* lead; sensitivity scale: ×1
e 2 × 10^{-3}*M* thallium(I); sensitivity scale: ×0·1
f 2 × 10^{-3}*M* tin(IV); sensitivity scale: ×0·01.

for variation in emission characteristics of the xenon arc lamp and response characteristics of the monochromators and the photomultiplier. Variation of the hydrochloric acid concentration between 6 and 10*M* produces no change in the wavelengths of maximum excitation and emission for the ions studied, with the exception of tellurium(IV).

Effect of hydrochloric acid concentration

The wavelengths of excitation and emission for the fluorescence observed from tellurium(IV) are affected by the hydrochloric acid concentration. Figure 2 shows the excitation and emission spectra obtained at hydrochloric acid concentrations between 6 and 10*M*. In 6*M* hydrochloric acid the excitation spectrum shows a maximum at 326 nm and a less intense peak at 380 nm. Under these conditions the wavelength of maximum emission occurs at 550 nm. When more concentrated hydrochloric acid solutions are used, the excitation maximum at 326 nm decreases, while that at 380 nm increases. The wavelength of maximum emission moves to longer wavelengths with increase in acid concentration, and in 10*M* hydrochloric acid occurs at 586 nm. These results suggest that the intense red fluorescence observed for tellurium(IV) is shown by two different tellurium chloro-complexes, and that the relative concentrations of these depend on the hydrochloric acid concentration. When the effect of additional chloride and hydronium ion on a 6*M* hydrochloric acid solution of tellurium(IV) was investigated, it was found that by increasing the acidity (by addition

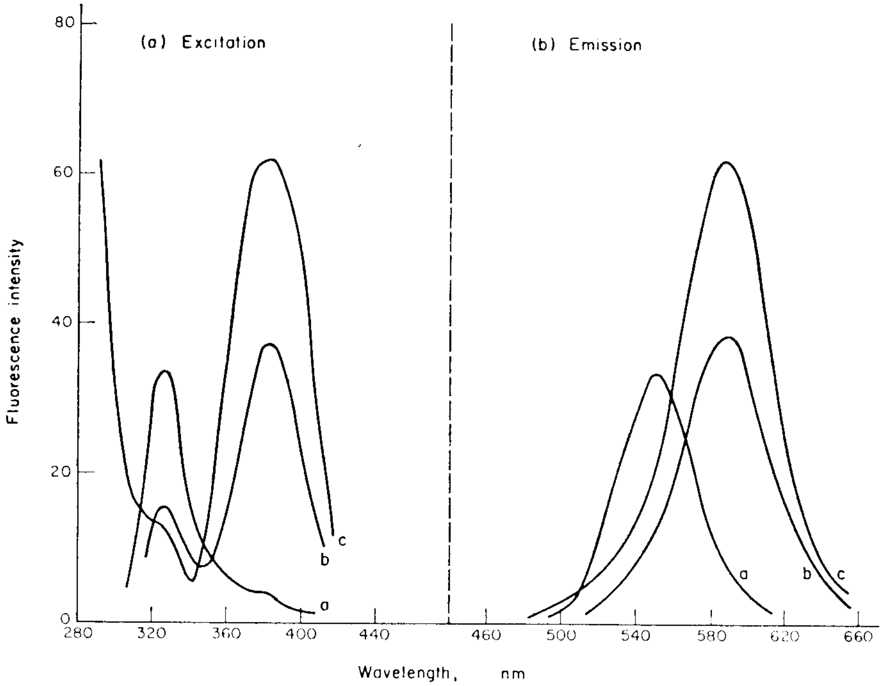

FIG. 2.—Excitation and Emission Spectra of $10^{-8}M$ Te(IV) complex in HCl solution.
a 6*M* HCl (sensitivity scale; ×0·1)
b 8*M* HCl (at half sensitivity setting for *a*)
c 10*M* HCl (at half sensitivity setting for *a*).

of concentrated sulphuric acid) the same changes in the absorption and emission spectra were produced. The addition of chloride to a 6*M* hydrochloric acid solution of tellurium(IV), on the other hand, has no effect on the wavelengths of excitation and emission. These observations suggest that the two species present might be $TeCl_6^{2-}$ and $HTeCl_6^-$ or H_2TeCl_6.

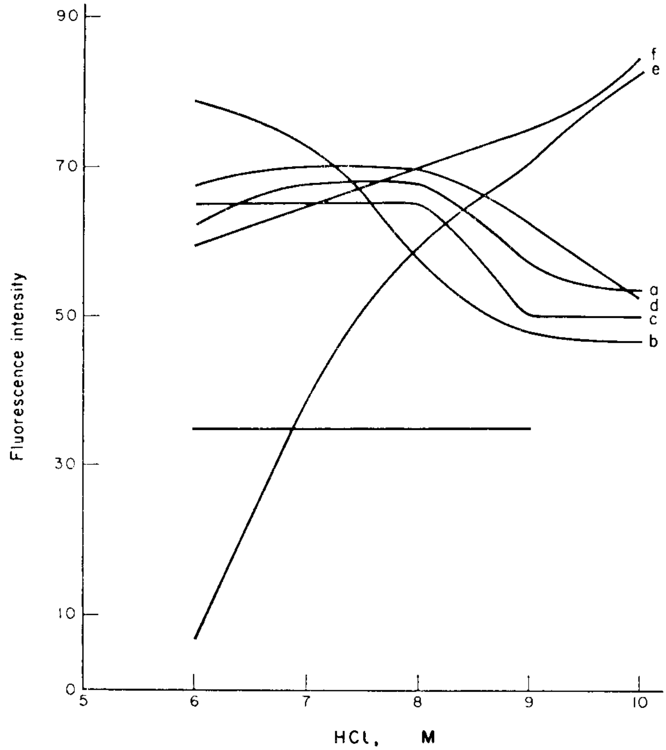

FIG. 3.—Variation of fluorescence intensity with hydrochloric acid concentration.
a 2 × $10^{-3}M$ antimony(III)
b 2 × $10^{-4}M$ bismuth(III)
c 2 × $10^{-3}M$ cerium(III)
d 2 × $10^{-4}M$ lead
e 2 × $10^{-3}M$ tellurium(IV) (Excitation at 380 nm, measurement of emission at 586 nm)
f 2 × $10^{-3}M$ thallium(I)
g 2 × $10^{-3}M$ tin(IV).

As mentioned above, no changes in the wavelengths of maximum excitation and emission occur over the range 6–10*M* hydrochloric acid for Sb(III), Bi(III), Ce(III), Pb, Tl(I) and Sn(IV). The emission intensity, however, is affected somewhat, and Fig. 3 shows the effect of hydrochloric acid concentration on the fluorescence intensity at the optimum wavelengths of excitation and emission. The curve for tellurium reflects the increase in intensity at 380 nm/586 nm and decrease at 326 nm/550 nm corresponding to the change in relative proportions of the two chloro-complexes present. The tellurium complex formed at high acid concentrations is also much more intensely fluorescent than that present at lower acidities, and consequently measurement of the fluorescence of the former species gives a higher analytical sensitivity.

Effect of time on fluorescence emission

The effect of time on the intensity of the fluorescence of the 7 ions studied was investigated at the optimal hydrochloric acid concentrations, (*a*) when the solution was stored in darkness for 2 hr, (*b*) when the solution was allowed to stand under normal laboratory conditions (fluorescent strip lighting) for 2 hr, and (*c*) on continuous irradiation of the solution in the spectrofluorimeter for 1 hr. The results are shown in Table II. The fluorescence of the chloro-complexes is quite stable, certainly over the time (1–2 min) required for measurement of the fluorescence emission intensity. Continuous irradiation of the thallium(I) solution for 1 hr causes a reduction in fluorescence intensity of 60%, probably owing to oxidation of thallium(I) to thallium(III).[10]

TABLE II.—EFFECT OF TIME ON FLUORESCENCE EMISSION INTENSITIES

Solution	Reduction in fluorescence intensity, % Standing in darkness (2 hr)	Under laboratory lighting (2 hr)	Continuous irradiation (1 hr)
$10^{-5}M$ Sb(III) in $7M$ HCl	not detectable	not detectable	5
$10^{-7}M$ Bi(III) in $6M$ HCl	7·5	14	10
$10^{-5}M$ Ce(III) in $7M$ HCl	not detectable	not detectable	13
$10^{-6}M$ Pb in $7M$ HCl	not detectable	6	4
$10^{-6}M$ Te(IV) in $10M$ HCl	3	6	5
$10^{-5}M$ Tl(I) in $10M$ HCl	4	7	60
$10^{-3}M$ Sn(IV) in $7M$ HCl	8	8	3

Calibration curves and sensitivity

Under optimum conditions the graph of fluorescence intensity *vs.* concentration is linear for each ion studied. Table III shows the concentration range for each ion over which this linearity was confirmed for a single setting of the gain control. The lower concentration limits of these calibration graphs represent a realistic detection limit (signal-to-noise ratio of unity) for the fluorescence of the element above the background blank for the hydrochloric acid employed. Thus even the trace impurities in the best available hydrochloric acid affect the available sensitivity. The thick-walled silica tubing also exhibits a slight "blank" fluorescence. The characteristics of this emission are similar to those of the lead, thallium and tin fluorescence, and consequently this blank limits the sensitivity for these elements. As only 0·5 ml of sample

TABLE III

Element	Concentration range of calibration curve
Sb(III) in $7M$ HCl	10^{-6}—$10^{-5}M$
Bi(III) in $6M$ HCl	10^{-8}—$5 \times 10^{-8}M$
Ce(III) in $7M$ HCl	10^{-7}—$10^{-6}M$
Pb in $7M$ HCl*	10^{-8}—$10^{-7}M$
Te(IV) in $10M$ HCl*	10^{-7}—$10^{-6}M$
Tl(I) in $10M$ HCl	10^{-6}—$8 \times 10^{-6}M$
Sn(IV) in $7M$ HCl	10^{-4}—$10^{-3}M$

* B.D.H. Aristar.

solution is required, the absolute detection limits are Sb(III), 0·06 μg; Bi(III), 0·001 μg; Ce(III), 0·007 μg; Pb, 0·001 μg; Te, 0·006 μg; Tl(I), 0·1 μg; Sn(IV), 6 μg. No attempt was made to establish the upper range of linearity by working with a lower gain setting.

CONCLUSIONS

Bi(III), Te(IV) and Sb(III) do not show fluorescence in hydrochloric acid at room temperature. Although fluorescence has been observed from Sn(II) in hydrochloric acid at room temperature,[10] Sn(IV) does not appear to fluoresce under these conditions. At −196°, however, Sn(IV) does fluoresce (although not strikingly intense), whereas we have been unable to detect fluorescence from Sn(II). With our experimental arrangement, thallium(I), cerium and lead show much increased fluorescence intensity (5, 50 and 1000-fold respectively) at −196° compared to that obtainable under otherwise similar conditions at room temperature.

Although the chloro-complexes of the ions examined exhibit relatively broad emission peaks at −196°, the half-intensity widths of the corresponding excitation peaks are relatively narrow. The intense fluorescence emission of the 7 elements examined in detail provides very sensitive methods for their determination. Owing to the separation of the excitation and emission maxima, it is possible to determine several of these elements simultaneously by selection of suitable excitation and emission wavelengths. Our current studies include an examination of the low-temperature fluorescence characteristics of ions in other halogen acids, and the application of the fluorescence at −196° to the determination of traces of elements in samples of practical importance. The results of these investigations will be reported later.

Zusammenfassung—Es wird über eine Untersuchung der Tieftemperaturfluoreszenzeigenschaften der Ionen von 55 Elementen in konzentrierter Salzsäure berichtet. Untersucht wurden die spektralen Eigenschaften, der Einfluß der Salzsäurekonzentration und der Zeit sowie die Eichlinearität und die Empfindlichkeit für Sb(III), Bi, Ce(III), Pb, Te(IV), Tl(I) und Sn(IV). Uran(VI), Kupfer(I) und Antimon(V) fluoreszieren unter diesen Bedingungen auch. Die Nachweisgrenzen mit einem handelsüblichen Spektrofluorimeter mit geänderten Probenküvetten sind: Sb(III) $10^{-6}M$; Bi(III) $10^{-8}M$; Ge(III) $10^{-7}M$; Pb $10^{-8}M$; Te(IV) $10^{-7}M$; Tl(I) $10^{-6}M$; Sn(IV) $10^{-4}M$. Auch die Eignung einiger anorganischer Säuren als Lösungsmittel zur Bildung klarer Gläser bei −196° wurde untersucht.

Résumé—On rapporte une étude des caractéristiques de fluorescence à basse température des ions de 55 éléments en acide chlorhydrique concentré. On a étudié les caractéristiques spectrales, les influences de la concentration de l'acide chlorohydrique et du temps, l'étalonnage, la linéarité et la sensibilité pour Sb(III), Bi, Ce(III), Pb, Te(IV), Tl(I) et Sn(IV). L'uranium(VI), le cuivre(I) et l antimoine(V) présentent aussi une fluorescence dans ces conditions. Les limites de détection en utilisant un spectrofluorimètre commercial avec des cellules à échantillon modifiées sont Sb(III), $10^{-6}M$; Bi(III), $10^{-8}M$; Ce(III), $10^{-7}M$; Pb, $10^{-8}M$; Te(IV), $10^{-7}M$; Tl(I), $10^{-6}M$; Sn(IV), $10^{-4}M$. On étudie aussi la valeur de quelques solvants acides inorganiques pour la formation de verres limpides à −196°.

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STUDIES IN ATOMIC-FLUORESCENCE SPECTROSCOPY—VIII

ATOMIC FLUORESCENCE AND ATOMIC ABSORPTION OF THALLIUM AND MERCURY WITH ELECTRODELESS DISCHARGE TUBES AS SOURCES

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Summary—Atomic-fluorescence measurements, with microwave-excited electrodeless discharge tubes as sources of excitation, are described for thallium and mercury. The limits of detection by atomic fluorescence are 0·12 ppm for thallium and 0·08 ppm for mercury; the corresponding limits by atomic absorption (using the same intrument and source) are 6 and 10 times as great. The preparation, operation and spectral characteristics of thallium and mercury discharge tubes are described and comparisons are made with a thallium hollow cathode lamp and thallium and mercury spectral discharge lamps.

The development of atomic-fluorescence spectroscopy in flames as an analytical technique in recent years has necessitated the design of suitable instrumentation in order to take advantage of its high inherent sensitivity.[1–7] This paper reports the use of the general purpose Perkin–Elmer Model 290 single-beam atomic-absorption spectrophotometer used in conjunction with microwave-excited electrodeless discharge tubes,[8] for both atomic absorption and fluorescence spectroscopy. This instrument has been described in detail by Slavin and Kahn.[9,10]

Thallium and mercury were studied because their principal resonance lines lie at wavelengths known to be accessible to the normal optics of the instrument.

EXPERIMENTAL

The following summarizes the instrumental modifications made.

Electrical

The electrodeless discharge tubes are effectively d.c. sources of excitation and hence all radiation entering the monochromator slit was mechanically chopped at 50 Hz in tune with the phase-sensitive amplifier. The chopper was made from a segmented aluminium disc fitted to a 300-rpm synchronous motor and operated from the 110-V supply at the accessory socket for spectral discharge lamps in the lamp compartment. It was placed immediately in front of the monochromator slit for simplicity. Under these conditions, the fluorescence signal, thermal emission and flame background radiation are recorded. However, there is little flame background with the air-hydrogen flame used in these studies, and negligible thermal emission from mercury and small concentrations of thallium.

Atomic-fluorescence measurements were made with a Servoscribe recorder connected to the flame emission accessory terminal at the rear of the instrument, *via* a circuit allowing variable electrical backing-off of the recorded signal and incorporating fixed time constants of 0, 1, 5 and 10 sec. Fluorescence readings were normally made on the 0–50 mV range, and source emission spectra were recorded on the 0–0·5 V range.

Spectra were scanned with a 0·5-rpm motor geared to the diffraction grating drive-shaft at the rear of the instrument to give a scanning rate of 10 divisions of the "coarse select element" control per min.

Burner

The long-path (50 × 0·5 mm) slot burner was replaced by a circular Unicam acetylene burner head, giving a flame with a maximum diameter of *ca.* 10 mm, for atomic-fluorescence measurements. This burner head was connected to the top of the nebulizing chamber *via* a drilled rubber bung.

Optical

In atomic-fluorescence studies the flame was irradiated with an electrodeless discharge tube at right-angles to the line from the flame to the monochromator entrance slit. The radiation, when the 210 L cavity[11] was used, was directed towards the flame by a translucent quartz tube (14 mm bore, *ca.* 50 mm length) wrapped with aluminium foil to prevent stray light from the source from entering the monochromator slit directly. The cavity was placed so that the end of the light guide almost touched the flame. Focussing the light from this cavity onto the flame with a short-focus quartz lens does not improve the fluorescence signals, because the exit aperture of the cavity is small and the "gathering power" of the lens is not used. With the more efficient 214 L cavity,[11] the use of a quartz lens of focal length 55 mm (and 40 mm diameter) incorporated into a 150-mm light guide made from black paper proved to be the most effective (Fig. 1). The lens produced a divergent beam giving an out-of-focus image approximately 10 mm across at the centre of the burner. This arrangement gave a 50-fold increase in the fluorescence signal as compared to the use of a light-guide tube with the same cavity.

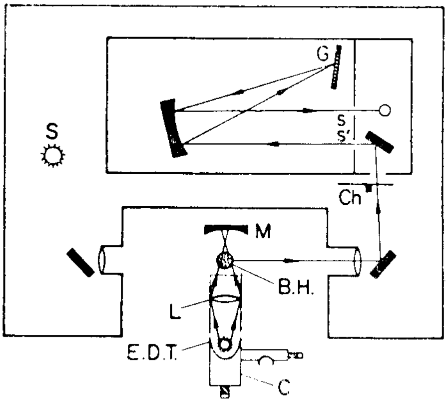

FIG. 1.—Atomic-fluorescence measurements with the Perkin–Elmer Model 290. B.H.—burner head; EDT—electrodeless discharge tube; C—214 L cavity; M—spherical mirror; S—source position for AAS; L—lens; Ch—chopper; SS′—monochromator slits; G—diffraction grating.

We have also used spherical front-silvered mirrors (53 mm diameter, 85 mm focal length) to reflect the source beam back through the flame, thereby producing a 3-fold increase in atomic fluorescence signal (Fig. 1) and to collect fluorescence radiation from that region of the flame opposite the detector system, thereby producing a 1·5-fold increase in fluorescence signal. The latter arrangement, however, also produced a 6-fold increase in the background signal and was, therefore, not used further. It is possible that mirrors of a different focal length might be more suitable.

No advantage was obtained by altering the focal length of the lens which focusses light from the flame, or by moving the flame closer to this lens. It was similarly considered unnecessary to alter the built-in fixed slit-width settings of 0·2, 0·7 and 2·0 nm, the last of which is suitable for most atomic-fluorescence measurements. A wider slit-width merely decreases the signal:noise ratio.

Determination of Thallium

Preparation and characteristics of discharge tube

The general method of preparation previously described was followed.[8] The most stable, intense and long-lived tubes were obtained by using *ca.* 5 mg of thallium(I) chloride (analytical grade) instead of the metal and iodine. The thallium(I) chloride was degassed by gentle heating under vacuum and the tubes (30–40 mm long) were finally sealed under an argon pressure of *ca.* 9 mbar.

The source of power was a "Microtron 200" (Electro-Medical Supplies) microwave (2450 ± 25 MHz) generator and initiation was achieved with a "Tesla" high-frequency vacuum tester.

Because of the comparative involatility of thallium(I) chloride only the 210 L cavity (Electro-Medical Supplies) is capable of giving long-term stability. Maximum stability was given when the tube was operated at 50 W (25 W reflected power). It was not necessary to cool the tube or cavity and there were no critical tuning characteristics, although there was minimum reflected power with the tuning probe fully screwed in. Under these conditions the tube assumed a very bright green colour. The output was stable ($\pm\frac{1}{2}$%) and drift over a period of 1 hr was less than 3%. The warm-up period was about 20 min.

The source intensity at the principal thallium resonance lines was compared with that from a Perkin–Elmer hollow-cathode lamp and a Wotan spectral discharge lamp operated under recommended conditions. The P.E. Model 290 spectrophotometer was used in its emission mode and all the sources were placed in focus in the normal lamp housing. The gain and slit-width (0·2 nm setting) were kept constant and only the calibrated recorder sensitivity was adjusted. The radiation from both the electrodeless and spectral discharge sources was mechanically chopped at 50 Hz. The results (Table I) show that the electrodeless discharge tube is 5 times more intense than the spectral discharge lamp at the most sensitive line for atomic-fluorescence measurements (377·6 nm) and *ca.* 60 times more intense than the hollow-cathode lamp at the most sensitive line for atomic-absorption measurements (276·8 nm). Table II shows the effect of power on intensity at 377·6 nm. The spectral discharge lamp gave no measurable intensity at 276·8 nm, owing to absorption by its glass envelope. Unlike some discharge lamps, it is not possible to cut a window in this envelope.

TABLE I.—COMPARISON OF THALLIUM SOURCE INTENSITIES

Wavelength, *nm*	Coarse select element setting*	Relative intensities		
		HCL†	SDL‡	EDT§
237·96	114·2	1	0	110
258·01	161·5	3	0	140
276·79¶	194·6	21	0	1300
377·57**	375·3	85	1950	9750
535·05	673·5	48	3900	7800

* Recommended for P.E. Model 290.

† Thallium molten hollow cathode lamp at 0·2 nm slit-width setting.

‡ Thallium spectral discharge lamp at 0·2 nm slit-width setting.

§ Thallium electrodeless discharge tube at 0·2 nm slit-width setting.

¶ Most sensitive for atomic absorption.

** Most sensitive for atomic fluorescence.

TABLE II.—DEPENDENCE OF INTENSITY ON OPERATING POWER FOR THALLIUM ELECTRODELESS DISCHARGE TUBE

Power, *W*	Discharge appearance	Intensity*, *recorder divisions*	Noise in signal, %
20	blue-pink	11	0
30	blue-purple	25	±0·25
40	green	51	±0·5
50	green	56	±0·5
60	green	56	±0·5

* Measurements at 377·6 nm with 0·2 nm slit-width setting and zero recorder damping.

Atomic-absorption measurements

The electrodeless discharge tube was suspended in the lamp compartment in approximately the same position as the cathode of the hollow-cathode lamp would have been and its output was mechanically chopped at 50 Hz. With an air-acetylene flame and the long-path burner under the recommended conditions,[12] the hollow-cathode lamp and electrodeless discharge tube gave comparable results as expected. The sensitivity for 1% absorption was 1·4 ppm and the detection limit (defined as that concentration of original solution which gives a signal equal to the noise) was 0·7 ppm. Both calibration curves were linear over the same concentration ranges.

Atomic-fluorescence measurements

These measurements were made under the optimum conditions outlined above. The amplifier was used at maximum gain and the recorder was used on its 0–50 mV range.

The Unicam emission head was used with a lean air–hydrogen flame adjusted to give minimum thermal emission for thallium. There was little variation in fluorescence signal with flame height or gas flow in the lower flame regions, so measurements were made *ca.* 25 mm above the top of the burner head. Under these conditions there was no reflected source radiation from the burner head.

Table III shows the relative fluorescence intensities at various wavelengths, with the electrodeless discharge tube being used. The hollow cathode and spectral discharge lamp did not give detectable signals, owing to low output and the difficulty of irradiating the flame efficiently with these sources.

TABLE III.—THALLIUM ATOMIC-FLUORESCENCE MEASUREMENTS

Wavelength, *nm*	Flame background	Flame and source background	Emission	
			Thermal	Fluorescence
	Recorder divisions			
276·79	30	30	0	8
377·57	20	20	7	44
535·05	15	25	2	16

Air–hydrogen flame; air flow 12·00 (instrument setting) at 40 psi external pressure; hydrogen flow 14·25 (instrument setting) at 15 psi external pressure.

Thallium solution 4 ppm; slit-width setting 2·0 nm.

Preliminary measurements indicate that the most sensitive fluorescence signals would probably be obtained by irradiating the flame at 377·57 nm *via* a filter which does not pass radiation of longer wavelength, and measuring the direct-line fluorescence signal at 535·05 nm. Under these conditions there would be negligible source scatter and lower flame background, and it would be possible to make better use of the detector response characteristics.

Figure 2 shows the calibration curves obtained over the range 1–100 and 1–1000 ppm thallium at 377·57 nm. The limit of detection was 0·12 ppm and is about 1/6 that obtainable by atomic absorption with the same instrument and source.

Determination of Mercury

Preparation and spectral characteristics of discharge tube

Mercury discharge tubes were prepared in the usual way by sealing a small amount (*ca.* 5 mg) of triply distilled mercury in tubes 40–50 mm long under an argon pressure of approximately 0·1 mbar. The most intense and stable discharge resulted from operation at *ca.* 20 W (2 W reflected power) in the 214L cavity with strong air-cooling *via* the inlet in line with the axis of the coaxial input connector. The output stability was ±½% within 4 min of initiation and the drift was less than 2%/hr. Warm-up time was about 4 min.

The output at the 253·66 nm intercombination line was 3 times that from a Wotan mercury spectral discharge lamp operated at 1·1 A. No detectable atomic-fluorescence signal was observed from a 100-ppm mercury(II) solution when the spectral discharge lamp was used, and it is suspected that this is because of extreme self-reversal occurring with such sources.

Atomic-absorption measurements

Linear calibration curves were obtained over the range 10–1000 ppm of mercury(I) and mercury(II) at 253·66 nm (coarse select element setting 153·7) in an air-acetylene flame, the sensitivities for 1% absorption being 7 and 12 ppm respectively, and the limits of detection 0·9 and 1·5 ppm. The addition of ascorbic acid and immediate spraying produced *ca.* a 5-fold increase in the mercury(II) signal. The calibration curves in our experiments were linear over a considerably wider concentration range than those previously obtained with an electrodeless discharge tube, but in view of the operating

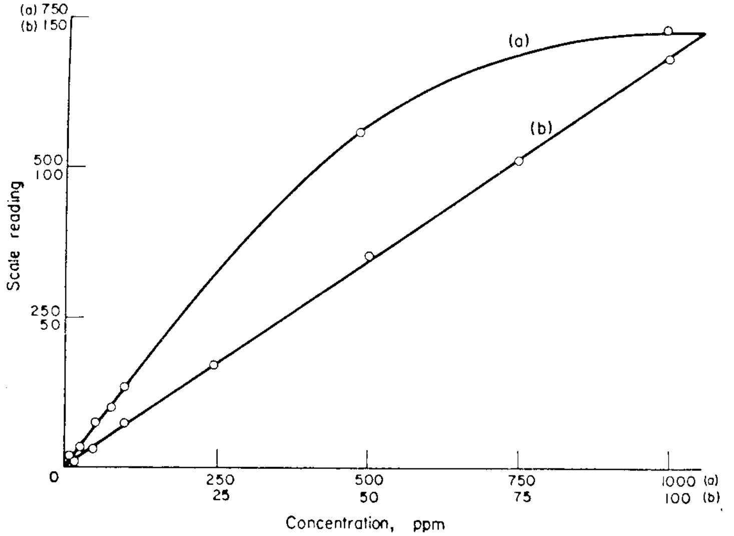

FIG. 2.—Analytical atomic-fluorescence curves for thallium at 377·6 nm, (*a*) 1–1000 ppm thallium, (*b*) 1–100 ppm thallium.
Air–hydrogen flame; 2·0 nm slit-width setting; E.D.T. source,

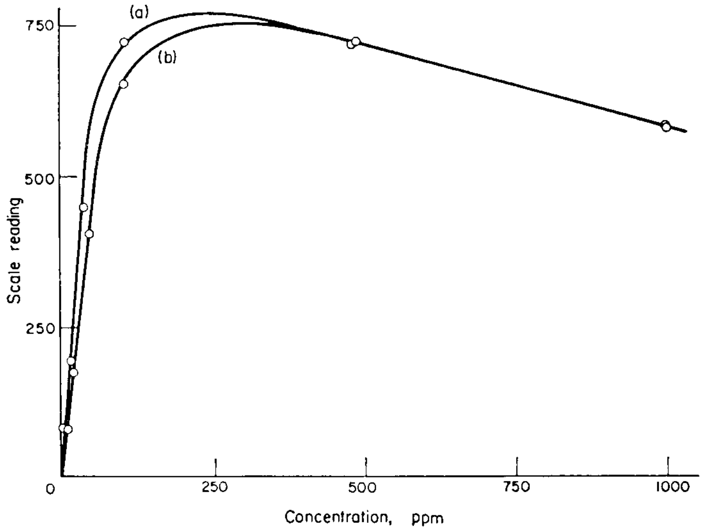

FIG. 3.—Analytical atomic-fluorescence curves for mercury, (*a*) 0·1–1000 ppm mercury(I), (*b*) 0·1–1000 ppm mercury(II).
Air-hydrogen flame; 2·0 nm slit-width setting; E.D.T. source

characteristics and warm-up period in these other studies there may have been some self-reversal of the source.[13]

Atomic-fluorescence measurements

The only fluorescence signal obtained was due to resonance fluorescence at the 253·66 nm intercombination line. The principal resonance line at 184·96 nm is in the vacuum ultraviolet beyond the reach of the Model 290 spectrophotometer.

An air–hydrogen flame was used with the same instrument settings as in the thallium study and the fluorescence characteristics of mercury(I), mercury(II) and mercury(II) plus ascorbic acid were examined. Linear calibration curves (Fig. 3) were obtained over the concentration range 0·1–100 ppm for mercury(I) and (II); the plot of fluorescence signal then curved rapidly towards the concentration axis because of self-absorption, the signal decreasing with mercury concentrations above about 250 ppm. The limit of detection for mercury(I) was 0·08 ppm and for mercury(II) 0·09 ppm. The difference in atomic-fluorescence signals between the same concentrations of mercury(I) and (II) is much less than that in the corresponding atomic-absorption signals.

The addition of excess of ascorbic acid to mercury(II) solutions produced about a 4-fold increase in fluorescence signal. However, at the high amplifier gain used in such measurements it is essential to use a long recorder time constant (*ca.* 10 sec) to obtain a stable baseline. Under these conditions the rapid aging of the solution produces erratic results and the true maximum signal is never reached. With shorter time constants a limit of detection of *ca.* 0·05 ppm was obtained, but at the expense of a poorer baseline. All these detection limits are at least one order of magnitude lower than can be obtained by atomic absorption with the same instrument and source of excitation.

DISCUSSION

The limits of detection by atomic fluorescence spectroscopy (0·12 ppm for thallium at 377·6 nm and 0·08 ppm for mercury at 253·7 nm) are significantly lower than the corresponding limits by atomic absorption (0·7 and 0·9 ppm) even with the largely unmodified and in completely optimized arrangement described. The most sensitive atomic-fluorescence measurements recorded to date are 0·1 ppm for mercury and 0·04 ppm for thallium,[2] made with specially designed apparatus and an oxy-hydrogen flame. These workers used a spectral discharge lamp for thallium and a commercial electrodeless mercury discharge tube which from the limit of detection quoted was probably not produced to give maximum intensity. An earlier study by the same authors with a less refined arrangement gave limits of detection for mercury and thallium of 0·1 and 2·0 ppm in an air–hydrogen flame.[14]

It was expected that the atomic-fluorescence sensitivity would be lower for mercury than for thallium because theoretical reasons[15] show that the signal:noise ratio in atomic fluorescence increases rapidly with decreasing wavelength and hence sensitivity is greater for elements with principal resonance lines in the far ultraviolet. On the other hand, the detector response and transmission characteristics of the instrument must be considered. The 210L cavity allows only a small fraction of the total radiation given by the source to reach the flame. The mercury study showed that the 214L cavity in conjunction with a lens to focus light onto the flame gave 50 times the atomic-fluorescence signal obtained with use of a light-guide tube. Work is under way to increase these sensitivities by incorporating better optics in general, especially for work around 200 nm, and to make a larger viewing aperture in the 210L cavity. Also, the use of a more sensitive photomultiplier (an RCA IP28 was used in these studies) should give further improvements.

The microwave-excited electrodeless discharge tubes used in this study have been shown to meet the requirements of both atomic-absorption and atomic-fluorescence spectroscopy, *i.e.*, they are intense and stable, and have short warm-up time and negligible drift. The warm-up period for the thallium tube is the longest (~20 min) we have encountered and is due to the low vapour pressure of thallium(I) chloride. Probably this might be improved by gently warming the tube just before initiation. This electrodeless discharge tube tends to be a little more noisy than a hollow-cathode lamp, but this is no disadvantage in atomic fluorescence where the source noise is reflected as a constant fraction of noise in the recorded signal. Increasing the amplifier gain to examine more dilute solutions does not affect this. In atomic absorption, however, the noise level of baseline and signal is critically dependent on source stability and is amplified by scale expansion. This is particularly noticeable for elements such as mercury, which have a poor absorption sensitivity.

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Zusammenfassung—Atomfluoreszenzmessungen mit mikrowellenerregten elektrodenlosen Entladungsröhren als Anregungslichtquellen werden für Thallium und Quecksilber beschrieben. Die Nachweisgrenzen durch Atomfluoreszenz betragen 0,12 ppm für Thallium und 0,08 ppm für Quecksilber; die entsprechenden Grenzen mit Atomabsorption (mit demselben Instrument und derselben Lichtquelle) sind 6 bzw. 10 mal so groß. Herstellung, Betrieb und spektrale Eigenschaften von Thallium- und Quecksilber-Entladungsröhren werden beschrieben und mit einer Thallium-Hohlkathodenlampe und einer Quecksilber Spektrallampe verglichen.

Résumé—On décrit, pour le thallium et le mercure, des mesures de fluorescence atomique avec, comme sources d'excitation, des tubes à décharge sans électrode excités par microondes. Les limites de détection par fluorescence atomique sont de 0,12 p.p.m. pour le thallium et 0,08 p.p.m. pour le mercure; les limites correspondantes par absorption atomique (en utilisant les mêmes instrument et source) sont 6 et 10 fois plus grandes. On décrit la préparation, le fonctionnement et les caractéristiques spectrales des tubes à décharge de thallium et de mercure et effectue des comparaisons avec une lampe à cathode creuse de thallium et des lampes à décharge spectrales de thallium et mercure.

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SPECTROPHOTOMETRIC DETERMINATION OF THALLIUM WITH 4-(2-PYRIDYLAZO)RESORCINOL AND 4-(2-THIAZOLYLAZO)RESORCINOL

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Summary—Thallium(III) gives sensitive reactions with PAR and TAR ($\varepsilon = 2 \times 10^4$ at 520 nm), forming 1:1 complexes at pH ~1–2, and a mixture of 1:1 and 1:2 complexes at higher pH values; hydrolysis sets in above pH ~3. The stability constants are evaluated.

THALLIUM(III) gives very sensitive analytical reactions with heterocyclic azo dyes of the pyridine and thiazole types in rather acidic medium, forming stable complexes with this group of dyes. 1-(2-Pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)-resorcinol (PAR) were earlier recommended as indicators for the EDTA titration or spectrophotometric determination of thallium.[1–3] A number of heterocyclic azo dyes such as PAR, PAN, 4-(2-thiazolylazo)resorcinol (TAR), 1-(2-thiazolylazo)-2-naphthol (TAN), 1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid, 2-(2-thiazolylazo)-4-phenol, 7-(2-pyridylazo)-8-hydroxyquinoline, 2-(2-thiazolylazo)chromotropic acid, 2-(2-thiazolylazo)-5-aminophenol and 2-(2-thiazolylazo)-5-dimethylaminophenol[4,5] as well as 2-(2-thiazolylazo)-4-methoxyphenol (TAMH) and 2-(2-thiazolylazo)-5-methoxyphenol (TAMR)[6] were found suitable as indicators for chelometric titrations of small amounts of thallium(III); 4-(2-*N*-methylanabasinoazo)resorcinol,[7] 5-(2-pyridylazo)-2-monoethylamino-*p*-cresol and its 5-bromo and 3,5-dibromo derivatives[8] have also been used.

Because of the need to define the working conditions closely when PAR was used as reagent for thallium(III) the reaction has been re-examined in detail and compared with the analogous reaction with TAR.

EXPERIMENTAL

Reagents

The purity of the PAR and TAR used was checked (*a*) by the mineral ash content found by treatment with concentrated sulphuric acid and ignition at 800°, (*b*) by drying at 120° to constant weight, (*c*) elemental analysis, (*d*) potentiometric titration with dichromate,[9] (*e*) descending paper chromatography with n-butanol-$2M$ acetic acid–methanol (3:1:1) or n-butanol-$2M$ ammonia–ethanol (3:1:1).

The PAR content can also be determined by spectrophotometric titration with copper sulphate at pH 3·1 in the presence of formate. Thallium(III) perchlorate standard solution was prepared by dissolving carefully washed thallium(III) hydroxide in perchloric acid (1 + 1), filtering the solution through a sintered-glass crucible and standardizing by EDTA titration with PAN as indicator.[1] The thallium(III) hydroxide was prepared by addition of $2M$ sodium hydroxide dropwise to $0·06M$ thallium(I)-sulphate that had been oxidized with 3% hydrogen peroxide solution. Thallium(III) perchlorate solutions ($0·07M$) in 1–$2M$ perchloric acid were stable for up to 5 months.

Buffers used were $1M$ monochloroacetic and formic acids adjusted to pH 2·4–3·1 with sodium hydroxide, or $0·25M$ potassium hydrogen phthalate.

Ionic strength was adjusted to 0·1 by addition of $1M$ sodium perchlorate. PAR was used in aqueous solution and TAR in solution in $0·01M$ sodium hydroxide.

Procedure

The thallium solution was added to the yellow solution of the dye in acid and the pH was finally adjusted to the required value. Results were interpreted as in previous papers from our laboratory.[10–12] The equations can become rather complicated if more than one ligand form and metal complex are simultaneously formed and absorb at the wavelength used.

The constancy of the values found for the molar absorptivity and the equilibrium constant of the system by calculation from a set of points over a broad range of pH verifies indirectly the equilibrium assumed, and also the composition of the complex formed and the number of protons liberated when a single equilibrium exists under selected working conditions.

Equations for the numerical analysis of the absorbance-pH plots for the formation of 1:1 complexes under various conditions are given here; the meaning of the symbols should be self-evident.

I. *Equimolar solutions*, $c_R = c_M$

A. Only one form of the reagent present; ε_{1H} calculated from two points, A_1, $[H]_1$ and A_2, $[H]_2$, on the curve.

$$M + H_3R^+ \rightleftharpoons MRH + 2H^+$$

$$\begin{aligned} c_R &= [MRH] + [H_3R] \\ c_M &= [MRH] + [M] \\ A &= \varepsilon_{1H}[MRH] + \varepsilon_{R1}[H_3R] \\ k_{12} &= [MRH][H]^2/[M][H_3R] \\ &= \frac{(A - \varepsilon_{R1}c_R)(\varepsilon_{1H} - \varepsilon_{R1})[H]^2}{(\varepsilon_{1H}c_R - A)^2} \end{aligned} \tag{1}$$

$$\varepsilon_{1H} = \frac{A_2[H]_1\sqrt{A_1 - \varepsilon_{R1}c_R} - A_1[H]_2\sqrt{A_2 - \varepsilon_{R1}c_R}}{c_R([H]_1\sqrt{A_1 - \varepsilon_{R1}c_R} - [H]_2\sqrt{A_2 - \varepsilon_{R1}c_R})} \tag{2}$$

B. Two forms of the reagent present; ε_{1H} is obtained from a cubic equation.

$$M + H_2R \rightleftharpoons MRH + H^+$$

$$\begin{aligned} c_R &= [MRH] + [H_3R] + [H_2R] \\ c_M &= [MRH] + [M] \\ A &= \varepsilon_{1H}[MRH] + \varepsilon_{R1}[H_3R] + \varepsilon_{R2}[H_2R] \\ k_{11} &= [MRH][H]/[M][H_2R] \\ &= \frac{(Ab - c_Rd)(\varepsilon_{1H}b - d)[H]}{b(\varepsilon_{1H}c_R - A)^2} \end{aligned} \tag{3}$$

$$\begin{aligned} c_R^2(a_1b_1 - a_2b_2)\varepsilon_{1H}^3 + c_R(2a_2b_2A_1 - 2a_1b_1A_2 + a_2d_2c_R - a_1d_1c_R)\varepsilon_{1H}^2 \\ + (2a_1d_1c_RA_2 - 2a_2d_2c_RA_1 + a_1b_1A_2^2 - a_2b_2A_1^2)\varepsilon_{1H} + a_2d_2A_1^2 - a_1d_1A_2^2 = 0 \end{aligned} \tag{4}$$

$$a = \frac{\{A(1 + [H]/K_{a1}) - c_R(\varepsilon_{R2} + \varepsilon_{R1}[H]/K_{a1})\}[H]}{1 + [H]/K_{a1}}$$

$$b = 1 + [H]/K_{a1} \qquad d = \varepsilon_{R2} + \varepsilon_{R1}[H]/K_{a1}$$

C. ε_1 is obtained from equation (4) with different values for a, b and d.

$$M + H_2R \rightleftharpoons MR + 2\,H^+$$

$$\begin{aligned} c_R &= [MR] + [H_2R] + [HR] \\ A &= \varepsilon_1[MR] + \varepsilon_{R2}[H_2R] + \varepsilon_{R3}[HR] \\ k_{12} &= [MR][H]^2/[M][H_2R] \end{aligned}$$

$$k_{12} = \frac{(Ab - c_Rd)(\varepsilon_1b - d)[H]^2}{b(\varepsilon_1c_R - A)^2} \tag{5}$$

$$a = \frac{\{A(1 + K_{a2}/[H]) - c_R(\varepsilon_{R2} + \varepsilon_{R3}K_{a2}/[H])\}[H]^2}{1 + K_{a2}/[H]}$$

$$b = 1 + K_{a2}/[H]$$

$$d = \varepsilon_{R2} + \varepsilon_{R3}K_{a2}/[H]$$

II. *Solutions with ligand excess*

A. $M + H_3R^+ \rightleftharpoons MRH + 2H^+$

$c_R \sim [H_3R]$ (concentration of reagent bound in complex is neglected).

$$\Delta A = A - \varepsilon_{R1}c_R = \varepsilon_{1H}[MRH]$$

$$k_{12} = \frac{\Delta A[H]^2}{(\varepsilon_1 c_M - \Delta A)c_R} \tag{6}$$

$$\varepsilon_{1H} = \frac{\Delta A_1\,\Delta A_2([H]_1^2 - [H]_2^2)}{c_M(\Delta A_1[H]_1^2 - \Delta A_2[H]_2^2)} \tag{7}$$

B. $M + H_2R \rightleftharpoons MRH + H^+$

$$c_R = [H_3R] + [H_2R]$$

$$\Delta A = A - (\varepsilon_{R1}[H_3R] + \varepsilon_{R2}[H_2R]) \sim \varepsilon_{1H}[MRH]$$

$$k_{11} = \frac{\Delta A[H](1 + [H]/K_{a1})}{(\varepsilon_{1H}c_M - \Delta A)c_R} \tag{8}$$

$$\varepsilon_{1H} = \frac{\Delta A_1\,\Delta A_2\{[H]_1(1 + [H]_1/K_{a1}) - [H]_2(1 + [H]_2/K_{a1})\}}{c_M\{\Delta A_1[H]_1(1 + [H]_1/K_{a1}) - \Delta A_2[H]_2(1 + [H]_2/K_{a1})\}} \tag{9}$$

III. The ΔA *vs.* ligand concentration curves at constant pH were also examined by means of graphical slope–intercept transformations of the apparent stability constant,[13] which have the following forms for equilibrium D.

D. $M(RH) + j(R)_0 \rightleftharpoons M(RH)_{1+j}$

$$\Delta A = \varepsilon_1 c_M + c_R^{\,j}(A_{02} - \Delta A)\,.\,\text{const.} \tag{10}$$

$$\Delta A = \varepsilon_2 c_M - (\Delta A - A_{01})/c_R^{\,j} \tag{11}$$

$$c_R \sim [R]_0 = [H_3R^+] + [H_2R]$$

$$c_M = [M(RH)] + [M(RH)_{1+j}]$$

$$\Delta A = \varepsilon_1[M(RH)] + \varepsilon_2[M(RH)_{1+j}]$$

The graphical plots $A = f\{c_R^{\,j}(\varepsilon_2 c_M - \Delta A)\}$ and $A = f'\{(\Delta A - \varepsilon_1 c_M)/c_R^{\,j}\}$ represent straight lines for the true value of j and true values of corresponding $A_{02} = \varepsilon_2 c_M$ or $A_{01} = \varepsilon_1 c_M$ respectively. One molar absorptivity was calculated from the intercept A_{01} of equation (10) by plotting at least three rough values of A_{02} against A since the true value of A_{02} could not be obtained from the horizontal part of the $\Delta A = f(c_R)$ curve even for solutions with a large excess of ligand.

The values of A_{01} and A_{02} were further refined by successive approximation. The concentration of the reagent was also corrected for the concentration bound in the complexes:

$$c_R' = c_R - \frac{A}{\varepsilon_2 - \varepsilon_1} - \frac{\varepsilon_2 c_M - 2\varepsilon_1 c_M}{\varepsilon_2 - \varepsilon_1} \tag{12}$$

assuming $M(RH)$ and $M(RH)_2$ complexes to be present.

The resulting values of A_{01} and A_{02} were only inserted in the logarithmic plot

$$\log\frac{\Delta A - A_{01}}{A_{02} - \Delta A} = j\log c_R' + \text{const.} \tag{13}$$

to check the number of co-ordinated ligand species from the slope.

In the thallium(III) systems only the absorbance-pH plots for equimolar solutions or those with a limited excess of the reagent, and the absorbance–ligand concentration plots for pH $\leqslant 2$ can be recorded and interpreted. The hydrolysis of thallium begins to interfere at pH $\geqslant 4$.

DISCUSSION

Equilibrium and stability constants

For equilibria A and B

$$k_{12} = k_{11}\,.\,K_{a1}. \tag{14}$$

The stability constant K_{1H} for the $TlRH^{2+}$ complex was calculated independently from equilibria **A** and **B** according to the equation

$$K_{1H} = [MRH]/[M][HR^*] = k_{11}/K_{a3} = k_{12}/K_{a1} \,.\, K_{a3} \tag{15}$$

where HR* is the hypothetical ligand form corresponding to the *o*-hydroxy proton dissociating before the *p*-hydroxy one. The earlier supposition[12] for the corresponding dissociation constant was again used:

$$[HR^*][H]/[H_2R] \sim [R][H]/[HR] = K_{a3} \,. \tag{16}$$

Characteristics of the ligands

Two forms of the reagent, H_3R^+ and H_2R, which absorb considerably at 500–530 nm, are involved in complexation of thallium(III). The parameters used for calculation were:

	PAR	TAR
$\varepsilon_{R1}([H^3R^+])$	2330 (520 nm)	3280 (550 nm)
$\varepsilon_{R2}[H_2R]$	180 (520 nm)	190 (550 nm)
pK_{a1}	3·1	1·0
pK_{a2}	5·6	6·2
pK_{a3}	11·9	9·4

Thallium(III)–PAR

For equimolar solutions there is a rather diffuse isobestic point at 475–480 nm which is characteristic for formation of a 1:1 metal complex from H_3R^+ at pH < 2 (Fig. 1). The two absorption maxima in the spectrum for solutions with metal ion excess, *i.e.*, the metal complex maximum at 520 nm and the smaller ligand maximum at 400 nm, are similar to those in the spectra of other protonated 1:1 metal–PAR complexes.[14]

The position of λ_{max} at 510–520 nm for ligand excess ($c_R = 1{\cdot}50 \times 10^{-4}M$) at pH 2·4 is considerably influenced by the method used to correct for the absorbance of the free reagent (Fig. 2).

Complexation of thallium(III) (present in excess) by PAR begins at a perchloric acid concentration of 7·9*M* and is quantitative at pH 0·6–1·1. The interpretation of curves at pH $> 1{\cdot}1$ is partly hindered by the thallium hydrolysis, which also influences the shape of curves for equimolar solutions at pH 2·7. The pH–absorbance curve at 530 nm becomes horizontal at pH 2–3 for solutions with an 8 to 35-fold excess of reagent and $c_M = 1{\cdot}37 \times 10^{-5}M$. The further change on increasing the pH shows formation of a new complex, but the solutions are easily hydrolysed and precipitates appear at pH $> 3{\cdot}5$. (Figure 3.)

The existence of equilibrium **A** was proved by calculation of k_{12} and ε_{1H} according to equations (1) and (2) for pH $\leqslant 0{\cdot}9$.

The equilibrium constants does not change over the pH range 0·35–0·90.

A maximum appears on the Job curves at a 1:1 = Tl:R ratio at pH 0·5–0·7 and 510–540 nm but the maximum shifts with increasing pH, eventually corresponding to Tl:R = 1:2 at pH 3·5 and 510–550 nm (Fig. 4). The position of the maximum is wavelength-dependent. This shift of the maximum indicates the presence of a 1:2

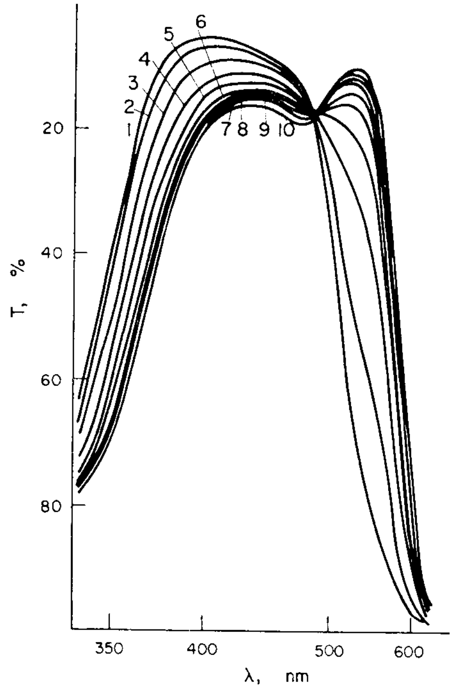

FIG. 1.—Transmittance curves for equimolar solutions of Tl(III) with PAR, as a function of pH.

$c_M = c_R = 6{\cdot}95 \times 10^{-5}M$. *1*—pH 0; *2*—pH 0·3; *3*—pH 0·6; *4*—pH 0·8; *5*—pH 0·98; *6*—pH 1·15; *7*—pH 1·29; *8*—pH 1·40; *9*—pH 1·70; *10*—pH 2·01.

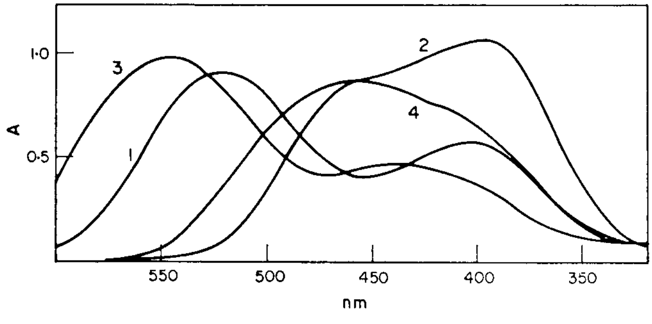

FIG. 2.—Absorbance curves for PAR or TAR solutions with Tl(III) in excess at pH 0·9. *1*—$c_R = 4{\cdot}91 \times 10^{-5}M$ (PAR), $c_M = 3{\cdot}81 \times 10^{-3}M$; *2*—$c_R = 4{\cdot}91 \times 10^{-5}M$ (PAR), $c_M = 0$; *3*—$c_R = 4{\cdot}27 \times 10^{-5}M$ (TAR), $c_M = 3{\cdot}81 \times 10^{-3}M$; *4*—$c_R = 4{\cdot}27 \times 10^{-5}M$ (TAR), $c_M = 0$.

complex with increasing pH rather than hydrolysis of the thallium species. The effect of hydrolysis was earlier discussed in one of our papers.[11]

The protonated complex $TlRH^{2+}$ is the only one formed in equimolar solutions or in those with metal ion excess at pH < 1. The familiar deprotonation usually observed for the PAR complexes of this type, to yield TlR^+, occurs at pH > 1 in solutions containing excess of thallium, and at pH $\geqslant 3$ in equimolar solutions, but is either partly overlapped by the simultaneous hydrolysis of the thallium species or interferes with equilibrium **B** at pH > 2 in equimolar solutions and cannot be examined by curve

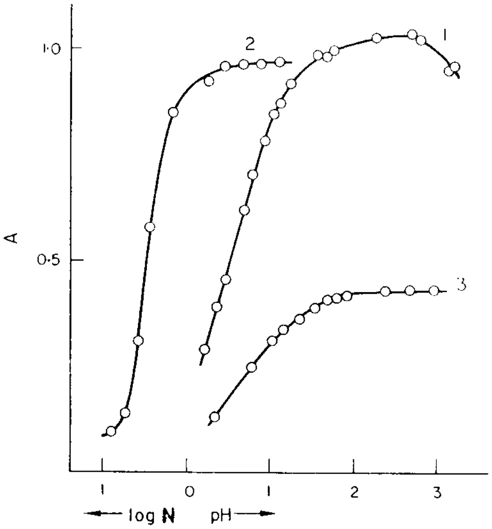

FIG. 3.—Absorbance-pH plots for Tl(III)-solutions with PAR.
1—$c_M = c_R = 6{\cdot}95 \times 10^{-5}M$, 520 nm; *2*—$c_R = 4{\cdot}66 \times 10^{-5}M$, $c_M = 3{\cdot}17 \times 10^{-3}M$, 520 nm; *3*—$c_M = 1{\cdot}71 \times 10^{-5}M$, $c_R = 1{\cdot}36 \times 10^{-4}M$, 530 nm (absorbance difference plotted).

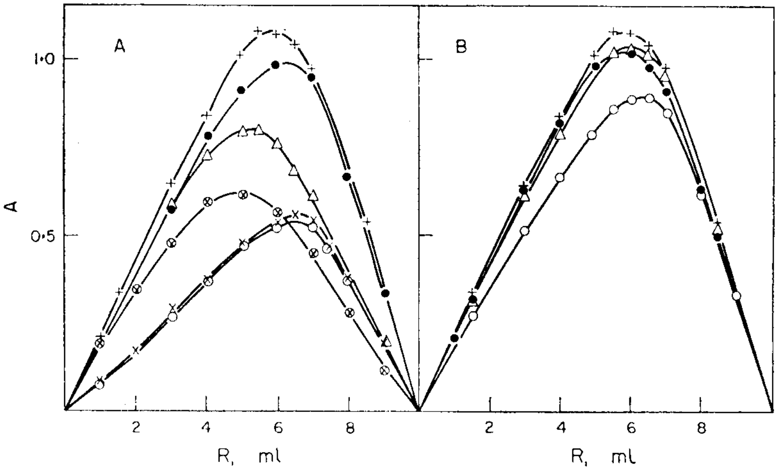

FIG. 4.—Job curves for the PAR-Tl(III) system.
A. *1*—pH 0·46; *2*—pH 0·71; *3*—pH 1·71; *4*—pH 2·14; *5*—pH 3·21; *6*—pH 3·52. Curves *1–4*: $c_0 = 1{\cdot}49 \times 10^{-4}M$, 530 nm, curves *5*, *6*: $c_0 = 2{\cdot}12 \times 10^{-5}M$, 530 nm, 40-mm cells. **B.** $c_0 = 1{\cdot}49 \times 10^{-4}M$; pH 1·71. *1*—510 nm; *2*—520 nm; *3*—530 nm.

analysis. However, the molar absorptivity of the TlR^+ complex may be calculated from the limiting parts of various absorbance curves at pH > 2. $Tl(RH)_2{}^+$ is also formed in solutions with excess of ligand at pH > 1·5 and according to the continuous variations results is the only one existing at pH 3·3–3·5. Some data for the complexes are given in Table I.

Thallium(III)-TAR

The diffuse isobestic point on the transmittance curves for equimolar solutions with $c_M = c_R = 6{\cdot}72 \times 10^{-5}M$, at 513–530 nm, arises from formation of a thallium

TABLE I

Reagent	MRH, ε_{1H} (520 nm)	MR, ε_1 (520 nm)	log k_{11}	log k_{12}	log K_{1H}
PAR	2·08 × 10^4*	2·93 × 10^4†	6·03‡	2·93‖	17·93**
	1·8 × 10^4	2·86 × 10^4‡‡			
	1·9 × 10^4††	2·90 × 10^4‖‖			
TAR	2·28 × 10^4*	3·34 × 10^4***	4·01‖‖‖	2·98‡	13·41**
		3·33 × 10^4†††			
		3·10 × 10^4‡‡‡			

* From $\varepsilon = A_{0l}/c_R$ for solutions with metal ion excess.

† From $\varepsilon = A_{0j}/c_M$ for solutions with reagent excess, A measured at pH 2–3.

‡ From equation (14).

‖ From equation (1), average of 6 values.

** From equation (15).

†† Busev and Tiptzova.[2]

‡‡ From $A = f(c_M)$ at pH 2·1 with metal ion excess.

‖‖ From horizontal of $A = f(c_R)$ at pH 2·1.

*** From $\varepsilon = A_{0l}/c_M$ for solutions with ligand excess in 30% v/v ethanol medium at pH 2·90, from $A = f(c_R)$.

††† From $A = f(\text{pH})$ for $c_M = 1{\cdot}71 \times 10^{-5}M$ and 10-fold excess of ligand.

‡‡‡ From $A = f(c_M)$ with metal ion excess and $c_R = 1{\cdot}71 \times 10^{-4}M$.

‖‖‖ From equation (3), average of 6 values.

complex from both H_3R^+ and H_2R at pH 0–2 (Fig. 5). The positions of the characteristic "complex" and "ligand" maxima are at 541–557 and 455–465 nm respectively for the 1:1 complex in acid solution, but are dependent on the relative concentrations of the components, *i.e.*, they are at 545 and 440 nm for solutions with metal ion excess at pH $\geqslant$ 0 (Fig. 2, curve 3) and at 540 nm for those with ligand excess ($c_M = 2{\cdot}74 \times 10^{-5}M$ and $c_R = 2{\cdot}20 \times 10^{-4}M$) in 30% v/v ethanolic medium if the absorbance of the ligand excess is corrected for. Complexation occurs at pH $\geqslant$ 0 in equimolar solutions ($c_M = c_R = 6{\cdot}72 \times 10^{-5}M$) and begins in 10$M$ perchloric acid with excess of thallium ($c_M = 3{\cdot}17 \times 10^{-3}M$, $c_R = 4{\cdot}27 \times 10^{-5}M$), the first complex being quantitatively formed even at pH 0–1. In both cases the pH–absorbance curves are considerably deformed by hydrolysis of the thallium species, at pH $> 2{\cdot}1$ and >1 respectively. For solutions with a 5 to 30-fold excess of ligand and $c_M = 1{\cdot}71 \times 10^{-5}$ M, the absorbance becomes constant at pH 2·6–3·7 but increases further at 540 nm for pH $> 3{\cdot}7$ (Fig. 6).

Mathematical treatment of the pH–absorbance curves according to equations (1)–(7) proves that equilibrium **A** exists at pH < 2 but is accompanied by equilibrium **B** in equimolar solutions. Both k_{12} and k_{11}, calculated according to equations (1) and (3), have constant values over a wide range of pH.

Analysis of the differential absorbance plots [equations (10) and (11)] gives clear evidence that only the 1:1 complexes are formed with up to 10-fold excess of TAR at pH 0·7, since the graphical plot $A = f(\varepsilon_2 c_R - \Delta A)c_R$ tends to zero ($A_{01} = \varepsilon_1 c_R = 0$). Measurements were made at 580 nm to diminish the interference of the excess of strongly absorbing ligand.

The co-ordination of a further ligand according to the two equilibria possible at pH 0·7:

$$\text{Tl(RH)} + H_3R^+ \rightleftharpoons \text{Tl(RH)}_2 + 2H^+ \qquad k_{2H}'$$

$$\text{Tl(RH)} + H_2R \rightleftharpoons \text{Tl(RH)}_2 + H^+ \qquad k_{2H}$$

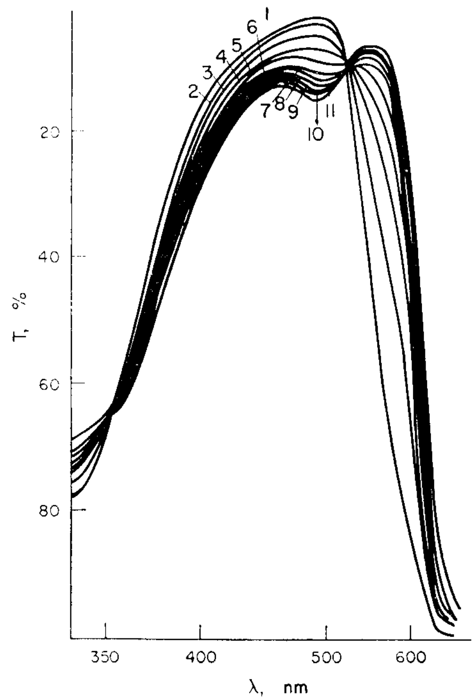

FIG. 5.—Transmittance curves of equimolar solutions of Tl(III) and TAR. $c_M = c_R = 6{\cdot}72 \times 10^{-5}M$. *1*—pH 0; *2*—pH 0·3; *3*—pH 0·57; *4*—pH 0·74; *5*—pH 0·96; *6*—pH 1·15; *7*—pH 1·26; *8*—pH 1·41; *9*—pH 1·56; *10*—pH 1·69; *11*—pH 1·92;

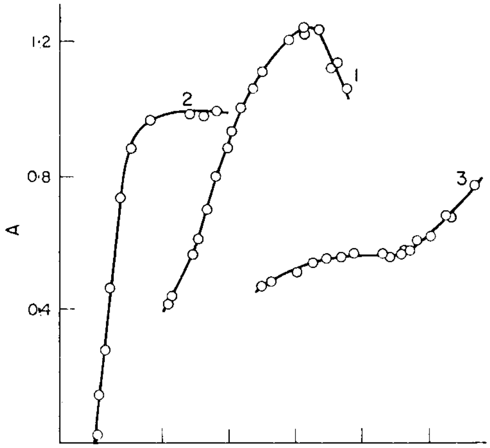

FIG. 6.—Absorbance-pH plots for Tl(III) solutions with TAR. *1*—$c_M = c_R = 6{\cdot}72 \times 10^{-5}M$, 550 nm; *2*—$c_R = 4{\cdot}27 \times 10^{-5}M$, $c_M = 3{\cdot}17 \times 10^{-3}M$, 550 nm; *3*—$c_M = 1{\cdot}91 \times 10^{-5}M$, $c_R = 1{\cdot}71 \times 10^{-4}M$, 540 nm. 30% v/v ethanol (absorbance difference between Tl(III) complex and reagent excess plotted).

was found only for TAR excesses larger than 14 to 33-fold ($c_M = 3{\cdot}17 \times 10^{-5}M$) (Figs. 7 and 8). A 30% v/v ethanol medium was used to keep TAR in solution.

The values of k_{2H} and k_{2H}' were obtained from the logarithmic plot of equation (13) *via* the equations

$$\log k_{2H} + \log c_R - \log (1 + [H]/K_{a1}) + pH = 0 \tag{17}$$

$$\log k_{2H}' + \log c_R - \log (1 + K_{a1}/[H]) + 2pH = 0 \tag{18}$$

K_{2H} was calculated similarly to K_{1H}, from $K_{2H} = k_{2H}'/K_{a1} \cdot K_{a3} = k_{2H}/K_{a3}$, and hence $\log \beta_{2H} = \log K_{1H} + \log K_{2H}$. The results obtained were $\log k_{2H} = 2{\cdot}9_5$; $\log k_{2H}' = 1{\cdot}9_5$; $\log K_2{:} = 12{\cdot}3_5$; $\log \beta_{2H} = 25{\cdot}8$.

On the $\Delta A = f(c_R)$ curve the rather short interval corresponding to formation of the 1:2 complex does not allow any further interpretation, but a mixture of complexes is obviously always present, even with the largest accessible excess of ligand in acid solutions.

A maximum corresponding to a 1:1 complex was found on the Job curves at 500–600 nm for a pH range 0·4–3·0 and various total reagent concentrations, but there was a slight shift of the maximum at $\leqslant$ 560 nm and pH 1·5–2·0, from formation of a small amount of 1:2 complex (Fig. 9).

The complexes and their regions of existence are similar to those with PAR, but the tendency to form 1:2 complexes is much lower, $Tl(RH)_2^+$ being found only in solutions with a considerable excess of TAR at pH > 0·7, but its concentration increases at pH $\geq$ 3·5. Some data for the PAR and TAR complexes are collected in Table I. The thallium(III) complexes of TAR are less stable than those of PAR but both reagents are about equally useful for the spectrophotometric determination of thallium, though the mixture of 1:1 and 1:2 complexes obtained means that the pH and the concentration of the reagent must be carefully kept controlled.

Spectrophotometric determination of thallium

With a final PAR concentration of $1{\cdot}5 \times 10^{-4}M$ at pH 2·1–2·5, Beer's law is obeyed up to 10 μg of thallium per ml at 530–540 nm in unbuffered solutions. The sensitivity is 0·08 μg/cm² for an absorbance of 0·010 at 530 nm, and the relative standard deviation is 1·3% for 3·5 μg/ml. The reagent concentration permissible is limited by the high absorptivity of PAR under these conditions. These conditions differ from those used by Busev and Tiptzova[1,2] who used pH 4–4·5. For TAR in 30% v/v ethanol medium, the corresponding figures are pH 2·5–3·0 (no buffer), $\lambda = 540$ nm, at least 10-fold reagent excess. Beer's law is obeyed up to 9 μg/ml for solutions with $c_R = 2{\cdot}7.10^{-4}M$, sensitivity 0·06 μg/cm².

All common buffers as acetate, hexamine, chloracetate, biphthalate, formate even in 0·05–0·1*M* concentrations decrease the absorptivity at pH 2–5; but Beer's law is often obeyed over a wider range of thallium concentration. Acetate and hexamine cause precipitation in the PAR system. The colour of the complexes fades whether the solution is buffered or not, and eventually precipitation occurs. The pH and buffer concentration must be kept constant for both samples and standards.

Nitrate, perchlorate, sulphate, fluoride (1 mg/ml) and phosphate (0·5 mg/ml) do not interfere, but chloride, bromide, iodide and other reductants, niobium, tantalum, zirconium, titanium, thorium and lanthanides and many other cations all interfere seriously. Some interferences are shown in Table II. Bromine cannot be used to oxidize thallium(I) but ammonium persulphate in 1*N* sulphuric acid is suitable.[1,2]

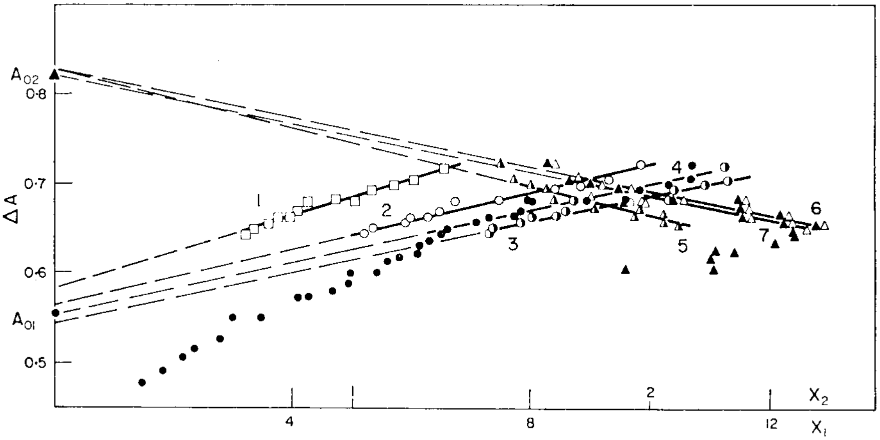

FIG. 7.—Graphical analysis of the plot of absorbance difference *vs.* concentration of TAR for solutions with $c_M = 3{\cdot}17.10^{-5}M$/pH 0·68 and 30% v/v ethanol (interpreted by successive approximation).

1—$x_2 = (A_{02} - \Delta A)c_R \,.\, 5 \cdot 10^3$; $A_{02} = 0{\cdot}970$
3—$x_1 = (A_{02} - \Delta A)c_R \,.\, 10^5$; $A_{02} = 0{\cdot}830$
5—$x_2 = (\Delta A - A_{01})/c_R' \,.\, 10^{-2}$; $A_{01} = 0{\cdot}565$
7—$x_2 = (\Delta A - A_{01})/c_R' \,.\, 10^{-2}$; $A_{01} = 0{\cdot}557$
2—$x_2 = (A_{02} - \Delta A)c_R \,.\, 10^4$; $A_{02} = 0{\cdot}910$
4—$x_1 = (A_{02} - \Delta A)c_R' \,.\, 10^5$; $A_{02} = 0{\cdot}830$
6—$x_2 = (\Delta A - A_{01})/c_R \,.\, 10^{-2}$; $A_{01} = 0{\cdot}545$
c_R' corrected values

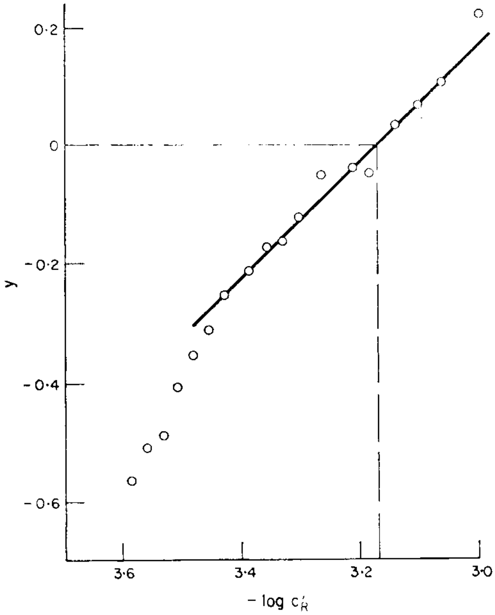

FIG. 8.—The logarithmic analysis of the curve $\Delta A = f(c_R')$ at pH 0·68. Conditions as for Fig. 7, $y = \log (\Delta A - A_{01})/(A_{02} - \Delta A)$.

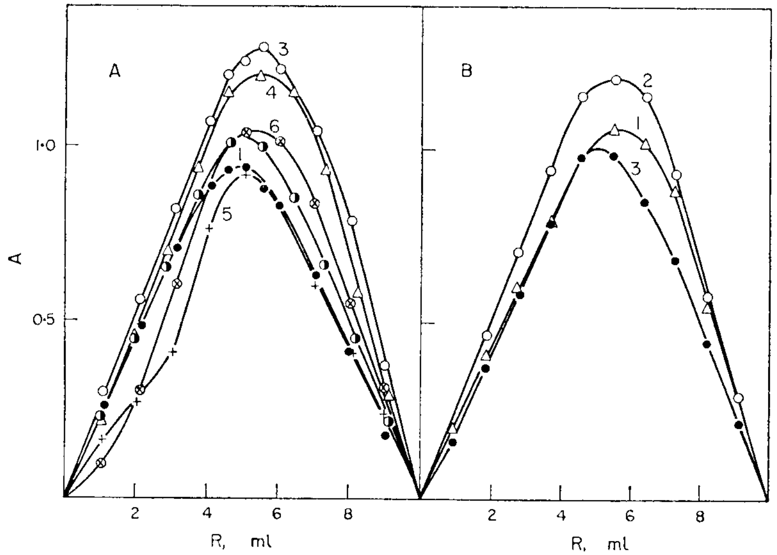

FIG. 9.—Job curves for the system Tl(III)-TAR.

A. 550 nm. *1*—pH 0·44; *2*—pH 1·20; *3*—pH 1·52; *4*—pH 2·02; *5*—pH 2·40; *6*—pH 2·96. *1*—c_0 = 1·48 × $10^{-4}M$, 2–4—c_0 = 1·34 × $10^{-4}M$, *5*, *6*—c_0 = 3·66 × $10^{-5}M$; 40-mm cells. **B.** c_0 = 1·31 × $10^{-4}M$, pH 2·02; *1*—530 nm; 2—550 nm; *3*—580 nm.

TABLE II.—CONCENTRATIONS OF VARIOUS IONS CAUSING A +5% ERROR IN THE ABSORBANCE OF 5 μg OF THALLIUM/ML*

Ion	PAR method	TAR method	Ion	PAR method	TAR method
	µg/ml	*µg/ml*		*µg/ml*	*µg/ml*
Cl^-†	3·0	5·0	Co^{2+}	1·5	0·9
Br^-†	4·6	5·0	Hg^{2+}	1·1	—
Mn^{2+}	1000	200	Bi^{3+}	0·7	0·4
Cd^{2+}	370	370	UO_2^{2+}	0·2	17
Al^{3+}	210	45	Ni^{2+}	0·2	0·8
Zn^{2+}	180	100	Cu^{2+}	0·2	0·2
Ag^+	4·0	—	Ga^{3+}	0·1	0·4
In^{3+}	4·3	0·4	Fe^{3+}	0·1	15
Pb^{2+}	2·7	55			

* c_R = 2·4.$10^{-4}M$, pH 2·3, 530 nm for PAR and c_R = 2·7.$10^{-4}M$, pH 2·9, 540 nm for TAR (without buffer).

† −5% error.

Procedure

Parameters for the TAR method are given in brackets. Add 10 ml (15) of 0·04% (0·06% in ethanol) solution of reagent to a nitric or sulphuric acid solution containing not more than 0·5 mg of thallium(III) in a 50-ml volumetric flask. Adjust the pH accurately to 2·1–2·2 (2·8–3·0) with dilute ammonia (check with pH-meter) and dilute to volume. Measure the absorbance at 530–540 nm (540–550) against a reagent blank adjusted to the sample pH not later than after 5 min. If desired, 5 ml of 1*M* chloracetate buffer at pH 2·4 may be added but the absorbance is related to calibration curves for the same concentration of buffer (valid for PAR only).

Zusammenfassung—Thallium(III) gibt empfindliche Reaktionen mit PAR und TAR ($\varepsilon = 2 \times 10^4$ bei 520 nm), wobei sich bei pH ~ 1–2 1:1-Komplexe, bei höheren pH-Wetren Gemische von 1:1- und 1:2-Komplexen bilden; über pH ~ 3 setzt Hydrolyse ein. Die Stabilitätskonstanten werden ermittelt.

Résumé—Le thallium(III) donne des réactions sensibles avec PAR et TAR ($\varepsilon = 2 \times 10^4$ à 520 nm), formant des complexes 1:1 à pH ~ 1–2 et un mélange de complexes 1:1 et 1:2 à des valeurs plus élevées du pH; l'hydrolyse se déclenche au-dessus de pH ~ 3. On a évalué les constantes de stabilité.

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UNTERSUCHUNGEN AN REAGENZIEN FÜR NIOB UND TANTAL—II

EIGENSCHAFTEN VON BRENZKATECHINDERIVATEN

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Zusammenfassung—Auf Grund theoretischer Überlegungen werden Möglichkeiten zur Erhöhung der Selektivität und der Empfindlichkeit analytisch anwendbarer Reaktionen für Niob und Tantal diskutiert, die auf der Bildung farbiger Metallchelate beruhen. Durch Variationen am Brenzkatechin als Grundkörper können die Bildungsreaktionen der Chelate beeinflußt werden. Als Ergebnis der systematischen Untersuchungen wird Dibromgallussäure als neues selektives und empfindliches Reagens empfohlen.

Die Bestimmung der Elemente Niob und Tantal—besonders wenn sie nebeneinander vorliegen—bereitet auch heute noch Schwierigkeiten, weil die Radien der beiden Ionen praktisch gleich sind und in der Lösung komplizierte Hydrolyse- und Polykondensationsreaktionen ablaufen. Für die Erfassung kleiner Gehalte der Erdsäuren mittels photometrischer Verfahren werden—neben anorganischen Reagenzien—meistens Pyrogallol,[2] Brenzkatechin,[3] Hydrochinon[4] und neuerdings auch Brompyrogallolrot[5] sowie 4-(2-Pyridylazo)-resorcin (PAR)[6] benutzt. Alle diese Reagenzien wurden rein empirisch gefunden. Systematische Untersuchungen zur Entwicklung neuer Reagenzien für die Bestimmung der Erdsäuren mit höherer Selektivi tät und Empfindlichkeit sind kaum bekannt. Über erste Versuche dazu haben wir früher berichtet.[7]

Niob(V) und Tantal(V) bevorzugen Bindungen zum Sauerstoff als Donatoratom. Fungieren zwei solcher Donatoren, so kommt es zur Bildung besonders stabiler fünf- oder sechsgliedriger Chelatringe. Diese Komplexe sind farbig, wenn bei ihrer Bildung ein π-Elektronensystem beteiligt ist (Polyphenole, Ascorbinsäure). Entscheidend ist der Abstand der Sauerstoff-Donatoratome untereinander. Da aus früheren Untersuchungen[7] bekannt war, daß für Niob und Tantal orthoständige OH-Gruppen analytisch funktionell wirken, benutzten wir Brenzkatechin als Grundkörper für die weiteren Versuche.

Ausgehend vom Brenzkatechin ergeben sich für neue Niob-Tantal-Reagenzien folgende Möglichkeiten:

(*a*) Steigerung der Empfindlichkeit

(*i*) Erhöhung des Reaktionsausmaßes

Ein erfolgversprechender Weg ist eine solche Veränderung des Liganden, daß eine größere Säuredissoziationskonstante resultiert, da der Ligand erst durch ein Säure-Base-Gleichgewicht gebildet wird. Andere Möglichkeiten, wie Erhöhung der Reagenskonzentration oder des pH-Wertes, scheiden aus praktischen Gründen (begrenzte Löslichkeit, Eigenabsorption und Oxydationsempfindlichkeit) aus.

(*ii*) Beeinflussung der Metall-Ligand-Bindung
Bei gegebenem Metallion können die Eigenschaften der Chelate auch durch Veränderungen am Grundgerüst beeinflußt werden. Dadurch werden auch die optischen Eigenschaften der Komplexe und somit auch die Nachweisgrenze beeinflußt.

(*b*) Erhöhung der Selektivität
Eine Verbesserung der Selektivität läßt sich auch durch eine Beeinflussung der Metall-Ligand-Bindung durch Variation am Liganden erreichen, da die Wirkung der Substituenten bei verschiedenen Metallionen unterschiedlich ist.

Variation am Grundkörper

Die Variation am Grundkörper Brenzkatechin soll durch Substitution erfolgen. Da die Wirkung von Substituenten in diesem System im wesentlichen von zwei Effekten (Resonanzeffekt und induktiver Effekt) bestimmt wird, erscheinen Halogene als Substituenten besonders geeignet.

Bei Vorversuchen zeigte es sich, daß sich Chlor und Brom als Substituenten in ihrer Wirkung kaum unterscheiden (4-Brombrenzkatechin und 4-Chlorbrenzkatechin) Die Untersuchungen wurden deshalb nur mit den bequemer zugänglichen Bromverbindungen fortgeführt. Tetrabrombrenzkatechin konnte nicht geprüft werden, weil es in Wasser praktisch unlöslich ist. Durch Einführen der hydrophilen Hydroxylgruppe (Tribrompyrogallol) wurde es möglich, die Wirkung von drei Bromatomen auf den Grundkörper zu studieren. Um die Löslichkeit der Reagenzien noch weiter zu steigern, machte es sich erforderlich, ein Bromatom des Tribrompyrogallols durch eine der Hydratisierung zugängliche Gruppe zu ersetzen. Die Wahl fiel auf die Carboxylgruppe, weil sie sich präparativ ohne größere Schwierigkeiten einführen läßt (Dibromgallussäure).

Zur Charakterisierung der Substanzen Brenzkatechin, 4-Chlorbrenzkatechin, 4-Brombrenzkatechin, Tribrompyrogallol und Dibromgallussäure wurden die Absorptionsspektren der Niob(V)- bzw. Tantal(V)-Chelate bei verschiedenen pH-Werten aufgenommen. Die benutzten Niob- bzw. Tantal-Lösungen enthielten Oxalsäure, da—wie entsprechende Untersuchungen ergaben—diese im Vergleich zu anderen Polycarbonsäuren für eine Nebeneinanderbestimmung der Erdsäuren am besten geeignet ist.

Als Beispiel sind in den Abbildungen 1 und 2 die erhaltenen Spektren von Brenzkatechin und Dibromgallussäure wiedergegeben. Zur Übersicht sind in Tabelle I die höchsten im Meßbereich erhaltenen Extinktionswerte zusammengestellt.

DISKUSSION DER ERGEBNISSE

Die Chelate von Niob(V) und Tantal(V) mit den hier untersuchten Polyphenolen absorbieren im ultravioletten und sichtbaren Spektralbereich. Die Banden der Chelate zeichnen sich bereits im Spektrum der Liganden ab, die Chelatspektren lassen sich deshalb wohl als Elektronenübergangsspektren (charge transfer) auffassen.

Nach Sommer[8] verschiebt sich das Absorptionsmaximum solcher Teilchen mit steigender Stabilität der Metall-Sauerstoff-Bindung bathochrom. Der Einfluß der Substituenten auf die Eigenschaften der Metallchelate läßt sich, abgesehen von sterischen Faktoren, durch zwei Effekte-Resonanzeffekt und induktiver Effekt-beschreiben. Bei den folgenden Betrachtungen soll der Einfluß der auch als Substituenten wirkenden zwei OH-Gruppen des Grundkörpers als konstant angesehen werden.

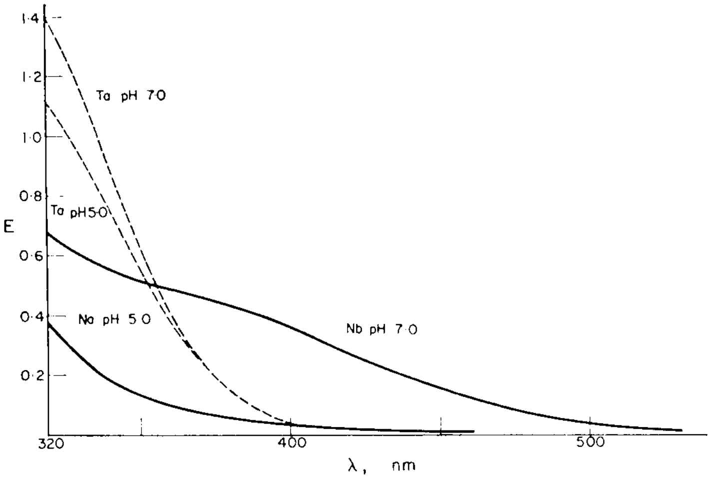

ABB. 1.—Absorptionsspektren der Brenzkatechin-Niob- und Tantal-Chelate bei unterschiedlichen pH-Werten (oxalsäurehaltige Lösungen).

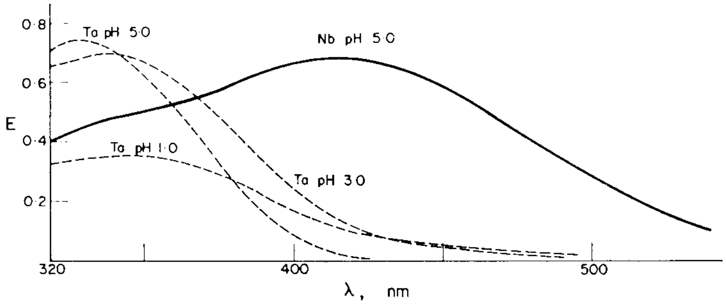

ABB. 2.—Absorptionsspektren der Dibromgallussäure-Niob- und Tantal-Chelate bei unterschiedlichen pH-Werten (oxalsäurehaltige Lösungen).

TABELLE I.—MAXIMALE EXTINKTIONSWERTE DER NIOB- UND TANTAL-POLYPHENOLCHELATE

Substanz	pH 1,0		pH 3,0		pH 5,0		pH 7,0	
	Nb	Ta	Nb	Ta	Nb	Ta	Nb	Ta
Brenzkatechin	—	—	—	—	0,19	0,58	0,47	1,09
4-Chlorbrenzkatechin	—	—	—	—	0,38	1,22	0,66	1,38
4-Brombrenzkatechin	—	—	—	—	0,37	1,12	0,67	1,41
Tribrompyrogallol	—	0,35 (345)	—	0,69 (340)	0,68 (415)	0,75 (330)	*	*
Dibromgallussäure	—	0,47	—	0,69	0,78 (380)	1,14	*	*

( ) Absorptionsmaxima, *nm*
— keine Reaktion
* wegen Oxydation des Polyphenols nicht gemessen

Die erhaltenen Meßergebnisse zeigen, daß durch Einführung des Halogens in der 4-Stellung die Reaktionen mit Niob(V) und Tantal(V) empfindlicher werden. Hierbei ist der Einfluß des induktiven Effekts von Bedeutung, da die Halogenderivate des Brenzkatechins stärker sauer sind als der Grundkörper. Parallel dazu kommt es aber auch zu einer Schwächung der Me-O-Bindung im Chelat. Außerdem besteht eine Wechselwirkung des Substituenten mit dem Kern (bzw. Chelatring) durch Resonanz. Verantwortlich dafür ist unter anderem eine Grenzstruktur mit einer Negativierung am Kohlenstoffatom 1 und damit auch am Donatoratom. Das würde auf eine Stabilisierung der Me-O-Bindung deuten. Experimentell zeigt sich das in der bathochromen Verschiebung der angedeuteten Maxima der Niobchelate bei pH = 7,0 der halogenierten Produkte gegenüber Brenzkatechin. Der ähnliche Verlauf der Absorptionskurven weist darauf hin, daß die Substitution die Chelatbildung hauptsächlich durch den Induktionseffekt und der damit verbundenen besseren Deprotonisierung der Liganden beeinflußt.

Die Niob- bzw. Tantalchelate des Tribrompyrogallols weisen auffällige Unterschiede in ihren optischen Eigenschaften im Vergleich mit den bisher betrachteten auf. Das Absorptionsmaximum ist bei Niob weit zum langwelligen Teil des Spektrums verschoben. Ähnlich liegen die Verhältnisse bei Tantal. Das ist auf eine Stabilisierung durch Resonanz zurückzuführen, weil Tribrompyrogallol stärker sauer ist als Brenzkatechin. Interessant ist die Bildung von Tantalchelaten mit Tribrompyrogallol bei pH = 1,0 und pH 3,0; die Beteiligung des induktiven Effektes hierbei ist sehr wahrscheinlich.

Bei der Dibromgallussäure werden zwar die Reaktionen wegen der besseren Löslichkeit des Reagens und damit wegen des höheren Angebots an Liganden empfindlicher, weniger stabile Me-O-Bindung im Vergleich mit Tribrompyrogallol sind jedoch wegen der hyposochromen Verschiebung der Absorptionsmaxima nicht ausgeschlossen.

Eng verbunden mit dem Einfluß der Substituenten sind die später zu diskutierenden analytischen Probleme. Unter den hier festgelegten Bedingungen sind 4-Chlorbrenzkatechin bzw. 4-Brombrenzkatechin für eine photometrische Niob-oder Tantalbestimmung bei pH = 7,0 dem Brenzkatechin vorzuziehen, da die halogenierten Produkte die Erfassung kleinerer Gehalte gestatten. Die für Tantal brauchbaren Reaktionen (pH = 5,0 und pH = 7,0) sind jedoch wenig selektiv gegenüber Niob.

Die recht intensiven Farbreaktionen der Erdsäuren mit Tribrompyrogallol (Niob pH = 5,0, Tantal pH = 1,0 und pH = 3,0) sind für analytische Zwecke geeignet, auch wenn beide Elemente nebeneinander vorliegen.

Die Dibromgallussäure verhält sich ähnlich, ist jedoch analytisch noch wertvoller als Tribrompyrogallol, weil ihre Reaktionen empfindlicher sind. Außerdem ist Dibromgallussäure besser wasserlöslich und gegen Oxydation weniger empfindlich als Tribrompyrogallol.

EXPERIMENTELLER TEIL

Herstellung der Stammlösung von Niob(V) und Tantal(V)

Es wurden 0,1329 g Nb_2O_5 (0,2209 g Ta_2O_5) mit 20 g Kaliumdisulfat in einem Quarztiegel aufgeschlossen, die erkaltete Schmelze in 400 ml Ammoniumoxalatlösung (40 g/l.) unter Erwärmen gelöst und mit der gleichen Lösung auf 500 ml aufgefüllt. Die erhaltene Lösung ist 0,002*M* an Niob (Tantal).

Bereitung der Lösungen

Es wurde 1,0 ml der Niob-(Tantal)-Lösung mit einer wäßrigen Lösung des entsprechenden Polyphenols versetzt, der pH-Wert mit Ammoniak und Perchlorsäure mit Hilfe eines pH-Messers eingestellt und mit Wasser auf 25 ml aufgefüllt. Die Messung erfolgte nach 10 Minuten gegen eine Blindprobe.

Um eine Oxydation der Polyphenole bei pH = 5,0 und pH = 7,0 zu vermeiden, wurden die Lösungen mit 5 ml 10%iger Natriumsulfitlösung stabilisiert. Das molare Verhältnis Chelatbildner zu Metall war 300:1. Bei Tribrompyrogallol konnte wegen dessen Löslichkeit in Wasser nur ein 50 facher Überschuß angewandt werden.

Summary—The possible improvement in sensitivity and selectivity of analytically useful reagents forming coloured chelates with niobium and tantalum is discussed on the basis of theoretical considerations. The formation of such chelates with compounds derived from pyrocatechol is affected by the substituents, and as a result of these studies, dibromogallic acid is recommended as a new selective and sensitive reagent for these two metals.

Résumé—On discute, sur la base de considérations théoriques, de l'amélioration possible en sensibilité et sélectivité des réactifs analytiquement utiles formant des chélates colorés avec le niobium et le tantale. La formation de tels chélates avec des composés dérivés du pyrocatéchol est influencée par les substituants et, comme résultat de ces études, on recommande l'acide dibromogallique comme nouveau réactif sélectif et sensible pour ces deux métaux.

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SHORT COMMUNICATIONS

A simple method for thermoanalysis of evolved gases

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In the study of the thermal properties of compounds—especially ammonium salts and amines—simultaneous or successive splitting-off of ammonia and water may occur. The interpretation of the decomposition processes then becomes extremely difficult, since stoichiometric computations cannot be applied because ammonia and water have almost the same molecular weight.

When a method for thermal analysis of nephroliths was developed[1,2] the question arose as to the temperature range over which struvite, $MgNH_4PO_4 \cdot 6H_2O$, loses ammonia. To solve this problem we have developed a method of determining the temperature at which splitting-off of volatile and oxidizable decomposition products—such as ammonia—will take place. The method can be adapted for observing the escape of halogens, acids, acid anhydrides and water.

EXPERIMENTAL

The derivatograph[3] was used in an air atmosphere, without pumping off the decomposition products. The heating rate was 10°/min. As a specimen-holder a 0·8-g double crucible of Pyrex glass (Fig. 1) was used. Platinum crucibles are not recommended, as platinum tends to oxidize ammonia exothermically.[4] A 3–7-mm thick layer of the specimen to be tested was placed in the bottom of the crucible, and covered with freshly heated aluminium oxide (200–300 mg). Above this inert material a solid reagent was placed, usually the thermal decomposition products of silver permanganate.[5] The crucible was placed in the furnace so that the thermocouple was in the upper third of the reagent.

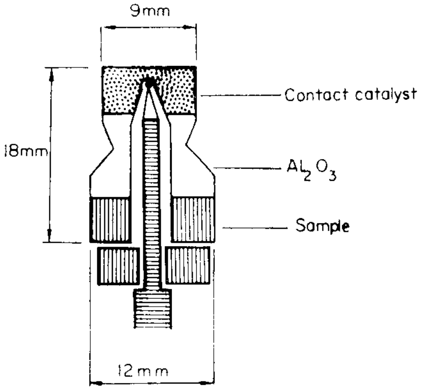

Fig. 1.—Double crucible.

The object of this arrangement was that enthalpy changes taking place within the sample should show only slightly on the DTA curve: in this way the escape of decomposition products which are split off endothermally but are oxidizable, would show exothermally on the DTA curve as a result of the oxidative process in the upper half of the crucible.

The thickness of the specimen layer can decisively affect the temperature of the onset and completion of the decomposition processes, and can even alter the sequence. In the double crucible used, the specimen is sealed off from the air-space of the furnace by relatively thick layers. In this way the decomposition conditions are those in the lower quarter of the specimen-holder (for 300–500 mg). The total space between the solid granules has a volume of only a few tenths ml and the gases and vapours evolved have difficulty in escaping. If the available void volume within the filled crucible is taken as 0·33 ml, this corresponds to 2% of the volume of 5 mg of ammonia at 300°. It may happen that ammonia release is immediately followed by a process that involves evolution of water. Any residual ammonia from the preceding process is then forced onto the catalyst by the water produced and a minor exothermic peak may appear on the DTA curve, but the size of this peak does not amount to 2% of the area of the principal process.

In comparative experiments, aluminium oxide was used without additional reagent, and the temperature was measured either in the upper half of the crucible (Figs. 4 and 5), or in the specimen (Figs. 2 and 3). The curves obtained when reagent was used are shown as dotted lines. Identical portions of curves have been left out for simplicity.

RESULTS

For exploring the performance and field of application of the double crucible, model compounds were used from which only ammonia and water escape in the course of thermal decomposition. Some interesting cases are described below.

Magnesium ammonium phosphate hexahydrate

On heating, this compound decomposes in two different ways. If an open dish of large surface is used as specimen-holder, three partially overlapping processes can be distinguished, in the course of which $6H_2O$, NH_3 and $0{\cdot}5H_2O$ are escaping. In a covered crucible, if there is relatively little free space above the specimen, or in our double crucible, the processes are clearly separated and correspond to escape of $5H_2O$, $H_2O + NH_3$, and $0{\cdot}5H_2O$ (Fig. 2).

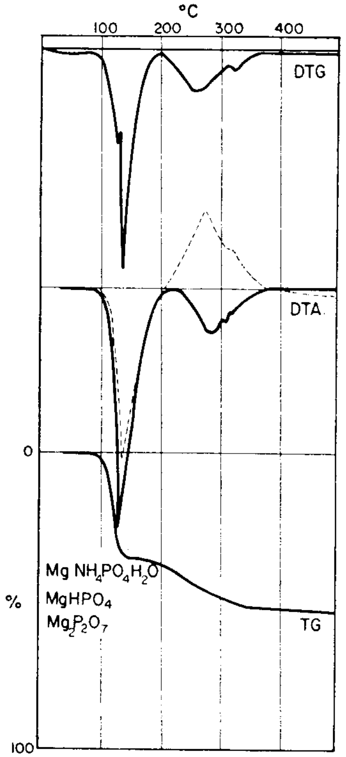

FIG. 2.—Decomposition curves of $MgNH_4PO_4{\cdot}6H_2O$ with (dotted line) and without (unbroken line) oxidizing catalyst. Quantity 100 mg.

However, when five nephroliths containing magnesium ammonium phosphate hexahydrate as principal component were analysed in this way, in no case were steps found corresponding to release of 5 of the 6 molecules of water of crystallization, so the thermal behaviour of magnesium ammonium phosphate hexahydrate appears to be influenced by its mode of formation.

Ammonium heptamolybdate tetrahydrate

The thermal decomposition of this compound has been studied by Erdey *et al.*[6] Molybdenum trioxide was found to be formed after escape of $4H_2O$, $3H_2O$, and $6NH_3$ in three distinctly separate processes.

However, it appears from the derivatogram (Fig. 3), obtained with reagent present, that the second and the third processes occur in a different way. On the DTA curve the first process is endothermic, while both the second and third are exothermic, which is only possible if ammonia escapes not in one but in two steps. In our opinion, $2NH_3 + H_2O$ split off in the second process and $4NH_3 + 2H_2O$ in the third, although it is equally possible that ammonia is already split off to a considerable extent in the first process. Comparison of the two DTA curves shows that the enthalpy changes are enhanced considerably by the oxidation of ammonia.

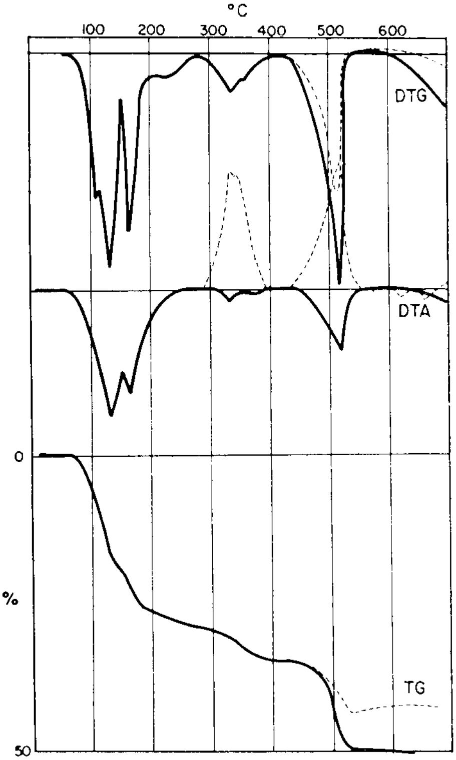

FIG. 3.—Decomposition curves of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. The DTA curve obtained with the use of a catalyst (silver permanganate heated to 160°) is shown by a dotted line. Quantity 127 mg.

Tetra-ammine copper(II) sulphate monohydrate

In agreement with Wendtlandt and Southern's mass-spectrometric studies,[7] our experiments show that ammonia escapes in all four decomposition processes. Since the weight loss is greatest in the first process, it is obvious that water is lost then. Flóra reached the same conclusions from the ammonia content of the sample after interruption of the heating.[8,9]

We succeeded in demonstrating this directly by using layers of freshly pulverized calcium carbide in the upper half of the crucible to give an exothermic reaction with water.

By dividing the conventional crucible into two compartments it has become possible to distinguish the products released during the various processes, by means of selective reactions induced in the crucible.

Not only an oxidizing agent can be used, but any substance that reacts unequivocally with one of the decomposition products. Several superimposed layers can be used simultaneously. Moreover, reactions between solids and gases can be studied.

The thermal decomposition of silver permanganate takes place in several steps. The greatest weight loss occurs during an extremely rapid exothermic process, at about 160°. The residual black powder—used as catalyst in Körbl's carbon and hydrogen method[5]—oxidizes ammonia at 140–160° with evolution of heat and loss in weight; after completion of the process most of the oxygen lost by the reagent is regained from the air.

The mixture formed in the first decompositon process of silver permanganate is not suitable for thermogravimetric tests, but from the areas under the peaks of the DTA curve conclusions can be drawn as to the amount of ammonia split off during the process studied. In calculating the areas it must be taken into account that the DTA curve is the resultant of one exothermic and one endothermic process.

If the reagent is kept at, say, 600° until weight constancy is reached, its activity at lower temperatures decreases. The higher the temperature to which silver permanganate has been heated, the higher is the temperature at which it begins to act as an oxidant. Silver permanganate loses weight gradually during its oxidation of other substances, and its specific gravity increases, while its capacity for binding sulphur trioxide and halogens increases. Utilization of this latter property is shown in Figs. 4 and 5.

Iron(II) ammonium sulphate hexahydrate

The DTA curve shows that after the gradual escape of the water of crystallization the first molecule of ammonia begins to split off at 280° (Fig. 4) and the second at 430–530°. It appears from the TG

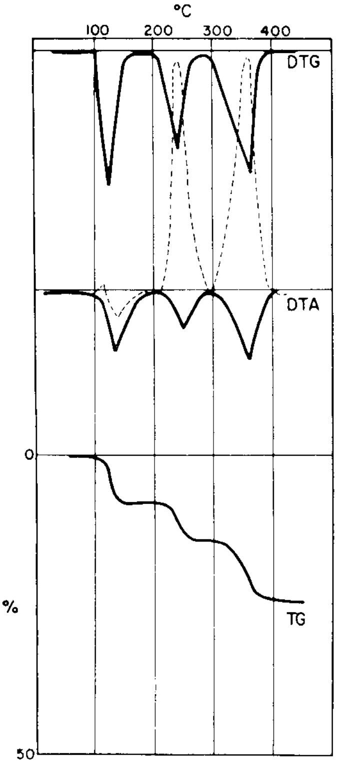

FIG. 4.—Decomposition curves of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The curves obtained with the use of a catalyst (silver permanganate heated to 530°) are shown as dotted lines. Temperature measured as in Fig. 1. Quantity 100 mg.

curve, obtained with reagent present, that in this latter process ammonia is accompanied by sulphur trioxide and water. The last loss in weight, compared to that obtained without reagent, is smaller by a value that corresponds to the weight of $0 \cdot 5SO_3$. After the catalyst reaction at 610°, there appears on the DTA curve the clearly visible endothermic peak at 660°, which is ascribable to the melting of silver sulphate.

Halogen-binding is shown on the DTA curve by the corresponding melting of silver halide, which is illustrated by the following example.

Copper(I) tetraiodomercuriate(II)

After a reversible modification at 80°, involving a colour change from red to black, the compound decomposes above 200° into HgI_2 and CuI (Fig. 5). Residual copper(I) iodide decomposes between 400 and 550° in the next process. If the decomposition product of silver permanganate previously heated to 710° is used, only mercury escapes, beginning at about 250°. There is only one step on the TG curve, as the reagent also binds the iodine originating from copper(I) iodide. The melting point of silver iodide is indicated on the DTA curve by the 550° peak. The weight loss at 420° corresponds to the mercury content of the compound.

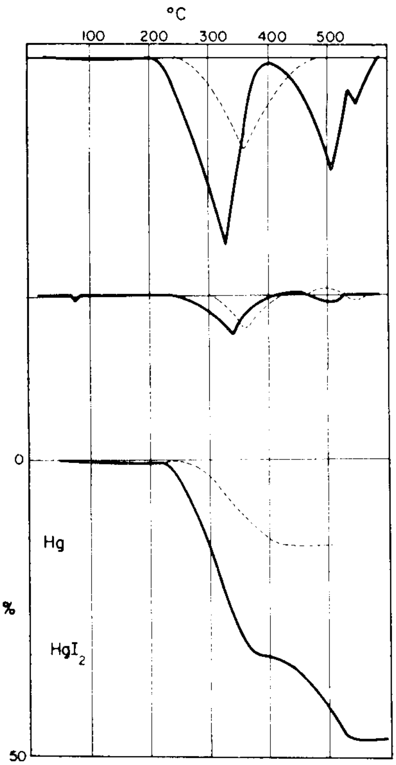

FIG. 5.—Decomposition curves of $Cu_2(HgI_4)$. The curves obtained with the use of silver permanganate heated to 710° are shown as dotted lines. Temperature measured as in Fig. 1. Quantity 68 mg.

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Summary—Thermoanalytical processes involving the splitting-off of ammonia, water, halogens, inorganic acids or acid anhydrides can be simply observed by using a specimen-holder in which specific reactions with the decomposition products can be induced. A special glass or quartz double crucible can be used for this purpose; the products arising in the lower part of the crucible can be oxidized selectively with reagents placed in the upper part, or can be bound or transformed into other compounds. This double crucible is also suitable for studying reactions taking place between solid and gaseous substances.

Zusammenfassung—Thermoanalytische Prozesse, bei denen Ammoniak, Wasser, Halogene, anorganische Säuren oder Säureanhydride abgespalten werden, lassen sich einfach beobachten durch Verwendung eines Probenhalters, in dem spezifische Reaktionen mit den Abspaltungsprodukten ausgeführt werden können. Ein besonderer Doppeltiegel aus Glas oder Quarz kann zu diesem Zweck verwendet werden; die im unteren Teil des Tiegels sich entwickelnden Produkte können mit Reagentien im oberen Teil selektiv oxidiert, gebunden oder in andere Verbindungen überführt werden. Dieser Doppeltiegel ist auch zur Untersuchung von Reaktionen zwischen Festkörpern und Gasen geeignet.

Résumé—On peut observer simplement les processus thermoanalytiques mettant en jeu le dégagement d'ammoniac, d'eau, d'halogènes, d'acides inorganiques ou d'anhydrides d'acide en utilisant un porte-échantillon dans lequel on peut provoquer des réactions spécifiques avec les produits de décomposition. On peut utiliser dans ce but un double creuset spécial en verre ou en quartz; les produits se formant dans la partie inférieure du creuset peuvent être oxydés sélectivement par des réactifs placés dans la partie supérieure, ou peuvent être liés ou transformés en d'autres composés. Ce double creuset convient aussi à l'étude de réactions se produisant entre des substances solides et gazeuses.

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Potentiometric studies of the complexes of chromium(VI), molybdenum(VI) and tungsten(VI) with some Azoxine S dyes

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CHROMIUM(VI), molybdenum(VI) and tungsten(VI) co-ordinate with a number of ligands, but very few equilibrium studies for these complexes have been made.[1–3]

In the usual potentiometric method for evaluating equilibrium constants, most information is obtained over the pH range 1–5,[4] but with sexivalent metals polymerization in this pH range makes it difficult to evaluate the equilibrium constants. Thus, it is preferable to utilize the reaction between the hydroxyl ion and the metal complexes at higher pH values for such studies, *viz.*, pH 6·5–9·5.

An earlier study[5] established that Azoxine S dyes form with molybdenum(VI) water-soluble 1:1 complexes in the pH range 2·5–6·5. The present paper describes the determination of the equilibrium constants of the complexes of chromium(VI), molybdenum(VI) and tungsten(VI) with 8-hydroxyquinoline-5-sulphonic acid (OXS), 7-phenylazo-8-hydroxyquinoline-5-sulphonic acid (PAZOXS), 7-(4-sulphophenylazo)-8-hydroxyquinoline-5-sulphonic acid (SPAZOXS) and 7-(4-sulphonaphthylazo)-8-hydroxyquinoline-5-sulphonic acid (SNAZOXS). The molybdenum co-ordinating species above pH 6·5 in all these systems is MoO_3 and it is assumed that chromium(VI) and tungsten(VI) behave analogously. The general reaction occurring during the titration may be represented as

$$MO_3A^{n-} + OH^- \rightleftharpoons MO_4^{2-} + HA^{(n-1)-}$$

where M represents Cr, Mo or W, and A the ligand.

EXPERIMENTAL

Reagents

Metal ion solutions. Requisite amounts of analytical grade K_2CrO_4, $Na_2MoO_4 . 2H_2O$ and $Na_2WO_4 . 2H_2O$ were dissolved in doubly distilled water.

Reagent solutions. The dyes used were prepared and purified as described earlier.[5,6] The stock solutions (0·01*M*) of 8-hydroxyquinoline-5-sulphonic acid and the monosodium salts of the dyes were prepared and the ionic strengths of the solutions were kept constant ($\mu = 0{\cdot}1$) by adding requisite amounts of potassium nitrate solution.

Procedures

Potentiometric titrations. Ten ml of 0·1*M* ligand solution were mixed with 20 ml of 0·1*M* metal solution followed by 5 ml of 1*M* potassium nitrate. The mixture was then made up to 50 ml with doubly distilled water. The titrant was 0·08*M* sodium hydroxide standardized against potassium hydrogen phthalate solution. For the determination of dissociation constants of the ligands, $4 \times 10^{-3}M$ solutions of ligand in 0·1*M* potassium nitrate was used.

The pH meter was standardized before and after each titration, with 0·05*M* potassium hydrogen phthalate and sodium borate solutions. All measurements were made at room temperature, 16 ± 1°.

Equilibrium calculations. The acid dissociation constants of the ligands were calculated by a method analogous to that of Martell *et al.*[7] The complex formation constants were calculated by the procedure of Kula.[3] 8-Hydroxyquinoline-5-sulphonic acid and monosodium salts of SPAZOXS and SNAZOXS contain two titratable hydrogen atoms, so the equilibrium constants (K_f) were calculated from the equation

$$K_f = \frac{\{H^+\}(1 - a) + K_b(2 - a)}{a\,M_t\{H^+\}^2K_b}$$

The monosodium salt of PAZOXS has only one titratable hydrogen atom and the following equation was used:

$$K_f = \frac{K_b(1 - a) - a\{H^+\}}{(1 + a)M_t\{H^+\}^2K_b}$$

where a = moles of alkali added per mole of ligand, M_t = total metal ion concentration, and K_b = the dissociation constant of $HA^{(n-1)-}$.

From the experimental titration curves the values of $\{H^+\}$ and a were obtained and K_f was calculated at different values of a.

RESULTS AND DISCUSSION

The titration curves obtained in SPAZOXS systems are shown in Fig. 1. These curves are quite similar to those obtained with iminodiacetic acid.[3] The reactions of the complexes with the added base were fairly rapid and equilibrium was achieved within 5 min of each addition.

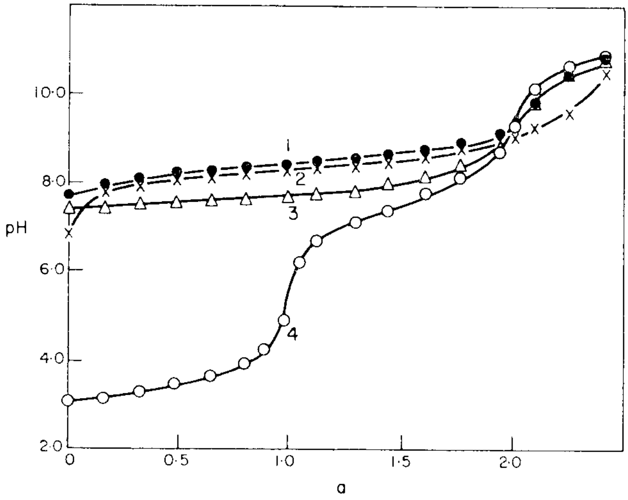

FIG. 1.—Titration curves for SPAZOXS systems.
SPAZOXS = $2 \times 10^{-3}M$; Cr(VI), Mo(VI) or W(VI) = $4 \times 10^{-2}M$.
1, W–SPAZOXS; 2, Mo–SPAZOXS;
3, Cr–SPAZOXS; 4, SPAZOXS blank.

A comparison of the equilibrium constants (Table I) shows that within experimental error there is almost no difference between the stabilities of the corresponding molybdenum and tungsten chelates; this can be attributed to the similar behaviour of the ions and their nearly equal ionic radii.[8] However, the corresponding values of chromium(VI) chelates are different, which may be due to their dissimilar nature. A comparison of the equilibrium constants for different ligands shows that the stabilities of the complexes decrease with decrease in the basicity of the ligands with respect to the addition of the first proton: OXS > PAZOXS > SPAZOXS > SNAZOXS.

TABLE I.—EQUILIBRIUM CONSTANTS OF Cr(VI), Mo(VI) AND W(VI) CHELATES

Ligand	pK_b	log K_f (16 ± 1°C; μ = 0·1, KNO_3)		
		Cr(VI)	Mo(VI)	W(VI)
OXS	8·47	17·43 ± 0·04	19·53 ± 0·05	19·87 ± 0·07
PAZOXS	7·85	16·78 ± 0·04	18·12 ± 0·04	18·34 ± 0·04
SPAZOXS	7·68	16·80 ± 0·07	17·98 ± 0·07	18·05 ± 0·07
SNAZOXS	7·62	16·77 ± 0·04	17·82 ± 0·05	18·00 ± 0·04

The equilibrium constants (K_f') independent of pH were calculated from the dissociation constants (K_m) of chromic,[9] molybdic[10] and tungstic[10] acids, by the equation $K_f' = K_f/K_m$ where K_m is $[Mo_4^{2-}][H^+]/[HMO_4^-]$ and has the values $10^{6\cdot5}$ for Cr(VI), $10^{7\cdot8}$ for Mo(VI) and $10^{8\cdot1}$ for W(VI).

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Summary—The equilibrium constants of the complexation reactions of Cr(VI), Mo(VI) and W(VI) with 8-hydroxyquinoline-5-sulphonic acid (OXS), 7-phenylazo-8-hydroxyquinoline-5-sulphonic acid (PAZOXS), 7-(4-sulphophenylazo)-8-hydroxyquinoline-5-sulphonic acid (SPAZOXS) and 7-(4-sulphonaphthylazo)-8-hydroxyquinoline-5-sulphonic acid (SNAZOXS) have been determined by potentiometric pH titration. The values in the case of chromate are different from those for molybdate and tungstate. The order of stabilities is OXS > PAZOXS > SPAZOXS > SNAZOXS.

Zusammenfassung—Die Gleichgewichtskonstanten der Komplexbildungsreaktionen von Cr(VI), Mo(VI) und W(VI) mit 8-Hydroxychinolin-5-sulfonsäure (OXS), 7-Phenylazo-8-hydroxychinolin-5-sulfonsäure (PAZOXS), 7-(4-Sulfophenylazo)-8-hydroxychinolin-5-sulfonsäure (SPAZOXS) und 7-(4-Sulfonaphthylazo)-8-hydroxychinolin-5-sulfonsäure (SNAZOXS) wurden durch potentiometrische pH-Titration ermittelt. Die Werte für Chromat sind von denen für Molybdat und Wolframat verschieden. Die Reihenfolge der Stabilitäten ist OXS > PAZOXS > SPAZOXS > SNAZOXS.

Résumé—On a déterminé par titrage pH potentiométrique les constantes d'équilibre des réactions de complexation de Cr(VI), Mo(VI) et W(VI) avec l'acide 8-hydroxyquinoléine 5-sulfonique (OXS), l'acide 7-phénylazo 8-hydroxyquinoléine 5-sulfonique (PAZOXS), l'acide 7-(4-sulfophénylazo) 8-hydroxyquinoléine 5-sulfonique (SPAZOXS) et l'acide 7-(4-sulfonaphtylazo) 8-hydroxyquinoléine 5-sulfonique (SNAZOXS). Les valeurs dans le cas du chromate sont différentes de celles du molybdate et du tungstate. L'ordre des stabilités est OXS > PAZOXS > SPAZOXS > SNAZOXS.

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Spectroscopic method of studying kinetics of consecutive reactions

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FEW methods have been proposed for studying the kinetics of consecutive reactions. They include the graphical method due to Powell and French,[1] the graphical integration time-variable transformation method of Widequist,[2] the time ratio method developed by Frost and Schweiner,[3] the steady-state method discussed by Rutherford *et al.*[4] and McMillan's simple ratio method.[5]

Recently a method has described[6,7] for studying the reaction kinetics of reversible and irreversible reactions, and determining the equilibrium constants of reversible reactions, based on the difference in molar absorptivities of reactants and products at a fixed wavelength. The method has been applied to first- and second-order reactions[6,7] and can be readily extended to reactions of higher order. Further consideration showed that the principle could also be applied to the study of kinetics of consecutive reactions, the necessary experimental observations being the absorbance as a function of time.

First-order consecutive reaction

Consider the irreversible consecutive reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

where k_1 and k_2 are the rate constants. The reaction consists of two first-order reactions, and to determine the rate constants, the concentrations of A, B and C must be determined at time t. Let the molar absorptivities of the three species be $\varepsilon_{\mathrm{A}1}$, $\varepsilon_{\mathrm{B}1}$ and $\varepsilon_{\mathrm{C}1}$ at wavelength λ_1 and $\varepsilon_{\mathrm{A}2}$, $\varepsilon_{\mathrm{B}2}$ and $\varepsilon_{\mathrm{C}2}$ at wavelength λ_2, and let the initial concentration of A be a, and the concentrations of A, B and C at time t be $(a - x)$, $(x - y)$ and y respectively. Then at time t the total absorbances A_1 and A_2 at λ_1 and λ_2 are

$$A_1 = \varepsilon_{\mathrm{A}1}(a - x) + \varepsilon_{\mathrm{B}1}(x - y) + \varepsilon_{\mathrm{C}1}y \tag{1}$$

$$A_2 = \varepsilon_{\mathrm{A}2}(a - x) + \varepsilon_{\mathrm{B}2}(x - y) + \varepsilon_{\mathrm{C}2}y \tag{2}$$

and the problem of obtaining the individual concentrations is purely algebraic. On rearrangement of equations (1) and (2):

$$x = \frac{(a\varepsilon_{\mathrm{A}2} - A_2) + R(A_1 - a\varepsilon_{\mathrm{A}1})}{(\varepsilon_{\mathrm{A}2} - \varepsilon_{\mathrm{B}2}) - R(\varepsilon_{\mathrm{A}1} - \varepsilon_{\mathrm{B}1})} \tag{3}$$

where $R = (\varepsilon_{\mathrm{C}2} - \varepsilon_{\mathrm{B}2})/(\varepsilon_{\mathrm{C}1} - \varepsilon_{\mathrm{B}1})$, and

$$y = \frac{(A_2 - a\varepsilon_{\mathrm{A}2}) - P(A_1 - a\varepsilon_{\mathrm{A}1})}{(\varepsilon_{\mathrm{C}2} - \varepsilon_{\mathrm{B}2}) - P(\varepsilon_{\mathrm{C}1} - \varepsilon_{\mathrm{B}1})} \tag{4}$$

where $P = (\varepsilon_{\mathrm{B}2} - \varepsilon_{\mathrm{A}2})/(\varepsilon_{\mathrm{B}1} - \varepsilon_{\mathrm{A}1})$.

Thus the concentrations of A, B and C can be determined at any time t from equations (3) and (4). The rate constants can then be evaluated from the usual expressions for first-order consecutive reactions:

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_1[\mathrm{A}] \tag{5}$$

which on integration gives

$$a - x = ae^{-k_1 t}, \tag{6}$$

and

$$\mathrm{d}[\mathrm{B}]/\mathrm{d}t = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{7}$$

which on integration gives

$$x - y = \frac{ak_1(e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1}\,. \tag{8}$$

An interesting example is the hydrolysis of glycol diacetate, catalysed by hydrochloric acid.

Second-order consecutive reactions

Consider the irreversible reactions

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_3} \mathrm{C} + \mathrm{E}$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{k_4} \mathrm{D} + \mathrm{E}$$

where k_3 and k_4 are the rate constants. Assume that only A, C and D absorb at the same wavelengths λ_1 and λ_2, and denote the absorptivities as before. Let the initial concentrations of A and B be a and b, and the concentrations of the four species at time t be $(a - x)$, $(b - x - y)$, $(x - y)$ and y for A, B, C and D respectively. Then x and y can be determined by means of equations (3) and (4) and define the concentrations of A and B.

The rate constant k_3 can be obtained from the rate expression

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_3[\mathrm{A}][\mathrm{B}] \tag{9}$$

which on integration gives

$$k_3 t = \frac{1}{(b - a)} \ln \frac{a(b - x - y)}{b(a - x)}\,. \tag{10}$$

Rate constant k_4 can then be obtained from the rate expression

$$\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_4[\mathrm{A}][\mathrm{B}] - k_2[\mathrm{B}][\mathrm{C}] \tag{11}$$

The ratio of equations (9) and (11), when integrated, gives the equation

$$x - y = \frac{a - x}{(k_4/k_3) - 1}\{1 - [(a - x)/a]^{(k^4/k_3)^{-1}}\} \tag{12}$$

from which, according to McMillan,[5] it is easy to determine the ratio k_4/k_3, and hence k_4 since k_3 is known from equation (10).

An interesting example of such a reaction is the saponification of a symmetrical diester, in which A is the diester, B the hydroxide, C the monoester and D the diacid.

The method would be expected to give reasonably accurate results if the values of the total absorbances and of the molar absorptivities are sufficiently different, and these factors impose a limit on the accuracy attainable.

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Summary—A simple absorbance measurement method is used to measure reaction kinetics of first- and second-order consecutive reactions.

Zusammenfassung—Zur Messung der Reaktionskinetik von Konsekutivreaktionen erster und zweiter Ordnung wird eine einfache Absorptionsmethode verwendet.

Résumé—On utilise une méthode de mesure d'absorbance simple pour mesurer les cinétiques de réactions de réactions consécutives d'ordres un et deux.

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Direct spectrophotometric method for determination of traces of boron in iron, steels and other compounds

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For the determination of boron in iron and steel samples titrimetry or colorimetry of boric acid has usually been employed after a previous separation of the boron from iron and other interfering elements. Separation techniques employed for the isolation of boron include precipitation,[1] distillation,[2,3] extraction,[4,5] ion-exchange[6,7] and electrolytic procedures.[8] Of these the distillation of boric acid as the methyl ester and the ion-exchange procedures are generally applied. For boron concentrations below 100 ppm extraction procedures seem to be more attractive however. So boron in steel can be converted into tetrafluoroborate, extracted as a coloured complex with Methylene Blue[4] or monomethylthionine[5] into dichloroethane and determined spectrophotometrically.

In iron and low-alloy steels boron can be determined by a Curcumin colour procedure[9,10] without previous separation of iron. If boron-free iron is used as a reference good results are obtained for concentrations over 20 ppm.[10]

We have developed a direct method for the determination of boron in the 1–200 ppm concentration range in iron and low-alloy steels, wherein no boron-free reference material is needed. The basis of our method is that the absorbance of the boron-Curcumin complex formed in the sample solution is compared directly with that of another aliquot of sample solution in which the boron is rendered inactive with fluoride before the Curcumin is added. For the formation of the boron-Curcumin complex the method of Grinstead and Snider[11] is used. In this procedure the acid required to develop the colour is partially neutralized with ammonium acetate.

Experiments show that our method can also be used for the analysis of boron in high-alloy steels and other materials.

EXPERIMENTAL

Reagents

Acid Reagent. Equal volumes of 96% sulphuric acid and glacial acetic acid.

Acetate buffer. Ammonium acetate (225 g) and glacial acetic acid (300 ml) in sufficient water to make 1 litre.

Fluoride reagent. Sodium fluoride solution, 4% w/v.

Curcumin reagent. A 0·125% w/v solution in glacial acetic acid.

Borax. Sodium tetraborate decahydrate stored over saturated aqueous sodium chloride solution.

Procedure

Dissolve about 250 mg of the sample in 10 ml of sulphuric acid (1 + 3) by gentle heating in a long-necked quartz vessel. If dissolution is incomplete, filter off the residue, wash it with water and transfer the filter pad to a platinum crucible; add 1 ml of 30% sodium carbonate solution, dry, ignite very carefully at low temperature and fuse for 15 min; cool the fused mass, dissolve it in the filtrate from the initial dissolution*, transfer the solution to a 25-ml calibrated flask and dilute to the mark with water. By pipette transfer 0·500-ml aliquots of the solution into two 30-ml polythene bottles, add to one of these 100 μl of the fluoride reagent, mix by swirling and allow both bottles to stand for 1 hr at room temperature. Add 3·00 ml of acid reagent to both bottles, wait at least 5 min, add 3·00 ml of Curcumin reagent to both solutions and allow to stand for 2 hr at 25° in a thermostat. Add 15·0 ml of acetate buffer, place the bottles back in the thermostat for 10 min, and read (at 555 nm) the absorbance of the solution without fluoride reagent against the "blank", which is the solution with fluoride reagent added. For boron concentrations up to 25 ppm use 50-mm cuvettes, and 10-mm cuvettes for higher concentrations.

For the preparation of boron standards for calibration add 0–50 μg of boron in the form of borax to 10 ml of sulphuric acid (1 + 3) and treat the solutions in the way mentioned above without fluoride reagent added. Use as a blank 10 ml of sulphuric acid (1 + 3) treated in the same way, inclusive of the addition of fluoride reagent.

RESULTS AND DISCUSSION

As a check on the method, increasing amounts of boron in the form of an aqueous borax solution were added to a series of aliquots corresponding to 250 mg of boron-free iron. After that the aliquots were treated by the general procedure and the boron concentrations were measured. The amounts of boron added corresponded to boron concentrations of 0·56–224 ppm in the iron. A correction was made for 0·4 ppm of boron impurity in the iron used. The results of these experiments are tabulated in Table I.

TABLE I.—RESULTS OBTAINED FOR INCREASING AMOUNTS OF BORON ADDED TO 250 mg PORTIONS OF BORON-FREE IRON

Boron added, *μg*	Boron concentration in the iron, *ppm*	Absorbance		Cuvette path-length, *mm*	Concentration found, *ppm*	
0·14	0·56	0·010	0·009	50	0·7	0·6
0·28	1·12	0·018	0·024	50	1·1	1·5
0·56	2·24	0·038	0·034	50	2·4	2·2
1·12	4·48	0·065	0·068	50	4·2	4·4
2·80	11·2	0·176	0·172	50	11·3	11·0
5·60	22·4	0·348	0·350	50	22·3	22·4
11·2	44·8	0·145	0·142	10	45·7	44·8
28·0	112	0·348	0·345	10	112	111
56·0	224	0·690	0·679	10	222	218

We conclude that boron can be determined in the concentration range of 1–220 ppm in iron by our procedure. The method can also be used for the analysis of boron in mild steels. This is demonstrated in Table II which shows the results obtained with British Chemical Standards and National Bureau of Standards mild steel standard samples. Our mean values correspond with the mean values given on the certificates. Our values for the standard deviation are lower than those calculated from the BCS results, though it has to be taken into consideration that the BCS figures were collected from various laboratories, all of which used the colorimetric dianthrimide method after isolation of the boron by ion-exchange.

In general, alloying elements have no influence on the determination of boron. This is demonstrated in Table III. The solutions used for these determinations were obtained by the addition of 25 mg of each of the elements mentioned, in aqueous solution, to 225 mg of boron-free iron. After the addition of 2·5 μg (10 ppm) or 25 μg (100 ppm) of boron (as aqueous borax solution) 10 ml of sulphuric acid (1 + 3) were added and the iron was dissolved by gently heating. After cooling, the solution was diluted with water to 25·0 ml. With vanadium, tungsten and molybdenum, however, the solutions were diluted to 50·0 ml on account of the low solubilities of the salts of these elements. After that the general procedure was followed.

The only interfering element in Table III is titanium, which forms complexes both with Curcumin and fluoride. Table IV shows that in our standard procedure a titanium concentration of 2% in the iron can be tolerated. For a higher amount a smaller sample than 250 mg has to be used.

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* If both soluble and insoluble boron have to be determined, the fused mass is treated separately.

TABLE II.—DETERMINATION OF BORON IN MILD STEEL STANDARD SAMPLES

Sample	Certificate value		Our value	
	Mean, *ppm*	*Std. devn., ppm*	Mean, *ppm*	*Std. devn., ppm*
BCS 271	133	18	141	1·8
BCS 272	38·0	3·3	39·9	0·6
BCS 273	23·0	4·0	26·2	0·4
BCS 274	81	6·0	85·0	1·4
BCS 275	12·5	4·5	12·0	0·2
BCS 277	<10	—	0·5	0·2
NBS 151	27	—	24·1	0·4

TABLE III.—INFLUENCE OF 25 mg OF ALLOYING ELEMENT IN 225 mg OF IRON ON THE DETERMINATION OF BORON

Alloying element added	Boron found, *ppm*	
	10 ppm added	100 ppm added
Al	10·8	100·0
Ce	10·7	101·3
Co	10·2	99·0
Cr	10·3	98·0
Cu	10·2	99·7
Mo	10·5	100·3
Mn	10·2	100·0
Nb	10·2	100·2
Ni	10·8	100·0
Pb	10·5	99·7
Sn	9·3	99·7
Ta	9·4	100·0
Ti	<0	80
U	9·6	100·3
V	11·0	99·7
W	10·4	99·7
Zn	10·6	100·9
Zr	10·2	101·5

TABLE IV.—INFLUENCE OF INCREASING AMOUNTS OF Ti IN Fe ON THE DETERMINATION OF BORON. TOTAL SAMPLE OF Fe PLUS Ti IS 250 mg IN ALL CASES

Ti in iron, %	Boron found, *ppm*		
	10 ppm added	50 ppm added	100 ppm added
2	10·5	49·2	99·2
5	6·0	43·6	91·5
10	0	34	80

TABLE V.—DETERMINATION OF BORON IN HIGH-ALLOY STEEL SAMPLE NBS 443 (18·5% Cr; 9·5% Ni) AND IN WASPALLOY NBS 349 (57% Ni; 14·0% Co; 19·5% Cr; 4·0% Mo; 1·2% Al; 3·0% Ti)

Sample	Certificate value mean,	Our value,	
	ppm	Mean, *ppm*	Std. devn., *ppm*
Steel sample NBS 443	12	11·9	0·8
Waspalloy NBS 349	46	48·1	0·8

TABLE VI.—DETERMINATION OF BORON IN ALUMINIUM WITH TOTAL IMPURITY LEVEL OF 1–2%

Sample	Boron			
	Direct method, *ppm*		Ion-exchange separation, *ppm*	
I	47·7	48·1	47·8	48·2
II	97·7	98·2	98·2	98·6
III	199	201	201	203

TABLE VII.—DETERMINATION OF BORON IN U_3O_8 STANDARD SAMPLES FROM USAEC

Sample	Certificate value, *ppm*	Our value	
		Mean, *ppm*	Std. devn., *ppm*
M 95-1	5·2	5·8	0·6
M 95-2	2·2	2·3	0·3

Boron can therefore also be determined in high-alloy steels. This is confirmed in Table V for the high-alloy steel standard sample NBS 443. The second sample in Table V—Waspalloy NBS 349—is a high-temperature nickel alloy. Notwithstanding its rather high titanium content good results were obtained. On account of the moderate solubility of nickel in the final solution (and the high titanium concentration) a 125-mg sample was used in this case.

Although aluminium is complexed by fluoride, our method can be used for the determination of boron in aluminium. In Table VI the results obtained with the direct method are compared with the results obtained after isolation of the boron by ion-exchange. The impurity level in these samples was 1–2%. All aluminium samples were dissolved in 5 ml of conc. hydrochloric acid.

Our last example is the determination of low boron concentrations in triuranium octaoxide standard samples M 95-1 and M 95-2 from USAEC. Here 295-mg samples were used, corresponding to 250 mg of uranium (Table VII).

Because oxidizing agents damage the Curcumin reagent, oxidizing acids cannot be used in the dissolution process. This seems to be the only serious limitation of our method. With iron and steel samples an oxidizing agent has the extra effect that the iron(III) formed may interfere in the determination of low boron concentrations. For this reason the samples must be cooled within 30 min after dissolution to limit oxidation by air. The only acid solvents used so far are sulphuric acid and hydrochloric acid. The quantity of acid solvent is not critical. The final determination is made in 0·5 ml of the sample solution, so the detection limit of 1 ppm in a solid sample corresponds to 0·005 μg of boron. This means that boron in water can be determined down to 5 ppm. If titanium is present complications are not expected if its quantity in the sample is kept below 5 mg.

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Summary—For the determination of traces of boron in iron, low- and high-alloy steels and other materials a direct spectrophotometric method was developed. In this method the absorbance of the boron-Curcumin complex formed in the sample solution is compared with the absorbance of another aliquot of sample solution wherein the boron is rendered inactive with fluoride before the Curcumin is added.

Zusammenfassung—Zur Bestimmung von Borspuren in Eisen, niedrig und hoch legierten Stählen und anderen Materialien wurde eine direkte spektrophotometrische Methode entwickelt. Bei diesem Verfahren wird die Extinktion des Bor–Curcumin–Komplexes in der Probelösung mit der Extinktion eines anderen Teiles der Probelösung verglichen, in dem das Bor vor dem Zusatz von Curcumin mit Fluorid getarnt wurde.

Résumé—On a élaboré une méthode spectrophotométrique directe pour le dosage de traces de bore dans le fer, les aciers à bas et haut alliage et d'autres produits. Dans cette méthode, on compare l'absorbance du complexe bore-curcumine formé dans la solution échantillon à l'absorbance d'une autre partie aliquote de la solution échantillon dans laquelle le bore est rendu inactif au moyen de fluorure avant addition de la curcumine.

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Substoichiometric determination of molybdenum in steels by neutron-activation analysis

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SUBSTOICHIOMETRIC separation substantially reduces the time needed for activation analysis by eliminating the chemical yield determination. Starý *et al.*[1] have described the substoichiometric determination of traces of molybdenum in germanium dioxide by neutron-activation and extraction of molybdenum oxinate into chloroform. However, this method involves a cooling period of three days after irradiation and is not suitable for the estimation of small amounts of molybdenum in alloy-steels, because the large excess of iron interferes. The selective extraction of molybdenum(VI) into chloroform with α-benzoinoxime[2] permits its separation from other elements, except tungsten with which it is commonly associated, and forms the basis of the method described here.

EXPERIMENTAL

Apparatus

The 66-hr ^{99}Mo activity was counted either with a Geiger counter through an aluminium absorber (0·135 mg/mm^2) or with a single-channel gamma-ray analyser coupled to a 38 × 38 mm NaI(Tl) crystal.

Irradiation

The samples of alloy-steel (10–60 mg in the form of fine turnings) and standards of molybdenum trioxide (1–4 mg) and sodium molybdate (100 μg of molybdenum) were sealed in quartz ampoules and simultaneously irradiated at a thermal neutron flux of $1·5–2·0 \times 10^{10}$ n/mm^2/sec. Irradiation times can be shortened by use of bigger samples and a higher neutron flux.

Reagents

Molybdenum trioxide $>99·9\%$ pure was used as the standard for some irradiations. Other standards were prepared by evaporating to dryness in quartz ampoules 0·1 ml of sodium molybdate (analytical grade) carrier solution (10 mg of Mo per ml). A 0·02*M* solution of α-benzoinoxime in twice distilled chloroform was used for extraction of molybdenum(VI) and a 0·07% benzidine hydrochloride solution in dilute hydrochloric acid was used to precipitate benzidine tungstate.

Development of method

Effect of pH and shaking time. The extraction of molybdenum(VI) from hydrochloric acid by a chloroform solution of α-benzoinoxime is complete when the hydrochloric acid concentration is in the range 0·6–0·8*M*, decreasing outside this range. In the extraction of 2–10 mg of molybdenum(VI) from 0·6–0·8*M* hydrochloric acid with 20 ml of 0·02*M* α-benzoinoxime in chloroform, the organic phase is turbid, but the extraction is not affected. The substoichiometric extraction is independent of the hydrochloric acid concentration in the range 0·6–0·8*M* and of shaking-time longer than 4 min. With shorter shaking-times, the extraction is lower and not reproducible.

Reproducibility of substoichiometric extraction. Increasing amounts of ^{99}Mo-labelled 0·1*M* sodium molybdate solution were taken in a series of separatory-funnels with 2 ml of 0·1*M* EDTA, were made 0·6–0·8*M* in hydrochloric acid and equilibrated for 4 min with 5 ml of 0·02*M* α-benzoinoxime in chloroform. A 4-ml portion of each organic phase was dried and its activity measured. The plot of activity against initial amount of molybdenum is linear (Fig. 1) till the reagent is substoichiometric to the molybdenum, a sharp break occurring at the Mo:α-benzoinoxime ratio of 1:2, whereafter the amount of molybdenum(VI) extracted remains constant. The EDTA does not affect the extraction of molybdenum but improves by a factor of 2 the decontamination of molybdenum from some other elements.

Selectivity

Tungsten will be extracted simultaneously and will interfere, so the solution is first scavenged with tungstic acid and then extracted with ethyl ether. Molybdenum(VI) is then stripped into the aqueous phase, which is then scavenged with benzidine tungstate before the substoichiometric molybdenum extraction.

A preliminary extraction with ether and stripping with water are necessary to ensure separation from nickel, chromium, *etc.*

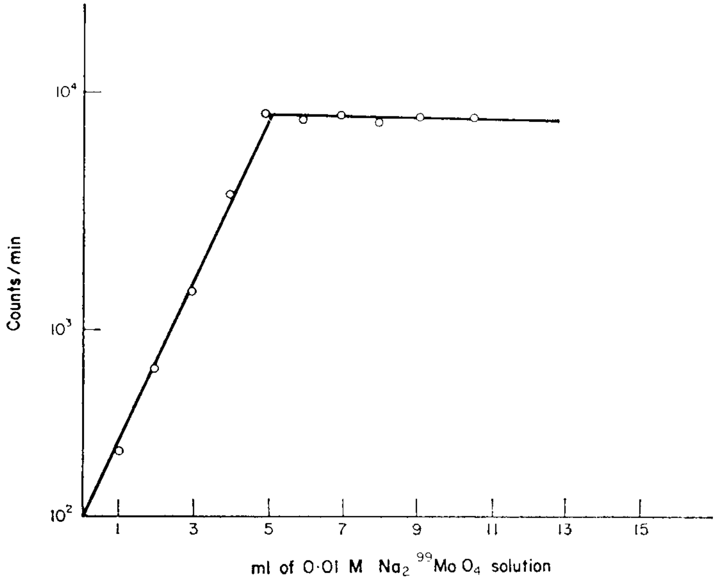

FIG. 1.—Substoichiometric extraction of molybdenum-α-benzoinoximate into chloroform.

Procedure

Dissolve the irradiated steel in a mixture of 10 ml of conc. hydrochloric acid, 2 ml of conc. nitric acid, 2 ml of bromine and 10 mg each of Mo(VI), W(VI), Ni(II), Mn(II), Si(IV), P(V) and S(VI) carriers. Centrifuge the solution to remove tungstic oxide, make it 6·5*M* in hydrochloric acid and extract with two 20-ml portions of ethyl ether saturated with 6·5*M* hydrochloric acid. Strip molybdenum by equilibrating the combined ether extracts with two 5-ml portions of water. Scavenge the aqueous phase with benzidine tungstate, add 2 ml of 0·1*M* EDTA and 2 drops of bromine, and make it 0·6–0·8*M* in hydrochloric acid. Shake the mixture for 4 min with 5 ml of 0·02*M* chloroform solution of α-benzoinoxime and wash the organic phase with 5 ml of 0·8*M* hydrochloric acid. Transfer 4 ml of the organic phase into a small beaker, and evaporate to dryness. Measure the activity of the residue with an end-window counter through 0·135 mg/mm^2 of aluminium absorber to eliminate counting of the conversion electrons of ^{99m}Tc, or after allowing molybdenum activity to attain equilibrium with the daughter ^{99m}Tc, count the sample on a gamma-ray spectrometer at the 0·147-MeV photopeak of ^{99}Mo. If tungsten is not present, it is unnecessary to add tungsten carrier and to scavenge. Dissolve a simultaneously irradiated molybdenum standard in dilute sodium hydroxide solution, dilute accurately to 100 ml with water, and process a 1- or 2-ml aliquot in the same way. Calculate the amount of molybdenum in the steel by simple proportion from the activities and the amount of molybdenum in the standard.

RESULTS AND DISCUSSION

The radiochemical purity of the samples of ^{99}Mo isolated was confirmed by gamma-ray spectra, half-life measurements and aluminium absorption curves. Decontamination studies with nuclides of some of the elements commonly occurring in steel are given in Table I. The separation of molybdenum from these elements is fairly good. Artificial mixtures containing Fe, Cr, Co, Mn and traces

TABLE I.—DECONTAMINATION STUDIES

Isotope used	Activity used, *cpm*	Decontamination factor
^{59}Fe(III)	4·96 × 10^4	6·2 × 10^3
^{32}P(V)	1·28 × 10^6	1·1 × 10^4
^{51}Cr(III)	3·80 × 10^5	2·5 × 10^4
^{185}W(VI)	1·90 × 10^6	9·7 × 10^4

of P, S and Mo were analysed for molybdenum by the proposed method and the results are given in Table II. A standard alloy–steel was also analysed. The 60-mg steel sample was counted for 1 min, and all others for 2·5 min (end-window counter).

TABLE II.—SUBSTOICHIOMETRIC DETERMINATION OF MOLYBDENUM BY NEUTRON-ACTIVATION ANALYSIS

Duration of irradiation	Sample	Molybdenum	
		Present	Found
7 days	Artificial mixture	47·0 ppm	47·7 ppm
7 days	Artificial mixture	376 ppm	385 ppm
7 days	Artificial mixture	470 ppm	462 ppm
7 days	Steel 60B (10 mg)	0·43%*	0·42%†
4 hr–7 days	Steel (16–60 mg)	0·43%	0·43‡

* Certificate value
† Average of 2 results
‡ Average of 8 results

The relative standard deviation is 1%. To test the sensitivity of the method, a sample containing 0·2 μg of molybdenum was irradiated at a neutron flux of 2×10^{10} n/mm^2/sec for 7 days, processed, and counted with the end-window counter. The activity of the sample 4 hr after the end of irradiation was 90 cpm, the background activity being 20 cpm. The activity measured on a gamma-ray spectrometer with a 5-V window was 460 cpm, including a background activity of 140 cpm. Two samples can be processed and counted with a Geiger counter within 30 min.

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Summary—A simple and rapid substoichiometric method for the determination of small amounts of molybdenum in steel by neutron-activation analysis is based on the extraction of molybdenum α-benzoinoximate into chloroform. The sensitivity of the method is 0·2 μg and the relative standard deviation is 1%. Two activated samples can be processed and counted within 30 min.

Zusammenfassung—Eine einfache und schnelle unterstöchiometrische Methode zur Bestimmung von kleinen Mengen Molybdän in Stahl durch Neutronenaktivierungsanalyse beruht auf der Extraktion von Molybdän-α-benzoinoximat in Chloroform. Die Empfindlichkeit der Methode beträgt 0,2 μg und die relative Standardabweichung 1 Prozent. Zwei aktivierte Proben können in 30 Min. verarbeitet und gezählt werden.

Résumé—Une méthode substoechiométrique simple et rapide pour le dosage de petites quantités de molybdène dans l'acier par analyse par activation de neutrons est basée sur l'extraction de l'α-benzoinoximate de molybdène en chloroforme. La sensibilité de la méthode est de 0,2 μg et l'écart type relatif est de 1%. On peut traiter et compter deux échantillons activés en 30 mn.

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Thiovioluric acid as an analytical reagent—I
Gravimetric determination of palladium

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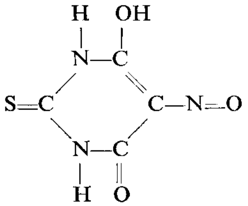
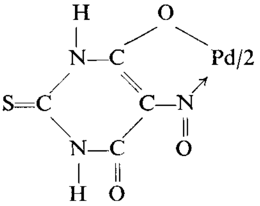
THE possibility of using violuric acid as an analytical reagent was pointed out by Baeyer,[1] Hantzsch[2] and Erlenmeyer.[3] Its co-ordination properties have been investigated by Leermaker and Hoffmann.[4] A considerable amount of work has been carried out on violuric acid and its derivatives as analytical reagents but no use seems to have been made of thiovioluric acid. The present work uses thiovioluric acid for gravimetric determination of palladium.

Thiovioluric acid (HTVA), under controlled conditions of pH, gives colours or precipitates with a large number of metal ions such as silver, copper, nickel, palladium, cobalt and iron.[5] The dark-brown complex $[Pd(TVA)_2]$ with palladium(II) can be weighed as such for determination of the metal; precipitation is quantitative at acidities ranging from pH 0·3 to 4·0. Some interferences can be eliminated by adjustments of pH or use of masking agents.

Consideration of the formula of thiovioluric acid (I) suggests that the metal salts are chelates, the enol form containing a hydrogen atom which can be replaced by a metal atom during salt formation, and a nitrogen atom in a suitable position to complete a five-membered ring by co-ordinate bond formation (II).



(I)



(II)

EXPERIMENTAL

Reagents

Palladium chloride solution. Prepared by dissolving palladium chloride in hot concentrated (analytical grade) hydrochloric acid and diluting with doubly distilled water, and standardized gravimetrically with dimethylglyoxime.

HTVA solution. HTVA was synthesized by the method of Lal and Dutt[6] and purified by repeated crystallization from absolute ethanol; m.p. 210°, purity established by thin-layer chromatography. A 1% w/v solution in 95% ethanol is used; it keeps for at least two days.

All other reagents were either chemically pure or of reagent grade quality. For the study of interferences, solutions of cations were prepared by dissolving the corresponding nitrates, chlorides or sulphates unless otherwise stated. For anions, alkali metal salts were used.

Physical characteristics of the complex

The complex is precipitated as a brown flocculent mass which can be filtered off easily after digestion. When freshly precipitated, it is somewhat soluble in hot 15% aqueous ethanol but after heating to constant weight is less soluble. However, the dried complex dissolves in isobutyl methyl ketone, acetone, ethanol, methanol and chloroform though not in isoamyl alcohol, ether, petroleum ether, carbon tetrachloride or 5% aqueous ethanol. It does not dissolve in alkalies but is decomposed by mineral acids on heating. The complex is thermally stable (m.p. >300°).

Procedure

Dilute the palladium solution to 200 ml with distilled water and adjust the pH to 0·3–4·0. Add about 100% excess of the reagent solution dropwise with constant stirring. Digest the precipitate for ∼5 min at 50–60° on a water-bath and then leave it for about 2 hr at room temperature. Collect the precipitate on a sintered glass crucible (porosity 4) and wash it two or three times with hot distilled water followed by hot 5% aqueous ethanol to remove excess of the reagent. Dry the complex at 110–130° to constant weight. The conversion factor for palladium is 0·2362, assuming the formula of the complex to be $Pd(C_4H_2N_3O_3S)_2$.

RESULTS

TABLE I.—DETERMINATION OF PALLADIUM WITH HTVA

Pd taken, *mg*	Wt. of complex, *mg*	Pd found, *mg*
2·93	12·44	2·94
5·86	24·72	5·84
9·75	41·72	9·75
12·68	53·80	12·71
15·61	66·03	15·60
19·50	82·83	19·57
22·43	95·03	22·45
25·36	107·34	25·37

Effect of pH and reagent concentration

The least amount of reagent found necessary for complete precipitation was about one and half times the theoretical amount. However, more than twice the theoretical quantity was added to ensure complete precipitation.

Effect of foreign ions

With 10 mg of palladium precipitated at pH 0·3, there was no interference from the following foreign ions in the amounts (mg) shown: Fe(III) 55, Co(II) 140, Ni(II) 110, Rh(III) 20, Os(IV) 12, Ir(IV) 25, Pt(IV) 55, Au(III) 22·8, Pb(II) 140. Zn(II) 60, Mn(II) 60, Cd(II) 50, Sb(V) 25, As(V) 80, Hg(II) 105, UO$_2$(II) 70, Mo(VI) 110, Ti(IV) 100, Se(VI) 40, Tl(IV) 30, Th(IV) 20, Zr(IV) 90, acetate 100, borate 50, tartrate 110, oxalate 75, citrate 100, fluoride 60 and phosphate 50; Cu(II) 65, Bi(III) 25, and Ru(III) 20 did interfere but could be masked with excess (100 mg) of citrate or tartrate. EDTA can only be used as masking agent above pH 2·5; the free acid precipitates at lower pH.

Results for precipitation of palladium(II) in synthetic mixtures at pH 0·3 are shown in Table II, and demonstrate that the method is applicable to alloys.

TABLE II.—ESTIMATION OF PALLADIUM (9·75 mg) IN SYNTHETIC MIXTURES WITH HTVA

Synthetic mixture	Amount of each ion, *mg*	Pd(II) found, *mg*	Error, *mg*
Fe(III), Co(II), Ni(II)	25	9·76	+0·01
Cu(II), Fe(III), citrate	20	9·70	−0·05
Zn(II), Mn(II), Cd(II)	20	9·71	−0·04
Pt(IV), Os(IV), Ir(IV)	10	9·72	−0·03
Rh(IV), Os(IV), Ir(IV)	10	9·74	−0·01

Conclusion

Many organic reagents have been used for gravimetric determination of palladium, including dimethylglyoxime,[7] nioxime,[8] β-furfuraldoxime,[9] 2-thiophene-*trans*-aldoxime[10] and oximidobenzotetronic acid.[11] Dimethylglyoxime continues to be the most favoured precipitant although it suffers from a number of drawbacks; several ions, *e.g.*, platinum(IV), iron(III) and nitrate, interfere and modified procedures have been suggested.[7,12] Although some of these ions do not interfere in the case of oximidobenzotetronic acid, cobalt is co-precipitated with palladium and has to be removed by washing with hot 50% aqueous ethanol. Gold(III), ruthenium(III) and osmium(IV) interfere in the determination of palladium(II) with 2-thiophene-*trans*-aldoxime as a precipitant. In the present method with HTVA as precipitant, platinum metals and several other metal ions do not interfere. The palladium complex has a high molecular weight and thus the conversion factor for palladium is low, which is an advantage over some other methods.

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Summary—Thiovioluric acid (HTVA) precipitates palladium(II) as the dark-brown complex Pd(TVA)$_2$ in the pH range 0·3–4·0. It can be used for the gravimetric estimation of palladium(II) alone or in the presence of diverse ions. EDTA, citrate or tartrate can be used to mask Cu(II) and Bi(III). Interference due to Ru(III) has been obviated by the use of citrate as masking agent.

Résumé—L'acide thioviolurique (HTVA) précipite le palladium(II) à l'état de complexe brun foncé Pd (TVA)$_2$ dans le domaine de pH 0,3–4,0. On peut l'utiliser pour le dosage gravimétrique du palladium(II) seul ou en présence de divers ions. On peut utiliser l'EDTA, le citrate ou le tartrate pour dissimuler Cu(II) et Bi(III). On a évité la gêne due au Ru(III) par l'emploi de citrate comme agent de dissimulation.

Zusammenfassung—Thioviolursäure (HTVA) fällt Palladium(II) im pH-Bereich 0,3–4,0 als dunkelbraunen Komplex Pd(TVA)$_2$. Sie kann zur gravimetrischen Bestimmung von Palladium(II) allein oder in Gegenwart verschiedener Ionen verwendet werden. Cu(II) und Bi(III) können mit EDTA, Citrat oder Tartrat getarnt werden. Die Störung durch Ru(III) ließ sich durch Citrat als Maskierungsmittel umgehen.

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Determination of traces of perchlorate in chlorate solutions

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PERCHLORATE can be determined in the presence or absence of chlorate spectrophotometrically with ferroin,[1,2] 2,2′-bipyridyl,[3] tetrahexylammonium erdmannate,[4,5] Methylene Blue,[6–8] Malachite Green,[9–11] or nitron,[12] titrimetrically after reduction to chloride,[13–17] or with tetraphenylphosphonium chloride.[18–21]

The method described below employs tetraphenylphosphonium chloride (TPPC) for the gravimetric determination of ppm-levels of perchlorate in the presence of approximately 3000 times as much chlorate and 5 times as much iron and chromium(III).

EXPERIMENTAL

Reagents

All reagents were of highest purity. Distilled or demineralized water was used throughout.

Iron standard, 1 *g/l.* Iron wire was dissolved in hydrochloric acid and the solution diluted to volume.

Chromium(III) *solution*, 1 *g/l.* Primary standard potassium dichromate (2·827 g) was reduced with hydrogen peroxide in acid solution, the excess of hydrogen peroxide removed by boiling, and the resulting solution diluted to 1 litre.

Procedure

A sodium chlorate solution was prepared containing in 1 litre, 500 g of sodium chlorate, 80 g of sodium chloride, 0·11 g of sodium dichromate and 0·04–0·08 g of sodium perchlorate. Aliquots were analysed for perchlorate after 5 min boiling with excess of hydrochloric acid to remove the chlorate, adjusting the pH, heating the sample to incipient boiling, and adding tetraphenylphosphonium chloride (5 ml of 2·25% w/v solution). The solution was then removed from the hot-plate, stirred vigorously for 2 min, and allowed to stand for 2 hr. The tetraphenylphosphonium perchlorate was filtered off on a fine Selas crucible, washed, and dried at 110° for 1 hr. The effect of varying the pH of precipitation is shown in Table I. The greenish hue of the precipitates was attributed to contamination by chromium(III) (resulting from reduction of dichromate by hydrochloric acid). Triethanolamine (TEA) was found to remove the green colour (Table II).

A number of determinations were made on the synthetic solution, 6 ml total of water being used for washing, TEA being added, and precipitation done at pH 5. In Table III these results are compared with those found by the ferroin method.

TEA clearly did not prevent precipitation of iron(III) and chromium(III), and other masking agents were investigated, namely EDTA, CDTA, and tartaric acid. Bromine was added to the hydrochloric acid solutions after reduction of chlorate, to oxidise iron before addition of tartaric acid. Results are shown in Table IV.

TABLE I.—TETRAPHENYLPHOSPHONIUM CHLORIDE PRECIPITATION OF PERCHLORATE AT VARIOUS pH VALUES

pH	$NaClO_4$, *ppm**		*s*†, *ppm*	*n*‡	Range of ppte. wt., *mg*
	Present	Found			
8	695	751	77	5	1·9–7·4
6	780	827	45	2	3·5–3·7
5	780	819	28	2	3·5–3·6
4	780	819	28	2	3·5–3·6
3	780	749	10	2	3·2–3·3

* In presence of $NaClO_3$.
† Standard deviation.
‡ Number of determinations.

TABLE II.—REMOVAL OF CR(III) FROM TETRAPHENYLPHOSPHONIUM PERCHLORATE

$NaClO_4$, *ppm**		*s*, *ppm*	*n*	ppte. wt., *mg*	Water, *ml*	Comment
Present	Found					
780	780	—	1	3·4	15	Green ppte.
780	840	17	3	3·6–3·8	30	
780	803	—	1	3·5	45	
780	718	—	1	3·1	60	
780	738	30	5	3·1–6·8	15–30	+ TEA, white ppte.

* In presence of $NaClO_3$.

DISCUSSION

Fritz *et al.*[1] report that chlorate is partially extracted by ferroin under the conditions used for quantitative perchlorate extraction, and we have confirmed this; in the work leading to Table III, standards and samples contained equal concentrations of chloride and chlorate. Dichromate was included in the standard solutions because it is commonly used as a depolarizer in commercial chlorate cells. Since chromium(VI) was shown to interfere, it was reduced with hydroxylamine

TABLE III.—PERCHLORATE DETERMINATION AS TETRAPHENYLPHOSPHONIUM PERCHLORATE AND WITH FERROIN

Method	$NaClO_4$, *ppm**		*s*, *ppm*	*n*	Range of ppte. wt., *mg*
	Present	Found			
TPPC	41	49	3	5	3·2–6·6
TPPC	390	405	19	12	3·3–9·7
TPPC	370	380	7	4	3·3–8·4
Ferroin†	370	308	105	4	

* In presence of $NaClO_3$.

† The slope of the calibration curve for $NaClO_4$ was 0·201 μg^{-1} (10-mm cell, $s = 0·010$, $n = 4$) in the absence of $NaClO_3$, and 0·160 μg^{-1} (10-mm cell, $s = 0.012$, $n = 4$) in the presence of an equal concentration of $NaClO_3$, after subtraction of the absorbance due to the $NaClO_3$-ferroin complex.

TABLE IV.—PERCHLORATE DETERMINATION: REMOVAL OF IRON AND CR(III)

Iron, *mg*	Cr(III), *mg*	$NaClO_4$, *mg*		Masking agent
		Present	Found	
0	0	4·0	4·0	None
10	10	4·0	4·0	50 ml 3% w/v CDTA
10	10	4·0	4·0	1·5 g of tartaric acid†
10	10	4·0	4·3	50 ml of 0·05*M* EDTA

* Duplicate analyses.

† Br_2 oxidation before addition of tartaric acid.

hydrochloride. Ferroin perchlorate instability in butyronitrile–xylene was also confirmed and the same instability was also observed when adiponitrile–xylene was used.

Previous studies in our Laboratory showed that hydrochloric acid is more effective than sodium bisulphite[19] for the decomposition of gross quantities of chlorate; hence, hydrochloric acid reduction was employed in the present work.

Results presented in Table III indicate the gravimetric TPPC determination of perchlorate in the presence of gross quantities of chlorate is more accurate and reproducible than the ferroin method. Table IV indicates that CDTA and tartaric acid are equally effective in removing interference from iron and chromium(III); EDTA was less effective under the conditions used.

The weighing uncertainty (± 0·1 mg) causes the relative error to be considerable when low perchlorate levels are determined gravimetrically as tetraphenylphosphonium perchlorate.

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Summary—Perchlorate present in chlorate solutions is determined gravimetrically as tetraphenylphosphonium perchlorate after destruction of chlorate by addition of hydrochloric acid. Interference of Fe(III) and Cr(III) is prevented by complexing with tarartic acid. Replicate analyses of a sodium chlorate solution containing $NaClO_3$, NaCl, $Na_2Cr_2O_7$, and 390 ppm $NaClO_4$ showed 405 ppm $NaClO_4$ (standard deviation 19 ppm, 12 results).

Zusammenfassung—Perchlorat in Chloratlösungen wird nach Zerstörung des Chlorats durch Zugabe von Salzsäure gravimetrisch als Tetraphenylphosphoniumperchlorat bestimmt. Die Störung durch Eisen(III) und Chrom(III) wird durch Komplexbildung mit Weinsäure verhindert. Mehrfachanalysen einer Natriumchloratlösung, die $NaClO_3$, NaCl, $Na_2Cr_2O_7$ und 390 ppm $NaClO_4$ enthielt, ergaben 405 ppm $NaClO_4$ (Standardabweichung 19 ppm, 12 Ergebnisse).

Résumé—On dose gravimétriquement le perchlorate présent dans les solutions de chlorate à l'état de perchlorate de tétraphénylphosphonium après destruction du chlorate par addition d'acide chlorhydrique. On évite les interférences de Fe(III) et Cr(III) par complexation avec l'acide tartrique. Des analyses répétées d'une solution de chlorate de sodium contenant $NaClO_3$, NaCl, $Na_2Cr_2O_7$ et 390 p.p.m de $NaClO_4$ ont donné 405 ppm de $NaClO_4$ (écart type 19 ppm, 12 résultats).

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Extraction of vanadium into isobutyl methyl ketone*

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THE increase in sensitivity gained in atomic-absorption spectroscopy by use of organic solvents, especially water-immiscible ones to concentrate a metal chelate in the organic phase, is well known.[1]

Determination of metals which form refractory oxides is possible only in a high-temperature, fuel-rich, reducing flame. Sachdev *et al.*[2] extracted vanadium as the cupferronate into a mixture of isobutyl methyl ketone (IBMK) and fatty acids (4:1 v/v) and used the solution for atomic-absorption work. The effect of chloroform, ethyl acetate, IBMK, and n-butanol on the absorption signal for standard vanadium solutions indicated that IBMK gave the greatest signal. Clearly, extraction of vanadium into IBMK would be the best choice for an atomic-absorption method. The present paper describes such an extraction.

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EXPERIMENTAL

Reagents

Reagent grade chemicals were used without further purification. Vanadium(V) stock solution (1 mg/ml) was prepared by dissolving 2·298 g of ammonium metavanadate in 1 litre of distilled water and standardized.[3,4] Working standards containing 0·1–100 μg/ml were prepared by appropriate dilutions.

Vanadium(IV) stock solution (1 mg/ml) was prepared by dissolving 3·907 g of purified grade vanadyl sulphate (Fisher) in 1 litre of distilled water. Working standards were prepared by dilution and assayed for vanadium(IV) and (V).[3,4]

Vanadium(III) stock solution (500 μg/ml) was prepared by dissolving 1·709 g of purified grade vanadium(III) acetylacetonate, tris-2,4-pentanedione vanadium(III), (Baker Chemical Co.) in 500 ml of reagent grade IBMK. An aliquot was treated with concentrated sulphuric and nitric acids to destroy organic matter, and then standardized.[3,4]

Atomic-absorption procedure

Aliquots (10 and 20 ml) of vanadium(III) 10 μg/ml standard and appropriate volumes of IBMK solutions of the chelating agents were placed in 100-ml volumetric flasks and diluted to volume with IBMK. The final concentration of chelating agent was that to be used in the proposed extraction procedure. A blank was also prepared.

The settings for the Perkin–Elmer model 303 atomic-absorption spectrophotometer were: grating, ultraviolet; wavelength, 314·8 nm; scale expansion, 10X; slit, 4 (1 mm ≡ 0·7 nm band-pass); source, shielded vanadium hollow-cathode lamp; lamp current, 40 mA; burner, nitrous oxide–acetylene; nitrous oxide pressure, 30 psi (6·0 on flow-meter); acetylene pressure, 8 psi (4·2 on flow-meter); noise suppression, 3; recorder, Servo/Riter II (Texas Instruments, Inc.), set at zero absorption with reagent blank.

Distribution measurements

Aliquots of 10 μg/ml vanadium(V) and (IV) solutions were made up to constant ionic strength, 0·10*M*, by addition of 1*M* sodium chloride, and diluted to 50 ml; 25 ml of each were equilibrated with the chelating agent dissolved in IBMK. The aqueous and organic phases were not presaturated (with IBMK and water respectively).

The phases were separated and the pH of the aqueous phase was measured. The atomic-absorption signal for the organic phase was compared with those obtained from standards, and the degree of extraction of the metal was calculated and plotted as a function of pH. The aqueous phase was analysed for vanadium by the phosphotungstate spectrophotometric method[5] after evaporation almost to dryness and removal of organic matter by treatment with concentrated sulphuric and nitric acids. This procedure is not very satisfactory and was used only to confirm the pH range required for quantitative extraction.

Study of interfering ions

A 5·0-ml aliquot of vanadium(V) or (IV) standard (10 μm/ml) and 5·0 ml of a solution of another metal (1000 μg/ml) were diluted to about 45 ml and the pH was adjusted to about 1·0 with hydrochloric acid. The solution was transferred to a 50-ml volumetric flask, diluted to the mark with water and mixed, and a 15-ml portion was transferred into a 125-ml separatory funnel and extracted with 15 ml of 5% cupferron in IBMK. The absorption signal of this solution was compared with that from a standard prepared in a similar manner but containing the vanadium only.

RESULTS AND DISCUSSION

Selection of the chelating agent was based on (*i*) a high degree of vanadium extraction, giving concentration in the IBMK, (*ii*) wide pH-range for extraction. Ease, simplicity and efficiency of extraction are more essential than selectivity, because specificity is conferred by the atomic-absorption method.

The chelating agents investigated were 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron),[6] *N*-nitrosophenylhydroxylamine (cupferron),[7] 8-hydroxyquinoline,[8] sodium diethyldithiocarbamate (NaDDC),[9] ammonium pyrrolidinedithiocarbamate (APDC),[10] α-benzoinoxime,[11] salicylic acid,[12] and salicylhydroxamic acid.[13] The optimum pH and concentration of the chelating agent for various solvents have been reported in numerous publications, and were investigated by us for IBMK. The quantitative extraction of vanadium with ferron into n-butanol or higher alcohols was confirmed, but no extraction into IBMK took place. Similarly, the vanadium complexes formed with α-benzoinoxime and salicylic acid could not be extracted into IBMK. NaDDC and APDC formed chelates with vanadium which were extractable into IBMK, but the rapid decomposition of NaDDC in acid solution and precipitation of the APDC complex in IBMK presented severe limitations.

Only cupferron, 8-hydroxyquinoline and salicylhydroxamic acid were at all suitable and were further investigated.

Extraction as the 8-hydroxyquinolinate

Figure 1 shows the effect of pH on the extraction of vanadium(V) by 0·01*M* 8-hydroxyquinoline in IBMK. Starý[14] reported a $pH_{1/2}$ value under similar conditions with IBMK as solvent as 1·75. The effect of pH on extraction of vanadium(IV) by 0·01*M* 8-hydroxyquinoline in IBMK is also shown in Fig. 1. The $pH_{1/2}$ value is 2·05 and no vanadium(IV) was extracted above pH 7·5. The curves show that vanadium can be separated as the 8-hydroxyquinolinate regardless of the original oxidation state of the vanadium. Since the complex is the same colour irrespective of initial vanadium oxidation state a redox reaction must occur. Because similar behavior is observed with many different chelating agents, the redox reaction does not involve the chelating agent itself. Rather it is our impression that the oxidation of vanadium(IV) to vanadium(V) is accomplished by dissolved oxygen. The presence of a chelating agent ties up the vanadium(V) as it is formed, making the oxidation of vanadium(IV) to (V) more easy.

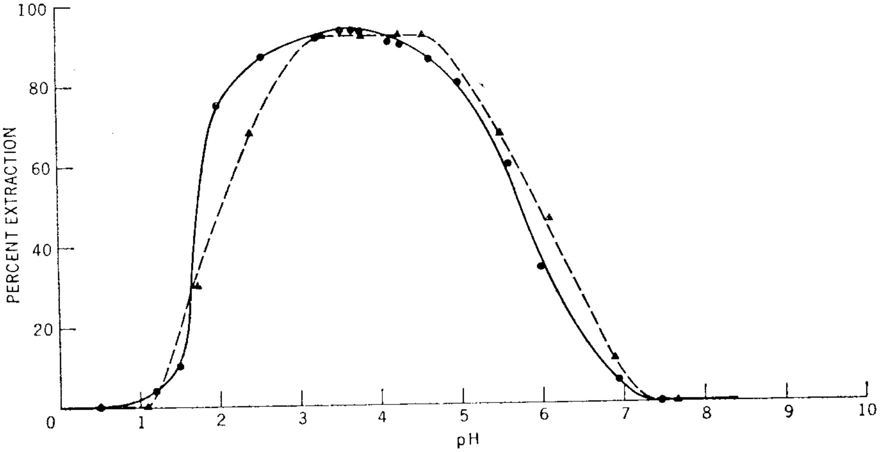

FIG. 1.—Effect of pH on the extraction of vanadium(V) and vanadium(IV) by 0·01*M* 8-hydroxyquinoline in IBMK.
●—Vanadium(V); ▲—vanadium(IV)

Vanadium(V) and (IV) can be extracted equally well from an aqueous solution buffered at pH 3·8 with acetic acid–sodium acetate. Proper control of the volume ratio makes it possible to concentrate the vanadium in the IBMK.

Extraction with salicylhydroxamic acid

Salicylhydroxamic acid was prepared by the method described by Jeanrenaud.[15] The acid is difficultly soluble in cold water and alcohol (about 0·5% at 30°). Extraction was incomplete with less than 0·03*M* salicylhydroxamic acid in the aqueous phase. Vanadium was completely extracted between pH 2·0 and 3·0. Vanadium(IV) was separated equally well, but the rate of formation of the complex was slower and a longer shaking time needed. The concentration conditions impose a severe limitation, and the nebulizer frequently became clogged, probably because of the low solubility of the reagent in IBMK.

Extraction as the cupferronate

Furman, Mason, and Pekola[7] made a systematic study of cupferron separations and considered extraction far superior for removal of microgram quantities of metals. Bertrand[16] extracted vanadium at pH 1·8. Vanadium(V) is completely extracted from 1*M* hydrochloric acid by cupferron and ethyl acetate.[17] Vanadium(IV) is quantitatively extracted from 0·5*M* hydrochloric acid if the concentration of the reagent in ethyl acetate is greater than 0·09*M*.[18]

In aqueous solution, cupferron is a weak acid and the partition coefficient between IBMK and water is 85 according to Dyrssen.[19] Furman *et al.*[7] derived a simplified relationship for the distribution coefficient of a metal cupferronate by assuming that extraction is favoured by low acidity and a large excess of cupferron. The effect of these two variables on the degree of extraction of vanadium in different oxidation states was investigated.

Figure 2 shows the effect of pH on the extraction of vanadium(V) and vanadium(IV) with different concentrations of cupferron in IBMK. Since the complexes formed with both vanadium standards have the same colour and an almost identical distribution of metal is obtained, a redox reaction must take place similar to that observed in the oxine extraction. Extraction was incomplete at pH 4·5. Vanadium could be concentrated in the IBMK by controlling the volume ratio of the phases and vanadium(V) and (IV) could be extracted equally well; the optimum pH was 2·0.

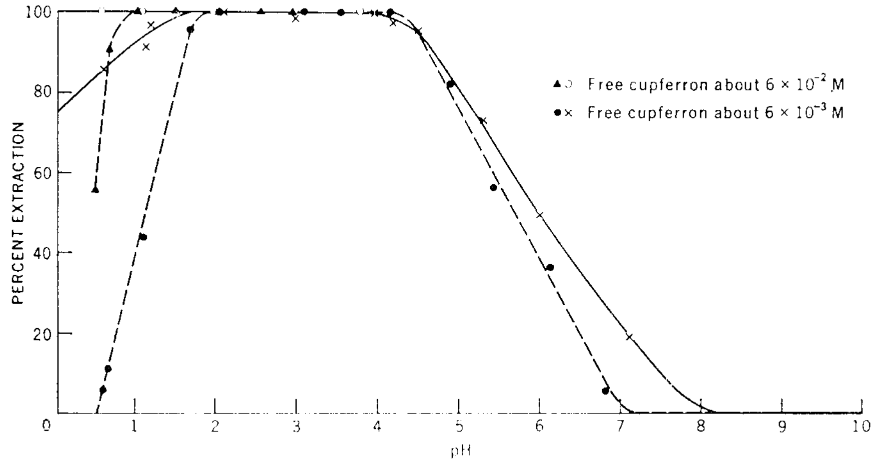

FIG. 2.—Effect of pH on the extraction of vanadium(V) and vanadium(IV) by cupferron in IBMK.

○ ×—Vanadium(V); ●▲—vanadium(IV).

The wide range of permissible operating conditions made cupferron the most suitable reagent, the only disadvantage being the relative instability of the amine, requiring the preparation of fresh solutions just before use. No erratic behaviour of the flame or clogging of the nebulizer was observed with 5% cupferron in IBMK.

Interferences

Some other metals may be extracted along with vanadium under the conditions used. Their effect on the absorption of the 318·4 nm line of vanadium was investigated. Results are given in Table I. Very little, if any, interference was expected, because the atomic-absorption method

TABLE I.—EFFECT OF INTERFERING IONS ON THE RECOVERY OF VANADIUM

Interfering ion added	Absorption, %	Vanadium recovered,* %
None	37·0	100
Fe^{3+}	38·0	103
Ni^{2+}	37·0	100
Cu^{2+}	37·0	100
Al^{3+}	36·6	99
Pb^{2+}	37·0	100
Zn^{2+}	35·8	97
Ce^{4+}	38·0	103
Bi^{3+}	37·0	100
Ti^{4+}	37·0	100
MoO_4^{2-}	36·0	97
Th^{4+}	37·0	100
Zr^{4+}	38·0	103
UO_2^{2}	37·5	101

* These values represent the average of three independent determinations. Concentration of vanadium in the aqueous solution: 1 μg/ml. Concentration of interfering ion in the aqueous solution: 100 μg/ml.

Permissible amounts of tungstate and tin(IV) were 5 and 10 μg/ml respectively.

should have been specific for vanadium. With two exceptions, essentially no interference was observed for all metals present at a concentration 100 times that of vanadium before extraction. The amount of interfering metal extracted with the vanadium was not determined.

Lundell and Knowles[20] stated that tungsten interferes in the separation of vanadium, a fact later confirmed by Clarke,[21] who reported that the low recovery could hardly be explained by removal of vanadium from solution but rather seemed due to the existence in solution of a complex rejected by cupferron. A vanadotungstate heteropoly anion is probably formed. The interference of tin was probably due to the formation of a basic tin vanadate. Recovery was found to be better at higher acidity, which indicated that the interference was due to incomplete separation rather than suppression in the flame. However, lower acidity was preferred because of the rapid deterioration of the reagent in more acidic solutions and the possibility of incomplete removal of vanadium(IV). If high concentrations of tungsten and tin are encountered, more drastic conditions of acidity and concentration of cupferron are required to eliminate interference, but only to an extent that will not jeopardize the quantitative removal of vanadium in either oxidation state. If only vanadium(V) is to be extracted, separation from more acidic solutions presents no problem.

Another discrepancy arose from the difference in volume of IBMK recovered from distilled water and saturated salt solutions. If 10 ml of IBMK are added to 100 ml of distilled water or saturated brine and shaken, approximately 7·61 and 9·75 ml respectively of IBMK are recovered after separation of the phases. The solubility of IBMK in distilled water had the effect of further concentrating the vanadium cupferronate in the organic phase, resulting in an increased absorption signal. The same absorption was obtained for equal concentrations of vanadium regardless of the salt content of the aqueous phase, if the separated organic layer was diluted to a fixed volume, indicating that no metal chelate was carried along with the IBMK into the aqueous layer.

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Summary—Because of its advantages in atomic-absorption spectroscopy, isobutyl methyl ketone was chosen as organic solvent for an extraction study on vanadium. Of eight chelating agents which were evaluated for completeness of extraction, ease of use, working pH range, and freedom from interference, cupferron was judged best.

Zusammenfassung—Wegen seiner Vorteile bei der Atomabsorptionsspektroskopie wurde Isobutylmethylketon als organisches Lösungsmittel zu einer Extraktionsuntersuchung an Vanadium herangezogen. Unter acht auf Vollständigkeit der Extraktion, Leichtigkeit der Handhabung, pH-Arbeitsbereich und Störungsfreiheit untersuchten Chelatbildnern wurde Kupferron am besten beurteilt.

Résumé—A cause de ses avantages en spectroscopie d'absorption atomique, on a choisi la méthylisobutylcétone comme solvant organique pour une étude d'extraction sur le vanadium. Des huit agents chélatants qui ont été évalués pour le caractère total de l'extraction, l'aisance d'emploi, le domaine de pH de travail et le fait d'être exempt d'interférences, le cupferron a été estimé le meilleur.

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The diffusion of fluoride with hexamethyldisiloxane

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USING fluoride-18 as radioactive tracer, Taves[1] has made the interesting observation that the silicone grease which many workers have used for sealing diffusion units can cause loss of fluoride because of the very greatly accelerated rate of diffusion of fluoride induced by the silicone.

In two more papers which the author has been privileged to see prior to publication in this journal[2,3] Taves further reported the application of hexamethyldisiloxane (HMDS) to the diffusion of fluoride from human blood serum. He demonstrated that under the conditions he used, fluoride was diffused about 10 times faster at room temperature than by the usual diffusion with 23–47% w/w perchloric acid at 50–60°, and attributed this to the formation of a methyl fluorosilane. This communication confirms that siliconed hydrochloric acid does induce the diffusion of hydrogen fluoride at room temperature and reports the separation of fluoride by use of hexamethyldisiloxane (HMDS) with other acids.

EXPERIMENTAL

Fluoride was diffused and estimated by the methods of Hall,[4,5] which use a 20-ml polythene bottle and absorption of the diffused HF on filter paper impregnated with 0·5*M* sodium hydroxide. Fluoride was determined by extracting the fluoride complex of lanthanum alizarin complexanate into isobutyl alcohol containing hydroxylammonium hydrochloride. Under the conditions used, the reaction is considered to be specific for fluoride. Suspensions of plants of the *Dichapetalum* species and of a soil in which one of them had been grown were examined for diffusible fluoride. These plants contain a mixture of organically bound fluorine and inorganic fluorides. The suspensions contained 20 mg of plant tissue or soil of less than 53 μm particle size, per ml of 0·1% agar solution. The diffusible fluoride content of the sample taken was usually less than 1 μg.

The perchloric acid was 72% w/w (sp. gr. 1·74) saturated with hexamethyldisiloxane (0·65 cSt). It was also used with the addition of 4% w/v silver sulphate to immobilize chloride. The hydrochloric acid was 6*M*. Most other diffusing acids were of molar concentration saturated with HMDS. The acids were saturated with the silicone by shaking with 1/10 their volume of HMDS for 2 min, not more than 20 ml being prepared at a time. In the case of perchloric acid the silicone is almost completely miscible and no untoward reactions were experienced but such a mixture should always be handled with caution.*

The diffusions were for 24 hr and at 25° except where indicated.

RESULTS

Table I shows a comparison of the fluoride absorbed by the papers and measured in terms of the absorbance of the fluoride complex at 570 nm in a standard volume of 4 ml (10-mm light path), after diffusion of 1 ml of plant or soil suspension with various volumes of siliconed and non-siliconed reagents.

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* NOTE: Tests by the Explosion Hazards Section of Imperial Chemical Industries Ltd. suggest that no explosive range exists with the mixture of perchloric acid and hexamethyldisiloxane under these conditions.

TABLE I.—THE DIFFUSION OF FLUORIDE FROM PLANT AND SOIL SUSPENSIONS

Material	Diffusing reagent	Volume, *ml*	Absorbance of fluoride complex at 570 nm*	
			Siliconed	Non-siliconed + Ag_2SO_4 at 60°C
D. cymosum stem (total F = 315 ppm, diffusible F^- = 58 ppm)	Hydrochloric acid	0·5	0·238 0·218 0·213	
	Hydrochloric acid	2·0	0 (acidic reaction)	
	Hydrochloric acid at 20°C	0·5	0·246 0·260 0·246	
	Hydrochloric acid at 20°C	2·0	0·176 0·176 0·176	
	Perchloric acid	0·5	0·243 0·243 0·233	0·281 0·278 0·284
	Perchloric acid	2·0	0·004 0·006 0·004	0·237 0·237 0·240
	Perchloric acid + Ag_2SO_4 at 20°C	0·5	0·266 0·270 0·280	
	Perchloric acid + Ag_2SO_4 at 20°C	2·0	0·236 0·236 0·236	
D. toxicarium leaf and stem	Hydrochloric acid	0·5	0·266 0·266 0·260	
	Hydrochloric acid	2·0	0·236 0·236 0·236	
(total F = 84 ppm, diffusible F^- = 67 ppm)	Perchloric acid	0·5	0·257 0·257 0·258	
	Perchloric acid	2·0	0·238 0·236 0·239	
	Perchloric acid + Ag_2SO_4	0·5	0·276 0·270 0·276	0·304 0·301 0·306
	Perchloric acid + Ag_2SO_4	2·0	0·236 0·239 0·231	0·334 0·320 0·348
D. toxicarium soil (total F = 178 ppm)	Hydrochloric acid	0·5	0·026 0·028 0·027	
	Hydrochloric acid	2·0	0 (acidic reaction)	
	Perchloric acid	0·5	0·016 0·018 0·013	0·113 0·113 0·110
	Perchloric acid	1·0	0·032 0·032 0·032	0·117 0·117 0·118
	Perchloric acid	2·0	0·035 0·038 0·033	0·233 0·232 0·233
	Perchloric acid + Ag_2SO_4	2·0	0·095 0·100 0·104	
Standard fluoride (1·0 μg F^-)	Perchloric acid	0·5		0·248

* Corrected for blank.

The results show quite clearly that the amount of fluoride measured in the plant material is influenced by the volume and temperature of the siliconed reagent used to induce diffusion. Generally, with the larger volume of reagent, the amount of fluoride measured is smaller. It is suggested that with perchloric acid, in the absence of silver sulphate, the lower readings are the effect of chloride in the samples being diffused as hydrogen chloride. In the case of the soil suspension increased volumes of siliconed perchloric acid released more fluoride as a result of decomposition of complex fluorominerals.

In Table II are the results of a more extensive selection of reagents used to induce diffusion of acid-labile fluoride from 20 mg of *D. toxicarium* root (total F = 109 ppm; maximum diffusible fluoride measured = 41 ppm). Except where indicated, the diffusions were at 25° for 24 hr with 0·5 ml of reagent (total diffusion volume 1·5 ml).

It is evident that the need for very strong siliconed acids is not a prerequisite to induce diffusion of the fluoride but that the stronger acids cause more fluoride to be diffused.

DISCUSSION

That siliconed hydrochloric acid readily induces diffusion of fluoride as reported by Taves[2,3] is established. According to Eaborn[6] the following reactions take place between hydrofluoric acid and hexamethyldisiloxane.

$$HF + (CH_3)_3SiOSi(CH_3)_3 \rightarrow (CH_3)_3SiF + (CH_3)_3SiOH$$

$$HF + (CH_3)_3SiOH \rightarrow (CH_3)_3SiF + H_2O$$

TABLE II.—DIFFUSION OF FLUORIDE FROM THE ROOT OF *D. toxicarium* WITH VARIOUS SILICONED AND NON-SILICONED ACIDS

Reagent	Absorbance of fluoride complex at 570 nm*					
	Siliconed			Non-siliconed		
Water		0			0	
Perchloric acid (72% w/w) with Ag_2SO_4 at 60°C				0·18	0·180	0·185
Perchloric acid (72% w/w) with Ag_2SO_4 at 25°C				0·103	0·108	0·098
Perchloric acid (72% w/w) at 25°C	0·170	0·172	0·175			
Hydrochloric acid (6*M*)	0·168	0·169	0·170	0·118	0·103	0·128
Citric acid (*M*)	0·145	0·147	0·150	0·017	0·017	0·017
Oxalic acid (*M*)	0·153	0·160	0·167	0·068	0·070	0·065
Succinic acid (*M*)	0·147	0·148	0·150	0·002	0	0·004
Tartaric acid (*M*)		0·147		0·002		
Potassium tetraoxalate (0·1*M*)	0·10	50·115	0·125	0	0	0
Standard fluoride (1·0 μg F) with 0·5 ml of $HClO_4 + Ag_2SO_4$ at 60°C				0·250	0·250	0·250
Standard fluoride (1·0 μg F) with 0·5 ml of $HClO_4$ at 25°C	0·248	0·248	0·251			

* Corrected for blank.

Peck and Smith[7] state that the silanol then condenses to reform the siloxane.

$$2(CH_3)_3SiOH \rightarrow (CH_3)_3SiOSi(CH_3)_3 + H_2O$$

As soon as the trimethylfluorosilane $(CH_3)_3SiF$ reacts with alkali the fluorine bond is split and hexamethyldisiloxane is again formed. Eaborn[8] noted that the formation of the fluorosilane can be achieved in very dilute acid. The results with succinic acid and 0·1*M* potassium tetraoxalate (Table II) show this to be the case in their reactions with the fluorine compounds present in the plant tissues used. These plants are particularly suitable materials with which to test the diffusion of fluoride because it is known[9,10] that they contain ω-fluorinated compounds from C_2 to C_{18} which are extremely stable to hot concentrated mineral acids. Any fluorine diffused from these plants can be presumed to be inorganic or loosely combined in an organic form or to protein, although no evidence has been found to support the existence of the latter forms. Under the conditions used for the determination of the fluoride ion with alizarin complexan it seems improbable that the reactions reported here could be due to compounds other than fluoride absorbed on the papers except that volatile halogen radicals such as chloride will compete with fluoride for the alkali. With low concentrations of siliconed hydrochloric acid, diffusion of chloride as hydrogen chloride does not appear to take place at 25° but there is clearly a maximum concentration which can be tolerated without this happening. With perchloric acid the situation is similar except that the inclusion of silver sulphate immobilizes chloride ions In the absence of the silver salt, 2 ml of the perchloric acid (Table I) caused the diffusible fluoride in *D. cymosum* stem to appear much lower and it is suggested that this was due to the presence of free chloride ions in the plant being diffused as hydrogen chloride. No positive reactions for fluoride were obtained from diffusions of these materials when 6*M* hydrochloric acid was used at 30° and 40°; the collecting papers were strongly acidic and contained free chloride. This was so in all the tests in which no diffused fluoride was measured after treatment with 2 ml of siliconed hydrochloric acid or perchloric acid without silver sulphate. A limiting factor, of course, is the amount of alkali on the papers. Under the conditions of the test 1 mg of hydrogen chloride can be present without interfering with the pH of the lanthanum alizarin reaction. The reagent, which also reacts as an acid/alkali indicator, rapidly shows the presence of excess of free acid.

As much as 30 mg of sodium chloride may be present in the fluoride determination without seriously influencing the result; more than this tends to depress the formation of the fluoride complex. Tests with perspex Conway units were inconsistent. Sometimes enough hydrogen chloride was absorbed by 1 ml of 0·1*M* sodium hydroxide or sodium bicarbonate to give strongly acidic solutions containing much free chloride when diffusion was induced with 2 ml of siliconized hydrochloric acid or 0·5 ml of siliconed hydrochloric acid plus 1 ml of non-siliconed 72% w/w perchloric acid without silver sulphate. No fluoride was measured from these tests. Diffusions with pure solutions of sodium fluoride and the siliconed acids showed that there was no interference with the actual formation of the lanthanum alizarin fluoride complex or its extraction.

The lower fluoride values obtained from *D. cymosum* stem with 2 ml of perchloric acid could be due to the effect of volume on the diffusion of hydrogen fluoride, but this is not so with *D. toxicarium* soil. These plants and soils are very unusual and contain a complex mixture of fluorine-containing compounds, some of which, particularly the fluoro-minerals, are only slowly degraded by perchloric acid. However, the findings shown in Table I do demonstrate that at ambient temperatures the silconed acids used in these experiments diffused only a small part of that fraction in soils which has been called[5] the "diffusible fluoride", *i.e.*, the fluoride diffused in not less than 24 hr at 60° by 47% w/w perchloric acid. It is also evident that the fluoride of the plant tissues diffused by the same volume of perchloric acid at 60° is higher than that diffused by siliconed acids at 25° though only marginally so in some cases. Perhaps this is due to the inability of the siliconed acids to render the more complex fluorides of soil and plants sufficiently labile at room temperature to react with the siloxane.

The observations recorded here may be of direct interest to workers dealing with the analytical chemistry of fluorine with special reference to biological materials containing relatively high levels of chloride. In an earlier publication, Tave,[11] using a technique with siliconed hydrochloric acid,[2,3] claimed that the true fluoride levels of human blood serum are only about a tenth of the values published by most other workers, his mean being 0·013 ppm compared with 0·15 ppm as the accepted average. The writer has rarely found any measurable free fluoride in the plasmas of various species of domestic animals;[4] his recent preliminary analyses of human plasma indicate the diffusible fluoride to be of the order of 0·033 ppm, by the procedures he normally uses for plants and soils, *i.e.*, direct diffusion at 60° with 47% perchloric acid containing silver sulphate.[4,5] Although higher than 0·013 ppm this figure is still only about a fifth of the generally accepted level. It is possible that siliconed acids at about 25° will only react with simple fluorides. It must be stressed that these findings relate only to the methods used the writer's laboratory but it is believed that similar procedures are widely employed elsewhere. The use of siliconed hydrochloric acid to induce the diffusion of fluoride as proposed by Taves might require the modification of some existing techniques and thereby introduce complications.

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Summary—Several acids, when saturated with hexamethyldisiloxane, induce the diffusion of fluoride at ambient temperatures. Observations with plant and soil suspensions which contain a mixture of complex fluorides including organically combined fluorine show that siliconed acids may not diffuse as much fluoride as does perchloric acid containing silver sulphate at 60°.

Zusammenfassung—Mehrere Säuren induzieren bei Sättigung mit Hexamethyldisiloxan die Diffusion von Fluorid bei Raumtemperatur. Beobachtungen mit Pflanzen- und Bodensuspensionen, die ein Gemisch von komplexen Fluoriden enthielten, darunter organisch gebundenes Fluor, zeigten, daß silikonisierte Säuren möglicherweise nicht so viel Fluorid diffundieren lassen wie Silbersulfat enthaltende Überchlorsäure bei 60°.

Résumé—Différents acides, lorsqu'ils sont saturés d'hexaméthyldisiloxane, provoquent la diffusion du fluorure aux températures ambiantes. Des observations avec des suspensions de plantes et de sols qui contiennent un mélange de fluorures complexes comprenant le fluor combiné organiquement montrent que les acides siliconés ne peuvent diffuser autant de fluorure que le fait l'acide perchlorique contenant du sulfate d'argent à 60°.

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Redox-complexometric determination of iron and cobalt and its application to the analysis of multi-component alloys

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THE potentiometric determination of iron(III) with EDTA was first described by Přibil, Koudela and Matyska[1] and found accurate by Siggia.[2] It was later recommended for the standardization of EDTA solutions. The iron can be titrated at pH 1·5–2·0 in the presence of aluminium, cobalt, nickel and other bivalent elements. Only elements forming very stable complexes with EDTA, such as thorium, zirconium, hafnium, thallium, gallium and bismuth, interfere or are co-titrated.

It is well known that complex-forming substances considerably alter the redox potential of simple redox systems such as Fe(III)/Fe(II) and Co(III)/Co(II). Analytically very useful is the redox system Fe(III)/Fe(II) in the presence of 1,10-phenanthroline (phen). It was found by Vydra and Přibil[3,4] that cobalt(II) can be titrated potentiometrically with iron(III) chlorine in acidic medium in the presence of phenanthroline:

$$Fe_2(phen)_4(OH_2{}^{4+}) + 2Co(phen)_3{}^{2+} + 2Hphen^+ = 2Fe(phen)_3{}^{2+} + 2Co(phen)_3{}^{3+} + 2H_2O \qquad (1)$$

This is the only reliable redox titration of cobalt in acidic medium known at present, but it cannot be performed in the presence of iron, because reaction (1) proceeds to the right immediately on addition of phenanthroline.

Successive determination of iron and cobalt in one aliquot would be very useful in the analysis of complex materials such as alloys containing iron, cobalt, nickel, copper and aluminium, and might be based on the principles outlined above.

At first we supposed that the mixture of cobalt and iron could be determined as follows. An excess of EDTA (Na_2H_2Y) was added to the solution at pH 1·5–2·0 and the mixture was titrated potentiometrically with standard iron(III) chloride solution. The consumption of EDTA should correspond to the amount of iron present. After addition of phenanthroline, the following reaction should proceed and the amount of EDTA liberated would correspond to the cobalt:

$$FeY^- + Co(phen)_2{}^{2+} + 3Hphen^+ = Fe(phen)_3{}^{2+} + Co(phen)_3{}^{3+} + Y^{4-} + 3H^+ \qquad (2)$$

The liberated EDTA was determined by titration with iron(III) chloride. In both titrations we got distinct potential breaks, but the results for iron were higher than theoretical and for cobalt lower. This failure can be easily explained. In the presence of free EDTA, even in acid medium (pH 2) a small amount of cobalt(II)–EDTA complex is formed and simultaneously oxidized:

$$CoY^{2-} + FeY^- = FeY^{2-} + CoY^- \qquad (3)$$

The iron(II)–EDTA complex is simultaneously oxidized by aerial oxygen to the more stable iron(III)–EDTA complex. If the titration is carried out in an inert atmosphere (*e.g.*, nitrogen) the oxidation of iron(II) does not take place.

Later we found that iron could be titrated directly with EDTA under the proper conditions, and the subsequent titration of cobalt with iron in the presence of phenanthroline could be carried out without difficulty. The consumption of iron(III) chloride in the second titration corresponds exactly to the amount of cobalt present. Neither determination is influenced by a moderate amount of aluminium, nickel, manganese, alkaline earths, *etc.* Copper up to 1:1 ratio to iron does not interfere. When the solution contains one more metal the total concentration can be determined complexometrically, and the three components estimated.

EXPERIMENTAL

Reagents

EDTA, 0·05*M*, was standardized complexometrically with 0·05*M* lead nitrate (pH 5·0–5·5, Xylenol Orange as indicator).

Solutions, 0·05*M*, of iron(III) chloride, cobalt(II) nitrate, copper sulphate, nickel sulphate and aluminium sulphate were prepared from reagent grade chemicals and checked complexometrically.

Buffer solution, pH 2·0, was prepared by dissolving 189 g of monochloracetic acid in distilled water, adding 66 ml of 5*M* sodium hydroxide and diluting to 1 litre.

TABLE I.—DETERMINATION OF Fe AND Co IN THE PRESENCE OF Al, Ni, Cu

Taken Fe, *mg*	Found Fe, *mg*	Taken Co, *mg*	Found Co, *mg*	Taken Me, *mg*	Found Me, *mg*
13·96	13·96	14·70	14·70	Al 33·77	33·74
27·92	27·78	14·70	14·77	33·77	33·90
55·86	55·93	8·82	8·67	67·54	67·54
13·96	14·10	29·40	29·25	33·77	33·84
8·38	8·52	58·80	58·65	33·77	33·84
13·96	14·03	14·70	14·70	67·54	67·61
13·96	13·89	14·70	14·77	Ni 29·40	29·40
27·92	27·92	14·70	14·63	58·80	58·51
55·86	56·00	8·82	8·67	88·20	88·42
13·96	14·03	29·40	29·33	29·40	29·49
8·38	8·45	58·80	58·80	17·60	17·63
13·96	14·03	14·70	14·70	Cu 15·27	15·19
27·92	27·99	14·70	14·85	30·54	30·23
55·86	55·93	8·82	8·82	30·54	30·54
13·96	14·10	29·40	29·21	15·27	15·27
8·38	8·52	58·80	58·61	9·16	9·04

Procedure

Dilute the solution, containing up to 60 mg each of iron and cobalt, to 100–150 ml, add 10 ml of buffer and titrate iron potentiometrically with 0·05*M* EDTA (use platinum and calomel electrodes). After the potential break is reached, add 1 g of solid phenanthroline per 50 mg total iron and cobalt, and titrate with 0·05*M* iron(III) to the second potential break. A temperature of 40–50° is convenient for both titrations. Apply a correction for the excess of EDTA added in the first titration. Some results are summarized in Table I.

The method gives reliable results over a broad range of Fe:Co concentration ratios in the presence of moderate amounts of aluminium and nickel or an amount of copper not exceeding the amount of iron. If the analysed solution contains one of these elements besides iron and cobalt, this can be easily determined from the sum of all three elements determined complexometrically as follows.

Dilute a suitable aliquot to 100–150 ml, add an excess of 0·05*M* EDTA, adjust the pH to 5·0–5·5 with hexamine, and boil the solution for 3 min. Cool the solution, add a few drops of Xylenol Orange and titrate the excess of EDTA with 0·05*M* lead nitrate. Some results for nickel, aluminium and copper are also included in Table I.

DISCUSSION

The proposed method is convenient not only for the determination of binary mixtures of iron and cobalt in ratios from 8:1 to 1:8, but also to complement complexometric analysis of more complicated materials. Further development of the combined complexometric method is now in progress. For example the combination iron–cobalt–nickel–aluminium can be analysed as follows. Iron and cobalt are determined by the method described above and in a second aliquot the sum of all four elements is determined by the back-titration method. Because the amount of iron and cobalt is known from the first titration, the amount of aluminium and nickel can be easily calculated. Use of other masking agents such as ammonium fluoride (for Al) or thiourea (for Cu) gives further possibilities for analysis of more complicated materials. Results of such studies will be published elsewhere in the near future.

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Summary—A redox-complexometric determination of iron and cobalt is based on potentiometric titration of iron with EDTA, followed by that of cobalt with iron(III) chloride after addition of 1,10-phenanthroline. This method simplifies the complexometric analysis of more complicated materials.

Zusammenfassung—Eine redox-komplexometrische Bestimmungsmethode für Eisen und Kobalt beruht auf einer potentiometrischen Titration von Eisen mit EDTA und anschließender Titration von Kobalt mit Eisen(III)chlorid nach Zugabe von 1,10-Phenanthrolin. Diese Methode vereinfacht die komplexometrische Analyse komplizierter zusammengesetzten Materials.

Résumé—Un dosage redox-complexométrique du fer et du cobalt est basé sur le titrage potentiométrique du fer à l'EDTA, suivi de celui du cobalt par le chlorure de fer(III) après addition de 1,10-phénanthroline. Cette méthode simplifie l'analyse complexométrique de matières plus compliquées.

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Simultaneous determination of sulphate and sulphonate type anionic surfactants

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SYNTHETIC detergents for household use make up over 80% of the world's production, and almost all of those produced in Western countries are of the anionic alkyl sulphate and alkylarylsulphonate type, the latter being mainly alkylbenzenesulphonates. In sewage and effluent analysis we are mainly concerned with these two types of detergent, as cationic surfactants are little used as yet (but we should remember that higher concentrations of them would interfere with the Methylene Blue method[1,2] though non-ionic surfactants would not).

Analytical differentiation between sulphates and sulphonates is important in effluent control, as the sulphonates are much more stable in sewage and effluents than are the sulphates, which are easily hydrolysed. We must recognize the distinct difference between chemical degradation due to hydrolysis and bidegradation caused by micro-organisms. Micro-organisms act specifically on the long aliphatic chain at a rate determined by its structure, straight chains usually being more easily degraded than branched ones. Attempts have been made to differentiate between sulphates and sulphonates by hydrolysis followed by the determination of the free acid or of the decrease in the Methylene Blue activity, but the acidity determinations have not been very successful.[3]

Sulphuric acid has been used for the hydrolysis in the Methylene Blue[4,5] method, but we found that we could not reproduce results reliably by this method, hydrolysis of the alkyl sulphates being still incomplete after 2 hr, and the alkylarylsulphonates being partially hydrolysed under the same conditions. Presumably this is caused by the common ion effect of the sulphate on the hydrolysis. Use of phosphoric acid as hydrolytic agent gave still less hydrolysis of the alkyl sulphates, possibly because phosphoric acid is not a particularly strong one ($\mathrm{p}K_1$ is about 2). Hydrochloric acid, however, was found to give quantitative hydrolysis of the alkyl sulphates but only 1–2% hydrolysis of the sulphonates.

EXPERIMENTAL

Procedure

Dilute the detergent sample (containing 150–250 μg of surfactant) to 30 ml with distilled water, add 10 ml of concentrated hydrochloric acid, and boil the mixture under reflux in a 100-ml round-bottomed flask (containing boiling-chips) for 1 hr. Cool the mixture to room temperature, adjust its pH to 10–11 with concentrated sodium hydroxide solution, and apply the Methylene Blue method[1] in the usual way. Run a non-hydrolysed sample for comparison, and blanks for both. The non-hydrolysed sample (corrected for the blank) gives the total surfactant concentration, the hydrolysed sample (corrected for its blank) gives the sulphonate-type surfactant concentration, and the difference corresponds to the alkyl sulphate.

TABLE I.—HYDROLYSIS OF SULPHATES AND SULPHONATES (150-μg SAMPLES)

[HCl], *M*	Time, *hr*	Surfactant	Degree of hydrolysis, %
1·6	1	Empicol	70
		SLS	61
2·8	1	SLS	99
	2	SLS	98
	3	SLS	99
		HS 90	1
3·3	1	Manoxol	99
		SLS	99
		HS 90	2

TABLE II.—ANALYSIS OF SYNTHETIC MIXTURES OF SURFACTANTS

Taken, μg		Recovery, %	
Sulphate	Sulphonate	Sulphate	Sulphonate
SLS 250	ABS 50	102	98
200	100	102	98
150	150	101	99
100	200	101	99
50	250	99	101
Manoxol 250	ABS 50	100	100
200	100	101	99
150	150	100	100
100	200	99	101
50	250	100	100
Empicol 250	ABS 50	98	102
200	100	98	102
150	150	100	100
100	200	100	100
50	250	101	99
SLS 250	Nansa* 50	101	99
200	100	100	100
150	150	99	101
100	200	101	99
50	250	98	102

* Nansa = sodium dodecylnaphthalenesulphonate.

RESULTS AND DISCUSSION

Manoxol O.T. (sodium dioctylsulphosuccinate), Empicol L.Z. (about 85% sodium lauryl sulphate), SLS (sodium lauryl sulphate) and HS 90 (sodium dodecylbenzenesulphonate) were used as reference materials in examining the proposed method. With $1{\cdot}7M$ sulphuric acid, Manoxol was completely hydrolysed after 1 hr, but Empicol was only 66% hydrolysed; if the sulphuric acid concentration was halved, Empicol was only 38% hydrolysed in 1 hr, but HS 90 was about 6% hydrolysed. With $1{\cdot}5M$ phosphoric acid, Manoxol was completely hydrolysed in 1 hr, but Empicol and SLS only 26% and 3% hydrolysed respectively, and HS 90 was 6% hydrolysed. When various concentrations of hydrochloric acid were used, however, the results were much better (Table I). The best conditions seem to be hydrolysis for 2 hr with $\sim 3M$ hydrochloric acid, even SLS being almost completely hydrolysed, but HS 90 being practically unaffected.

The high concentration of sodium chloride, produced by the neutralization, was found not to affect the Methylene Blue method significantly. Results for mixtures (of known composition) of both types of surfactant are shown in Table II and show that the method is of adequate accuracy for this type of work.

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Summary—A method is described for the simultaneous determination of organic sulphates and sulphonates, based on hydrolysis of the sulphates in $3M$ hydrochloric acid. The total concentration of anionic surfactants is determined by the Methylene Blue method, then the sulphates are hydrolysed by boiling with $3M$ hydrochloric acid for 2 hr, and the sulphonates are determined by the Methylene Blue method. The concentration of the alkyl sulphates is obtained by difference. The large amounts of sodium chloride introduced during the procedure do not affect the Methylene Blue method.

Zusammenfassung—Eine Methode zur gleichzeitigen Bestimmung organischer Sulfate und Sulfonate wird beschrieben, die auf Hydrolyse der Sulfate in $3M$ Salzsäure beruht. Die Gesamtkonzentration an anionischen oberflächenaktiven Substanzen wird nach dem Methylenblauverfahren ermittelt; dann werden die Sulfate durch zweistündiges Kochen mit $3M$ Salzäure hydrolysiert und die Sulfonate nach dem Methylenblauverfahren bestimmt. Die Konzentration der Alkylsulfate wird durch Differenzbildung festgestellt. Die durch die Methode eigebrachten großen Mengen Natriumchlorid beeinflussen das Methylenblauverfahren nicht.

Résumé—On décrit une méthode pour la détermination simultanée des sulfates et sulfonates organiques, basée sur l'hydrolyse des sulfates en acide chlorhydrique $3M$. On détermine la concentration totale des surfactants anioniques par la méthode au bleu de méthylène, puis on hydrolyse les sulfates par ébullition avec l'acide chlorhydrique $3M$ pendant 2 h, et détermine les sulfonates par la méthode au bleu de méthylène. On obtient la concentration des alkylsulfates par différence. Les fortes quantités de chlorure de sodium introduites durant la technique n'affectent pas la méthode au bleu de méthylène.

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Vanadox—A new reagent for the photometric determination of vanadium

(*Received* 14 *March* 1968. *Accepted* 10 *June* 1968)

MORE that 70 organic reagents have been proposed for the spectrophotometric determination of vanadium, but most have poor selectivity. Derivatives of hydroxamic acids, especially *N*-benzoylphenylhydroxylamine,[1-3] are promising reagents for the extraction and photometric determination of vanadium, but molybdenum(VI), titanium, zirconium *etc.* interfere. Recently, derivatives of diphenylamine, such as diphenylbenzidine,[4] diphenylaminesulphonic acid,[5-7] and phenylanthranilic acid[7-9] have been suggested as vanadium reagents, but iron(III) interferes and phosphoric acid or fluoride cannot be used to mask iron in the strongly acidic media used.

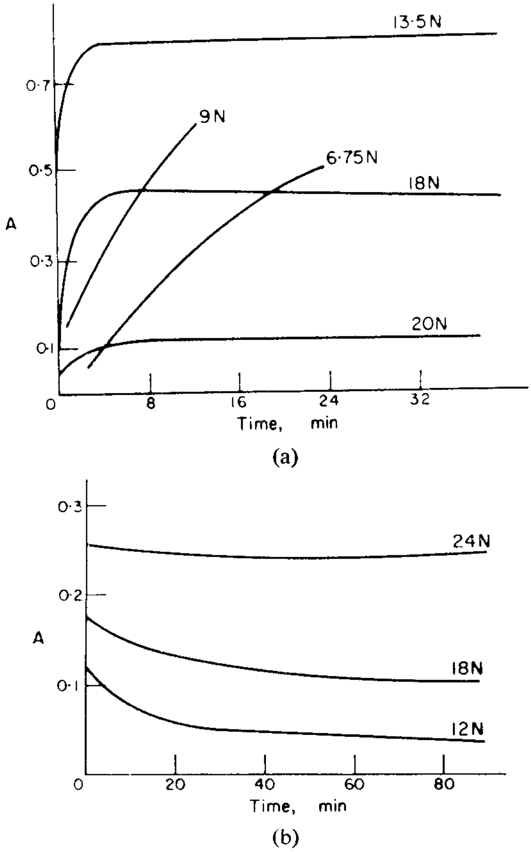
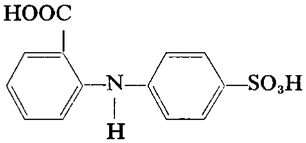
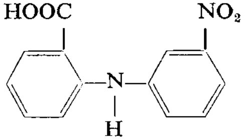
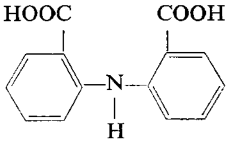
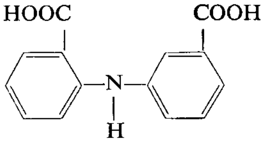


FIG. 1.—Rate of colour development in reaction of vanadium(V) at various sulphuric acid concentrations with (*a*) phenylanthranilic acid, (*b*) 2,2′-dicarboxydiphenylamine.

Since derivatives of diphenylamine have a relatively high sensitivity for vanadium(V) and only iron(III) interferes, it seemed worth while to find such a compound which would not react with iron(III). Substances containing one or more electrophilic substituents were therefore examined, because their redox potentials should be much higher than those of the parent compounds, and the reagents should be more selective because the potential of the vanadium(V)/IV) couple increases with increasing acidity of the medium whereas that of the iron(III)/(II) couple does not change significantly.[10,11] The compounds examined are listed in Table I.

The main difficulty in using these reagents is the instability of their oxidation products in the presence of excess of oxidant. However, when an excess of reagent is present, the stability of the oxidation product increases with increase in acidity[12] and it is possible to determine the optimum

Table I.—Properties of the reagents tried

No.	Name	Optimum $[H_2SO_4]$, *M*	λ_{max}, *nm*	ε	Sensitivity *μg/ml*	$E°$, *V*
I	2-Carboxy-4′-sulphodiphenylamine 	9	560–570	$1{\cdot}60 \times 10^4$	0·40	
II	2-Carboxy-2′-nitrodiphenylamine 	12	592–598	$1{\cdot}85 \times 10^4$	0·08	0·90 (9*M* H_2SO_4)
III	2,2′-Dicarboxydiphenylamine 	12	608–612	$2{\cdot}31 \times 10^4$	0·08	0·88 (9*M* H_2SO_4)
IV	2,3′-Dicarboxydiphenylamine 	12	575–582	$1{\cdot}04 \times 10^4$	0·20	—

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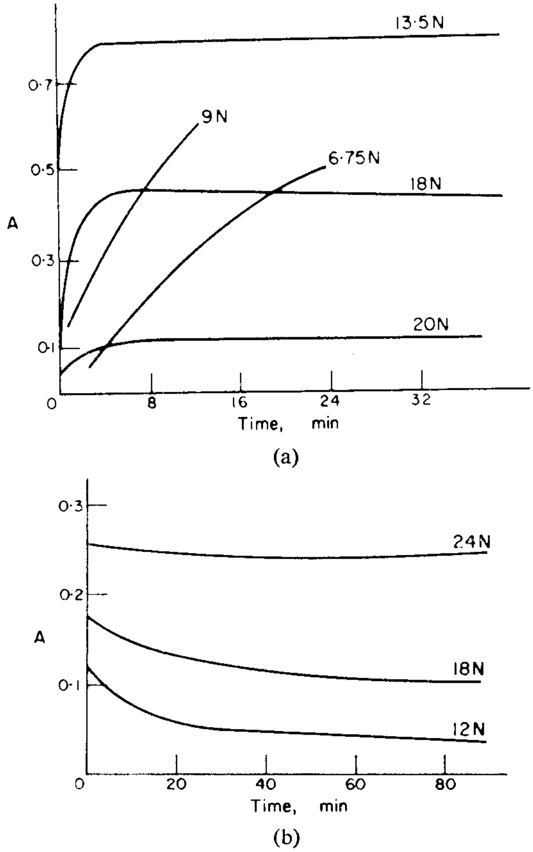

(a)

(b)

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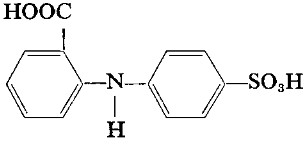
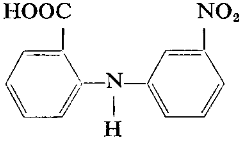
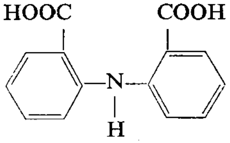
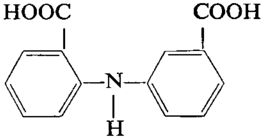
I	2-Carboxy-4′-sulphodiphenylamine 	9	560–570	1.60×10^4	0·40	
II	2-Carboxy-2′-nitrodiphenylamine 	12	592–598	1.85×10^4	0·08	0·90 (9*M* H_2SO_4)
III	2,2′-Dicarboxydiphenylamine 	12	608–612	2.31×10^4	0·08	0·88 (9*M* H_2SO_4)
IV	2,3′-Dicarboxydiphenylamine 	12	575–582	1.04×10^4	0·20	—

TABLE I (*contd*)

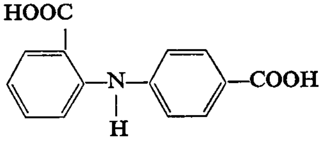
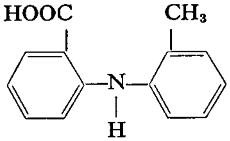
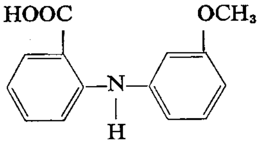
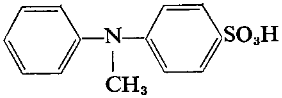
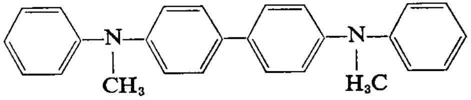
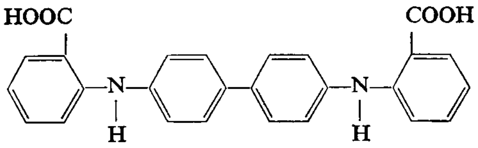
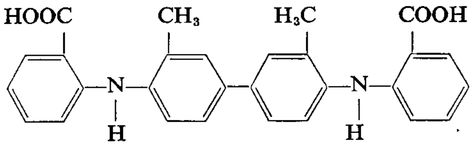
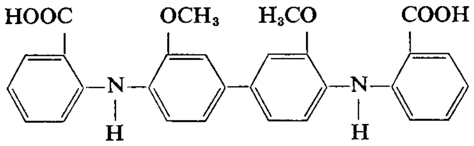
V	2,4′-Dicarboxydiphenylamine 	12	565–572	1·80 × 10^4	0·12	—
VI	2-Carboxy-2′-methyldiphenylamine 	9	554–560	2·86 × 10^4	0·10	0·92 (0·5*M* H_2SO_4)
VII	2-Carboxy-2′-methoxydiphenylamine 	9	622–624	3·13 × 10^4	0·20	1·00 (0·5*M* H_2SO_4)
VIII	*N*-Methyldiphenylaminesulphuric acid 	9	520–525	2·64 × 10^4	0·10	0·86 (0·5*M* H_2SO_4)
IX	*N*,*N*′-Dimethyl-*N*,*N*′-diphenylbenzidine 	9	525–532	4·50 × 10^4	0·02	—

Table I (*contd*)

No.	Name	Optimum[H_2SO_4], *M*	λ_{max}, *nm*	ε	Sensitivity *μg/ml*	$E°$, *V*
X	Diphenylbenzidine-2,2′-dicarboxylic acid 	12	556–562	$4·27 \times 10^4$	0·10	—
XI	Diphenylditolidine-2,2′-dicarboxylic acid 	12	564–574	$5·20 \times 10^4$	0·06	—
XII	Diphenyldianisidine-2,2′-dicarboxylic acid 	12	618–630	$6·36 \times 10^4$	0·04	—

acidity for stability and intensity of colour of the oxidation product. Table I also lists the oxidation characteristics of the compounds studied. Reagents II, III, IX and XII were further studied. Because the rate of oxidation of these compounds limits their utility, the kinetics of oxidation were studied. Phenylanthranilic acid rapidly gives stable colours at sulphuric acid concentrations above 13·5*N*, but the intensity decreases sharply with increasing acidity, whereas the new group of reagents gave increasing sensitivity with increase in acid concentration above 18*N*. Figure 1 shows some typical kinetic curves.

Curves showing the dependence of absorbance on vanadium(V) concentration showed that benzidine derivatives are useless for photometric determination of vanadium(V) because they give non-linear graphs on account of the complicated oxidation mechanism. Moreover, they react with iron(III) even in high concentrations of sulphuric acid. On the other hand, 2,2′-dicarboxydiphenylamine and 2-carboxy-2′-nitrodiphenylamine give linear calibration curves over the range 5–80 μg of vanadium in 25 ml of 24*N* sulphuric acid, the former giving the more stable colour and hence being preferred as the reagent. Up to 50 mg of iron(III), manganese(II), nickel, cobalt(II), copper(II), molybdenum(VI) and tungsten(VI) do not interfere; more than 3 mg of chromium(III) of niobium(V) increase the absorbance, and cerium(IV) interferes when its ratio to vanadium exceeds 2:1.

EXPERIMENTAL

Procedures

High-temperature alloys and high-alloy steels. Dissolve 0·4–1 g of sample (according to vanadium content) in 30 ml of *aqua regia*, add 20 ml of 9*M* sulphuric acid and evaporate to fumes of sulphur trioxide. Cool, add 20–30 ml of water, 1–2 drops of 30% hydrogen peroxide [to reduce chromium(VI)], heat to boiling, and filter off the precipitate and wash it several times with hot water. Collect the filtrate and washings in a 100-ml standard flask, dilute to the mark and mix. Take a 2-ml aliquot of this sample solution in a 50-ml beaker and to oxidize vanadium(IV) add 0·1*N* permanganate dropwise till a pink colour appears that remains for 3 min. Discharge the pink colour by dropwise addition of 0·05*M* sodium nitrate followed immediately by 0·3–0·5 g of urea. Transfer the solution to a 25-ml standard flask, add 12*M* sulphuric acid almost to the mark, then 0·2 ml of 0·1% vanadox solution (2,2′-dicarboxydiphenylamine), and dilute to the mark with 12*M* sulphuric acid. Mix the solution, and after 5 min measure the absorbance in a 10-mm cell at 610 nm against distilled water as reference.

TABLE II.—ANALYSES OF ALLOYS, STEELS AND ORES

Sample	Vanadium		Vanadium recovery			
	Certificate value, %	Found, %	Added, μg	Recovered, μg	V in sample	
					μg	%
Iron-alloys						
461	1·85	1·93, 1·93, 1·67	40	72	32	1·72
462	1·54	1·44, 1·39, 1·32	30	68	38	1·39
464	0·79	0·87, 0·85, 0·91	30	78	48	0·88
471	0·06	$0{\cdot}06_5$, $0{\cdot}06_0$, $0{\cdot}05_1$	30	58	28	0·06
472	0·25	0·25, 0·25, 0·25	30	52	22	0·25
Ferrotitanium ores						
25 b	0·33	0·29, 0·31	20	55	35	0·30
25 v	0·42	0·42, 0·43	30	58	28	0·43
Steels						
105	1·86	1·86, 1·86, 1·86				
26 v	1·17	1·20, 1·15, 1·17				
249	0·25	0·25, 0·25, 0·24	600	840	240	0·24
122	1·85	1·86, 1·85, 1·84	200	575	375	1·87
158 a	0·16	0·16	500	650	150	0·15
Nickel-base high-temperature alloy						
	0	—	20	20	—	—
			40	40		
			60	60		
			80	80		

Ferrotitanium ores. Fuse about 0·4 g of sample in an iron crucible with 6–8 g of sodium peroxide, cool, and leach the melt with 100 ml of hot water. If the solution is green add a spatula-tip of sodium peroxide and boil the solution for 15–20 min. Cool the solution and transfer it to a 250-ml standard flask, dilute to the mark, mix, and leave until the precipitate has settled out. Filter through a dry paper into a dry beaker and take 5 ml of filtrate in a 50-ml beaker, boil it for 5 min to decompose the peroxide, neutralize with sulphuric acid, add 0·05*M* iron(II) ammonium sulphate dropwise till the solution is decolourized, followed by 0·1*N* permanganate until a permanent pink appears, then proceed as for alloys and steels, discharging the pink colour with nitrite *etc*.

Results

Typical results are shown in Table II, including some for spiked samples.

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N.G. Chernyshevsky University
Saratov, U.S.S.R.

N. S. Frumina
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Summary—A new reagent, 2,2 -dicarboxydiphenylamine, vanadox, is proposed for the photometric determination of vanadium in steels, high temperature alloys and ferrotitanium ores. In strongly acidic medium the reagent is selective for vanadium(V) and only cerium(IV) interferes.

Zusammenfassung—Zur photometrischen Bestimmung von Vanadium in Stählen, Hochtemperaturlegierungen und Ferrotitanerzen wird ein neues Reagens, 2,2′-Dicarboxydiphenylamin, Vanadox, vorgeschlagen. In stark saurem Medium ist das Reagens selektiv für Vanadium(V) und nur Cer(IV) stört.

Résumé—On propose un nouveau réactif, la 2-2′-dicarboxydiphénylamine pour le dosage photométrique du vanadium dans les aciers, les alliages à haute tempétature et les minerais au ferrotitane. En milieu fortement acide, le réactif est sélectif pour le vanadium(V) et seul le cérium(IV) interfère.

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p-nitroaniline as a colorimetric reagent for sulphur dioxide

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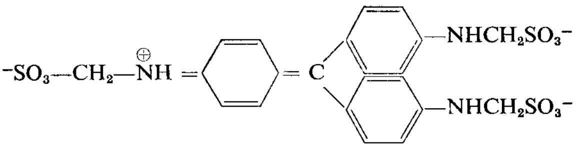
THE intense colour of an aqueous solution of *p*-rosaniline disappears when the solution is acidified. If formaldehyde and sulphur dioxide or sulphite are added to the decolorized solution, a colour closely resembling the original appears. This reaction, and similar ones with other triphenylmethane dyes, have long[1] been used for detecting and determining sulphur dioxide and sulphites. From a spectrophotometric examination of the reaction and parallel studies with aniline, Nauman *et al.*[2] found that the final product was a methanesulphonic acid (R—NH—CH_2—SO_3H). Further study by others[3–5] led to the conclusion that the coloured substance is a mixture of mono-, di- and trisubstituted reaction products. For the trisubstituted product the following structure was proposed:



As the sulphonic acid groups are most probably protolyzed, the structure is written here in its ionic form.

The fact that several coloured species are formed, together with the difficulty of obtaining a well-defined reagent[3,6] impairs the precision of the *p*-rosaniline method. In principle, any aromatic amine (in its ionic form), would be likely to react similarly. The electronic configurations of the neutral amine and the end product, the sulphonic acid, are similar, and for a potential reagent for sulphur dioxide simple coloured amines should be examined. The focus of our attention accordingly fell on the nitroanilines, all of which form intensely yellow aqueous solutions. The p*K* values for the corresponding acids are[7] *p*-nitroaniline 2·0; *m*-nitroaniline 2·5; *o*-nitroaniline −0·29.

As the reacting species are the colourless acid forms, the use of *o*-nitroaniline would call for a strongly acid reaction mixture. Pilot experiments showed that the reaction products became unstable when the acid concentration was increased beyond 1*N*. *o*-Nitroaniline is therefore not a suitable colorimetric reagent for sulphur dioxide.

The absorption spectra of the amines in neutral and acid solution are shown in Figs. 1 and 2, and those of the reaction products in Fig. 3. As the molar absorptivity of the *p*-nitroaniline product is much greater than that of the *meta* compound, only the former was studied.

Optimal conditions for the colour development were found to be 0·8*M* acid, 0·02*M* formaldehyde and 0·3*mM* *p*-nitroaniline. This covers a sulphite concentration up to 0·1*mM* in the final solution, 10-mm cells being used for 10–300 μg of sulphur dioxide in 10 ml of sample, and 100-mm cells for 1 μg. The colour develops fairly slowly but is stable after 25–30 min. The precision is good and Beer's law holds. The sensitivity is of the same order as that of the *p*-rosaniline method.

The procedure below is given as an example. It is intended for the analysis of sodium tetrachloromercurate(II) solution used for absorbing sulphur dioxide from the atmosphere,[8,9] but can be modified for other purposes.

EXPERIMENTAL

Reagents

Sodium tetrachloromercurate(II) solution, 0·1*M*. Dissolve 27·2 g (0·1 mole) of mercury(II) chloride and 11·7 g (0·2 mole) of sodium chloride in distilled water and dilute to 1 liter.

Sulphamic acid, 0·6%. Freshly prepared.

Hydrochloric acid, 4*M*.

p-*Nitroaniline solution*, 0·001*M*. Dissolve 0·138 g of reagent in 25 ml of ethanol in a 1-litre volumetric flask and make up to the mark with distilled water.

Formaldehyde solution, 0·1*M*.

Standard sulphur dioxide solution, ca. 50 ppm SO_2. Add 0·0742 g of sodium metabisulphite, $Na_2S_2O_5$, to 50 ml of the sodium tetrachloromercurate solution in a 1-litre volumetric flask and make up to the mark with distilled water. Standardize by iodometric titration.

All reagents should be of analytical grade.

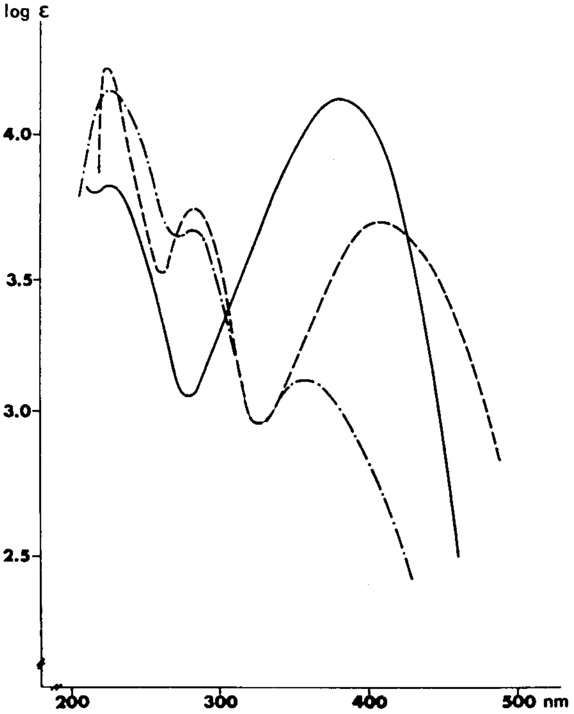


FIG. 1.—Spectra of the nitroanilines in aqueous solution. ——, *para*; – –, *ortho*; —●—, *meta*.

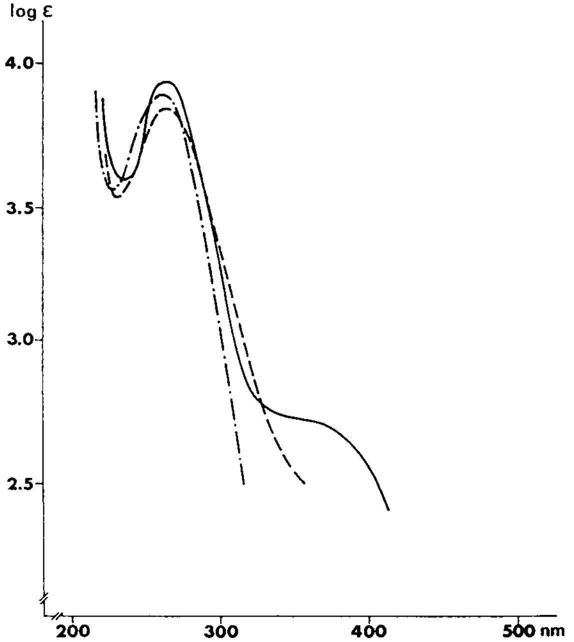


FIG. 2.—Spectra of the nitroaniline hydrochlorides in hydrochloric acid, 1·6M for the *para* compound, and 5·9 and 2·9M for the *ortho* and *meta* compounds, respectively. Code as for Fig. 1.

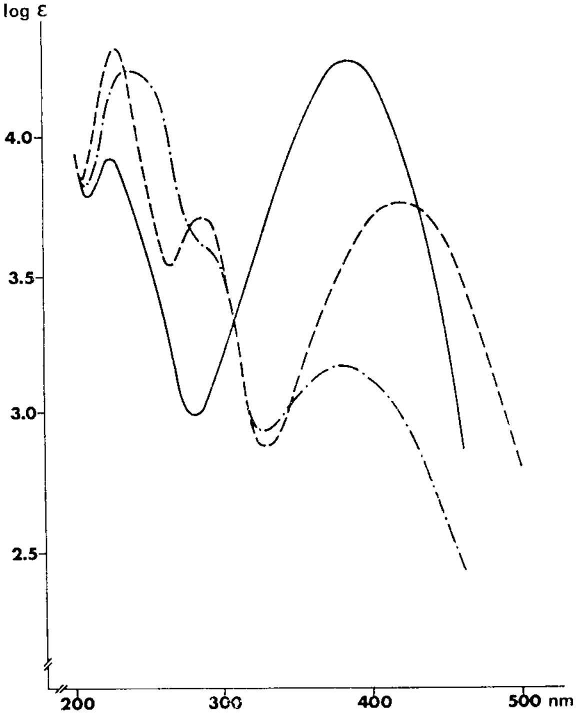


FIG. 3.—Spectra of the nitroaniline-methanesulphonic acids, aqueous solutions of their sodium salts. Code as for Fig. 1.

Procedure

The following method applies to 10-ml samples of 0·1*M* tetrachloromercurate solution containing 10–300 μg of sulphur dioxide. Samples containing more than 300 μg of sulphur dioxide can be analysed after dilution with distilled water, provided that the tetrachloromercurate solution used for the preparation of the reagent blank is diluted correspondingly. Hydrogen sulphide is precipitated by the tetrachloromercurate and does not interfere. Nitrogen dioxide may be present in a concentration not exceeding four times that of the sulphur dioxide.

Into a 50-ml volumetric flask measure 10·0 ml of the sample solution and 1 ml of the sulphamic acid solution. Mix 10 ml of the hydrochloric acid, 15 ml of *p*-nitroaniline solution and 10 ml of formaldehyde solution and add the mixture to the flask. Make up to the mark with distilled water. Prepare a reagent blank with 10 ml of the sodium tetrachloromercurate solution (or a corresponding dilution thereof) instead of the sample solution. After 30 min measure the absorbance in 10-mm cells at 387 nm with the reagent blank as a reference. Read off the sulphur dioxide content from a calibration curve covering the range 0–200 μg of sulphur dioxide, and prepared by applying the procedure to suitable portion of the standard solution.

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PER OLOF BETHGE
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Summary—The merits of the nitroanilines as an alternative to *p*-rosaniline and fuchsine in the colorimetric determination of sulphur dioxide and sulphites have been investigated. *p*-Nitroaniline was found to be a stable, well-defined reagent, with which sulphur dioxide can be determined to a high level of precision, the sensitivity being of the same order of magnitude as for *p*-rosaniline.

Zusammenfassung—Die Vorzüge der Nitraniline statt *p*-Rosanilin und Fuchsin bei der kolorimetrischen Bestimmung von Schwefeldioxid und Sulfiten wurden untersucht. *p*-Nitranilin wurde als stabiles, wohldefiniertes Reagens befunden, mit dem Schwefeldioxid sehr genau bestimmt werden kann, wobei die Empfindlichkeit in der selben Großenordnung liegt wie bei *p*-Rosanilin.

Résumé—On a étudié les mérites des nitranilines comme une alternative de la *p*-rosaniline et de la fuchsine dans le dosage colorimétrique de l'anhydride sulfureux et des sulfites. On a trouvé que la *p*-nitraniline est un réactif stable, bien défini, avec lequel on peut doser l'anhydride sulfureux avec un haut degré de précision, la sensibilité étant du même ordre de grandeur que pour la *p*-rosaniline.

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PRELIMINARY COMMUNICATION

Electrogravimetric trace analysis on a piezoelectric detector*

(*Received* 16 *April* 1968. *Accepted* 6 *May* 1968)

ELECTRODEPOSITION has long proved useful for the separation and quantitative analysis of metals in solution. Selectivity can often be obtained by masking agents or by varying the applied voltage, since metals have different characteristic plating potentials. The method requires little attention and is quite accurate for metal concentration as low as about $10^{-3}M$. The major limitations are the long times required for complete deposition from dilute samples, the care necessary to prevent oxidation or dissolution of the plated metal before weighing, and the useful lower concentration limit imposed by the sensitivity of the analytical balance. In this paper a method is presented which takes advantage of the piezoelectric effect and thus overcomes all three of these restrictions.

Piezoelectric crystals have been used for the determination of very small mass changes.[1,2,3] It is well known that the fundamental frequency of a quartz crystal is dependent on the total mass of the crystal element and its associated metallic electrodes. If the crystal is incorporated in an oscillator circuit, it will control the frequency of the oscillator. In the present work, the metallic electrodes of such a crystal are used as cathodes during the incomplete electrodeposition of cadmium from aqueous solutions. The resultant change in the total mass of the quartz crystal and its electrodes leads to a corresponding shift of the oscillator frequency. It has been shown that the magnitude of this shift is such that mass differences of the order of 10^{-9} g should be detectable with a 6·0-MHz crystal.[3] At the concentrations used in this investigation the weight of cadmium deposited on the electrodes is related linearly to the change in the fundamental crystal frequency.

EXPERIMENTAL

Stock solutions of cadmium perchlorate and sodium perchlorate were prepared from reagent grade $Cd(ClO_4)_2 \cdot 6H_2O$ and anhydrous $NaClO_4$. Demineralized water from a mixed-resin column was used to prepare all solutions.

A 3·0-MHz quartz crystal, with gold electrodes and having an AT cut, was used in a tuned plate-tuned grid oscillator circuit.[4] The oscillator output frequency was monitored to ±1 Hz with a frequency meter (Model 5246L Electronic Counter, Hewlett-Packard Company, Palo Alto, California) or recorded on a potentiometric recorder after digital-to-analogue conversion (Model 580A Digital-Analog Converter, Hewlett-Packard Company).

A three-electrode electrodeposition circuit consisting of a conventional d.c. polarograph and a potentiostat was employed. The cathode consisted of the gold electrode surfaces of the crystal, and the reference electrode was a commercial saturated calomel electrode. A platinum wire counter-electrode was isolated from the solution by a medium-porosity glass frit to prevent any anodic products from being swept to the cathode. All three electrodes were mounted in holes drilled through a plastic disc which also served as the cell cover during electroplating. Stirring was accomplished with a magnetic stirrer. A simple switching circuit was designed to change the crystal electrodes from the electroplating circuit to the frequency measuring circuit. Provision for a nitrogen purge was built into the cell.

For each determination a 40·0-ml aliquot of the cadmium solution in $0{\cdot}1M$ sodium perchlorate was placed in the cell, covered with a plastic cap, and purged with nitrogen to remove oxygen. Meanwhile the initial frequency of the crystal was determined and the crystal switched into the electrodeposition circuit. Next the cover with the electrodes suspended on insulated support wires was lowered into the cell and a voltage of −0·90 V applied for a known time interval. At the end of this interval the electrodes were raised from the sample solution and the crystal was rinsed with water, dried, and switched into the frequency measuring circuit. The final frequency, which was lower than that observed before electrodeposition, was then noted. After each analysis the deposit was dissolved in dilute nitric acid. A complete analysis can be performed in 15 min.

RESULTS AND DISCUSSION

With a 3·0-MHz crystal operated on the harmonic at 6·0 MHz, a calibration curve was obtained for plating times of 2·0 min. The calibration curve is simply a plot of the total frequency change in

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* This work was conducted in partial fulfillment of the requirements for the Ph.D. degree at Texas A & M University.

Hz *vs.* the initial cadmium concentration. A linear relationship resulted over a concentration range from $2{\cdot}0 \times 10^{-6}M$ to $2{\cdot}0 \times 10^{-4}M$ cadmium. The average values of three determinations at each of five concentrations in this range were used to establish the relationship. The reproducibility at these concentrations was very satisfactory. The relative standard deviation for six determinations at $4{\cdot}0 \times 10^{-5}M$ cadmium, which yielded an average frequency change of 163 Hz, was 2·8%. In view of the linearity and the precision obtained, it must be concluded that surface oxidation or dissolution are either absent or reproducible. It was estimated that during a 2-min plating interval only about 0·5% of the total cadmium was removed from solution. Thus the method is essentially non-destructive.

The useful concentration range was extended to lower values by depositing for longer periods of time to obtain greater frequency changes. When a 20-min plating time was used, a linear relationship was observed over a concentration range from $3{\cdot}0 \times 10^{-7}M$ to $1{\cdot}0 \times 10^{-5}M$ cadmium. The empirical relationship describing this particular group of experiments is

$$C = k\Delta f$$

where C is in mole.l.$^{-1}$, $\Delta f = (f_{\text{initial}} - f_{\text{final}})$, and $k = 3{\cdot}33 \times 10^{-8}$ mole.l.$^{-1}$ Hz^{-1}. The proportionality factor is constant for a given crystal, stirring rate, and deposition time. The averages of two determinations at each concentration are shown in Table I.

TABLE I.—DETERMINATION OF CADMIUM WITH 20-MINUTE DEPOSITION TIME

Sample molarity	Molarity found*	Relative error, %
$3{\cdot}00 \times 10^{-7}$	$3{\cdot}49 \pm 0{\cdot}16 \times 10^{-7}$	16
$6{\cdot}00 \times 10^{-7}$	$6{\cdot}33 \pm 0{\cdot}33 \times 10^{-7}$	5·5
$2{\cdot}00 \times 10^{-6}$	$2{\cdot}00 \pm 0{\cdot}03 \times 10^{-6}$	0·0
$5{\cdot}00 \times 10^{-6}$	$4.94 \pm 0{\cdot}02 \times 10^{-6}$	1·2
$1{\cdot}00 \times 10^{-5}$	$0{\cdot}996 \pm 0{\cdot}004 \times 10^{-5}$	0·4

* Averages of 2 determinations.

The accuracy and precision of the method were improved by this longer plating time, partly because of the lower relative error in timing. The total timing error in either case is less than 1 sec.

Several means of increasing the sensitivity and accuracy of this method are currently being pursued before the method is extended to include other metals. Most notable of these approaches is the use of crystals of higher frequency since the sensitivity is proportional to the square of the fundamental frequency of the crystal.[2]

Acknowledgement—We wish to thank Phillips Petroleum Company for a fellowship to J. P. M.

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Summary—A novel and rapid electroanalytical method for the determination of cadmium at micromolar concentrations is described. The method utilizes the piezoelectric effect to follow small mass changes which result from electrodeposition.

Zusammenfassung—Eine neue und schnelle elektroanalytische Methode zur Bestimmung von Cadmium in Mikromol-Konzentrationen wird bescrieben. Die Methode benutzt den piezoelektrischen Effekt, um kleinen Massenänderungen zu folgen, die mit der Bildung von elektrolytischen Niederschlägen einhergehen.

Résumé—On décrit une méthode électroanalytique nouvelle et rapide pour le dosage du cadmium à des concentrations micromolaires. La méthode utilise l'effet piézoélectrique pour suivre de faibles changements de masse qui résultent de l'électrodéposition.

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Extraction of metals with methyltricaprylammonium chloride—I. Selective extraction of zinc chloride: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (11 *November* 1968)

Talanta, 1969, Vol. 16, p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Marine Chemistry: Dean F. Martin. Arnold London, 1968, Pp.viii + 280. 55s.

This is the first volume of a two-volume work dealing with the chemistry of natural water. In it are given analytical methods for the determination of a number of ions, of particulate matter suspended in water and of dissolved gases. In addition to accounts of classical methods there are descriptions of the more recent techniques of flame photometry and atomic-absorption spectrometry. The second volume, which justifies the title, is to deal with the theoretical aspects.

Glassblowing for Laboratory Technicians: R. Barbour. Pergamon Press, Oxford, 1968. Pp. 245. 40s.

This book does not pretend that anyone can become a competent glassblower simply by reading, but it will supply answers to most of the questions that arise during practice in connection with materials and techniques. There are many diagrams showing the sequences in making various standard pieces. A chapter on vacuum technique deals with pumps and the measurement of low pressures, as well as the special glassblowing problems. A useful book for the practical chemist as well as the technician.

Polarography: D. R. Crow and J. V. Westwood. Methuen, London, and Barnes & Noble, New York, 1968. Pp 174. 30s.

For its size, there is a surprisingly large amount of information packed into this small book, which is good value for money. The use of practical examples to illustrate the sections on Fundamental Principles and on the Study of Inorganic Complex Formation helps to make the discussions easier to follow for newcomers to the field. A section on A.C. Polarography and Related Techniques summarizes the many newer developments in the art, and compares the performances of instruments based on them. This book can be recommended for senior students of analytical chemistry, and more experienced chemists will find it a useful text for refreshing their memory or bringing them up to date.

Thermometric titrimetry: H. J. V. Tyrrell and A. E. Beezer. Chapman and Hall, London, 1968. Pp. vii + 207. 48s.

The authors clearly and concisely discuss the principles of, the apparatus for and applications of thermometric titrations. The work is notable for its fairness and comprehensiveness; the authors have not overstated the advantages of the methods described, but have preferred to let the facts, conveniently presented in tabular form with the accuracy and precision stated, speak for themselves. Many analysts and physical chemists may be convinced by the book that the method is another useful "working tool." The book must become the standard work on the subject.

Reagent chemicals. 4th Ed.: American Chemical Society, Washington, 1968. Pp. xviii + 651. $14.00.

The new edition of this valuable work lists the specifications of 38 new reagents as well as the revised ones for all but one of the reagents listed in the 3rd edition of 1960. Additional specifications are given for the solvents commonly used for ultraviolet spectroscopy, and polarographic and gas chromatographic tests are introduced. The work is very similar to the 1967 edition of *AnalaR Standards*, but there are differences in detail, the British standards being, usually, slightly more rigorous. Analysts concerned with trace analysis, who like to know what the figures on the label really mean, will not be disappointed. Supplements are provided at no extra charge as they become available.

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For details and registration forms contact Dr. H. G. McAdie, Ontario Research Foundation Sheridan Park, Ontario, Canada.

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SUMMARIES FOR CARD INDEXES

A critical review of atomic absorption, spectrochemical, and X-ray fluoresence methods for the determination of the noble metals—II: F. E. Beamish, C. L. Lewis and J. C. Van Loon, *Talanta*, 1969, **16**, 1. (Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada.)

Summary—The review is a continuation of the initial reviews and covers the period of abstracting up to and including April, 1967. Work on the atomic-absorption determination of noble metals is also included.

Semipermeable ion-exchange membranes as a preconcentration matrix for trace analysis by electrochemical and neutron-activation techniques: Uri Eisner and Harry B. Mark, Jr., *Talanta*, 1969, **16**, 27. (Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.)

Summary—Ion-exchange membranes were used in conjunction with neutron-activation analysis and anodic stripping voltammetry for the determination of certain trace metal ions. The various parameters which govern the applicability, limitations and sensitivity of the methods were investigated. A new membrane "barrier" electrode assembly was introduced and found to be useful for the anodic stripping determination of trace metal ions in the presence of surface active materials.

Determination of rhenium in molybdenite by X-ray fluorescence. A combined chemical-spectrometric technique: M. W. Solt, J. S. Wahlberg and A. T. Myers, *Talanta*, 1969, **16**, 37. (U.S. Geological Survey, Denver, Colo., U.S.A.)

Summary—Rhenium in molybdenite is separated from molybdenum by distillation of rhenium heptoxide from a perchloric–sulphuric acid mixture. It is concentrated by precipitation of the sulphide and then determined by X-ray fluorescence. From 3 to 1000 μg of rhenium can be measured with a precision generally within 2%. The procedure tolerates larger amounts of molybdenum than the usual colorimetric methods.

КРИТИЧЕСКИЙ ОБЗОР ИСПОЛЬЗОВАНИЯ МЕТОДОВ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ, СПЕКТРОРАФИЧЕСКОГО И РЕНТГЕНОВСКОГО ФЛУОРЕСЦЕНТНОГО АНАЛИЗА ДЛЯ ОПРЕДЕЛЕНИЯ БЛАГОРОДНЫХ МЕТАЛЛОВ(II):

F. E. Beamish, C. L. Lewis and J. C. Van Loon, *Talanta*, 1969, **16**, 1.

Резюме—Этот обзор представляет собой продолжение начальных обзоров и охватывает период литературы опубликованной до апреля 1967 г. включительно. В обзоре приведены также данные о определении благородных металлов методом атомно-абсорбционной спектрометрии.

ИСПОЛЬЗОВАНИЕ ПОЛУНЕПРОНИЦАЕМЫХ ИОНООБМЕННЫХ МЕМБРАН ДЛЯ ПРЕДВАРИТЕЛЬНОГО КОНЦЕНТРИРОВАНИЯ В СЛЕДОВОМ АНАЛИЗЕ МЕТОДАМИ ЭЛЕКТРОХИМИЧЕСКОГО И НЕЙТРОННО-АКТИВАЦИОННОГО АНАЛИЗА:

Uri Eisner and Harry B. Mark, *Talanta*, 1969, **16**, 27.

Резюме—Ионообменные мембраны использованы вместе с методами нейтронно-активационного анализа и анодной стриппинг вольтамперометрии в определении некоторых следов ионов металлов. Изучены параметры влияющие на применимость, пределы определения и чувствительность исследованных методов. Предложен новый электрод с мембранным «барьером», который оказался полезным для определения следов ионов металлов методом анодной стриппинг воьтамперометрии в присутствии поверхностно-активных веществ.

ОПРЕДЕЛЕНИЕ РЕНИЯ В МОЛИБДЕНИТЕ МЕТОДОМ РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНЦИИ. КОМБИНИРОВАННЫЙ ХИМИЧЕСКО-СПЕКТРОФОТОМЕТРИЧЕСКИЙ МЕТОД:

M. W. Solt, J. S. Wahlberg and A. T. Myers, *Talanta*, 1969, **16**, 37.

Резюме—Рений в молибдените отделяют от молибдена дистилляцией семиокиси рения из смеси хлорной и серной кислоты. Рений концентрируют осаждением в форме сульфида и его затем определяют методом рентгеновской флуоресценции. Можно определять 3 до 1000 мкг рения точностью обычно больше чем 2%. Процедура позволяет присутствие количеств молибдена больше чем обыкновенные колориметрические методы.

Cation-exchange separation of hafnium and zirconium from accompanying metal ions: J. Korkisch and K. A. Orlandini, *Talanta*, 1969, **16**, 45. (Chemistry Division, Argonne National Laboratory, Argonne, Illinois, U.S.A.)

Summary—Hafnium and zirconium are not retained on the strongly acidic cation-exchange resin Dowex 50 from a mixture of methanol and $12M$ nitric acid (19:1) which is $0{\cdot}1M$ in trioctylphosphine oxide. On the other hand most other elements investigated are strongly adsorbed on the resin from this medium so that they are readily separated from hafnium and zirconium. These elements include titanium, rare earths, alkali metals, alkaline earth metals, iron, cobalt, manganese and zinc. This separation technique has been found to be suitable for the separation of tracer and milligram amounts of hafnium and zirconium from accompanying metal ions. If in place of methanol other organic solvents such as acetone, tetrahydrofuran and methyl glycol are used the selectivity of the separation of zirconium and hafnium from the other elements is decreased. The same effect is observed when hydrochloric acid is used in the mixtures instead of nitric acid.

Substituted hydroxylamines as analytical reagents: A. D. Shendrikar, *Talanta*, 1969, **16**, 51. (Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La.70803, U.S.A.)

Summary—The review deals with analytical applications of hydroxylamine derivatives. The defects of cupferron and versatility of *N*-benzoyl-*N*-phenylhydroxylamine in reaction with various metal ions is discussed. The application of the latter in chemical analysis is summarized and separation factors for some pairs of elements included. Suggestions for further use of this compound and other hydroxylamines are given.

КАТИОНООБМЕННОЕ ОТДЕЛЕНИЕ ГАФНИЯ И ЦИРКОНИЯ ОТ СОПРОВОЖДАЮЩИХ ИОНОВ МЕТАЛЛОВ:

J. Korkisch and K. A. Orlandini, *Talanta*, 1969, **16**, 45.

Резюме—Гафний и цирконий не удерживаются на сильнокислой катионообменной смоле дауекс 50 из смеси метилового спирта и 12*M* азотной кислоты (19:1), содержащей 0,1*M* триоктилфосфиноксида. Большинство других изученых элементов сильно адсорбируются на смоле из этого раствора и потому могут легко отделяться от гафния и циркония. Эти элементы включают титан, редкоземельные элементы, щёлочные металлы, щёлочноземельные металлы, железо, кобальт, марганец и цинк. Эта процедура оказалась подходящей для отделения индикаторных и миллиграммовых количеств гафния и циркония от сопровождающих ионов металлов. В случае использования других органических растворителей, на пример ацетона, тетрагидрофурана и метилгликола вместо метилового спирта селективность отделения циркония и гафния от других элементов уменьшается. Тот же самый эффект обнаружен если в смесях азотная кислота заменяется соляной кислотой.

ЗАМЕЩЕННЫЕ ГИДРОКСИЛАМИНЫ КАК АНАЛИТИЧЕСКИЕ РЕАГЕНТЫ:

A. D. Shendrikar, *Talanta*, 1969, **16**, 51.

Резюме—Обзор посвящен применении в анализе дериватов гидроксиламина. Обсуждены недостатки купферрона а многосторонность *N*-бензоил-*N*-фенилгидроксиламина в реакциях с различными ионами металлов. Описано применение последного реагента в химическом анализе и приведены факторы разделения некоторых парах элементов. Предложены другие применения этого реагента и других гидроксиламинов.

Fluorescence characteristics of inorganic complexes in hydrochloric acid medium at liquid-nitrogen temperature: G. F. Kirkbright, C. G. Saw and T. S. West, *Talanta*, 1969, **16**, 65. (Chemistry Department, Imperial College, London, S.W.7.)

Summary—A study of the low-temperature fluorescence characteristics of the ions of 55 elements in concentrated hydrochloric acid is reported. The spectral characteristics, effects of hydrochloric acid concentration and time, calibration linearity and sensitivity for Sb(III), Bi, Ce(III), Pb, Te(IV), Tl(I) and Sn(IV) have been investigated. Uranium(VI), copper(I) and antimony(V) also exhibit fluorescence under these conditions. The detection limits using a commercial spectrofluorimeter with modified sample cells are Sb(III), $10^{-6}M$; Bi(III), $10^{-8}M$; Ce(III), $10^{-7}M$; Pb, $10^{-8}M$; Te(IV), $10^{-7}M$; Tl(I), $10^{-6}M$; Sn(IV), $10^{-4}M$. The suitability of some inorganic acid solvents for clear glass formation at $-196°$ is also investigated.

Studies in atomic fluorescence spectroscopy—VIII. Atomic fluorescence and atomic absorption of thallium and mercury, electrodeless discharge tubes being used as sources: R. F. Browner, R. M. Dagnall and T. S. West, *Talanta*, 1969, **16**, 75. (Chemistry Department, Imperial College, London, S.W.7, U.K.)

Summary—Atomic-fluorescence measurements, with microwave-excited electrodeless discharge tubes as sources of excitation, are described for thallium and mercury. The limits of detection by atomic fluorescence are 0·12 ppm for thallium and 0·08 ppm for mercury; the corresponding limits by atomic absorption (using the same instrument and source) are 6 and 10 times as great. The preparation, operation and spectral characteristics of thallium and mercury discharge tubes are described and comparisons are made with a thallium hollow cathode lamp and thallium and mercury spectral discharge lamps.

ХАРАКТЕРИСТИКИ ФЛУОРЕСЦЕНЦИИ НЕОРГАНИЧЕСКИХ КОМПЛЕКСОВ В СОЛЯНОКИСЛОЙ СРЕДЕ ПРИ ТЕМПЕРАТУРЕ ЖИДКОГО АЗОТА:

G. F. Kirkbright, C. G. Saw and T. S. West, *Talanta*, 1969, **16**, 65.

Резюме—Изучены характеристики флуоресценции при низкой температуре ионов 55 элементов в концентрированной соляной кислоте. Исследованы спектральные характеристики, влияние концентрации соляной кислоты и времени, линейность калибровочных кривых и чувствительность для Sb(III), Bi, Ce(III), Pb, Te(IV), Tl(I) и Sn(IV). Уран(VI), медь(I) и сурьма(V) также показуют флуоресценцию в этих условиях. Пределы обнаружения пользуясь коммерческим спектрофлуорометром и модифицированными кюветками равны: Sb(III) $10^{-6}M$; Bi(III), $10^{-8}M$; Ce(III), $10^{-7}M$; Pb $10^{-8}M$; Te(IV) $10^{-7}M$; Tl(I) $10^{-6}M$; Sn(IV) $10^{-4}M$. Также изучена применимость некоторых неорганических кислых растворителей для образования прозрачного стекла при —196°.

ИЗУЧЕНИЕ АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ —VIII. АТОМНАЯ ФЛУОРЕСЦЕНЦИЯ И АТОМНАЯ АБСОРБЦИЯ ТАЛЛИЯ И РТУТИ С ИСПОЛЬЗОВАНИЕМ БЕЗЭЛЕКТРОДНЫХ РАЗРЯДНЫХ ТРУБОК В КАЧЕСТВЕ ИСТОЧНИКОВ:

R. F. Browner, R. M. Dagnall and T. S. West, *Talanta*, 1969, **16**, 75.

Резюме—Описаны измерения атомной флуоресценции для таллия и ртути с использованием возбужденных микроволнами безэлектродных разрядных трубок в качестве источников. Предел обнаружения атомно-флуоресцентным методом 0,12 мг/л для таллия, а 0,08 мг/л для ртути; соответсвующие пределы обнаружения атомно-абсорбционным методом (с использованием того же прибора и источника) 6 и 10 раз больше. Описани приготовление, использование и спектральные характеристики разрядных трубок таллия и ртути и эти трубки сравнены с лампой с полым катодом таллия и с спектральными разрядными лампами таллия и ртути.

Spectrophotometric determination of thallium with 4-(2-pyridylazo)-resorcinol and 4-(2-thiazolylazo)resorcinol: M. HNILIČKOVÁ and L. SOMMER, *Talanta*, 1969, **16**, 83. (Department of Analytical Chemistry, J. E. Purkyně-University, Brno, Czechoslovakia.)

Summary—Thallium(III) gives sensitive reactions with PAR and TAR ($\varepsilon = 2 \times 10^4$ at 520 nm), forming 1:1 complexes at pH $\sim$1–2, and a mixture of 1:1 and 1:2 complexes at higher pH values; hydrolysis sets in above pH $\sim$3. The stability constants are evaluated.

Untersuchungen an Reagenzien für Niob und Tantal—II. Eigenschaften von Brenzkatechinderivaten: G. ACKERMANN and S. KOCH, *Talanta*, 1969, **16**, 95. (Institut für Anorganische und Analytische Chemie der Bergakademie Freiberg, Freiberg (Sachs), DDR.)

Summary—The possible improvement in sensitivity and selectivity of analytically useful reagents forming coloured chelates with niobium and tantalum is discussed on the basis of theoretical considerations. The formation of such chelates with compounds derived from pyrocatechol is affected by the substituents, and as a result of these studies, dibromogallic acid is recommended as a new selective and sensitive reagent for these two metals.

A simple method for thermoanalysis of evolved gases: MIHÁLY BERÉNYI, *Talanta*, 1969, **16**, 101. (Urological Clinic, Medical University of Budapest, Budapest VIII, Üllöi ut 78/b, Hungary.)

Summary—Thermoanalytical processes involving the splitting-off of ammonia, water, halogens, inorganic acids or acid anhydrides can be simply observed by using a specimen-holder in which specific reactions with the decomposition products can be induced. A special glass or quartz double crucible can be used for this purpose; the products arising in the lower part of the crucible can be oxidized selectively with reagents placed in the upper part, or can be bound or transformed into other compounds. This double crucible is also suitable for studying reactions taking place between solid and gaseous substances.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ТАЛЛИЯ 4-(2-ПИРИДИЛАЗО)-РЕЗОРЦИНОМ И 4-(2-ТИАЗОЛИЛАЗО)РЕЗОРЦИНОМ:

M. Hniličková and L. Sommer, *Talanta*, 1969, **16**, 83.

Резюме—Таллий дает чувствительные реакции с ПАР и ТАР ($\varepsilon = 2 \times 10^4$ при 520 ммк), с образованием 1:1 комплексов при pH $\sim$1–2, а смеси 1:1 и 1:2 комплексов при выших значениях pH; гидролиз является выше pH $\sim$3. Определены константы устойчивости.

ИЗУЧЕНИЕ РЕАГЕНТОВ ДЛЯ НИОБИЯ И ТАНТАЛА—II. ХАРАКТЕРИСТИКИ ПРОИЗВОДНЫХ ПИРОКАТЕХИНА:

G. Ackermann and S. Koch, *Talanta*, 1969, **16**, 95.

Резюме—На основе теоретических рассмотрений обсуждена возможность улучшения чувствительности и избирательности реагентов пользуемых в анализе, образующих окрашенные хелаты с ниобием и танталом. Заместители влияют на образование таких хелатов с производными пирокатехина; в результате этих исследований предложена дибромогалловая кислота в качестве нового селективного и чувствительного реагента для этих двух металлов.

НЕСЛОЖНЫЙ МЕТОД ТЕРМЧЕСКОГО АНАЛИЗА ВЫДЕЛЕННЫХ ГАЗОВ:

Mihály Berényi, *Talanta*, 1969, **16**, 101.

Резюме—Несложный метод наблюдения термоаналитических процессов включающих выделение аммиака, воды, галогенов, неорганических кислот и ангидридов кислот пользуется держателем образца в котором можно провести специфические реакции с продуктами разложения. Этой цели отвечает специальный стеклянный или кварцевый двойной тигель; образующиеся в нижней части тигеля продукты могут окисляться селективно с реагентами помещенными в высшей части или связываться или превращаться в другие соединения. Этот двойной тигель также применимый в изучении реакций между твёрдыми и газообразными веществами.

Potentiometric studies of the complexes of chromium(VI), molybdenum(VI) and tungsten(VI) with some Azoxine S dyes: S. S. Goyal and J. P. Tandon, *Talanta*, 1969, **16**, 106. (Chemical Laboratories, University of Rajasthan, Jaipur, India.)

Summary—The equilibrium constants of the complexation reactions of Cr(VI), Mo(VI) and W(VI) with 8-hydroxyquinoline-5-sulphonic acid (OXS), 7-phenylazo-8-hydroxyquinoline-5-sulphonic acid (PAZOXS), 7-(4-sulphophenylazo)-8-hydroxyquinoline-5-sulphonic acid (SPAZOXS) and 7-(4-sulphonaphthylazo)-8-hydroxyquinoline-5-sulphonic acid (SNAZOXS) have been determined by potentiometric pH titration. The values in the case of chromate are different from those for molybdate and tungstate. The order of stabilities is OXS > PAZOXS > SPAZOXS > SNAZOXS.

Spectroscopic method of studying kinetics of consecutive reactions: R. S. Roy, *Talanta*, 1969, **16**, 109. (Science College, Mosul University, Mosul, Iraq.)

Summary—A simple absorbance measurement method is used to measure reaction kinetics of first- and second-order consecutive reactions.

Direct spectrophotometric method for determination of traces of boron in iron, steels and other compounds: A. Tolk, W. A. Tap and W. A. Lingerak, *Talanta*, 1969, **16**, 111. (Reactor Centrum Nederland, Petten, Netherlands.)

Summary—For the determination of traces of boron in iron, low- and high-alloy steels and other materials a direct spectrophotometric method was developed. In this method the absorbance of the boron-Curcumin complex formed in the sample solution is compared with the absorbance of another aliquot of sample solution wherein the boron is rendered inactive with fluoride before the Curcumin is added.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ КОМПЛЕКСОВ ХРОМА(VI), МОЛИБДЕНА(VI) И ВОЛЬФРАМА(VI) С НЕКОТОРЫМИ КРАСИТЕЛЯМИ ТИПА АЗОКСИНА S:

S. S. Goyal and J. P. Tandon, *Talanta*, 1969, **16**, 106.

Резюме—Определены методом потенциометрического титрования pH константы равновесия реакций комплексообразования Cr(VI), Mo(VI) и W(VI) с 8-оксихинолин-5-сульфоной кислотой (OXS), 7-фенилазо-8-оксихинолин-5-сульфоновой кислотой (PAZOXS), 7-(4-сульфофенилазо)-8-оксихинолин-5-сульфоновой кислотой (SPAZOXS) и 7-(4-сульфонафтилазо)-8-оксихинолин-5-сульфоновой кислотой (SИAZOXS). Величины для хромата различны от величин для молибдата и вольфрамата. Порядок устойчивости OXS > PAZOXS > SPAZOXS > SИAZOXS.

ИЗУЧЕНИЕ КИНЕТИКИ КОНСЕКУТИВНЫХ РЕАКЦИЙ СПЕКТРОСКОПИЧЕСКИМ МЕТОДОМ:

R. S. Roy, *Talanta*, 1969, **16**, 109.

Резюме—Предложен несложный метод измерения светопоглощения для определения кинетики консекутивных реакций первого и второго порядка.

ПРЯМОЙ СПЕКТРОФОТОМЕТРИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ СЛЕДОВ БОРА В ЖЕЛЕЗЕ, СТАЛЯХ И ИНИХ ВЕЩЕСТВАХ:

A. Tolk, W. A. Tap and W. A. Lingerak, *Talanta*, 1969, **16**, 111.

Резюме—Разработан прямой спектрофотометрический метод определения следов бора в железе, высоко- и низколегированных сталях и других материалах. В этом методе светопоглощение образованного в растворе пробы комплекса бора с куркумином сравнивается с светопоглощением другой аликвотной части раствора пробы, в которой бор дезактивирован фторидионом прежде добавления куркумина.

Substoichiometric determination of molybdenum in steels by neutron-activation analysis: R. A. Nadkarni and B. C. Haldar, *Talanta*, 1969, **16,** 116. (Inorganic and Nuclear Chemistry Laboratory, Institute of Science, Bombay-1, India.)

Summary—A simple and rapid substoichiometric method for the determination of small amounts of molybdenum in steel by neutron-activation analysis is based on the extraction of molybdenum α-benzoinoximate into chloroform. The sensitivity of the method is 0·2 μg and the relative standard deviation is 1%. Two activated samples can be processed and counted within 30 min.

Thiovioluric acid as an analytical reagent—I. Gravimetric determination of palladium: R. S. Chawla, Yag Dutt and R. P. Singh, *Talanta*, 1969, **16,** 119. (Department of Chemistry, University of Delhi, Delhi-7, India.)

Summary—Thiovioluric acid (HTVA) precipitates palladium(II) as the dark-brown complex $Pd(TVA)_2$ in the pH range 0·3–4·0. It can be used for the gravimetric estimation of palladium(II) alone or in the presence of diverse ions. EDTA, citrate or tartrate can be used to mask Cu(II) and Bi(III). Interference due to Ru(III) has been obviated by the use of citrate as masking agent.

Determination of traces of perchlorate in chlorate solutions: D. L. Fuhrman, *Talanta*, 1969, **16,** 121. (PPG Industries, Inc., Chemical Division, P.O. Box 4026, Corpus Christi, Texas 78408, U.S.A.)

Summary—Perchlorate present in chlorate solutions is determined gravimetrically as tetraphenylphosphonium perchlorate after destruction of chlorate by addition of hydrochloric acid. Interference of Fe(III) and Cr(III) is prevented by complexing with tartaric acid. Replicate analyses of a sodium chlorate solution containing $NaClO_3$, NaCl, $Na_2Cr_2O_7$, and 390 ppm $NaClO_4$ showed 405 ppm $NaClO_4$ (standard deviation 19 ppm, 12 results).

СУБСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МОЛИБДЕНА В СТАЛЯХ МЕТОДОМ НЕЙТРОННОАКИВАЦИОННОГ АНАЛИЗА:

R. A. Nadkarni and B. C. Haldar, *Talanta*, 1969, **16**, 116.

Резюме—Быстрый и несложный субстехиометрический метод определения небольших количеств молибдена в стали методом нейтронно-активационного анализа основывается на извлечении α-бензоиноксимата молибдена хлороформом. Чувствительность метода 0,2 мкг а относительная стандартная ошибка 1%. Можно обработать и считать две активированных пробы в течение 30 мин.

ТИОВИОЛУРОВАЯ КИСЛОТА В КАЧЕСТВЕ АНАЛИТИЧЕСКОГО РЕАГЕНТА—I. ГРАВИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ:

R. S. Chawla, Yag Dutt and R. P. Singh, *Talanta*, 1969, **16**, 119.

Резюме—Тиовиолуровая кислота (HTVA) осаждает палладий(II) в форме тёмнокоричневого комплекса $Pd(TVA)_2$ в области pH 0,3–4,0. Комплексом можно пользоваться для гравиметрического определения палладия(II) самого или в присутствии различных ионов. ЭДТА, цитрат или тартрат маскируют Cu(II) и Bi(III). Влияние Ru(III) избегнуто использованием цитрата в кауестве маскирующего агента.

ОПРЕДЕЛЕНИЕ СЛЕДОВ ПЕРХЛОРАТА В РАСТВОРАХ ХЛОРАТА:

D. L. Fuhrman, *Talanta*, 1969, **16**, 121.

Резюме—Присутствующий в растворах хлората перхлорат определяют гравиметрическии методом в форме перхлората тетрафенилфосфония после разорения хлората добавлением соляной кислоты. Влияние Fe(III) и Cr(III) избегалось комплексированием с винной кислотой. Повторные анализы раствора хлората натрия, содержающего $NaClO_3$, $NaCl$, $Na_2Cr_2O_7$ и 390 мг/л $NaClO_4$ дали 405 мг/л $NaClO_4$ (стандартная ошибка 19 мг/л, 12 результатов).

Extraction of vanadium into isobutyl methyl ketone: Hans J. Crump-Wiesner and William C. Purdy, *Talanta*, 1969, **16**, 124. (Department of Chemistry, University of Maryland, College Park, Md. 20742, U.S.A.)

Summary—Because of its advantages in atomic-absorption spectroscopy, isobutyl methyl ketone was chosen as organic solvent for an extraction study on vanadium. Of eight chelating agents which were evaluated for completeness of extraction, ease of use, working pH range, and freedom from interference, cupferron was judged best.

The diffusion of fluoride with hexamethyldisiloxane: R. J. Hall, *Talanta*, 1969, **16**, 129. (Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service, Government Buildings, Kenton Bar, Newcastle upon Tyne, U.K.)

Summary—Several acids, when saturated with hexamethyldisiloxane, induce the diffusion of fluoride at ambient temperatures. Observations with plant and soil suspensions which contain a mixture of complex fluorides including organically combined fluorine show that siliconed acids may not diffuse as much fluoride as does perchloric acid containing silver sulphate at 60°

Redox-complexometric determination of iron and cobalt and its application to the analysis of multi-component alloys: Jan Horáček and R. Přibil, *Talanta*, 1969, **16**, 133. (Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Prague 1, Jilská 16, Czechoslovakia.)

Summary—A redox-complexometric determination of iron and cobalt is based on potentiometric titration of iron with EDTA, followed by that of cobalt with iron(III) chloride after addition of 1,10-phenanthroline. This method simplifies the complexometric analysis of more complicated materials.

ИЗВЛЕЧЕНИЕ ВАНАДИЯ ИЗОБУТИЛМЕТИЛКЕТОНОМ:

Hans J. Crump-Wiesner and William C. Purdy, *Talanta*, 1969, **16**, 124.

Резюме—Изобутилметилкетон использован в качестве органического растворителя для извлечения ванадия на основе его преимуществ для атомно-абосрбционной спектроскопии. Найлучшим комплексообразующим агентом выбран купферрон из восемь агентов на основе полноты извлечения, удобного применения, адэкватной области pH и отсутствия мешающих эффектов.

ДИФФУЗИЯ ФТОРИДА ГЕКСАМЕТИЛДИСИЛОКСАНОМ:

R. J. Hall, *Talanta*, 1969, **16**, 129.

Резюме—Ряд насыщенных гексаметилдисилоксаном кислот индуцируют диффузию фторида при комнатной температуре. Опыты с суспензиями растений и почвы содержащих смеси сложных фторидов включая фтор в органических соединениях показуют что силиконированные кислоты дифундируют менее фторида чем хлорная кислота, сопержащая сульфат серебра при 60°.

ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНОЕ КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА И КОБАЛЬТА И ПРИМЕНЕНИЕ ЭТОГО МЕТОДА В АНАЛИЗЕ МНОГОКОМПОНЕНТНЫХ СПЛАВОВ:

Jan Horáček and R. Přibil, *Talanta*, 1969, **16**, 133.

Резюме—Описанный метод окислительно-восстановительного комплексонометрического определения железа и кобальта основывается на потенциометрическом титровании железа с ЭДТА, с последующим титрованием кобальта с хлоридом железа(III) после добавления 1,10-фенантролина. Описанный метод позволяет упрощение комплексонометрического анализа более сложных материалов.

Simultaneous determination of sulphate and sulphonate type anionic surfactants: G. W. Ströhl and D. Kurzak✠, *Talanta*, 1969, **16**, 135. (Research Department, Imperial Chemical Industries, Modderfontein, Transvaal.)

Summary—A method is described for the simultaneous determination of organic sulphates and sulphonates, based on hydrolysis of the sulphates in 3*M* hydrochloric acid. The total concentration of anionic surfactants is determined by the Methylene Blue method, then the sulphates are hydrolysed by boiling with 3*M* hydrochloric acid for 2 hr, and the sulphonates are determined by the Methylene Blue method. The concentration of the alkyl sulphates is obtained by difference. The large amounts of sodium chloride introduced during the procedure do not affect the Methylene Blue method.

Vanadox—a new reagent for the photometric determination of vanadium: N. S. Frumina, I. S. Mustafin, M. L. Nikurashina and M. K. Vechera, *Talanta*, 1969, **16**, 138. (Department of Analytical Chemistry, N. G. Chernyshevsky University, Saratov, U.S.S.R.)

Summary—A new reagent, 2,2′-dicarboxydiphenylamine, vanadox, is proposed for the photometric determination of vanadium in steels, high temperature alloys and ferrotitanium ores. In strongly acidic medium the reagent is selective for vanadium(V) and only cerium(IV) interferes.

***p*-nitroaniline as a colorimetric reagent for sulphur dioxide:** Per Olof Bethge and Margareta Carlson, *Talanta*, 1969, **16**, 144. (Swedish Forest Products Research Laboratory and Central Laboratory of the Swedish Cellulose Industry, Stockholm 11728, Sweden.)

Summary—The merits of the nitroanilines as an alternative to *p*-rosaniline and fuchsine in the colorimetric determination of sulphur dioxide and sulphites have been investigated. *p*-Nitroaniline was found to be a stable, well-defined reagent, with which sulphur dioxide can be determined to a high level of precision, the sensitivity being of the same order of magnitude as for *p*-rosaniline.

Electrogravimetric trace analysis on a piezoelectric detector: James P. Mieure and Jerry L. Jones, *Talanta*, 1969, **16**, 149. (Department of Chemistry, Texas A & M University, College Station, Texas 77840, U.S.A.)

Summary—A novel and rapid electroanalytical method for the determination of cadmium at micromolar concentrations is described. The method utilizes the piezoelectric effect to follow small mass changes which result from electrodeposition.

ОДНОВРЕМЕННОЕ ОПРЕДЕЛЕНИЕ АНИОННЫХ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ ТИПА СУЛЬФАТА И СУЛЬФОНАТА:

G. W. Ströhl and D. Kurzak†, *Talanta*, 1969, **16**, 135.

Резюме—Описан метод одновременного определения органических сульфатов и сульфонатов, основывающийся на гидролизе сульфатов в $3M$ соляной кислоте. Общую концентрацию анионных поверхностно-активных веществ определяют методом метиленового голубого, а затем сульфаты гидролизируют кипячением с $3M$ соляной кислотой в течение 2 ч. и сульфонаты определяют методом метиленового голубого. Концентрация алкилсульфатов получается из разницы. Большие количества хлорида натрия внесенные в процедуре не влияют на метод метиленового голубого.

ВАНАДОКС—НОВЫЙ РЕАГЕНТ ДЛЯ ФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ВАНАДИЯ:

N. S. Frumina, I. S. Mustafin, M. L. Nikurashina and M. K. Vechera, *Talanta*, 1969, **16**, 138.

Резюме—Предложен новый реагент, 2,2'-дикарбоксидифениламин, ванадокс, для фотометрического определения ванадия в сталях, высокотемпературных сплавах и ферротитановых рудах. В сильнокислых средах реагент является избирательным для ванадия(V) и только церий(IV) мешает определению.

П-НИТРАНИЛИН КАК КОЛОРИМЕТРИЧЕСКИЙ РЕАГЕНТ ДЛЯ ДВУОКИСИ СЕРЫ:

Per Olof Bethge and Margareta Carlson, *Talanta*, 1969, **16**, 144.

Резюме—Изучены преимущества нитранилинов в сравнении с п-розанилином и фуксином для колориметрического определения двуокиси серы и сульфитиона. п-Нитранилин оказался устойчивым, хорошо определенным реагентом которым можно определять двуокись серы высокой точностью, а чувствительность равна чувствительности п-розанилина.

ЭЛЕКТРОГРАВИМЕТРИЧЕСКИЙ СЛЕДОВЫЙ АНАЛИЗ С ИСПОЛЬЗОВАНИЕМ ПЬЕЗОЭЛЕКТРИЧЕСКОГО ДЕТЕКТОРА:

James P. Mieure and Jerry L. Jones, *Talanta*, 1969, **16**, 149.

Резюме—Описан новый и быстрый электроаналитический метод определения микромолярных концентраций кадмия. Метод пользуется пьезоэлектрическим эффектом для определения небольших перемен массы, происходящих из электродепозиции.

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