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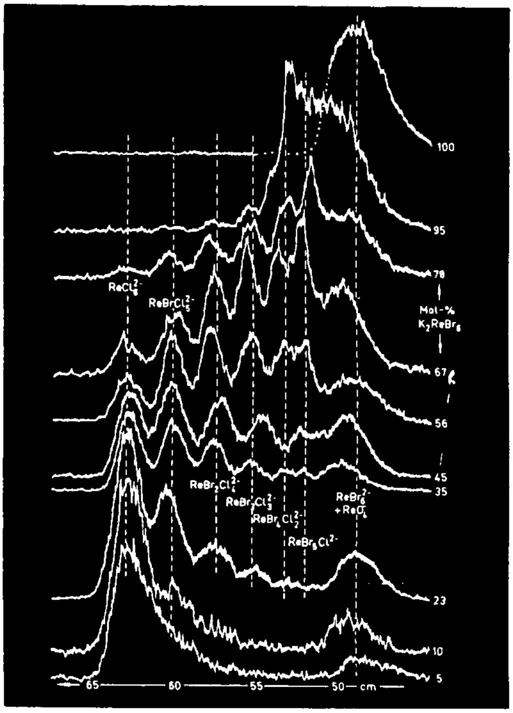

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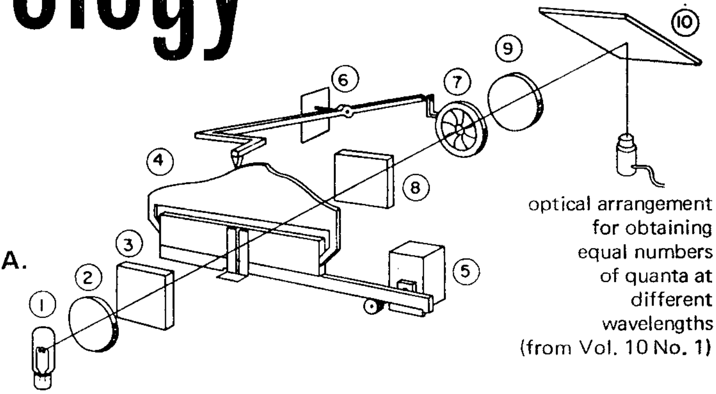

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E. BEN-HUR and I. ROSENTHAL: Photosensitized splitting of pyrimidine dimers

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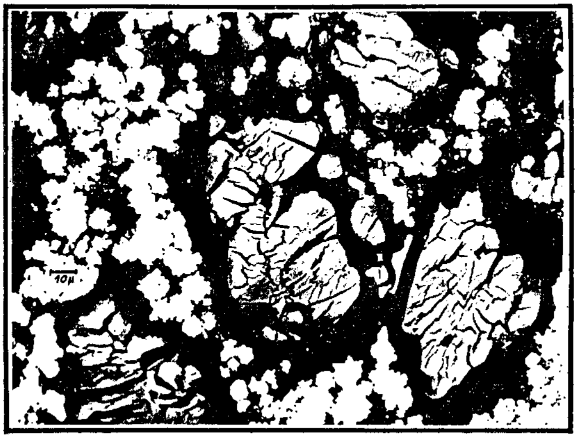

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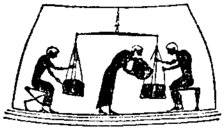

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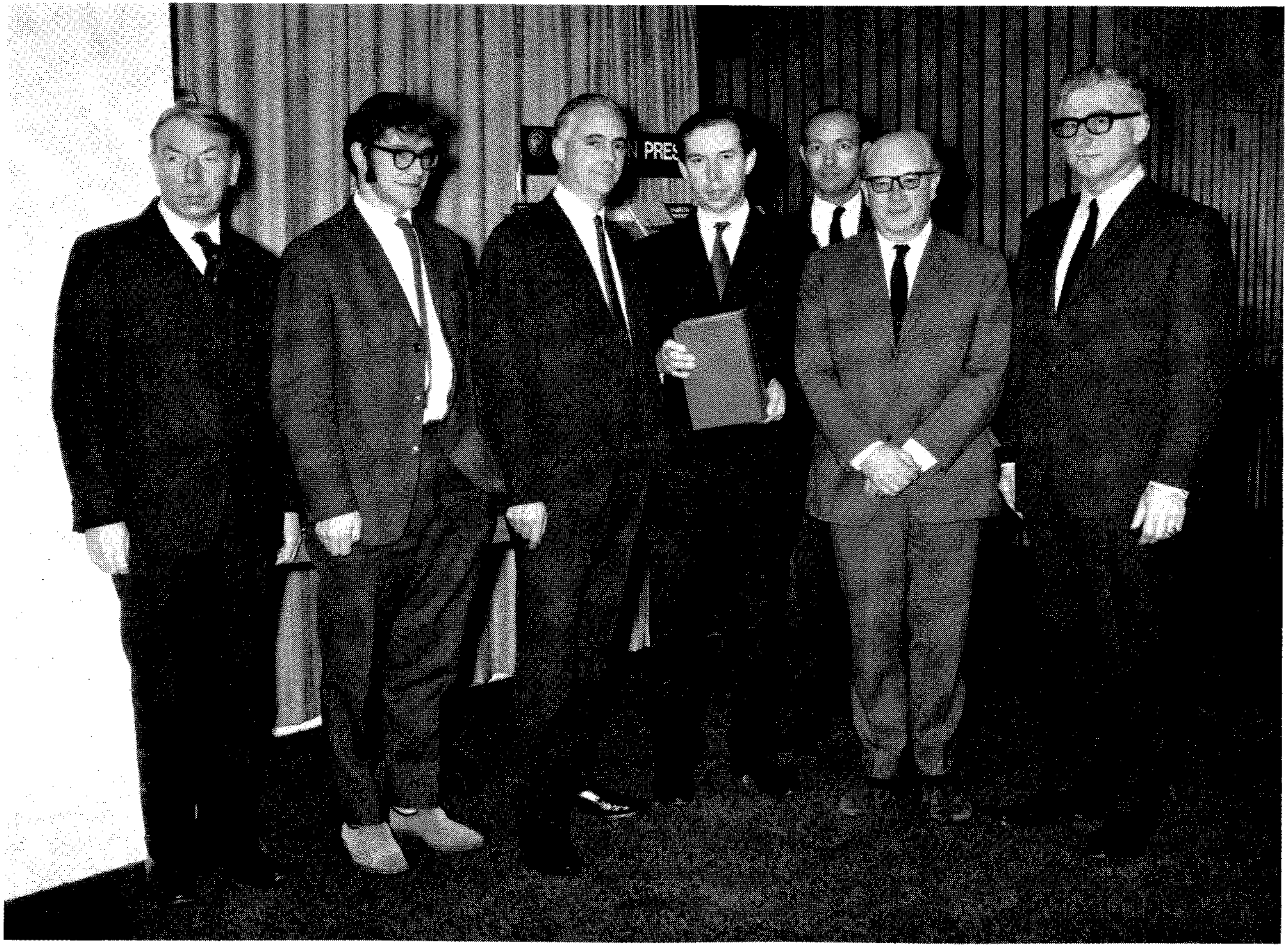
DR. S. J. LYLE (right) thanks Prof. R. BELCHER, Chairman of the Editorial Board of *Talanta*, after receiving a specially bound 1969 volume of the journal. His paper with Mr. V. C. NAIR "Reversed-phase Partition Chromatographic Separations with 2-Ethylhexyl Dihydrogen Phosphate and Di-2-Ethylhexyl Hydrogen Phosphate" (*Talanta*, 1969, **16,** 813) was adjudged the best-written, stylistically, of the year.



The presentation was made at Pergamon Press in Oxford on 11 November 1970 during the course of a meeting of the Editorial Board of *Talanta* (from left to right): Dr. J. R. Majer, Dr. D. Betteridge, Dr. M. Williams, Dr. Lyle, Mr. G. F. Richards, Prof. Belcher, Dr. F. Kalinski.

Talanta, 1971, Vol. 18, pp. 1 to 19. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

RECENT DEVELOPMENTS IN SUBSTOICHIOMETRIC ANALYSIS

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(*Received* 11 *March* 1970. *Accepted* 17 *April* 1970)

Summary—A review of recent developments in substoichiometric analysis is presented.

IN 1968 the monograph *Substoichiometry in Radiochemical Analysis*[1] surveyed the theory and application of the method in neutron-activation analysis, isotope-dilution analysis and radioactive material analysis. Since that time more than 60 further publications have dealt with this method. Such a great interest in substoichiometry is due to its high selectivity and simplicity. Furthermore, the necessity of determining the chemical yield is eliminated. This is of special importance in isotope-dilution analysis because it increases considerably the sensitivity of the determination. Substoichiometric analysis may be easily automated, which permits the rapid analysis of a large number of samples with good accuracy and reproducibility.

In the monograph were described procedures for the substoichiometric determination of some 23 elements: antimony, arsenic, bismuth, cadmium, chlorine, cobalt, copper, fluorine, gallium, gold, indium, iodine, iron, lead, manganese, mercury, molybdenum, rare earths, rhenium, scandium, silver, yttrium and zinc. During the last three years several of these procedures have been improved and procedures for determining beryllium, carbonate, caesium, hafnium, phosphorus, palladium, platinum, sulphur, thallium, tin, tungsten, uranium and zirconium have been developed.

NEUTRON-ACTIVATION ANALYSIS

The quantity of an element to be determined (y) can be calculated from the activities isolated from the test sample (a) and from a simultaneously irradiated standard sample (a_s), according to the equation

$$y = y_s \frac{a}{a_s}. \tag{1}$$

where y_s is the quantity of the element in the standard sample (Ref. 1, p. 6).

Equation (1) is valid if the following two conditions are fulfilled:

(*i*) after irradiation and dissolution, to both the test and standard samples is added an exactly equal amount (by weight) of non-active isotopic carrier;

(*ii*) for measurement of the activity, an exactly equal amount (by weight) of the element to be determined is isolated from the solutions of the test and standard samples.

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* For reprints of this paper, see Publisher's announcement near end of issue.

† Present address: Chemistry Department A, Technical University of Denmark, Building 207, Lyngby, Denmark.

There are no difficulties in fulfilling the first condition. The second requirement can be fulfilled by substoichiometric isolation *i.e.*, by the addition to the test and standard samples of an exactly equal amount of reagent which is smaller than that corresponding stoichiometrically to the quantity of carrier present. The reagent used must be consumed quantitatively (or at least to the same extent) in the reaction with the element to be determined and the compound formed must be easily separable from the excess of unreacted element.

An interesting substoichiometric technique proposed by Suzuki and Kudo,[2] consists of dividing the irradiated sample solution into two equal portions to one of which a known amount of carrier (x) is added. When from both portions the same amount of element to be determined is substoichiometrically isolated (activities a_1 and a_2), the amount of the element (y) can be calculated by means of the equation

$$\left(y = x\frac{a_2}{a_1 - a_2}\right) \tag{2}$$

An analogous equation has also been proposed by Cappadona.[3]

This modified substoichiometric technique has been applied to the determination of copper in aluminium and tin (12–460 ppm)[4] and of zinc in zinc-doped gallium arsenide (about 100 ppm).[5] Miller[6] modified this procedure for the determination of copper (0·2 ppm) in zinc: from the irradiated test-sample solution a substoichiometric amount of copper negligible in comparison with its total amount (y) was isolated. Increasing known amounts of non-active copper (x) were then added to the test sample solution. After each addition the same substoichiometric amount of copper was isolated and its activity measured (a). The intercept of the plot of x *vs.* $1/a$ gives the value of y.

The method of Suzuki and Kudo has the following advantages: the use of a standard sample is not necessary; secondary nuclear reactions and self-shielding do not interfere in the determination. The sensitivity is, however, limited because the reagent blank must be taken into account.

Solvent extraction of metal chelates

The use of organic reagents (HA) forming extractable chelates (MA_N) still remains the most important application of substoichiometry (see *Procedures for Substoichiometric Determination of Elements*). The reason is that the conditions for substoichiometric isolation can be easily calculated from a knowledge of the extraction constant (K) according to

$$\text{pH} \geqslant -0{\cdot}01 \log c_{\text{HA}} - 1/N \log K + 1/N \log \beta_s[\text{B}]^s \tag{3}$$

where c_{HA} is the total concentration of the reagent HA, β_s is the stability constant of the complex MB_s, and [B] is the equilibrium concentration of the anion of any masking agent HB.

Equation (3) (Ref. 1, p. 22) is valid only when the dissociation of the organic reagent in the aqueous phase can be neglected, *i.e.*, when

$$\text{pH} \leqslant \text{p}K_{\text{HA}} + \log p_{\text{HA}} \tag{4}$$

where K_{HA} is the dissociation constant of the reagent HA and p_{HA} is the distribution coefficient of the reagent HA.

The selectivity of the separation can be easily calculated from the values of K for other metals. Those metals having higher extraction constants interfere and must be removed or masked by a suitable agent.

Recently, a new technique called *multielement substoichiometric separation*[7,8] has been proposed. This technique is based on the substoichiometric extraction of metal M (charge $N+$, extraction constant K) under such conditions that metal M′ (charge $N'+$, extraction constant K') is quantitatively extracted (more than 99%) whereas interfering metal M″ (charge $N''+$, extraction constant K'') is left in the aqueous phase. The conditions for such a separation are given by

$$(10^{-2}K')^{1/N'} \gg K^{1/N} \gg (10^{2}K'')^{1/N''}. \tag{5}$$

In this case the content of two metals M′ and M can be determined providing that the activity of all extracted species can be distinguished, *e.g.*, by gamma spectrometry. Equation (5) has been verified for the determination of silver ($\log K' = 7{\cdot}2$) and copper ($\log K = 10{\cdot}5$) in cobalt ($\log K'' = 1{\cdot}5$) with dithizone in carbon tetrachloride as the chelating agent.[8] Similarly, the content of gold, mercury and copper in tin and organic reagents has been determined.[9]

Another important improvement in substoichiometric separation has been proposed by Obrusník and Adámek[10] and independently by Braun and Ladányi.[11,12] This technique, called *replacement substoichiometry*, is based on the extraction of metal M^{N+} with an excess of reagent, removal of the excess of reagent and replacement of the metal to be determined from the organic phase by a substoichiometric amount of another metal $M^{N'+}$:

$$N'(\mathrm{MA}_N)_{\mathrm{org}} + N\,\mathrm{M}^{N'+} = N(\mathrm{M'A}_{N'})_{\mathrm{org}} + N'\,\mathrm{M}^{N+}. \tag{6}$$

Metal M can be quantitatively replaced (more than 99·9%) from the organic phase by a substoichiometric amount of metal M′ if the following equation applies:

$$\mathrm{N}\log K' - N'\log K \gg 3N. \tag{7}$$

There is no difficulty in finding a suitable replacement metal from its known extraction constant; furthermore, the selectivity of the determination does not depend on the nature of the replacement metal.

The ratio of the concentrations of two metals M and M″ replaced from the chelates MA_N and $\mathrm{M''A}_{N''}$ by a metal M′ can be calculated from the following relationship*

$$\frac{[\mathrm{M}^{N+}]}{[\mathrm{M}^{N''+}]} = \frac{K''}{K}\left(\frac{[\mathrm{H}^+]}{[\mathrm{HA}]_{\mathrm{org}}}\right)^{N-N''}\frac{[\mathrm{MA}_N]_{\mathrm{org}}}{[\mathrm{M''A}_{N''}]_{\mathrm{org}}}. \tag{8}$$

In substoichiometric separation, the selectivity of the separation of two metals is greater than in separation with an excess of reagent. Consider a simple case where the organic phase contains equal concentrations of chelates MA_N and $\mathrm{M''A}_{N''}$, and suppose $N = N''$. For quantitative separation of metal M from metal M″ (*i.e.*, $[\mathrm{M}^{N+}]/[\mathrm{M}^{N''+}] > 100$) by use of an amount of replacement metal M′ corresponding stoichiometrically to half the quantity of M present, the value K''/K has to be greater than 200 because $[\mathrm{MA}_N]_{\mathrm{org}}/[\mathrm{M''A}_{N''}]_{\mathrm{org}}$ is then 0·5. Thus, metals with sufficiently higher extraction constants do not interfere; interference can be expected from metals

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* There is an error in equation (21) of the paper cited in ref. 10.

having about the same or a smaller extraction constant than that of the metal to be determined. This technique is of special importance for the determination of metals with low values of K; however, equations (3) and (4) must be fulfilled. Replacement substoichiometry has been applied to the determination of thallium ($\log K = -3{\cdot}3$) in biological materials[13] and of indium ($\log K = 4{\cdot}8$) in granite[14] with dithizone as reagent.

Solvent extraction of ion-association compounds

The theory of the extraction of an anion Z^- with a heavy organic cation T^+ has been discussed by Alimarin and Perezhogin.[15] For substoichiometric isolation the following condition must be fulfilled:

$$\log K > 2 - \log (c_Z - c_T) \qquad (9)$$

where c_Z is the concentration of the carrier, and c_T is the concentration of the organic cation (Ref. 1, p. 31).

The upper limit of concentration of the carrier is defined by the solubility of the extracted species in the solvent used, and the lower limit is given by the value of K:[15]

$$\log c_Z > 2{\cdot}3 - \log K. \qquad (10)$$

For the extraction of rhenium (as ReO_4^-) by a substoichiometric amount of tetraphenylarsonium chloride, 1,2-dichlorobenzene ($10^{-2}\,M > c_Z > 5 \times 10^{-5}\,M$) is a more suitable solvent than chloroform ($2 \times 10^{-3}\,M > c_Z > 5 \times 10^{-4}\,M$).

Also, the selectivity of a substoichiometric separation is here much higher than in cases when an excess of reagent is being used. The threshold concentration of an interfering anion c_Z' can be calculated from[15]

$$c_{Z'} < 0{\cdot}005 \left(\frac{K}{K'} + 1\right) c_Z \qquad (11)$$

where K' denotes the extraction constant of TZ'.

Alimarin and Perezhogin[15] have verified these conditions experimentally for the substoichiometric determination of various elements. Thus, iodide was extracted by a substoichiometric amount of tetraphenylarsonium chloride ($\log K = 5$) into chloroform, while bromide (up to $0{\cdot}01M$) and chloride (up to $0{\cdot}15M$) did not interfere. Anionic complexes of tantalum, bismuth, molybdenum(V) and tungsten(V) with halides, cyanide, and thiocyanate were found to be suitable for substoichiometric determination with tetraphenylarsonium chloride. Also, thallium(I), caesium, rubidium, and partially potassium, can be substoichiometrically extracted as tetraphenylborates.[15]

Other separation techniques

It is a little surprising that complexation with a substoichiometric amount of ethylenediaminetetra-acetic acid (or other strong complexing agent) followed by isolation of the unreacted metal by ion-exchange has not found a wider application.[16] Removal of the unreacted metal by extraction with a weaker chelating agent[17] (see later) also seems to be a promising technique.

The use of precipitating agents is not very advantageous, because various radioisotopes can be easily co-precipitated. Nevertheless, precipitation with a substoichiometric amount of reagent brings two advantages: the necessity of determining the chemical yield is avoided, and the selectivity of the separation is higher than when an excess of reagent is used.[18,19].

For the determination of traces of copper[6] the spontaneous deposition of microquantities of Cu^{2+} on a platinum wire cathode has been used. Within definite ranges of pH and concentration, the quantity of copper deposited depends only on the surface area and, for the same surface, it is constant, independent of the copper and other metal concentrations and the volume of the solution.

ISOTOPE-DILUTION ANALYSIS

The quantity of an element to be determined (y) can be calculated from the activities isolated from a standard sample (a_s) and from the mixture of the test and standard samples (a) according to the equation

$$y = y_s \left(\frac{a_s}{a} - 1\right) \tag{12}$$

where y_s is the amount of radioisotope added to the test sample.

For successful determination of the test element it is necessary to fulfil the following two conditions:

(*i*) complete isotopic exchange in the mixture of test and standard samples must be established;

(*ii*) for measurement of the activities a_s and a, an exactly equal quantity of the element in question must be isolated.

Fulfilment of the second condition is much more difficult than in the case of neutron-activation analysis because a much smaller (<1 μg) quantity of the element to be determined has to be isolated with sufficient reproducibility.

Solvent extraction of metal chelates

Chelating agents forming extractable chelates can be widely used for the substoichiometric determination of very small amounts of various metals providing that the extraction constants are sufficiently high. The pH for such a determination can also be calculated according to equations (3) and (4). Because the substoichiometric concentration of reagent is much smaller than in the case of neutron-activation analysis, the working range of pH is narrower. The selectivity of the separation follows the same pattern as in the case of neutron-activation analysis: metals with higher extraction constants again interfere and must be masked or removed. If replacement substoichiometry (see above) is used, interference from these metals can be avoided; however, interference from metals with lower extraction constants must be considered.

Formation of water-soluble complexes

The theory of the formation of water-soluble complexes (MY) with a substoichiometric amount of strong complexing agent (H_nY), followed by removal of the excess of unreacted metals by ion-exchange has been discussed earlier (Ref. 1, p. 35, 48).

Recently, an interesting method has been proposed by Briscoe and Dodson.[17] For removing the excess of unreacted metal, extraction with an excess of weaker chelating agent (HA) was proposed.

The conditions of a such isolation (*i.e.*, pH and concentration of the reagent $[HA]_{org}$) can be ascertained from the equation

$$\frac{K}{\beta_1} = \frac{[H^+]^N \, 10^{-3} \, [Y^{n-}]}{[HA]_{org}^N} \tag{13}$$

where K is the extraction constant of the chelate MA_N, β_1 is the stability constant of the complex MY, and $[Y^{n-}]$ is the equilibrium concentration of the anion of the complexing agent H_nY at a given pH.

The value of $[HA]_{org}$, calculated from equation (13), represents the maximum concentration of the reagent HA which may be used to remove the unreacted metal from a solution without breaking down more than 0·1 % of the complex MY.

The equation above has been verified experimentally for the substoichiometric determination of rare earths.[17] Rare earths were complexed with a substoichiometric amount of ethylenediaminetetra-acetic acid and the excess of unreacted metal was removed by extraction with thenoyltrifluoracetone.

The use of extraction for removing the excess of unreacted metal has in comparison with ion-exchange separation the following advantage: the sample may contain higher concentrations of electrolytes which would interfere in separation by ion exchange.

Other separation techniques

The precipitation of sulphates and carbonates with a substoichiometric amount of barium ions has been used for the determination of these anions.[20] An analogous technique has been applied to the determination of iodide,[21,22] silver,[21] and iron.[21] Precipitation was carried out on filter paper and the excess of the unreacted element washed out by a suitable solvent, using ring-oven technique[21] or electrophoresis.[22] The quantity of the element to be determined (y) was calculated from the modified equation (12):

$$y = y_s \left(\frac{a_s - a_s^0}{a - a^0} - 1 \right) \tag{14}$$

where a_s^0 and a^0 are the activities of the standard sample and of the mixture of the standard and test samples in the absence of precipitating agent, respectively.

Landgrebe *et al.*[23] used a controlled potential procedure with two identical electrolysis cells connected in series for the determination of traces of cadmium. Under prescribed conditions the same amount of the element is deposited in each cell. The procedure involves the addition of a known amount (x) of the element to be determined to the control cell and an unknown amount (y) to the sample cell. An equal amount (y_s) of a radioisotope of that element (activity a_t) is added to each cell. Because the same amount of the element is deposited in each cell, the difference ($y - x$) can be determined by measuring the radioactivity left in the control (a') and sample (a'') cells after a finite electrolysis time, according to the relationship

$$(y - x) = (x + y_s) \frac{a'' - a'}{a_t - a''} \, . \tag{15}$$

If a carrier-free radioisotope is used ($y_s \ll x$), the equation is simplified.

PROCEDURES FOR SUBSTOICHIOMETRIC DETERMINATION OF ELEMENTS

In this section the principles for substoichiometric determination of different elements by neutron-activation analysis and isotope-dilution analysis are briefly summarized. Where appropriate, detailed procedures are also included.

Beryllium

Isotope-dilution analysis. Beryllium can be determined by using a substoichiometric amount of actylacetone.[24] The complex formed is extracted from borate buffer (pH ~ 9) into benzene. Ethylenediaminetetra-acetic acid may be used as a suitable masking agent. As little as 1 ppm of beryllium can be determined.

Carbonate

Isotope-dilution analysis. Carbonate (10–400 ppm) can be determined by using a substoichiometric amount of barium hydroxide as precipitating agent.[20] The method is not very selective because anions forming stable complexes or sparingly soluble precipitates with barium interfere.

Cadmium

Neutron-activation analysis. Cadmium can be extracted from 1*M* sodium hydroxide with a substoichiometric amount of dithizone.[25] The selectivity of the determination can be increased *via* a preliminary extraction using cyanide as masking agent.

Determination of cadmium in metallic aluminium and zinc.[25] Simultaneously irradiate the samples (0·1–0·7 g) together with a cadmium standard in a flux of 4 × 10^{11} neutrons.mm^{-2}.sec^{-1} for 130 hr. Dissolve the irradiated samples in a small volume of hydrochloric acid in the presence of 400 μg of cadmium carrier and evaporate the resulting solution to dryness. Add 5 ml of 0·1*M* sodium tartrate, 15 ml of 10*M* sodium hydroxide, 1 ml of 20% hydroxylamine solution and 1 ml of 0·1*M* potassium cyanide. Shake with an excess of dithizone solution in carbon tetrachloride for 2 min; repeat the extraction. Wash the organic extracts with 2*M* sodium hydroxide, then strip the cadmium with 10 ml of 0·1*M* nitric acid. Adjust the aqueous phase to be 1*M* in hydroxide concentration with sodium hydroxide solution containing tartrate and hydroxylamine. Extract with 1 ml of $10^{-3}M$ dithizone solution in carbon tetrachloride for 1–2 min. By measurement of the activity of the extracts from the test and standard samples (treated in exactly the same way) the contents of cadmium in aluminium (0·5–4 ppm) and in zinc (0·3–14 ppm) have been determined.

An analogous method has been used for determination of cadmium in gallium arsenide.[26]

Isotope-dilution analysis. Extraction with a substoichiometric amount of dithizone (Ref. 1, p. 84) has been applied to the determination of cadmium in beef liver (0·16 ppm), beef kidney (1·56 ppm) and other biological materials.[27,28]

Caesium

Fission-product analysis. Caesium can be extracted by a substoichiometric amount of lithium dipicrylaminate in nitrobenzene.[29] The dilithium salt of ethylenediaminetetra-acetic acid is used as masking agent. This procedure seems much simpler than precipitation with a substoichiometric amount of sodium tetraphenylborate in dilute acetic acid.[18]

Determination of ^{137}Cs in fission products.[29] To a solution of fission products or nuclear fuel materials in 0·2*M* nitric acid, add dilithium ethylenediaminetetra-acetate and caesium carrier in such amounts that their concentrations, after dilution to a constant volume, are 0·05*M* and 0·0012*M* respectively. Neutralize the resulting solution with 1*M* lithium hydroxide, using *o*-Cresol Red as indicator. Extract by shaking with an equal volume of 6 × $10^{-4}M$ lithium dipicrylaminate in nitrobenzene for 30 sec. Simultaneously, treat a standard solution containing a known absolute activity of ^{137}Cs in exactly the same way. Determine the ratio of activities of an equal volume of extract from the test and standard samples.

This method can also be used for the preparation of radiochemically pure ^{137}Cs.

Cobalt

Isotope-dilution analysis. Cobalt can be complexed by a substoichiometric amount of 2-nitroso-1-naphthol ($10^{-6}M$ solution in 10% dimethylformamide solution).[30] The excess of unreacted cobalt is removed with acetone–isopentanol mixture (4:1) by ascending paper chromatography. Iron(III), copper and nickel do not interfere.

Copper

Neutron-activation analysis. Extraction with a substoichiometric amount of dithizone (Ref. 1, p. 87) has been applied to the determination of copper in gallium arsenide (0·2–0·02 ppm).[31] A substoichiometric amount of sodium diethyldithiocarbamate (Ref. 1, p. 88) has been employed for the determination of copper in iron (0·8–2·6 ppm) and gallium (3·6 ppm).[32] Multielement substoichiometric separation has been applied to the analysis of cobalt,[8] tin and biological materials.[9]

Determination of copper in tin and biological materials.[9] Simultaneously irradiate samples of metallic tin in aluminium foil and samples of biological materials in quartz ampoules together with a copper standard in a flux of 10^{11} neutrons mm^{-2} sec^{-1} for 1–20 hr. Dissolve the samples in a mixture of sulphuric and perchloric acids in the presence of 1 mg of copper and 0·01 mg of gold and mercury as carriers. Dilute with water to obtain a final concentration of $1M$ sulphuric acid and $0{\cdot}1M$ perchloric acid. Extract for 1–2 min with 10 ml of $0{\cdot}002M$ zinc diethyldithiocarbamate in chloroform. The content of copper in tin (38 ppm), dried blood (4·6 ppm) and flour (1·4 ppm) as well as of gold and mercury quantitatively extracted have been determined from the corresponding gamma peaks of the extracts from test and standard samples.

Gold

Neutron-activation analysis. Gold can be extracted from dilute hydrochloric acid solution by a substoichiometric amount of triphenylguanidine (TPG) in 1,2-dichlorethane.[33] This method is more selective than that proposed previously,[34] based on extraction of the complex $TPG[Au(SCN)_4]$ into chloroform. A substoichiometric amount of Rhodamine B has been suggested for the determination of gold in commercial- (2·4 ppm) and in 99·99% pure copper (0·04 ppm).[35] Extraction of gold from $1M$ hydrochloric acid by ethyl acetate followed by its re-extraction with a substoichiometric amount of zinc diethyldithiocarbamate (the complex formed is quantitatively transferred into the aqueous phase) has been utilized for determination of this element in iron.[36,37]

Determination of gold in rocks.[33] Dissolve 0·1–0·5 g of irradiated rock sample in *aqua regia* in the presence of 2·0 mg of gold as a carrier. Evaporate the solution to dryness and heat for some minutes to remove iodine. Dissolve the residue in 3–4 ml of *aqua regia* and heat again to decrease the volume to 1–2 ml. Add 2–3 ml of hydrochloric acid and repeat the heating procedure. Filter and make up to 10 ml with water, then heat to boiling for about 3 min to convert antimony into its non-extractable hydroxide. After cooling, add 2·0 ml of $2{\cdot}5 \times 10^{-3}M$ triphenylguanidine in 1,2-dichlorethane and shake the mixture for 3 min. Transfer the organic phase to a centrifuge tube, add 1·5 ml of $0{\cdot}5M$ hydrochloric acid and shake for 3 min. After centrifugation, measure the activity of 1 ml of extract from the test and standard samples (treated in exactly the same way), using a 100-channel analyser.

By this method gold (0·1–100 ppm) has been determined in 25 samples of various rocks.

Isotope-dilution analysis. Gold can be extracted from $0{\cdot}5N$ sulphuric acid by a substoichiometric amount of zinc diethyldithiocarbamate in chloroform.[38] To increase the selectivity of the method a preliminary extraction of gold by diethyl ether should be carried out.

Determination of gold in ores and silicon.[38] To the test sample in a Teflon beaker add a known amount of labelled gold (y_S). Dissolve the sample in a mixture of nitric acid and hydrochloric acid with gradual addition of hydrofluoric acid. Evaporate to 0·5 ml and repeat the evaporation twice, each time after the addition of 5 ml of hydrochloric acid. Dilute the resulting solution with water to give finally 10 ml of 2*M* hydrochloric acid solution and shake with 20 ml of diethyl ether for 3 min. Scrub the ether phase with 5 ml of 2*M* hydrochloric acid and transfer it to a beaker; then add 0·5 ml of 3*M* hydrochloric acid and heat the solution at 50° on a water-bath to remove the ether. Transfer the resulting solution to a separatory funnel and dilute to 20 ml with 0·5*N* sulphuric acid. If necessary, add ethylenediaminetetra-acetic acid and remove palladium with dimethylglyoxime. Finally, add 1 ml of 1 % ascorbic acid solution and extract the gold with a substoichiometric amount of zinc diethyldithiocarbamate in chloroform for 5 min. From the activity of the extracts from the test sample and from a standard sample, treated in exactly the same way, the amount of gold is calculated. By this procedure down to 0·1 ppm of gold has been determined.

Hafnium

Neutron-activation analysis. Hafnium is precipitated as Ba_2HfF_8 in 1*M* hydrofluoric acid solution with a substoichiometric amount of barium ions.[18] Because the method is not very selective many preliminary separation steps must be carried out. It has been used for the determination of hafnium (0·01 ppm) in aluminium.

Indium

Neutron-activation analysis. Indium is extracted from alkaline cyanide solution with an excess of dithizone. After the extract has been washed with borate buffer solution, indium is replaced from indium dithizonate by a substoichiometric amount of aqueous mercury(II) solution.[14]

Determination of indium in granite.[14] Seal the granite powder (2–3 g) and an indium standard in glass ampoules and irradiate simultaneously with a flux of $7{\cdot}5 \times 10^8$ neutrons . mm^{-2} . sec^{-1} for 200 hr. To the irradiated samples add 300 μg of indium carrier and dissolve them with a mixture of hot hydrofluoric and sulphuric acids. Neutralize with aqueous ammonia, then add 5 ml of 0·2*M* sodium tartrate, a few mg of ascorbic acid, and potassium cyanide and sodium thiosulphate to give final concentrations of 3 % and 4 %, respectively. Adjust the pH to 8–9, and extract the indium with two portions (15 and 5 ml) of $7{\cdot}7 \times 10^{-4}M$ dithizone in carbon tetrachloride. Wash the combined extracts three times with 40 ml of 0·01*M* sodium tetraborate. Add tartrate buffer (4 ml of 0·2*M* sodium tartrate containing enough ammonia to give a pH of 7·5 when 2 ml of mercury solution are added) and 2·0 ml of mercury solution (200 μg of Hg(II)/ml in 0·1*M* nitric acid) and shake the mixture for 30 sec. Measure the activity of the indium in the aqueous phase. Apply the same procedure to a standard sample.

The sensitivity of the determination is about 0·01 ppm.

Iodine

Isotope-dilution analysis. Iodide can be precipitated on filter paper by a substoichiometric amount of silver cations. The excess of unreacted iodide is washed out of the paper by ammonium nitrate, using ring-oven technique[21] or electrophoresis in 0·1*M* tartaric acid.[22]

Iron

Isotope-dilution analysis. A substoichiometric amount of ethylenediaminetetra-acetic acid (Ref. 1, p. 100) has been used for the determination of iron in soil solution by double isotope-dilution technique.[39] Also, precipitation of iron(III) on filter paper by a substoichiometric amount of potassium hexacyanoferrate(II) has been recommended.[21] The unreacted iron is removed by dilute hydrochloric acid, using ring-oven technique.

Manganese

Neutron-activation analysis. The extraction of permanganate with a substoichiometric amount of tetraphenylarsonium chloride (Ref. 1, p. 102) has been applied to the determination of manganese (20 ppb) in pure lead.[40] In the procedure given, the manganese was first separated as dioxide and for the extraction procedure 1,2-dichlorethane was used as solvent. Similarly, the content of manganese (5 ppb) in gallium arsenide has been determined.[26] In this procedure arsenic was distilled off and gallium removed by extraction with isopropyl ether. To increase the selectivity of the separation, a preliminary extraction of manganese(II) with thenoyltrifluoroacetone and sodium diethyldithiocarbamate was carried out. A simpler but not so selective method consists in the extraction of manganese(II) with a substoichiometric amount of thenoyltrifluoroacetone.[41]

Determination of manganese in aluminium, zirconium, potassium fluoride and biological materials.[41] Seal the samples in polyethylene ampoules and irradiate simultaneously with a manganese standard in a flux of $7{\cdot}5 \times 10^{10}$ neutrons.mm^{-2}.sec^{-1} for 2 hr. Samples of aluminium and zirconium may be dissolved in a mixture of hydrofluoric and nitric acids, potassium fluoride in water, and ash from biological samples in hydrochloric acid. Add successively 2 mg of manganese(II) carrier, 3 ml of 10% tartaric acid solution, 3 ml of 20% potassium fluoride solution and 10 mg of hydroxylamine hydrochloride and adjust the pH to 8–8·5. Then add 0·50 ml of 0·11*M* thenoyltrifluoroacetone in ethanol and extract for 2–3 min with 10 ml of ethyl acetate. After separating the phases, measure the gamma spectrum of the organic extract with a 200-channel analyser. By comparison of the areas under the 0·84-MeV photopeaks of the test sample and of the manganese standard, the manganese content may be determined.

By this method the following contents of manganese have been determined: 0·058 ppm in pure zirconium, 0·010 ppm in zone refined aluminium, 0·1 ppm in potassium fluoride, and 40 ppm in ash from fish.

Mercury

Neutron-activation analysis. Mercury can be extracted from slightly alkaline solution by a substoichiometric amount of sodium diethyldithiocarbamate. Ethylenediaminetetra-acetic acid and citric acid are used as masking agents.[42]

Determination of mercury in gallium and in biological materials.[42] Simultaneously irradiate samples of gallium (0·2–0·3 g) in quartz ampoules, samples of flour (1·5–2 g) in polyethylene ampoules, and a mercury standard, in a flux of 7×10^{10} neutrons.mm^{-2}.sec^{-1} for 20 hr. After the addition of 14 mg of mercury carrier, dissolve the gallium in hydrochloric acid and the flour in a mixture of sulphuric and perchloric acids. Dilute with water, add 5 ml of 5% EDTA solution and 10 ml of 25% citric acid solution, then neutralize with aqueous ammonia to about pH 10 (the colour of phenolphthalein must be red). Add 1·0 ml of 0·02*M* sodium diethyldithiocarbamate and extract the mercury chelate into 20 ml of chloroform by shaking for 2 min. Wash the extract with a solution of EDTA and citric acid (pH ~ 10) and measure its activity, using a 200-channel analyser at 0·068–0·077 MeV.

Amounts of mercury in high purity gallium of 0·023 ppm and in flour of 0·35–0·42 ppm have been detected.

Isotope-dilution analysis. Mercury can be extracted as $HgBr_2$ into ethyl ether in the presence of a substoichiometric amount of bromide ions.[43] This method seems to be less sensitive and selective (chloride, iodide, thiocyanide, cyanide, *etc*, interfere) than by extraction with a substoichiometric amount of dithizone (Ref. 1, p. 104).

Molybdenum

Neutron-activaton nalysis. Extraction with a substoichiometric amount of 8-hydroxyquinoline (Ref. 1, p. 105) has been applied to the determination of molybdenum (0·15 ppm) in germanium dioxide.[44] Molybdenum can also be determined by substoichiometric extraction as its cupferronate[44] or α-benzoinoximate[45] into chloroform.

Determination of molybdenum in steel.[45] Simultaneously irradiate the test samples and a molybdenum standard in a flux of 2×10^{10} neutrons.mm^{-2}.sec^{-1} for 4 hr–7 days. Dissolve them in a mixture of 10 ml of hydrochloric acid, 2 ml of nitric acid and 2 ml of bromine in the presence of 10 mg of each of molybdenum(VI), tungsten(VI), nickel, manganese(II), silicon, phosphorus(V), and sulphur(VI) carriers. Centrifuge to remove tungstic acid, adjust to 6·5*M* in hydrochloric acid and extract with two 20-ml portions of diethyl ether saturated with 6·5*M* hydrochloric acid. Strip the molybdenum by equilibrating the combined 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 adjust to 0·6–0·8*M* in hydrochloric acid. Shake the mixture with 5 ml of 0·02*M* α-benzoinoxime in chloroform for 4 min. Wash the organic extract with 5 ml of 0·8*M* hydrochloric acid. Evaporate 4 ml of the extracts from test and standard samples to dryness and count at the 0·147-MeV photopeak of ^{99}Mo.

Palladium

Neutron-activation analysis. Palladium can be extracted from 3*M* hydrochloric acid with a substoichiometric amount of diethyldithiophosphoric acid into carbon tetrachloride.[46] Thiourea can be used to mask copper, silver and platinum. The method has been applied to the analysis of palladium concentrates and ores. For the determination of palladium in silver alloys extraction with a substoichiometric amount of isonitrosoacetophenone has been recommended.[47] Also, substoichiometric extraction of palladium diethyldithiocarbamate[48] seems to be a suitable method for determination of this element.

Determination of palladium in silver alloys.[47] Simultaneously irradiate the silver-alloy samples and a palladium standard in a flux of $1–2 \times 10^{11}$ neutrons.mm^{-2}.sec^{-1} for 2–20 hr. Dissolve the samples in a minimum volume of hot nitric acid (1 + 1) in the presence of 5 mg of palladium, 2 mg of gold, and 1 mg of osmium as carriers. Evaporate nearly to dryness with 0·4 ml of 6*M* hydrochloric acid; take up the residue in 2 ml of water and remove silver chloride by centrifugation. Transfer the supernatant solution to a 50-ml separatory funnel and adjust to 1*M* with respect to acetic acid and a total volume of 10 ml. Extract with 10 ml of 0·1% solution of isonitrosoacetophenone in benzene by shaking for 3 min. Centrifuge and count 5 ml of the organic extract in a gamma spectrometer, at the 0·087-MeV photopeak of ^{109}Pd.

In the presence of gold and osmium, which interfere, the test solution should be pretreated with 1 ml of 2% hydroquinone solution, boiled, and centrifuged.

Phosphorus

Neutron-activation analysis. Phosphomolybdic acid forms with a substoichiometric amount of tetraphenylarsonium chloride (TPACl) a compound (P:Mo:TPA = 1:12:3) which may be extracted into 1,2-dichlorethane; phosphomolybdic acid itself is not extracted into this solvent.[49]

Determination of phosphorus in semiconductor silicon.[49] Simultaneously irradiate the samples of silicon and a phosphorus standard in a flux of $1{\cdot}2 \times 10^{11}$ neutrons.mm^{-2}.sec^{-1} for 20–60 hr. After cooling for 5–6 days, dissolve the samples in a mixture of hydrofluoric and nitric acids in the presence of 0·20 ml of 0·01*M* phosphoric acid and evaporate to dryness. Then add 2 ml of 0·15*M* sulphuric acid and 0·2 ml of 0·2*M* ammonium molybdate and extract with 1·0 ml of $4 \times 10^{-3}M$ TPACl in dichlorethane. Calculate the amount of phosphorus present from the activity of the organic extract from a sample and that of a phosphorus standard treated in exactly the same way.

The sensitivity of the method is 2 ppb; arsenic(V) and antimony (V) do not interfere.

Isotope-dilution analysis. Phosphomolybdic acid forms in dilute mineral acids, with a substoichiometric amount of zirconium, a ternary complex (Zr:P:Mo = 1:1:12) which remains in the aqueous phase, whereas excess of phosphomolybdic acid may be extracted into a 1:1 butanol-chloroform mixture.[50]

Determination of traces of phosphorus.[50] To a test sample containing 0·4–50 μg of phosphorus, add a known amount of radioactive standard phosphorus followed by 0·3–1 ml of 1*M* ammonium molybdate and a substoichiometric amount of zirconium nitrate. Adjust the acidity to 0·35*M* in nitric acid (volume 20 ml). After standing for 1 min, extract the solution with 5 ml of 1:1 butanol-chloroform mixture for 20–60 sec. Compare the activity of the aqueous phase with that of a standard phosphorus sample treated in exactly the same way.

From many cations and anions studied, only arsenate, chromate, vanadate, fluoride, thorium and zirconium interfere. A preliminary extraction of phosphomolybdic acid with butanol followed by stripping into 0·2*M* potassium hydroxide increases the selectivity of the method.

Platinum

Neutron-activation analysis. Platinum(II) is extracted from dilute mineral acids by a substoichiometric amount of copper diethyldithiocarbamate [$Cu(DDC)_2$] in chloroform. Mercury, palladium and gold may be removed by a preliminary extraction; platinum should then be present in the non-extractable quadrivalent state.[51]

Determination of platinum in aluminium, gallium and biological samples.[51] Simultaneously irradiate the samples in polyethylene ampoules with a platinum standard in a flux of 7×10^{10} neutrons.mm^{-2}.sec^{-1} for 20 hr. After the addition of 12·5 mg of platinum carrier, dissolve metallic samples in hydrochloric acid and biological materials in a mixture of sulphuric and perchloric acids. If hydrogen peroxide is used during dissolution, it must subsequently be removed by boiling. Dilute the solutions thus prepared, with water, to be 1–2*M* in hydrochloric acid or 1·5–2·5*M* in sulphuric acid. Remove gold from hydrochloric acid solutions by extraction with diethyl ether, then extract the aqueous phase with two 20-ml portions of 0·1*M* diethylammonium diethyldithiocarbamate in chloroform to remove mercury, palladium and gold. To the remaining aqueous phase add 1 ml of tin(II) chloride (8 g of $SnCl_2$ dissolved in 20 ml of hot hydrochloric acid followed by dilution with 20 ml of water) to reduce platinum to the bivalent state. Then extract the platinum with 5 ml of $10^{-3}M$ $Cu(DDC)_2$ in chloroform for some minutes. Wash the organic extract with dilute hydrochloric acid and measure its activity, using a 200-channel analyser at the 0·077-MeV peak.

By this method the following amounts of platinum have been found: 0·11 ppm in aluminium, 1·5 ppm in gallium, 0·027 ppm in tea, and 0·01 ppm in fish ash.

Rare earths

Isotope-dilution analysis. Rare earth metals can be complexed with a substoichiometric amount of EDTA in hexamine/hexamine nitrate buffer solution (pH ~ 6). The excess of unreacted metal is removed by extraction with 0·01*M* thenoyltrifluoroacetone in xylene.[17] The method has been applied to the determination of microgram amounts of terbium and ytterbium.[17] Because the method is not very selective, a preliminary separation must be carried out to remove interfering elements.

Scandium

Neutron-activation analysis. Scandium is complexed with a substoichiometric amount of EDTA. The excess of unreacted scandium and any foreign cations are separated from the negatively charged scandium chelate on a cation-exchange column.[52]

Determination of scandium in meteorites.[52] Simultaneously irradiate the samples of iron meteorites (1 g) or stony meteorites (0·05–0·2 g) in quartz ampoules with a scandium standard in a flux of $1{\cdot}2 \times 10^{11}$ neutrons.mm^{-2}.sec^{-1}. for 20 hr or 2–7 days, for stony or iron meteorites respectively. After cooling for 10 days, dissolve samples of iron meteorites in the presence of 5·0 mg of scandium carrier by heating in *aqua regia*. Extract the bulk of iron with diethyl ether; remove the remaining traces of iron by passing the solution through a column of Dowex-1-X8 (Cl^--form). Mask zirconium in the eluate by the addition of 2 ml of 0·01*M* tartaric acid and precipitate the hydroxides by the addition of aqueous ammonia. Dissolve the hydroxides in 6*M* hydrochloric acid and evaporate to dryness. Then add 2 ml of 0·01*M* hydrochloric acid and 1·0 ml of 0·05*M* EDTA and pass the solution through a column of Dowex-50 (Na^+-form; 200 × 7 mm) at a rate of 0·3 ml/min. Elute with 0·01*M* hydrochloric acid and determine the ^{46}Sc by measuring the activity of 5 ml of the eluate at the 1·12-MeV peak.

Fuse stony meteorites with sodium peroxide at 500–600°, then dissolve the melt in the presence of 10 mg of scandium as carrier. Precipitate silicic acid by evaporating with $6M$ hydrochloric acid and remove by centrifugation. The subsequent operations are the same as described above for iron meteorites.

The sensitivity of the method is 0·1 ppm of scandium.

Silver

Isotope-dilution analysis. For the determination of silver in small volumes, precipitation with a substoichiometric amount of sodium sulphide has been recommended.[21] Excess of silver is removed by aqueous ammonia, using ring-oven technique. This procedure is less selective than that based on extraction with a substoichiometric amount of dithizone (Ref. 1, p. 111).

Sulphur

Neutron-activation analysis. Sulphur can be determined by means of the nuclear reaction $^{32}S(n, p)^{32}P$. Phosphorus can be isolated by extraction as vanadomolybdophosphoric acid (P:V:Mo = 1:1:11) in the presence of a substoichiometric amount of molybdate.[52,53] Arsenate, fluoride and iron(III) interfere in the determination.

Determination of sulphur in organic polymers.[52,53] Irradiate the polymer samples (30–300 mg) and an ammonium sulphate standard in silica tubes with a flux of 10^{10} neutrons.mm^{-2}.sec^{-1} for 6–8 hr. Oxidize the organic samples by oxygen-flask technique, using 10 ml of $4M$ nitric acid as absorbent, then add 10 ml of $0{\cdot}01M$ phosphate solution and 3 ml of saturated bromine water. Heat the mixture on a hot-plate, without boiling, so that phosphorus is completely converted into orthophosphate and excess of bromine is expelled. After cooling, make the solution up to 50 ml with water.

To a 10-ml aliquot add 1 ml of 60% perchloric acid, 4 ml of $0{\cdot}01M$ vanadate and 12 ml of $0{\cdot}01M$ molybdate (pH 0·7–0·8). Extract with 10 ml of isobutyl methyl ketone by shaking for three 1-min periods at 1-min intervals. Measure the activity of 8·0 ml of the extract and compare with the activity of the same volume of the extract from the standard sample treated in exactly the same way.

In the presence of fluoride, the solution must be evaporated three times with 5 ml of hydrochloric acid at a temperature below 80°.

By this method a content of 0·1–10% of sulphur has been determined. However, by an increase in the irradiation time, much lower concentrations may be determined.

Thallium

Neutron-activation analysis. Thallium(I) is extracted from alkaline solution with a small excess of dithizone in chloroform. After washing the organic extract with aqueous ammonia, thallium is replaced from thallium(I) dithizonate by a substoichiometric amount of an aqueous solution of mercury.[13] This method is more selective than that previously described, based on the extraction of thallium(III) from $4M$ hydrochloric acid by a substoichiometric amount of diethylammonium diethyldithiocarbamate in carbon tetrachloride.[54]

Determination of thallium in dried milk.[13] Simultaneously irradiate samples of milk powder and a thallium standard with a flux of 7 × 10^{10} neutrons.mm^{-2}.sec^{-1} for 160 hr. After cooling for 20 days, mineralize the samples with a mixture of sulphuric, nitric and perchloric acids in the presence of 0·50 mg of thallium(I) carrier. Neutralize, add potassium cyanide (final concentration about 10%) and a small amount of sodium sulphite (to reduce the thalium). Adjust the pH to about 11 and filter off the precipitated phosphates. Extract the thallium(I) with three 7·5 ml portions of $0{\cdot}001M$ dithizone in chloroform. Wash the combined extracts with 10 ml of $5M$ aqueous ammonia. To the separated extract add 1·0 ml of mercury(II) solution, containing 100 μg of mercury, and 1 ml of $5M$ aqueous ammonia. After shaking for 30 sec, measure the β-activity of the aqueous phase and compare it with the activity obtained from the standard sample treated in exactly the same way.

A content of thallium in dried milk of about 0·02 ppm has been determined.

Tin

Neutron-activation analysis. Because radioindium is formed by the reaction $^{112}Sn(n, \gamma)\,^{113}Sn \rightarrow {}^{113m}In$, the determination of tin as well as indium can be carried out by measurement of the activity of ^{113m}In and of ^{114m}In, respectively.

Determination of tin in granite and gallium.[14] Seal the samples in aluminium capsules (granite powder) or quartz ampoules (gallium) and irradiate them simultaneously in a flux of 5×10^8 neutrons.mm^{-2}.sec^{-1} for 160 hr; the cooling time should be about 20 days. Dissolve the granite samples in a mixture of hot hydrofluoric and sulphuric acids and the gallium samples in hot nitric acid in the presence of 300 μg of indium carrier. Isolate the indium by using replacement substoichiometry (see under *Indium*) and measure its activity by means of a multichannel gamma spectrometer. Calculate the content of tin from the 0·39-MeV peak area (^{113m}In) and that of indium from the 0·19-MeV peak area (^{114m}In).

The sensitivity of the method is about 0·01 ppm for indium and 0·5 ppm for tin.

Tungsten

Isotope-dilution analysis. Tungsten can be extracted with a substoichiometric amount of toluene-3,4-dithiol into chloroform. Molybdenum must be removed previously by extraction with the same reagent.[55]

Determination of tungsten in tungsten-molybdenum alloys.[55] Dissolve the sample (about 5 mg) in 10 drops of hydrofluoric acid and 3 drops of nitric acid, heat until nitrogen oxides are driven off and then dilute to 5 ml with 1*M* hydrochloric acid. Add 8·5 ml of 3·5*M* hydrochloric acid, a known amount of tungsten labelled with ^{181}W of high specific activity (0·5 mg) and 4 drops of 10% hydroxylamine hydrochloride solution. After mixing, add 0·15 ml of 0·5% dithiol solution. Stand for 5 min, then extract the molybdenum–dithiol complex with four 3-ml portions of carbon tetrachloride Evaporate the aqueous phase very carefully to a volume of 2 ml; add 25 ml of hot titanium(III) sulphate solution (1 g of titanium metal dissolved in 1·5*M* sulphuric acid) and 20 ml of hot 11·7*M* hydrochloric acid. Then add 0·20 ml of 0·5% dithiol solution, mix and allow to stand for 90 min, then extract the tungsten-dithiol complex into 10 ml of chloroform. Measure the activity of an aliquot of the organic phase and compare with that of the same volume of solution obtained from a standard sample treated in exactly the same way.

Uranium

Isotope-dilution analysis. Uranium(VI) can be extracted in the presence of a substoichiometric amount of arzenazo III by thenoyltrifluoroacetone in chloroform.[56] The method does not, however, seem to be very selective.

Zinc

Neutron-activation analysis. Extraction with a substoichiometric amount of dithizone (Ref. 1, p. 113) has been applied to the determination of zinc in pure gallium (1·7 ppm).[57] The bulk of the gallium is first removed by extraction with diethyl ether and the zinc is then separated from interfering metals on a Dowex 1-8 column. A similar procedure has been used for the analysis of gallium arsenide.[5,26,58,59] A preliminary distillation by heating with hydrobromic acid is used to remove arsenic.

Isotope-dilution analysis. The procedure proposed (Ref. 1, p. 113) has been verified for the determination of zinc in germanium dioxide.[60,61]

Zirconium

Neutron-activation analysis. Zirconium can be precipitated as Ba_2ZrF_8 with a substoichiometric amount of barium ions from 1*M* hydrofluoric acid.[18] Because this procedure is not very selective, many separation steps have to be carried out before the substoichiometric separation is applied.

The method has been used for the determination of zirconium in very pure aluminium (0·1 ppm).

AUTOMATION

Substoichiometric separation by solvent extraction can be automated on a continuous flow basis (Ref. 1, p. 119). In this technique individual samples are placed in a sample changer and inserted into the analysis system by a proportioning pump so that they follow each other in a continuously flowing stream. To this stream, buffers, masking agents, organic reagent and organic solvent are added in such proportions and concentrations that in the finally separated organic phase the element in question is contained in the desired quantity. The radioactivity of the element in the stream of the organic phase is then measured by a scintillation or Geiger–Müller flow counter and displayed on a strip-chart recorder. In such a system each sample is treated in exactly the same manner because factors such as concentrations, pH, time of extraction, *etc*, are always the *same* for all samples; the only variable is the quantity of the species to be determined. Obviously, this is advantageous for the substoichiometric separation of such very small quantities of elements as those met with in isotope-dilution analysis.

In the first practical work[62,63] these considerations were confirmed and later[64] it was concluded that automation makes it possible to use extraction systems having lower K-values than those imposed by equation (3). The reason is that in the manual operations the reproducibility of the substoichiometric separation is obtained through *quantitative* consumption of the reagent used in substoichiometric quantity. This, of course, requires relatively high K-values, but allows less strict control of pH and of other conditions. In continuous flow analysis, on the other hand, the requirement of quantitative consumption of the reagent may be substituted by an *incomplete*, but *reproducible* consumption. This means that always the same quantity of the element in question is separated from the sample of that particular concentration under those fixed conditions as maintained in the automated analysis system. Any deviation from the "ideal" case [separation of equal quantities, *i.e.*, equation (12)] is then reflected on the calibration graph.

Further advantages of automation are the higher output of analyses than by manual methods (up to 20 samples per hour can be analysed) and the ease of measurement of the radioactivity. This is also automated because the separated organic phase (or aqueous phase) is measured by a flow counter and the signal is monitored by a ratemeter and registered *via* a pen recorder. On the chart record thus obtained each sample is represented by a peak, the height of which is used for calculations or for construction of a calibration graph.

For practical analysis either a *one-detector system* (as described above) or a *two-detector system* (Fig. 1) can be used. In the one-detector system only the substoichiometrically separated activity is measured, whereas in the two-detector system both the total and substoichiometrically separated activities of each sample are measured and recorded. The purpose of this latter approach is explained here for the determination of traces of mercury in biological material. The analytical procedure consists of three main stages:

(*i*) manual destruction of the sample material in the presence of a standard quantity of radiomercury;
(*ii*) manual preconcentration and separation of mercury from interfering species;
(*iii*) automated substoichiometric separation and measurement of the separated activity.

Oxygen-flask combustion and solvent extraction are used in steps (*i*) and (*ii*), and the automated stage is based on solvent extraction of mercury by dithizone, and on a one-detector system.[65] In this manner quantities of mercury ranging from 0·04 ppb to 2 ppm in various materials such as flour, milk, bread, apples, eggs, beef, liver, chemicals, paper, as well as in standard biological materials, have been determined.[65] However, it was realized that by controlling the yield of the preliminary separation the operational errors of the manual stage would be avoided and ensure the validity of all results. If the total activity is registered by recorder I (Fig. 1) while the substoichiometrically separated activity is registered by recorder II, it can easily be seen whether the yield has by some error dropped so low that the subsequent automated separation is no longer substoichiometric but is quantitative. A detailed theory of the two-detector system has been published[64] and its full experimental verification is now being prepared.[66]

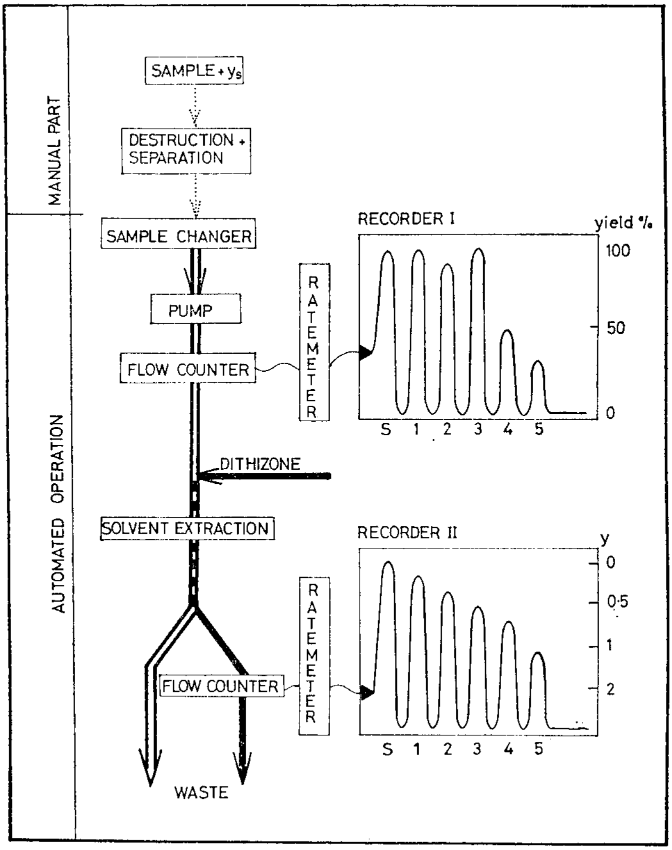

FIG. 1.—Flow diagram for continuous substoichiometric determination with two-detector system.

Besides the method for mercury, an automated determination of phosphorus in amounts down to 0·01 ppm has also been developed. In this case the activity of substoichiometrically separated phosphozirconium-molybdic acid in the aqueous phase is measured (see *Phosphorus*).[50] Here again automation proved to be superior to the manual operation in respect of productivity, reproducibility and sensitivity.

The drawbacks of automation should, however, also be mentioned here. First, the equipment—Technicon AutoAnalyzer—until now used exclusively for this purpose, is rather expensive. This situation is likely to improve because a similar instrument has recently become available from another manufacturer (C. Erba, Italy). Secondly, the development of automated procedures is not merely the mechanization of manual methods, because kinetic factors and the adsorption of traces of the element in question on various parts of the instrument must always be considered and investigated.[50,63] These, in fact, may prove to be the factors limiting the sensitivity of determination.

Finally, the use of automation for substoichiometric determination of the specific activity of ^{32}P as obtained from plants fertilized with labelled phosphate should be mentioned here as an example of the automated analysis of radioactive material.[67]

MISCELLANEOUS APPLICATIONS

The procedures described above can easily be applied to the analysis of radioactive materials, *e.g.*, for the determination of radioactive impurities in radioactive preparations, radiochemical analysis of fission products, and determination of isotopic carrier in radioactive preparations. Substoichiometric separations can also be used for a simple preparation of radiochemically pure radioisotopes.[29]

Recently, the theory of substoichiometric separation has found application in other radiochemical methods, *e.g.*, for predicting the optimal conditions for the determination of antimony, bismuth and iron, by the method of radiometric correction[68,69] (method analogous to the micromethod of Schumacher and Friedli[70]) and of bismuth by using an isotope exchange between two bismuth complexes in the organic phase.[71]

In conclusion, the method of substoichiometric masking[72,73] should be mentioned. The masking agent is added in a smaller amount than stoichiometrically corresponds to the amount of the element to be masked; thus the amount of free interfering element is reduced below the interference threshold. This approach is advantageous in cases where the available masking agents when added in excess profoundly affect the element to be determined, and has found practical application in the determination of traces of cobalt in nickel salts and metallic nickel.

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Zusammenfassung—Es wird eine Übersicht über neue Entwicklungen in der unterstochiometrischen Analyse gegeben.

Résumé—On présente une revue de développements récents dans l'analyse substoechiométrique.

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STUDIES ON THE EXTRACTION AND DETERMINATION OF METAL SALTS WITH ISOBUTYL METHYL KETONE—XIII*

EXTRACTION OF THORIUM AND URANIUM†

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Summary—The work deals with the extraction of thorium or uranium from hydrochloric, perchloric, sulphuric or nitric acid solutions of various concentrations, or from mixed acid solutions, by means of isobutyl methyl ketone. When the extraction is made from 5–8*M* hydrochloric acid that is 10*M* in lithium chloride or from 7–8*M* hydrochloric acid that is 1*M* in magnesium chloride, uranium is extracted quantitatively (>99%), whereas thorium is hardly extracted at all.

RESULTS for the distribution of thorium[1,2] and uranyl[2–11] nitrates between isobutyl methyl ketone (IBMK) and nitric acid in the presence of various nitrates as salting-out agent have been published by a number of investigators, but extractions from other mineral acids, either alone or mixed, have not hitherto been studied.

From the work of Hardwick and Smith[9] an analytical separation procedure is available for extraction of a trace of uranium in irradiated thorium into isobutyl methyl ketone from a dilute nitric acid solution saturated with ammonium nitrate. However, the separation seems to be incomplete, because the thorium is slightly extracted. According to Peppard *et al.*,[12] Ishimori *et al.*,[13] and Ishii and Takeuchi,[14] in the extraction of thorium and uranium with tributyl phosphate from hydrochloric acid solution, thorium is partly extracted together with uranium and the complete separation of these two elements is impossible.

The results obtained in the present work show that the addition of lithium chloride or magnesium chloride as salting-out agent markedly enhances the extractability of uranium(VI) from hydrochloric acid into isobutyl methyl ketone, while under the same conditions no thorium can be extracted. The difference in the extractabilities is such that the two elements can readily be separated from each other. The process should be applicable to the analytical separation and purification of thorium and uranium.

EXPERIMENTAL

Reagents

Standard thorium solution (10 mg/ml). Thorium dioxide (99·99% pure), 11·380 g, was dissolved by heating in 20 ml of hydrochloric acid (1 + 1) containing a few drops of hydrofluoric acid (1 + 9), and the solution was evaporated to dryness. After dissolution of the residue with hydrochloric acid,

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the solution was evaporated again to dryness. This treatment was repeated until the residue was free from fluoride. The final residue was dissolved in about 20 ml of 6*M* hydrochloric acid, and the solution diluted with 6*M* hydrochloric acid to 1 litre in a volumetric flask. For solutions in other acids, an aliquot of this standard thorium solution was heated to dryness, the residue dissolved in the desired acid, and the solution evaporated again to dryness. This treatment was repeated until the residue was free from chloride. The final residue was dissolved in the desired acid and diluted to known volume.

Standard uranium solution (10 mg/ml). Triuranium octaoxide (99·9% pure), 11·804 g, was dis-dissolved in 40 ml of *aqua regia* by heating, and then the solution was evaporated to dryness. After dissolution of the residue with hydrochloric acid, the solution was evaporated again to dryness. This treatment was repeated until the residue was free from nitrate. The subsequent treatment was the same as for thorium.

Other reagents used were all of analytical reagent grade.

Extraction procedure

Ten ml of an acid solution containing 10 mg of thorium or uranium(VI) were shaken vigorously for about 1 min (120 shakes) with an equal volume of IBMK in a 100-ml separatory funnel. After equilibration, the degree of extraction was calculated by determining the amount of metal in equal volumes of each phase according to the procedures given below. A correction was applied for any volume change during equilibration. All experiments were performed at 15° (temperature-controlled water-bath). Preliminary experiments established that equilibrium was reached in <30 sec.

Analytical procedures

An aliquot of the organic or aqueous phase was transferred into a 50-ml beaker and heated to dryness. After dissolution of the residue with *aqua regia*, the solution was again evaporated to dryness. The residue was dissolved in 5 ml of 0·15*M* nitric acid for thorium or in 5 ml of 0·2*M* hydrochloric acid for uranium, and the solution diluted with the same acid to give a known volume of solution with a metal concentration in the range 2–30 ppm.

Determination of thorium. A 5·00-ml aliquot of the thorium solution was transferred into a 25-ml volumetric flask, 1 ml of 0·1% Neothorone solution [15–17] was added, the solution was diluted with water to the mark and the absorbance measured at 580 nm against a reagent blank. The lower limit of determination was 0·4 ppm of thorium and the coefficient of variation of the results was <3·4% in the thorium concentration range 0·4–6 ppm.

Determination of uranium. A 5·00-ml aliquot of the uranium solution was transferred into a 50-ml beaker, and diluted with water to about 25 ml. The pH was adjusted to about 1·8 (pH-meter) by dropwise addition of dilute ammonia solution or dilute hydrochloric acid. The solution was transferred into a 50-ml volumetric flask, 1 ml of 0·1% arsenazo III solution[18–20] was added, the solution was diluted with water to the mark and the absorbance was measured at 655 nm against a reagent blank. The lower limit was 0·2 ppm of uranium, and the coefficient of variation of the results was <3·1% in the uranium concentration range 0·2–3 ppm.

RESULTS AND DISCUSSION

Extraction from pure acid media

Thorium ($4{\cdot}17 \times 10^{-3}M$) and uranium(VI) ($4{\cdot}20 \times 10^{-3}M$) in hydrochloric, perchloric, sulphuric or nitric acid media of various concentrations were equilibrated with IBMK as described above. The results are presented in Figs. 1 and 2.

As will be seen from these graphs, thorium was <0·1% extracted from hydrochloric acid over the range of concentrations tested; extraction of uranium increased rapidly from hydrochloric acid >5*M*. The behaviour of thorium was similar to that of uranium in perchloric acid media. The extraction behaviour in nitric acid was roughly the same as that already described by Rydberg and Bernström.[2]

Extractions from mixed acids

Results of extraction of thorium and uranium(VI) from nitric–perchloric acid solution and of uranium from hydrochloric–perchloric acid and hydrochloric–nitric acid media are shown in Figs. 3, 4 and 5.

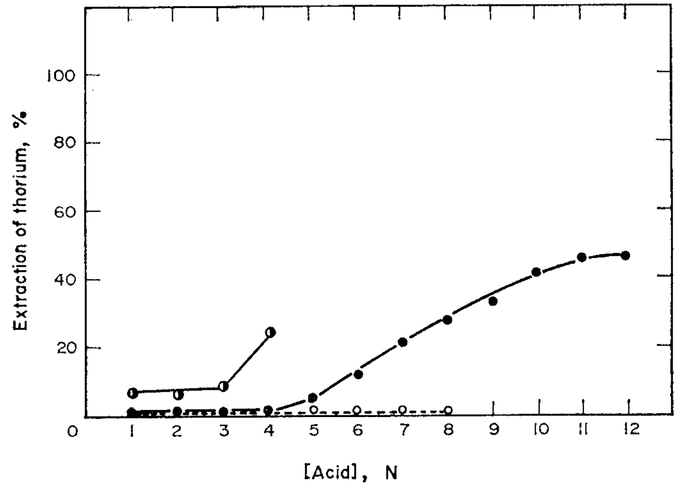

FIG. 1.—Extraction of thorium from various acid solutions with IBMK.
Th: 4·17 × $10^{-3}M$
---○---: HCl, —◑—: $HClO_4$, —●—: HNO_3.

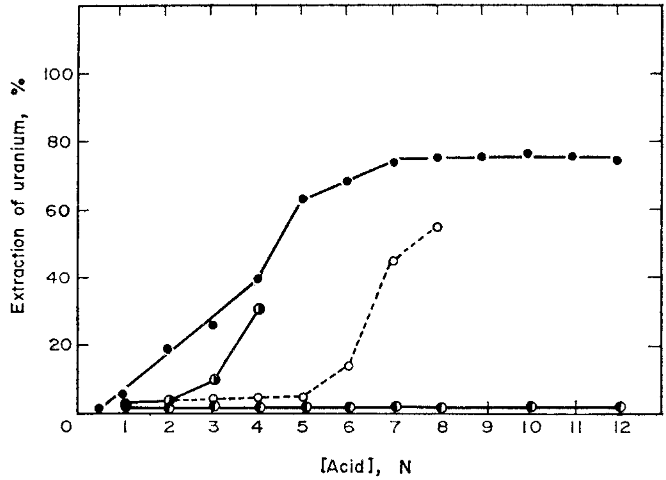

FIG. 2.—Extraction of uranium from various acid solutions with IBMK.
U(VI): 4·20 × $10^{-3}M$
---○---: HCl, —◑—: $HClO_4$, —◐—: H_2SO_4, —●—: HNO_3.

These experiments show that perchloric acid enhances the extraction of thorium and uranium from nitric acid and that of uranium from hydrochloric acid.

Effect of salting-out

Rydberg and Bernström[2] studied in detail the extraction of thorium and uranyl nitrates with IBMK from nitric acid containing various amounts of calcium nitrate. Distribution of thorium and uranyl nitrates between IBMK and nitric acid containing various nitrates such as lithium,[1] magnesium,[1] zinc,[1] calcium,[1,4] aluminium,[1,10,11]

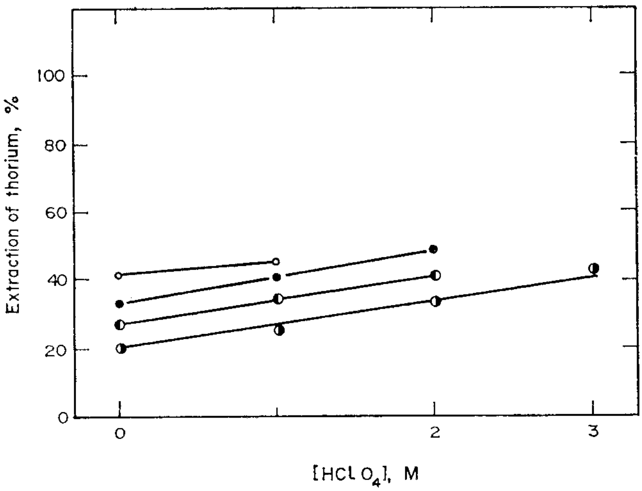

FIG. 3.—Extraction of thorium from nitric–perchloric acid solution with IBMK.
Th: 4·17 × 10^{-3} M
◑: 7M HNO_3, ◐: 8M HNO_3, ●: 9M HNO_3, ○: 10M HNO_3.

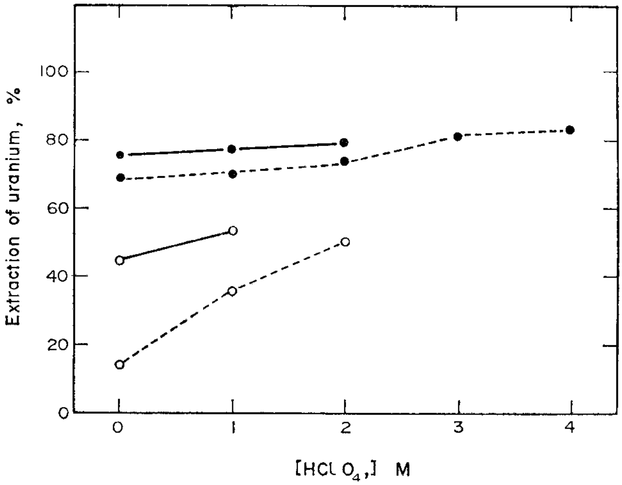

FIG. 4.—Extraction of uranium from hydrochloric–perchloric or nitric–perchloric acid solutions with IBMK.
U(VI): 4·20 × $10^{-3}$$M$
---○---: 6M HCl, —○—: 7M HCl, ---●---: 6M HNO_3,
—●—: 8M HNO_3.

sodium[4] or ammonium[5,9] as salting-out agent has already been studied by other workers. However, the effects of salting-out on the extraction from other mineral acid media do not appear to have been examined.

From the results shown in Figs. 1 and 2, separation of thorium from uranium seemed to be possible by extraction of the latter from hydrochloric acid. The effect of various chlorides of cations with comparatively small ionic radius was examined under the conditions given for Figs. 1 and 2. The results are shown in Fig. 6 which shows that from 5M hydrochloric acid–10M lithium chloride or $>$7M hydrochloric acid–1M

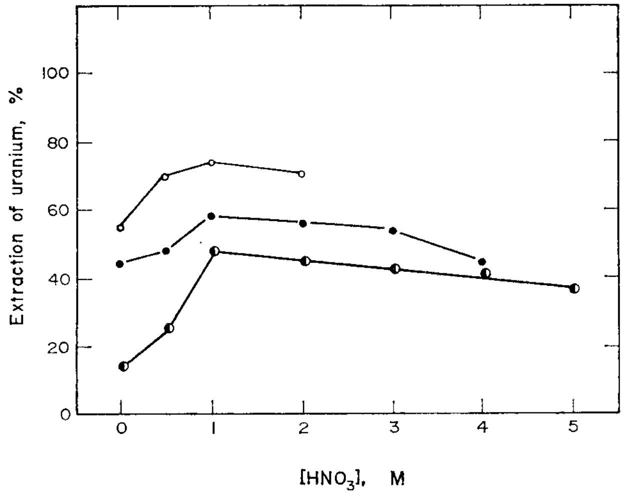

FIG. 5.—Extraction of uranium from hydrochloric-perchloric acid solution with IBMK.

U(VI): $4{\cdot}20 \times 10^{-3}M$

◑: $6M$ HCl, ●: $7M$ HCl, ○: $8M$ HCl.

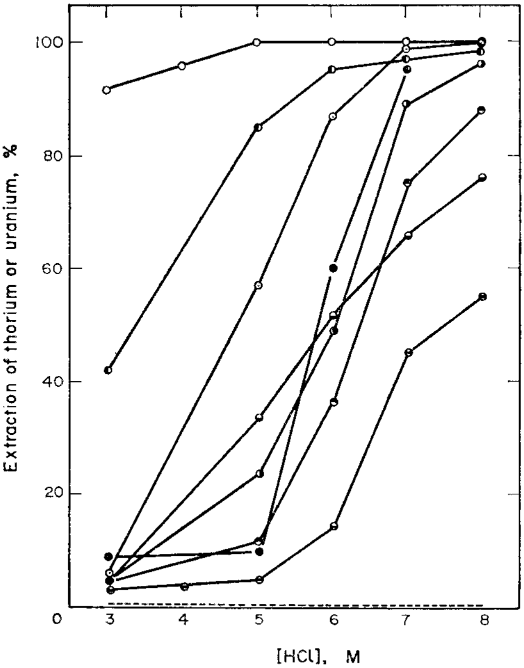

FIG. 6.—Effect of various chlorides on the extraction of thorium and uranium from hydrochloric acid solutions with IBMK.

Th: $4{\cdot}17 \times 10^{-3}M$, U(VI): $4{\cdot}20 \times 10^{-3}M$

○: U-$10M$ LiCl, ⊙: U-$1M$ $MgCl_2$, ◐: U-$5M$ $CaCl_2$, ●: U-$1M$ $AlCl_3$, ◑: U-$1M$ $CaCl_2$, ◓: U-$1M$ LiCl, ◒: U-$1M$ $ZnCl_2$, ⊖: U,
----: Th-$10M$ LiCl and Th-$1M$ $MgCl_2$.

magnesium chloride, uranium was quantitatively extracted (>99%); while thorium remained quantitatively (>99·9%) in the aqueous phase.

Although the concentration of the anion of the salting-out agent seems to be a major factor of the remarkable enhancement in the extractability of uranium from hydrochloric acid solution, the cation also plays some part.

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Zusammenfassung—Die Arbeit befaßt sich mit der Extraktion von Thorium oder Uran mit Isobutylmethylketon aus salzauren, überchlorsauren, schwefel- oder salpetersauren Lösungen verschiedener Konzentration sowie aus Lösungen in Säuregemischen. Bei Extraktion aus 5–8 M Salzsäure, die 10 M Lithiumchlorid enthält, oder aus 7–8 M Salzsäure mit 1 M Magnesiumchlorid wird Uran quantitativ (über 99%) extrahiert, Thorium dagegen fast gar nicht.

Résumé—Le travail traite de l'extraction du thorium or de l'uranium de solutions en acide chlorhydrique, perchlorique, sulfurique ou nitrique de diverses concentrations, ou de solutions d'acides mzlangzs, au moyen de mzthylisobutylcztone. Lorsque l'extraction est effectuze a partir d'acide chlorhydrique 5–8*M* qui est 10*M* en chlorure de lithium, ou d'acide chlorhydrique 7–8*M* qui est 1*M* en chlorure de magnesium, l'uranium est extrait quantitativement (>99%) tandis que le thorium ne l'est pratiquement pas.

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ÜBER DIE GENAUIGKEIT UND ANWENDBARKEIT DER RÖNTGENFLUORESZENZ FÜR DIE BESTIMMUNG DER KONZENTRATION DER ELEMENTE PHOSPHOR BIS URAN IN LÖSUNG

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Zusammenfassung—Die Anwendung der Röntgenfluoreszenzanalyse für die Bestimmung der Elemente der Ordnungszahl größer als 14, in Lösung, wird beschrieben. Interelementeffekte wurden untersucht, und die Brauchbarkeit eines inneren Standards (benachbartes Element) gegen einen äusseren Standard wird verglichen. In verdünnten Lösungen (weniger als $5 \cdot 10^{-3}$ *M*) sind Interelementeffekte vernachlässigbar. Die Fehlerquelle und die Wahl sowohl der Meßbedingungen als auch des optimalen Konzentrationsbereichs werden diskutiert.

ZUR QUALITATIVEN ANALYSE mit Hilfe von Röntgenfluoreszenz (für Literatur über die Methode siehe Citaten 1 und 2) können feste Proben, Pulver und Lösungen ohne besondere Vorbehandlung untersucht werden. Das beruht darauf, daß die Wellenlänge der charakteristischen Strahlung, abgesehen von den ganz leichten Elementen, vom Chemismus des betreffenden Elementes unabhängig ist.

Bei der quantitativen Bestimmung muß aber berücksichtigt werden, daß die Intensität der Fluoreszenzstrahlung nicht nur von der Konzentration des betreffenden Elementes, sondern auch von der Art und Konzentration der Begleitelemente abhängt. Dieser sogenannte Matrixeffekt ist durch die Absorption von sowohl der Primär-, als auch der Fluoreszenzstrahlung in der Probe bedingt und weiter kann die Fluoreszenzstrahlung gewisser Elemente andere Elemente zur Fluoreszenz anregen (Interelementenanregung).

Bei festen Proben und Pulvern spielen auch die Größe der Körner und deren Oberflächeneigenschaften, sowie die Homogenität der Probe eine wichtige Rolle. Bei der Untersuchung von Lösungen fallen Letztere weg und die Matrixeffekte lassen sich leichter numerisch erfassen[3] bzw. kompensieren.[4]

Eine praktisch vollständige Kompensation der Interelementeneffekte kann bei der Analyse von verdünnten Lösungen durch die Anwendung eines inneren Standards erreicht werden. Bei dieser Methode wird ein zweites Element ("Innerer Standard", S) der Lösung des zu bestimmenden Elementes A beigemischt und die Fluoreszenzintensität jedes Elements gemessen. Als S-Element sollte ein Element gewählt werden, dessen Fluoreszenzintensität durch die übrigen Begleitelemente im gleichen Maße beeinflußt wird wie die Fluoreszenzstrahlung des zu bestimmenden Elementes A. Seine Wahl erfolgt nach folgenden Kriterien:[5]

(*a*) Keine Fluoreszenzlinie eines dritten Elementes sollte zwischen den Absorptionskanten von A und S liegen.

(*b*) Keine Absorptionskante eines Begleitelementes darf zwischen den Fluoreszenzlinien von A und S anwesend sein. Diese Bedingungen sind im allgemeinen erfüllt, wenn man bei der Anregung der gleichen Schale (K oder L) als S ein benachbartes Element von A wählt.[6] Sind nun die Interelementeneffekte für beide Elemente gleich, so ist das Verhältnis der Nettointensitäten dem Verhältnis der Konzentrationen direkt proportional:

$$\frac{N_A}{N_S} = k \frac{[A]}{[S]} \qquad (1)$$

Die Proportionalitätskonstante k bestimmt man an Lösungen, welche A und S in bekannter Konzentration enthalten. Bei der Analyse von sehr verdünnten Lösungen ($\Sigma M_i < 0{,}01$) kann im allgemeinen auf die Verwendung eines inneren Standards verzichtet werden, da die Nettointensität N_A zu [A] direkt proportional ist und die Proportionalitätskonstante K von den Begleitelementen vernachlässigbar wenig beeinflußt wird.

In dieser Arbeit soll nun beschrieben werden, wie diese Methoden allgemein anwendbar und was für apparative und meßtechnische Vorbereitungen hierzu erforderlich sind.

EXPERIMENTELLER TEIL

Die verwendete Apparatur bestand aus einem Universal-Vakuum-Spektrographensatz PW 1540 der Firma Philips mit einem Generator für 54 kV maximale Hochspannung und mit einer Silberröhre. Der Probenraum wurde vom Raum mit dem Analysatorkristall mit Hilfe einer Kunststoffolie (Mylarfolie) an der Eintrittsöffnung des Kollimators getrennt. Für die Messung wurde der Kristallraum auf $1{,}3 \cdot 10^{-2}$ mbar evakuiert, während der Probenraum ~660 mbar Helium enthielt.

Analysatorkristalle und Zählrohre

Da der Analysatorkristall und das Zählrohr der Wellenlänge der zu messenden Strahlung angepaßt werden müssen, benötigt man mindestens zwei verschiedene Kristalle und Zählrohre, wenn die zu bestimmenden Elemente sich stark in der Ordnungszahl voneinander unterscheiden. Man verwendete für die K_α-Strahlung der leichten Elemente und als Analysatorkristall Äthylendiamin-*d*-tartarat (EDDT, $2d = 0{,}8808$ nm) und ein Durchflußzählrohr (DFZ). Für die schweren Elemente stand ein LiF-Kristall ($2d = 0{,}4028$ nm) und ein Szintillationszählrohr (SZZ) zur Verfügung.

Impulshöhenanalysator (Diskriminator)

Für genaue Analysen ist die Verwendung eines Impulshöhenanalysators empfehlenswert. Der verwendete Verstärker-Diskriminator (Philips PW 4280) verstärkt alle Impulse und läßt je nach Wahl nur solche hindurch, dern verstärkte Amplitude über einem bestimmten Schwellenwert (Unteres Niveau UN = 0–5 Volt) oder zwischen zwei bestimmten Schwellenwerten (zwischen UN und UN + F, Fenster F = 0–2,5 Volt) liegt. Hierdurch wird die unerwünschte Untergrundstrahlung verringert, weil die Reflexionen höherer Ordnung eliminiert werden

Die Impulshöhe (IH) eines Durchfluß- oder Szintillationszählrohres hängt von der an das Rohr angelegten Spannung V_D und von der Energie ($h\nu$) des einfallenden Röntgenquantes ab. Wird die Hochspannung V_D am Detektor konstant gehalten, so ist die Impulshöhe zur Photonenenergie direkt proportional. Mißt man nun die von einer bestimmten Strahlung erzeugte Impulsrate I in Abhängigkeit der eingestellten Impulshöhe, so kann man eine maximale Impulsrate feststellen. Bei der praktischen Ausführung wird eine konstante Fensterbreite F eingestellt und das untere Schwellenpotential UN variiert. Das Spektrometer bleibt dabei auf die betreffende Wellenlänge eingestellt. Trägt man nun I gegen (UN + F/2) auf, so entstehen Glockenkurven (s. Abb. 1), welche ihr Maximum M bei verschiedenen (UN + F/2)-Werten haben. Für die Impulshöhe am Maximum gilt die folgende Proportionalität:

$$\mathrm{IH_M} = (\mathrm{UN} + \mathrm{F}/2)_\mathrm{M} = \mathrm{prop.}\ (h \cdot \nu) = \mathrm{prop.}\ (1/\lambda) \qquad (2)$$

Gemäß Gleichung 2 muß die Funktion $\mathrm{IH_M}(1/\lambda)$ eine Gerade ergeben. In Abb. 2 ist sowohl $\mathrm{IH_M}$, als auch die zugehörigen Halbwertsbreite Δ_{IH} für den verwendeten Szintillationszähler gegen die reziproke Wellenlänge aufgetragen. Beide Grössen ergeben praktisch eine Gerade.

Damit ist die Möglichkeit gegeben, die günstigsten Werte von UN und F für die Einstellung des Diskriminators mit Hilfe dieser Geraden zu ermitteln. Dazu liest man in Abb. 2 bei der betreffenden reziproken Wellenlänge die Werte von Δ_{IH} und $\mathrm{IH_M}$ ab. Wenn man nun eine Fensterbreite von

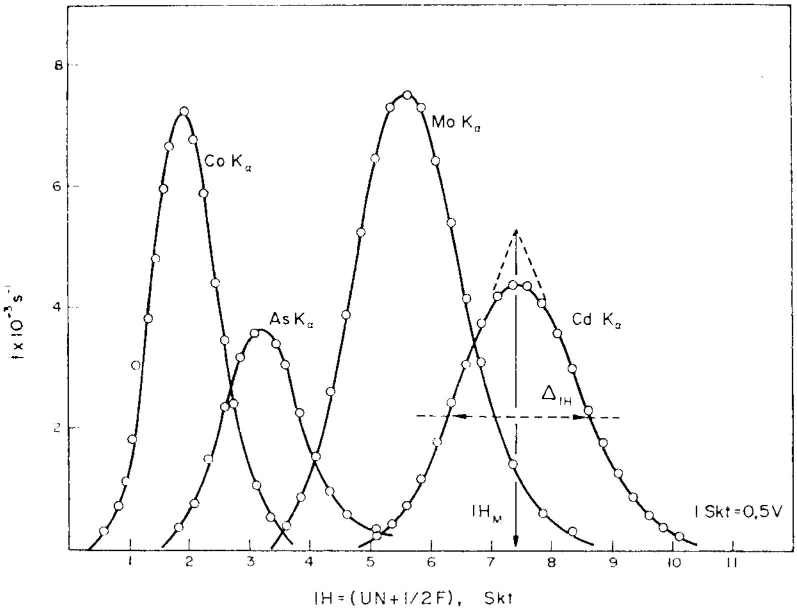


ABB. 1.—Impulshöhenanalyse.
Häufigkeitsverteilung der Impulse bei variabler Impulshöhe für Fluoreszenzlinien verschiedener Quantenenergie und konstante Spannung (V_D = 760 Volt) am Detektor (SZZ).

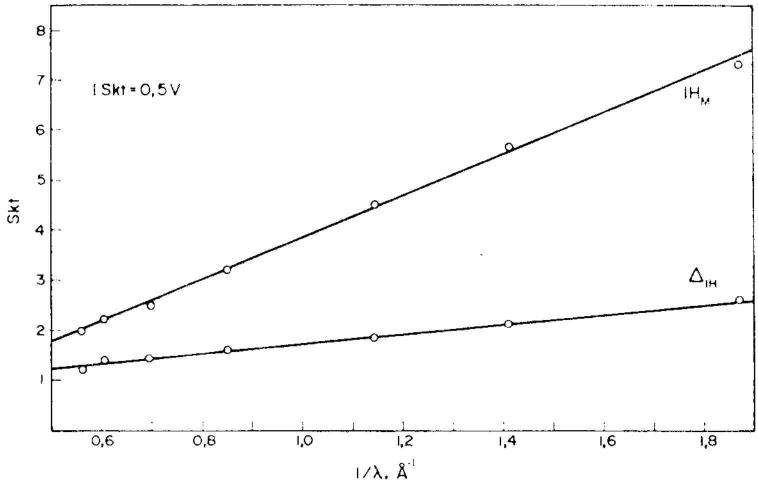


ABB. 2.—IH_M-Gerade: Abhängigkeit der Impulshöhe mit maximaler Impulsrate von der reciproken Wellenlänge der Fluoreszenzstrahlung (Szintillationszähler, V_D = konst. = 760 Volt). Δ_{IH}-Gerade: Halbwertsbreite der I, IH-Kurven in Funktion der Wellenlänge.

$2\Delta_{IH}$ einstellt, so werden praktisch alle Impulse der betreffenden Strahlung gezählt. Im allgemeinen kann also die folgende Diskriminatoreinstellung verwendet werden:

$$F = 2 \cdot \Delta_{IH} \quad \text{und} \quad UN = IH_M - \Delta_{IH} \tag{3}$$

Es ist zweckmässig, für benachbarte Elemente eine gemeinsame Diskriminatoreinstellung (UN_g und F_g) zu wählen:

$$F_g = 2 \cdot \Delta_{IH,k} + (UN_k - UN_l) \quad \text{und} \quad UN_g = UN_l \tag{4}$$

Der Index g bedeutet hier "gemeinsam" und k bzw. l deuten die "kurzwelligere", bzw. die "langwelligere" Fluoreszenzstrahlung der beiden zu vergleichenden Elemente an. Wenn man die Bedingungen 3 und 4 erfüllt, werden praktisch alle Impulse beider Linien gezählt. Es kann aber keine gemeinsame Fensterbreite F_g gewählt werden, wenn diese noch eine Störstrahlung umfaßt, welche mit einer der beiden Linien überlappt. In solchen Fällen kann natürlich keine gemeinsame Diskriminatoreinstellung vorgenommen werden. Vielmehr müssen für die Elemente A und S eigene und engere Fensterbreiten als $2\Delta_{IH}$ gewählt werden.

RESULTATE UND DISKUSSION

Fluoreszenzintensität von molaren Lösungen der Elemente (K)

Die Fluoreszenzintensität von Lösungen ist in einem recht großen Konzentrationsbereich zu der Molarität [A] direkt proportional. Dieses ist aus Abb. 3 ersichtlich, wo log N_A (N_A = Nettointensität des Elementes A) gegen −log [A] für einige Linien graphisch aufgetragen ist. Man wählte eine doppellogarithmische Darstellung, damit die Proportionalität auch bei kleinen Konzentrationen sichtbar ist. Für viele Fluoreszenzlinien ist die Linearität zwischen der Intensität und Konzentration über mehrere Zehnerpotenzen in Konzentration gut erfüllt. Die Abweichung bei größeren Konzentrationen ist auf die zunehmende Absorption der Lösung zurückzuführen. Im allgemeinen beginnt die Abweichung von der Linearität oberhalb

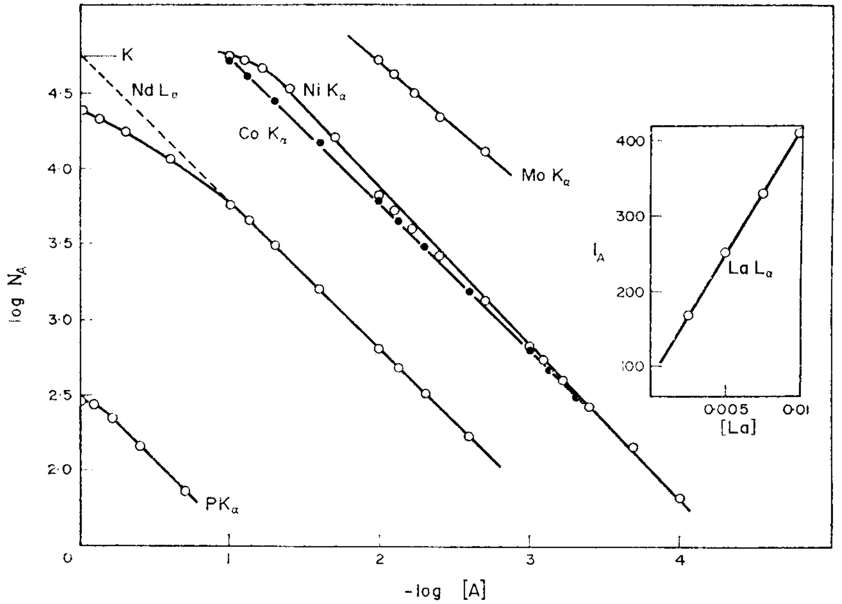
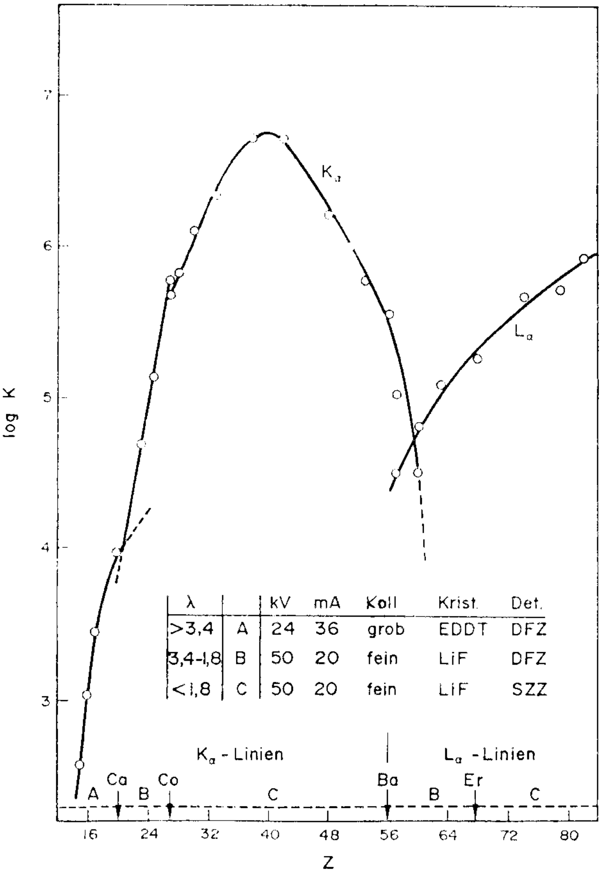


ABB. 3.—Abhängigkeit der Fluoreszenzintensität von der Konzentration für eine bestimmte Linie (K_α oder L_α) des Elementes A.
(N_A = Nettointensität, I_A = Bruttointensität = $N_A + I_A^\circ$, wobei I_A° die Untergrundintensität bedeutet).

ca. 0,1*M*. Diese Regel gilt dann, wenn nur leichte Begleitelemente in der Lösung anwesend sind. Für die Ermittlung der N_A, [A]-Geraden sollten daher Nitrate bzw. Ammonium oder Natrium-Salze eingesetzt werden, je nachdem das zu bestimmende Element als Kation oder Anion vorliegt.

Die Fluoreszenzintensität K für molare Lösungen erhält man durch Extrapolation auf $-\log [A] = 0$. Dieses ist in Abb. 3 für die Neodym L_α-Linie veranschaulicht. Nur wenig schlechtere Werte erhält man mit weniger Aufwand, wenn man ausgehend von einer 0,01*M* Lösung eine Verdünnungsreihe herstellt und die totale Intensität I_A an der Stelle der betreffenden Linie ausmißt. Die Neigung der I_A, [A]-Geraden ergibt dann direkt K. Eine I_A, [A]-Gerade ist in Abb. 3 für die Lanthan L_α-Linie ebenfalls eingezeichnet.

Eine graphische Darstellung von log K in Abhängigkeit der Ordnungszahl Z zeigt Abb. 4. Der ansteigende Teil dieser Kurve ist offensichtlich durch die Zunahme der Fluoreszenzausbeute mit der Ordnungszahl bedingt. Die Kurve erreicht in der Nähe von Silber ein Maximum, da die vor Silber liegenden Elemente durch die K_α-Strahlung der verwendeten Silberröhre sehr intensiv angeregt werden. Nach dem



λ		kV	mA	Koll	Krist.	Det.
>3,4	A	24	36	grob	EDDT	DFZ
3,4-1,8	B	50	20	fein	LiF	DFZ
<1,8	C	50	20	fein	LiF	SZZ

ABB. 4.—Fluoreszenzintensität von molaren Lösungen der Elemente.
A, B und C bedeuten je einen Satz der wählbaren Größen, bzw. Bauelementen des Spektrometers.

Silber sinkt aber K rapide ab, da die Anregung der folgenden Elemente nun mehr einzig durch die Bremsstrahlung der Röhre erfolgt, deren Intensität bei kürzeren Wellenlängen rasch abnimmt. Die K-Kurve würde dann bei Eu den Wert Null erreichen, da die Anregungsenergie von Europium *ca.* 50 keV beträgt. Hat man nur 50 kV maximale Hochspannung zur Verfügung, so kann bei den schweren Elementen nur die L-Schale angeregt werden. Die log K-Kurve für die L_α-Linien steigt wiederum mit zunehmender Ordnungszahl, da die Fluoreszenzausbeute auch für die L_α-Linien mit zunehmender Z größer wird.

Der K-Wert für eine bestimmte Linie hängt natürlich von der Konstruktion (Geometrie) des Spektrometers, von der elektrischen Leistung der Röhre (kV, mA), der Durchlässigkeit des Kollimators (Koll), des Reflexionsvermögens des Analysatorkristalls (Krist) und vom Wirkungsgrad des Detektors (Det) ab. Optimale Versuchsbedingungen hat man dann gewählt, wenn für K ein möglichst hoher Wert resultiert.

Zur Vereinheitlichung der experimentellen Bedingungen wurden drei Sätze A, B und C von wählbaren Größen bzw. Bauelementen des Spektrometers ausgewählt, die in der Tabelle in Abb. 4 angegeben sind. Welcher dieser Sätze jeweils am günstigsten ist—weil er den größten K-Wert liefert—ist auf der Abszisse der Abbildung (Ordnungszahl) angegeben. Die K-Werte der Figur gelten für den betrefenden jeweils günstigsten Satz der experimentellen Bedingungen.

Benötigte Konzentration der Elemente für die quantitative Bestimmung

Um die Stabilität der Meßanordnung zu prüfen, wurde die Impulsrate an der Stelle der Kupfer K_α-Linie für eine $5 \cdot 10^{-4} M$ Kupfersulfat-Lösung in $0{,}1 M$ Schwefelsäure während einer Stunde registriert. Die zeitliche Änderung der mittleren Impulsrate I über je 100 Sekunden ist in Abb. 5 graphisch dargestellt. I zeigt offensichtlich eine kleine Zeitabhängigkeit. Die statistische Auswertung von mehreren solchen Geraden ergab, daß der Meßfehler der Impulszählung mit dem statistischen Fehler abgeschätzt werden kann. Gewöhnlich arbeitet man mit der Zeitvorwahl-Meßtechnik, d.h. man mißt die totale Anzahl Z_{tot} der Impulse, die während der vorgewählten Meßzeit T akkumuliert werden. Die statistische Standardabweichung der Impulsrate I_{A} beträgt:

$$\mathrm{S}(I_{\mathrm{A}}) = (Z_{\mathrm{tot}})^{1/2}/T = (I_{\mathrm{A}}/T)^{1/2} \tag{5}$$

Die Nettoimpulsrate N_{A} für eine bestimmte Strahlung des Elementes A erhält man durch Subtraktion der Untergrundintensität $I_{\mathrm{A}}{}^{\circ}$ von der totalen Intensität I_{A} an der Stelle der betreffenden Linie. Bei verdünnten Lösungen ist $I_{\mathrm{A}}{}^{\circ}$ mit der Streustrahlung am Lösungsmittel identisch. Sie wird daher am einfachsten dadurch ermittelt, daß man die Impulsrate I_{A} an Stelle der betreffenden Linie auch für das Lösungsmittel ermittelt. Die relative Standardabweichung (%) der Nettointensität beträgt nun:

$$(\%) = \frac{\mathrm{S}(N_{\mathrm{A}})}{N_{\mathrm{A}}} \cdot 100 = \frac{(I_{\mathrm{A}}/T + I_{\mathrm{A}}{}^{\circ}/T)^{1/2}}{I_{\mathrm{A}} - I_{\mathrm{A}}{}^{\circ}} \cdot 100 = \frac{[(I_{\mathrm{A}}{}^{\circ} + K[\mathrm{A}])/T + I_{\mathrm{A}}{}^{\circ}/T]^{1/2}}{K[\mathrm{A}]} \cdot 100 \tag{6}$$

Die kleinste erforderliche Konzentration $[\mathrm{A}]_{\mathrm{e}}$ des zu bestimmenden Elementes A kann mit Hilfe von Gleichung 6 für eine bestimmte Meßzeit T und einen bestimmten relativen Fehler (%) abgeschätzt werden. Löst man die Gleichung 6 nach [A] auf,

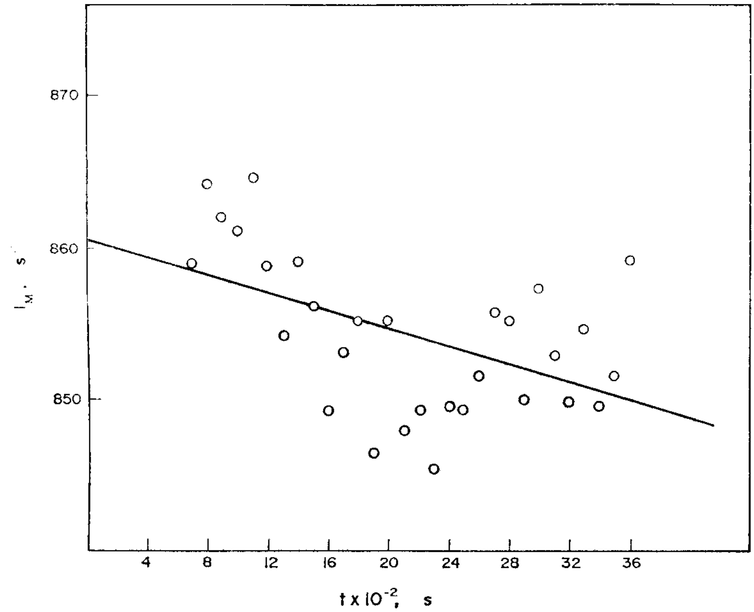


Abb. 5.—Zeitliche Schwankung der Fluoreszenzintensität einer 4,98.$10^{-4}M$ $Cu(NO_3)_2$-Lösung in 0,1M H_2SO_4. I_M bedeutet die mittlere Impulsrate über je 100 Sekunden.

erhält man für $[A]_e$:

$$[A]_e = \frac{5 \cdot 10^3}{(\%)^2 \cdot T \cdot K} + \frac{10^2}{(\%) \cdot T \cdot K}\left(\frac{2{,}5 \cdot 10^3}{(\%)^2} + 2 \cdot T \cdot I_A^{\circ}\right)^{1/2} \tag{7}$$

Die erforderliche Konzentration der Elemente wurde nun nach Gleichung 7 für eine Meßzeit von 100 s und einem Fehler von 0,5% berechnet und in Abb. 6 in Abhängigkeit der Ordnungszahl graphisch dargestellt.

Gemäß dieser Darstellung können die meisten Elemente in einer Konzentration von 0,01M bestimmt werden. Für die leichten Elemente Chlor, Schwefel und Phosphor benötigt man aber unter diesen Bedingungen recht konzentrierte Lösungen. Durch Verlängerung der Meßzeit auf 1000 Sekunden, können auch diese Elemente in einer Konzentration von *ca.* 0,1M bestimmt werden. Eine noch längere Zähldauer wäre sehr unpraktisch und zudem von wenig Nutzen, da der durch die langzeitige Instabilität der Impulszählung verursachte Fehler den statistischen Zählfehler übersteigen würde.

Durch die Anwendung eines Diskriminators wird die Untergrundintensität herabgesetzt. Daher kommt man nach Gleichung 7 für die erforderliche Mindestkonzentration $[A]_e$ kleinere Werte (s. ausgefüllte Kreise in Abb. 6). Den grßöten Gewinn erzielt man für die Arsen K_α-Linie, da hier die Untergrundintensität infolge der Compton Silber K_α-Strahlung in zweiter Ordnung sehr hohe Werte annimmt. Diese störende Strahlung wird durch die Verwendung eines Diskriminators weitgehend unterdrükt. Die Compton Silber K_α-Strahlung in erster Ordnung kann natürlich mit einem Disktriminator nicht unterdrückt werden. Die Bestimmung der Elemente Rhodium, Palladium, Silber und Cadmium (s. Pfeil C in Abb. 6) wird daher durch diese Strahlung erheblich gestört. Bei der Messung mit dem Diskriminator wurde stets eine Einstellung gemäß Gleichung 3 verwendet. In einigen Fällen (wie z.B.

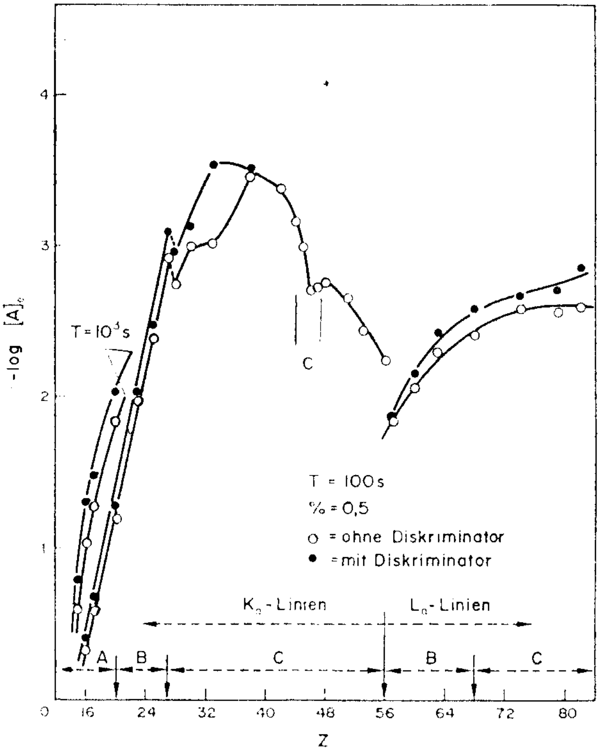


Abb. 6.—Erforderliche Mindestkonzentration $[A]_e$ der Elemente für die quantitative Bestimmung, wenn die statistische Standardabweichung der Nettoimpulsrate bei einer Messzeit T von 100 Sekunden 0,5% nicht übersteigen soll.

Arsen K_α-Linie) könnte man etwas günstigere Zählverhältnisse, durch die Verwendung einer engeren Fensterbreite F des Diskriminators erreichen. Dann würde aber nicht nur $I_A{}^\circ$, sondern auch K für die betreffende Linie eine Funktion der Fensterbreite, sodaß die verschiedenen Elemente miteinander mit Hilfe der Kurven in Abb. 4 und 6 nicht verglichen werden könnten.

Interelementeneffekte in Lösung

Im Vergleich zu festen Proben wird die gegenseitige Störung der Elemente in Lösung stark unterdrückt. Die Nettointensität eines Elementes hängt daher nur wenig und linear von der Konzentration [D] des störenden Elementes D ab. Das ist aus Abb. 7 ersichtlich, wo die Nettointensität für $2 \cdot 10^{-3}M$ Lösungen von Arsen, Selen, Kobalt und Nickel in Abhängigkeit der Konzentration vom störenden Nickel, bzw. Zink graphisch dargestellt ist. Die Geraden N_A wurden durch lineare Regression ermittelt. Ihr Ordinatenabschnitt $N([D] = 0)$, Neigung $n(N)$, sowie die zugehörigen Standardabweichungen $S(N)$, bzw. $S(n)$ sind in Tabelle I zusammengestellt.

Vergleicht man die Neigung $n(N)$ mit ihrer Standardabweichung $S(n)$, so ergibt sich Folgendes: Der Einfluß vom Nickel auf die Fluoreszenzintensität von Arsen und Selen ist nicht vernachlässigbar. Die Abnahme beider Nettointensitäten N_{As} und N_{Se} mit zunehmender Nickel-Konzentation ist hauptsächlich auf die Absorption der Arsen- und Selen-Strahlung durch das Nickel zurückzuführen. Im Falle von Kobalt

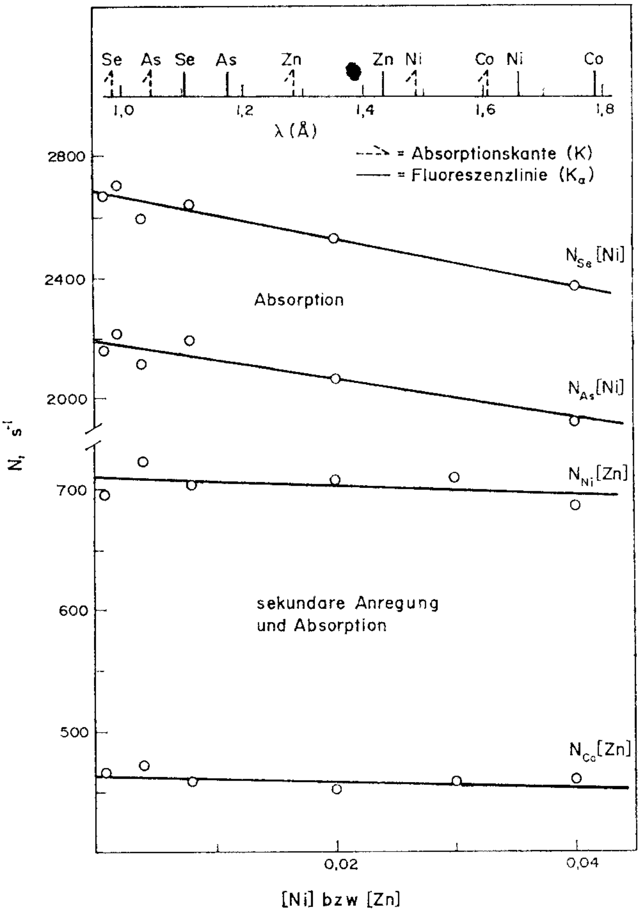


ABB. 7.—Interelementeneffekte in Lösung.
Nettointensität von $2 \cdot 10^{-3}M$ Lösungen der Elemente Se, As, Ni und Co in Abhängigkeit der Konzentration von den störenden Elementen Ni, bzw. Zn.

TABELLE I.—INTERELEMENTENEFFEKTE IN LÖSUNG

No. Meßgröße	A = As	S = Se	A = Co	S = Ni
1. $N([D] = 0)$ (s^{-1})	2195,2	2684,1	462,86	712,05
2. $S(N)$ (s^{-1})	25,5	13,2	3,94	7,10
3. $100.S(N)/N$ (%)	1,07	0,49	0,85	1,00
4. $n(N)$ (s^{-1} $l.mol^{-1}$)	−6516	−7768	−142	−386
5. $S(n)$ (s^{-1} $l.mol^{-1}$)	1260	1085	177	319
6. $k([D] = 0)$	0,8183 ± 0,0033		0,6501 ± 0,0081	
7. $n(k)$ ($l.mol^{-1}$)	−0,105 ± 0,177		+0,162 ± 0,363	
8. $[D]_{kr}$ ($mol/l.$)	$9{,}8 \cdot 10^{-3}$	$3{,}9 \cdot 10^{-3}$	0,224	0,210

Lösung 1: D = Ni	*Lösung 2:* D = Zn
$2 \cdot 10^{-3}M$ H_3AsO_3	$2 \cdot 10^{-3}M$ $Co(NO_3)_2$
$2 \cdot 10^{-3}M$ H_2SeO_3	$2 \cdot 10^{-3}M$ $Ni(NO_3)_2$
$8 \cdot 10^{-4}$–$4 \cdot 10^{-2}M$ $Ni(NO_3)_2$	$8 \cdot 10^{-4}$–$4 \cdot 10^{-2}M$ $Zn(NO_3)_2$
$5 \cdot 10^{-2}M$ $HClO_4$	

und Nickel könnte das zugesetzte Zink die Fluoreszenzstrahlung der beiden erstgenannten Elemente durch sekundäre Anregung erhöhen, da die Wellenlänge der K_α-Strahlung vom Zink kurzwelliger ist, als die Absorptionskante von Kobalt und Nickel (s. Abb. 7). Dieser Effekt konnte jedoch nicht nachgewiesen werden ($|n(N)| \leq \mathrm{S}(n)$). Die Zeile 6 der Tabelle I enthält die Proportionalitätskonstante k der Gleichung 1 für die beiden Elementenpaare. Sie ist innerhalb der Fehlergrenzen auch im Falle des Arsen–Selen-Paares von der Konzentration des störenden Elementes (Nickel) unabhängig ($\mathrm{S}(k) > |n(k)|$). Selen und Arsen können daher gegenseitig als Standardelemente verwendet werden.

Nun wird es möglich, mit Hilfe der Gleichung 8 abzuschätzen, bei welcher Konzentration des Störelementes die Verwendung eines inneren Standards erforderlich ist:

$$[\mathrm{D}]_{\mathrm{kr}} = \frac{2 \cdot \mathrm{S}(N)}{[n(N) + \mathrm{S}(n)]_{\mathrm{min}}} \tag{8}$$

Ist die Konzentration des störenden Elementes D größer als $[\mathrm{D}]_{\mathrm{kr}}$, so sollte die Methode des inneren Standards verwendet werden. Der Faktor 2 in Gleichung 8 berücksichtigt, daß der totale Zählfehler bei der Verwendung eines inneren Standards *ca.* das Doppelte beträgt, da für eine Bestimmung die doppelte Anzahl von Intensitäten gemessen werden muß. Index "min" im Nenner bedeutet Folgendes: Die Neigung $n(N)$ und ihre Standardabweichung $\mathrm{S}(n)$ müssen so summiert werden, daß sie einen minimalen Absolutwert ergeben. Nach Gleichung 8 wurde nun diese kritische Konzentration von Nickel für die Lösung 1 und von Zink für die Lösung 2 berechnet und in der achten Zeile der Tabelle I angegeben.

Im allgemeinen kann der Einfluß eines störenden Elementes vernachlässigt werden, wenn seine Konzentration $5 \cdot 10^{-3} M$ nicht übersteigt. Ein Blick auf Abb. 6 überzeugt davon, daß eine große Anzahl von Elementen ohne inneren Standard bestimmt werden kann, wenn die Elemente als Hauptkomponente der Lösung in einer Konzentration von *ca* $[\mathrm{A}]_{\mathrm{e}}$ vorliegen.

PRAKTISCHE AUSFÜHRUNG DER ANALYSE

Zur Unterdrückung der Interelementeneffekte ist es am besten, möglichst verdünnte Lösungen zu analysieren. Damit aber der Zählfehler einen bestimmten Wert (0,5%) nicht überschreitet, wählt man zweckmäßigerweise die erforderliche Mindestkonzentration. Wie man dabei die Methode des äusseren, bzw. inneren Standardes allgemein anwendet, soll nun beschrieben werden.

(*a*) *Methode des inneren Standardes*

Wie bereits erwähnt worden ist, wählt man für die Bestimmung des Elementes A ein diesem benachbartes Element als inneren Standard S. Die beiden Elemente können dann in etwa gleicher Konzentration vorliegen ($[\mathrm{A}]_{\mathrm{e}} \approx [\mathrm{S}]_{\mathrm{e}}$). Für den Diskriminator kann ebenfalls eine gemeinsame Einstellung nach Gleichung 4 gewählt werden. Die Strahlungen der beiden Elemente dürfen sich gegenseitig nicht stören. Um diese zu prüfen, wird die Proportionalitätskonstante k der Gleichung 1 an zwei Eichlösungen bestimmt. Die Zusammensetzung der Lösungen und die zu messenden Intensitäten sind in der Tabelle II zusammengestellt.

Setzt man nun die bekannten Konzentrationen und ermittelten Nettointensitäten für die beiden Eichlösungen in Gleichung 1 ein, so erhält man zwei Werte für die Proportionalitätskonstante k. Sind diese innerhalb 1% identisch, so sind sie nur mit dem statistisch bedingten Zählfehler behaftet. Mit dem Mittelwert beider Konstanten, den Intensitäten N_{A}, N_{S} und der bekannten Konzentration des Standardelements in der Probelösung [S] erhält man schließlich aus Gleichung 1 die unbekannte Konzentration [A].

Als Lösungsmittel werden vorteilhaft Wasser, 0,1M Schwefelsäure, 0,1M Perchlorsäure und Dimethylformamid (DMF) verwendet. Bei Verwendung von Schwefel- bzw. Perchlorsäure als Lösungsmittel können Schwefel bzw. Chlor für die benachbarten Elemente als innerer Standard

TABELLE II.—ZUSAMMENSETZUNG DER LÖSUNGEN UND MEßGRÖßEN FÜR METHODE *a*

Lösung	Zusammensetzung		Meßgrößen		Nettointensität	
	[A]	[S]			N_A	N_S
0 Lösungsmittel	0	0	$I_A°$	$I_S°$	0	0
1 Eichlösung	1.$[A]_e$	2.$[S]_e$	I_{A1}	I_{S1}	$(I_{A1} - I_A°)$	$(I_{S1} - I_S°)$
2 Eichlösung	2.$[A]_e$	2.$[S]_e$	I_{A2}	I_{S2}	$(I_{A2} - I_A°)$	$(I_{S2} - I_S°)$
x Probelösung	(1-2)$[A]_e$	2.$[S]_e$	I_A	I_S	$(I_A - I_A°)$	$(I_S - I_S°)$

I_A = Intensität am Maximum der Linie vom Element A für eine Lösung dieses Elementes.
$I_A°$ = Intensität am Maximum der Linie vom Element A für das Lösungsmittel.
$N_A = I_A - I_A°$ = Nettointensität des Elementes A.

dienen. Auf die Verwendung von flüchtigen Säuren (Salzsäure, Salpetersäure) wird bei ständigem Gebrauch des Spektrometers am besten verzichtet, damit das dünne Beryllium-Fenster der Röntgenröhre geschont wird.

Feste Substanzen löst man zweckmäßigerweise im betreffenden Lösungsmittel zu einer Konzentration der dreifachen Mindestkonzentration und mischt zur Bestrahlung im Verhältnis von 1:1 mit der Lösung des Standardelementes im gleichen Lösungsmittel, wobei $[S] = 4[S]_e$ betragen soll. Steht wenig Substanz zur Verfügung, kann die Probe auch direkt in der Lösung des Standardelementes gelöst werden. Den prozentualen Gehalt von A in der Substanz erhält man folgendermassen:

$$\% A = \frac{[A] \cdot AG_A \cdot V_A° \cdot V}{E} \cdot 100 \pm 2\% \text{ rel. F} \tag{9}$$

[A] bedeutet hierbei die Konzentration in der bestrahlten Lösung (mMol/ml), die aus Gleichung 1 berechnet wird, AG_A das Atomgewicht des Elementes A, $V_A°$ das Volumen (ml) der Lösung, in welcher die Einwaage E (mg) gelöst wurde und V die Verdünnung beim Mischen der Lösungen von A und S. Das Resultat ist mit einem maximalen Zählfehler von 2% behaftet, welcher etwa dem totalen Fehler dieser Methode entspricht.

Die Methode wurde erfolgreich zur Analyse von Komplexverbindungen eingesetzt. Die folgende Tabelle III zeigt einige Beispiele.

TABELLE III.—ANALYSE VON KOMPLEXVERBINDUNGEN

Zu bestimmendes Element		Standard El.		Lösungsmittel	%A theor	%A gef.
A	in Komplex	S	in			
S	$NiC_{23}H_{34}S_2P_2J_2$	Cl	$HClO_4$	0,1*M* $HClO_4$ in 90%-iger DMF	8,56	8,9
Cl	$ZnC_{18}H_{18}N_4(ClO_4)_2$	S	H_2SO_4	0,1*M* H_2SO_4	12,78	12,0
Zn	$ZnC_{18}H_{18}N_4(ClO_4)_2$	Cu	$CuSO_4 \cdot 5H_2O$	0,1*M* H_2SO_4	11,78	11,4
Cl	$MnC_{26}H_{28}N_6(ClO_4)_2$	S	H_2SO_4	0,1*M* H_2SO_4	10,45	10,2
Br	$CuC_8H_{18}N_6O_2Br_2$	Se	H_3SeO_3	0,1*M* H_2SO_4	35,23	35,3
J	$CoC_6H_{17}N_7O_7J_2$	Ba	$Ba(NO_3)_2$	DMF	45,00	45,1

(*b*) *Methode des äusseren Standards*

Diese wird nur dann angewandt, wenn die Konzentration von störenden Begleitelementen die kritische Konzentration $[D_{kr}]$ nach Gleichung 8 nicht überschreitet. $[D_{kr}]$ muß im allgemeinen nicht bestimmt werden, wenn die Konzentration des störenden Begleitelementes $5 \cdot 10^{-3}M$ nicht übersteigt.

Man mißt die Intensität für die betreffende Linie an drei Lösungen aus, deren Konzentration in der folgenden Tabelle IV angegeben ist.

TABELLE IV.—KONZENTRATION UND MEßGRÖßEN FÜR DIE METHODE *b*

Lösung	[A]	Meßgröße	Ermittelte Größe
O Lösungsmittel	O	$I_A°$	—
E Eichlösung	$[A]_E = 2.[A]_e$	I_{AE}	$K = (I_{AE} - I_A°)/[A]_E$
X Probelösung	$[A]_X = (1-2)[A]_e$	I_{AX}	$[A]_X = (I_{AX} - I_A°)/K$

Man hat experimentell gefunden, daß ein gleichzeitig bestimmter K-Wert ein genaueres Resultat ergibt, als ein im voraus bestimmter K-Wert. Dieses ist eine Folge der langzeitigen Instabilität der Meßanlage, welche durch die Veränderung der Intensität der Röntgenröhre, Änderung des Reflexionsvermögens der Analysatorkristalle und durch Veränderung des Wirkungsgrades des Detektors verursacht wird.

Herrn Prof. G. Schwarzenbach danke ich bestens für sein Interesse an dieser Arbeit und für die Hilfe bei der Vorbereitung des Manuskriptes, sowie der Eidg. Stiftung zur Förderung Schweizerischer Volkswirtschaft durch wissenschaftliche Forschung für finanzielle Unterstützung.

Summary—X-Ray fluorescence spectroscopy has been used for the determination in solution of elements of atomic number greater than 14. Interelement effects have been investigated, and the use of internal (neighbouring element) standards and of external standards has been compared. In dilute solutions (less than $5 \times 10^{-3}M$) matrix effects can be ignored. The sources of error and their effect on the choice of operating conditions and the optimum concentration range are discussed.

Résumé—On a utilisé la spectroscopie de fluorescence aux rayons X pour la détermination en solution d'éléments de nombre atomique plus grand que 14. On a étudié les influences inter-éléments et comparé l'emploi d'étalons internes (élément voisin) et d'étalons externes. En solutions diluées (moins que $5 \times 10^{-3}M$), on peut ignorer les influences de matrice. On discute des sources d'erreur et de leur influence sur le choix des conditions opératoires et du domaine de concentration optimal.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF PALLADIUM BY RADIOACTIVE ISOTOPE-DILUTION ANALYSIS

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Summary—A radioactive isotope-dilution method for the determination of traces of palladium has been developed. It is based on the solvent extraction of palladium dithizonate from acid solution by means of a substoichiometric amount of dithizone in carbon tetrachloride. The separation has been applied to the determination of traces of palladium in platinum, the rocks W-1 and PCC-1 and a biological material (kale). Amounts of palladium down to 3 ng have been determined.

FOLLOWING the success of a neutron-activation method for the determination of traces of palladium involving the substoichiometric separation of palladium diethyldithiocarbamate,[1] it was thought that a radioactive isotope-dilution method using the same kind of separation could be developed. However, the solvent extraction of palladium diethyldithiocarbamate by means of a substoichiometric amount of copper diethyldithiocarbamate in chloroform was found to be unreliable at concentrations lower than $10^{-5}M$ (in the organic phase). This was thought to be due to the reaction of low concentrations of palladium being so slow, even under optimum conditions, that the reagent was decomposed before the reaction was complete. As suggested by Růžička,[2] an alternative reagent for this type of extraction was dithizone, the palladium complex of which is known to have a high extraction constant in chloroform or carbon tetrachloride. Although this reagent was unsuitable for activation analysis (at high concentrations the secondary dithizonate PdDz, where Dz is the dithizonate ion, precipitated), it was expected that at concentrations suitable for isotope-dilution analysis, the secondary complex would either not be formed or if it were, would be soluble.

Where amounts of palladium greater than 1 μg are to be determined, isotope-dilution analysis has little to offer compared with the large variety of spectrophotometric methods available.[3] This work has therefore concentrated on amounts below this level. Isotope-dilution analysis has been applied to the determination of a large number of elements,[4] but no reference can be found to its application to the determination of palladium.

EXPERIMENTAL

Apparatus

Scintillation counter. The detector used for the measurement of the palladium-103 activity was a 76 × 76 mm NaI(Tl) well-type crystal associated with a single channel gamma-ray spectrometer. In all experiments counting was carried out in a 10–50-keV channel, at least 10^4 counts being accumulated in each case.

Reagents

These were prepared from analytical reagent grade chemicals unless otherwise stated.

Unlabelled palladium solutions. A weighed amount of spectrographically standardized palladium sponge was dissolved in *aqua regia*. The resulting solution was evaporated to dryness with hydrochloric acid many times to remove oxides of nitrogen, and finally diluted to give an approximately 0·01*M* solution of palladium chloride in 1*M* hydrochloric acid.

This solution was standardized against $3 \times 10^{-3}M$ EDTA by the back-titration method developed by MacNevin and Kriege.[5] Palladium solutions of lower concentrations were prepared by dilution of this solution.

Labelled palladium solutions. Carrier free palladium-103 as palladium chloride in 1*M* hydrochloric acid (Radiochemical Centre, Amersham, England) had to be treated as follows to ensure that the palladium was in the correct chemical form to enable rapid isotopic equilibration with non-labelled palladium chloride to take place.

The palladium-103 solution was evaporated to dryness, 5 ml of *aqua regia* were added, and the solution was evaporated to dryness, many times, to destroy any organic material. A few ml of hydrochloric acid were added to dissolve the residue, and the solution was diluted to about 200 ml with distilled water and then transferred to a 500-ml separating funnel. To this solution were added 10 ml of a 10% solution of recrystallized sodium diethyldithiocarbamate in water, and the resulting precipitate was extracted by shaking with several successive 5-ml portions of chloroform. The combined chloroform extracts were evaporated to dryness, and the residue was dissolved in *aqua regia* and evaporated to dryness. Three further evaporations with hydrochloric acid were carried out to remove oxides of nitrogen and the residue was dissolved in a few ml of hydrochloric acid. This solution was diluted so that the hydrochloric acid concentration was 1*M* and then used to label the non-active palladium chloride solutions prepared as above.

Dithizone solution. Dithizone was purified by dissolving in chloroform, extracting into ammonia solution, acidifying the separated aqueous layer with hydrochloric acid and re-extracting the precipitate into carbon tetrachloride to form a saturated solution (about $2 \times 10^{-3}M$). The concentration was checked by 100-fold dilution with carbon tetrachloride and measurement of the absorbance at 620 nm in a 10-mm cell against pure carbon tetrachloride. The molar absorptivity at this wavelength[6] is $3{\cdot}28 \times 10^{3}$ l. mole^{-1}. mm^{-1}. Lower concentrations were prepared by dilution of this solution with carbon tetrachloride.

Distilled water. Doubly distilled water obtained from a Scorah Type 4 glass distillation unit (L. V. D. Scorah, 44 Northfield Road, Birmingham 30, England) was used in all experiments.

Development of method

Preliminary experiments. Experiments carried out at fairly high dithizone concentrations (10^{-4}–$10^{-5}M$) indicated that:

(*a*) the substoichiometric extraction of palladium was much faster into carbon tetrachloride than into chloroform;

(*b*) high chloride ion concentrations slowed down the extraction dramatically; therefore hydrochloric acid was an unsuitable medium for the aqueous phase;

(*c*) complexes of dithizone with other metals such as copper, zinc, mercury, bismuth or silver in carbon tetrachloride, either reverted to free dithizone on shaking with an acid aqueous phase, or caused the extraction of palladium to be slower than with the free acid. Therefore such complexes appeared to have little to offer as extraction reagents.

Time to reach extraction equilibrium. At low concentrations the substoichiometric extraction of palladium with dithizone was expected to be slow. Therefore, in order to ascertain the conditions for the most rapid extraction of any given amount of palladium, the effects of variations in the chloride ion concentration, acidity, stoichiometry and reagent concentration were investigated. In all the following experiments the required volume of labelled palladium chloride solution was added to a series of 50-ml separating funnels. The acid and chloride ion concentrations were adjusted as required (see below) with 5*M* sulphuric acid, 1*M* potassium hydroxide and hydrochloric acid to give a final volume of 10 ml. To each was added 5 ml of dithizone solution of the required concentration in carbon tetrachloride, and the funnels were shaken for different lengths of time. The organic phase was filtered and a 3-ml aliquot evaporated to dryness and counted. (This was necessary because chlorinated solvents absorb the low energy palladium-103 radiation).

Chloride ion concentration. The chloride ion concentrations of 1·0-ml portions of $10^{-6}M$ labelled palladium chloride solution in 2·5*M* sulphuric acid were varied from 0·005*M* to 0·1*M*. The dithizone solution concentration was $10^{-7}M$. The results (Fig. 1) show that at concentrations above 0·01*M*, chloride ions slow down the extraction, while at this level and below, the extraction is complete in about 15 min.

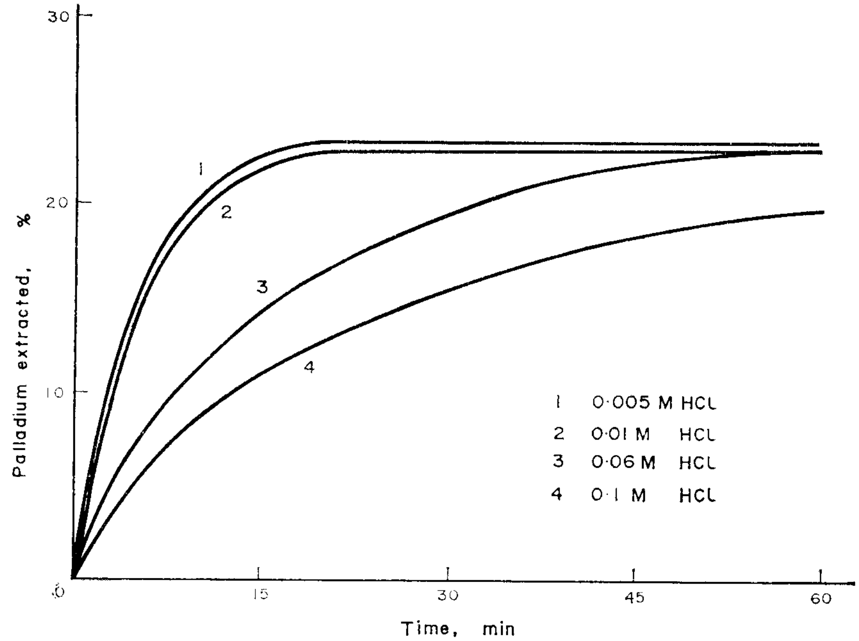

FIG. 1.—Effect of chloride ion concentration on the extraction of palladium with dithizone ($10^{-6}M$ labelled palladium chloride; 2·5*M* sulphuric acid; $10^{-7}M$ dithizone).

Acidity. Using the same labelled palladium chloride and dithizone concentrations as above and a chloride ion concentration of 0·01*M*, experiments were carried out with 0·005*M*, 0·05*M*, 0·5*M* and 5*M* sulphuric acid. The results (Fig. 2) show that the acid concentration has no significant effect on the rate of extraction.

In order to ascertain the effect of high pH values on the extraction, experiments were carried out at the same concentrations as above, with the pH adjusted over a wide range. A constant shaking time of 30 min was used. The results (Fig. 3) show that the extraction is unaffected up to about pH 3, but above this low results were obtained, probably because of kinetic effects.

Stoichiometry. All the previous experiments were carried out at 25% stoichiometry, *i.e.*, sufficient dithizone was present to combine with one quarter of the palladium present, as $Pd(HDz)_2$ (formation of PdDz was not observed). Higher stoichiometry is an advantage as a higher measured activity would be obtained for a given quantity of palladium. But as the conditions approach equivalence the extraction would almost certainly be slower. Using $10^{-7}M$ dithizone, 0·01*M* chloride ion and 0·05*M* sulphuric acid, experiments were carried out with 0·5, 1·0 and 2·0 ml of $10^{-6}M$ labelled palladium chloride solution, *i.e.* 12·5%, 25% and 50% stoichiometry. The results (Fig. 4) show that at 50% stoichiometry the extraction is slow, while at 25% and 12·5% stoichiometry complete extraction occurs in about 15 min. Hence nothing is gained by lowering the stoichiometry.

Reagent concentration. The optimum conditions having been determined for a dithizone concentration of $10^{-7}M$, *i.e.*, chloride ion 0·01*M* or less, acidity from 5*M* sulphuric acid to pH 3, and stoichiometry 25%, it was necessary to determine the effect of reagent concentration on the time needed to reach extraction equilibrium. Experiments were carried out with $10^{-6}M$, $10^{-7}M$ and $10^{-8}M$ dithizone, all at 25% stoichiometry in 0·01*M* chloride ion and 0·05*M* sulphuric acid. The results (Fig. 5) show, as expected, that increasing the reagent concentration increases the rate of extraction.

For all further experiments a shaking time of 30 min was used for dithizone concentrations down to $10^{-7}M$ and a shaking time of 45 min for $10^{-8}M$ dithizone. An experiment was carried out at $10^{-9}M$ dithizone, but the results were too erratic to be meaningful.

Reproducibility

In order to test for substoichiometric reproducibility a series of solutions of 0·01*M* chloride ion and 0·05*M* sulphuric acid containing increasing amounts of labelled palladium chloride solution were extracted for a constant time with 5-ml portions of dithizone solution. Several different dithizone

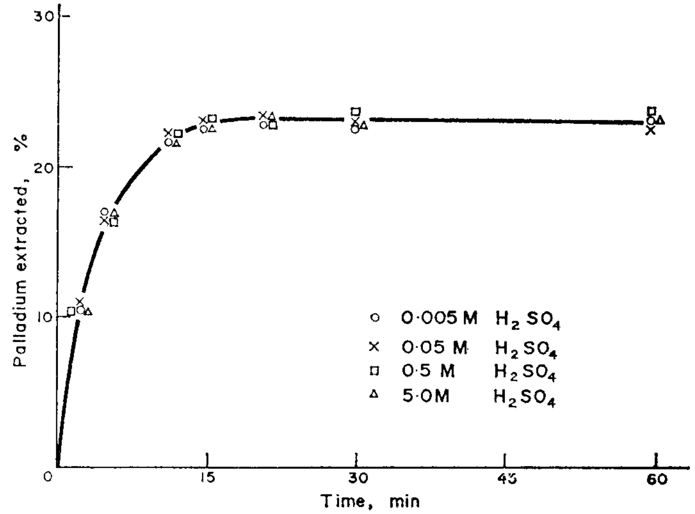

Fig. 2.—Effect of acid concentration on the extraction of palladium with dithizone ($10^{-6}M$ labelled palladium chloride; $10^{-2}M$ chloride; $10^{-7}M$ dithizone).

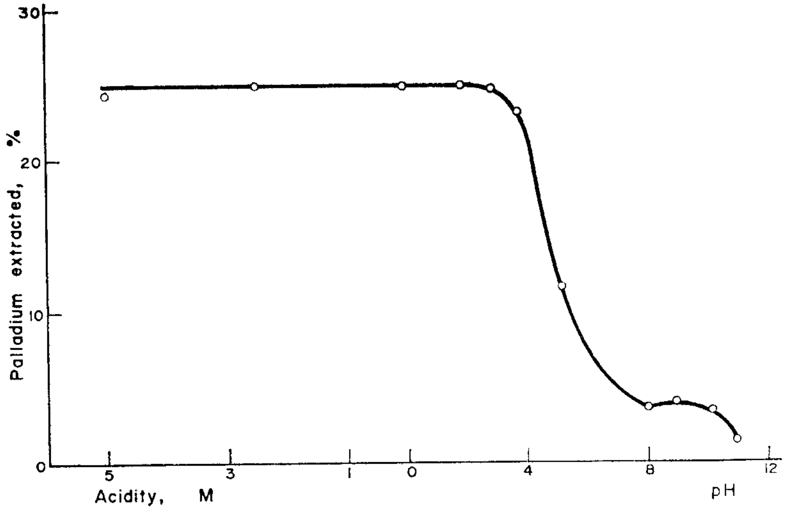

Fig. 3.—Effect of pH on the extraction of palladium with dithizone ($10^{-6}M$ labelled palladium chloride; $10^{-2}M$ chloride; $10^{-7}M$ dithizone; 30 min extraction time).

concentrations were used (Fig. 6). In all cases the reproducibility is good, except near the equivalence point where the reaction has not gone to completion. With $10^{-6}M$ dithizone a slight upward slope indicates that some PdDz formation has occurred. At concentrations below $5 \times 10^{-9}M$, results were not reproducible and less palladium was extracted than had been expected, probably owing to decomposition of the reagent before the reaction was complete. This was not surprising since dilute dithizone solutions decompose fairly rapidly. The approximate half-lives and maximum usable periods (10% decomposition) at various concentrations are given in Table I.

To estimate the precision of the extraction at various reagent concentrations, equal volumes of labelled palladium chloride solution diluted to 10 ml in 0·01*M* chloride ion and 0·05*M* sulphuric acid were extracted for equal lengths of time with 5 ml of dithizone solution at 25% stoichiometry. A 3-ml aliquot of the separated organic phase was evaporated to dryness and counted and the standard deviation of the measured activities calculated. The results are given in Table II.

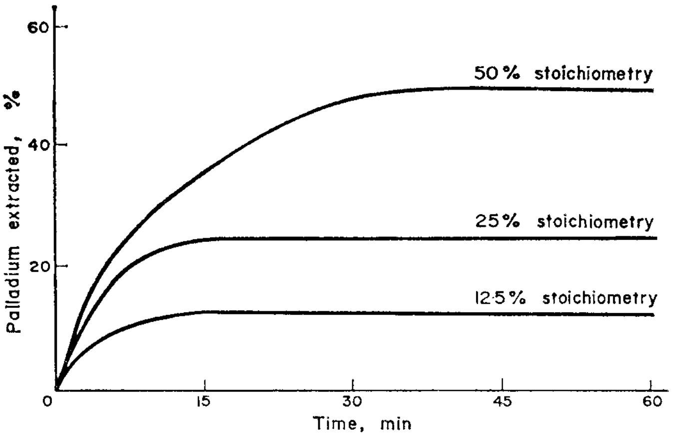

FIG. 4.—Effect of stoichiometry on the extraction of palladium with dithizone ($10^{-7}M$ dithizone; $10^{-2}M$ chloride; $5 \times 10^{-2}M$ sulphuric acid).

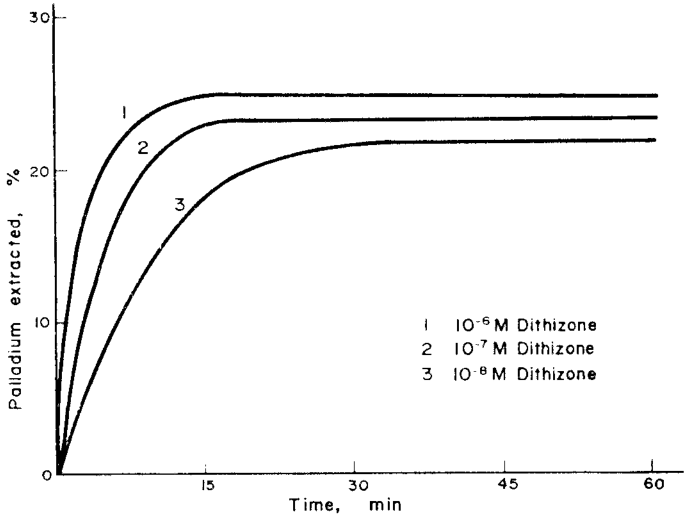

FIG. 5.—Effect of reagent concentration on the extraction of palladium with dithizone ($10^{-2}M$ chloride; $5 \times 10^{-2}M$ sulphuric acid; 25% stoichiometry).

Selectivity

The selectivity of the extraction was examined in the presence of a large number of foreign ions which could be present in test samples. The effect of high concentrations of substances that might be used to dissolve samples was also investigated. The extractions were carried out as in the precision experiments, using $10^{-7}M$ dithizone solution. Foreign ions were usually present in quantities of 1000 μg (*i.e.* a 10000-fold weight excess over the palladium), but if they interfered, lower concentrations were investigated. The foreign ion was considered to interfere if the difference in activities between the sample and a standard in which no foreign ion was present was greater than 4%. The results are given in Table III, and it can be seen that the extraction is very selective. Of the ions which interfered down to a 10-fold excess, mercury and gold were presumed to do so by competing for the dithizone, while cerium(IV) probably oxidized the dithizone. Other strong oxidizing agents might also interfere by the same mechanism.

ANALYSIS OF TEST SAMPLES

The samples tested were: the standard rocks W-1 and PCC-1, a biological material (kale) and a sample of platinum, all of which have previously been analysed for palladium by a substoichiometric neutron-activation analysis method.

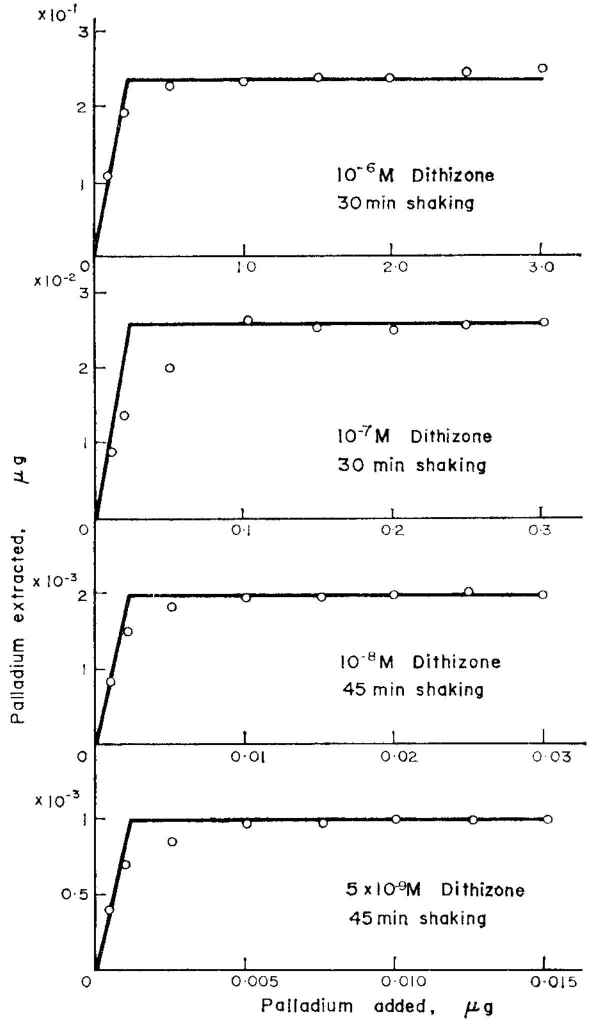

Fig. 6.—Substoichiometric reproducibility of the extraction of palladium with dithizone ($10^{-2}M$ chloride; $5 \times 10^{-2}M$ sulphuric acid).

Dissolution of the platinum posed a problem as it does not readily go into solution except in the presence of a fairly high chloride ion concentration. Therefore, in order to remove the chloride ions, a preliminary separation of the palladium with dimethylglyoxime was carried out. The other samples could be dissolved in the absence of chloride ions, but although a number of different combinations of acids were tried, the results were not sufficiently reproducible to be of value. As the dimethylglyoxime method was successful for the platinum sample, it was decided to use it for the remaining samples.

Procedures

Rocks. To the test sample in a 25-ml Teflon beaker a weight (y) of labelled palladium was added (as labelled palladium chloride solution) approximately equal to the expected weight of palladium in the sample. The matrix was dissolved in a mixture of hydrofluoric (5 ml), hydrochloric (1 ml) and nitric (5 ml) acids. After boiling had reduced the volume to 3–4 ml, 5 ml of *aqua regia* were added and the solution was boiled until no more brown fumes were evolved. The resulting solution was cooled, transferred to a 100-ml separating funnel and diluted to about 50 ml. The addition of 3 ml of a 1% solution of dimethylglyoxime in ethanol to this solution was followed by extraction with two 5-ml

TABLE I

H_2Dz concentration, *M*	Approximate half-life *hr*	Time for 10% decomposition, *hr*
10^{-5}	59	8·5
10^{-6}	12·5	1·9
10^{-7}	1·9	0·3
10^{-8}	1·3	0·2

TABLE II

Weight of palladium present, *μg*	H_2Dz concentration, *M*	Mean activity of extract, $\bar{x}$, *cps*	Standard deviation s^*, *cps*
0·01	10^{-8}	34·9	1·23 (3·5%)
0·1	10^{-7}	77·4	1·08 (1·4%)
1	10^{-6}	90·0	1·22 (1·4%)

$* \; s = \left(\frac{\Sigma(x - \bar{x})^2}{n - 1}\right)^{1/2}$ where x is the activity of an individual extract.

In all cases the number of tests, n, was 8.

TABLE III

Foreign ion present				Foreign ion interfering	
1000 *μg*			100 *μg*	1000 *μg*	100 *μg*
Al(III)	Sb(V)	Sb(III)	Ce(IV)	Ce(IV)	Ce(IV)*
As(V)	As(III)	Ba(II)	Au(III)	Au(III)	Au(III)*
Be(II)	Bi(III)	Cd(II)	Sb(III)	Sb(III)	Hg(I)*
Ca(II)	Ce(IV)	Ce(III)	Ir(IV)	Ir(IV)	Hg(II)*
Cr(III)	Co(II)	Cu(II)	Hg(I)	Hg(I)	
Ga(III)	Ge(IV)	Au(III)	Hg(II)	Hg(II)	
In(III)	K(I)	Na(I)	Nb(V)	Nb(V)	
Ir(IV)	Fe(II)	Fe(III)	Re(VII)	Re(VII)	
Pb(II)	Mg(II)	Mn(II)	Sn(II)	Sn(II)	
Hg(II)	Hg(I)	Mo(VI)	EDTA	EDTA	
Ni(II)	Nb(V)	Os(VI)			
Pr(IV)	Re(VII)	Rh(IV)			
Ru(IV)	Se(VI)	Se(IV)			
Si(IV)	Ag(I)	Sr(II)			
Te(VI)	Te(IV)	Tb(I)			
Th(IV)	Sn(IV)	Sn(II)			
Ti(IV)	Ti(III)	W(VI)			
U(VI)	V(IV)	Zn(II)			
Zr(IV)					
	BO_3^-				
	F^-				
	I^-				
	Cl^-				
	SO_3^{2-}				
	EDTA				
	$CH_3CO_2^-$				
	1*M* Br^-				
	1*M* PO_4^{3-}				
	1*M* ClO_4^-				
	1*M* NO_3^-				
	1*M* SO_4^{2-}				

* These ions did not interfere when 1 *μg* was present.

TABLE IV

Sample	Sample weight, *g*	Palladium standard weight, *μg*	Palladium standard activity, *cps*	Palladium sample activity, *cps*	Palladium found, *ppm*	Mean, *ppm*	Standard deviation, %	Activation analysis results, *ppm*	Results of other authors, *ppm*
W-1*	0·2501	0·108	16·8	15·5	0·036				
	0·2497	0·108	26·9	24·6	0·040				
	0·2510	0·108	26·9	24·5	0·042				
	0·4772	0·108	50·1	42·0	0·044				
	0·5086	0·108	50·1	41·6	0·043				
	0·4987	0·054	35·1	25·4	0·041				
	0·4869	0·054	35·1	26·0	0·039	$4{\cdot}1 \times 10^{-2}$	6·9	$3{\cdot}9 \times 10^{-2}$	$1{\cdot}9 \times 10^{-2}$ (ref. 7)
	0·7549	0·054	42·0	27·2	0·039				$1{\cdot}4 \times 10^{-2}$ (ref. 8)
	0·7408	0·054	42·0	27·0	0·040				
	0·5125	0·027	19·1	11·0	0·039				
	0·7671	0·027	19·1	9·2	0·038				
	0·1001	0·0054	13·0	7·1	0·045				
	0·0944	0·0054	11·1	6·2	0·045				
PCC-1*	0·2512	0·108	24·7	23·2	0·028				
	0·2498	0·108	49·3	46·1	0·030				
	0·2495	0·108	49·3	46·5	0·026				
	0·4932	0·108	50·1	44·7	0·026				
	0·5049	0·108	50·1	45·6	0·021				
	0·4935	0·054	35·1	28·0	0·028				
	0·5013	0·054	35·1	26·8	0·033	$2{\cdot}8 \times 10^{-2}$	11·9	$2{\cdot}9 \times 10^{-2}$	$0{\cdot}7 \times 10^{-2}$ (ref. 8)
	0·7710	0·054	42·0	30·1	0·028				
	0·7548	0·054	42·0	29·0	0·032				
	0·4917	0·027	19·0	12·1	0·031				
	0·7610	0·027	19·0	10·2	0·031				
	0·0868	0·0054	7·3	5·2	0·025				
	0·1061	0·0054	7·3	4·6	0·030				

Kale†	0·2522	0·108	24·7	23·0	0·032				
	0·4792	0·108	50·1	45·0	0·026				
	0·4815	0·108	50·1	44·2	0·030				
	0·4821	0·054	35·1	27·1	0·033	3·2 × 10^{-2}	11·2	2·6 × 10^{-2}	
	0·7499	0·054	42·0	30·1	0·028				
	0·5101	0·027	19·0	11·5	0·034				
	0·7564	0·027	19·0	9·5	0·036				
	0·0895	0·0054	7·3	4·5	0·037				
Pt§	0·0396	0·054	45·8	19·8	1·79				
	0·0384	0·054	45·8	22·0	1·52				
	0·0309	0·054	35·8	17·9	1·75				
	0·0135	0·054	35·8	25·1	1·71				
	0·0593	0·054	20·0	7·1	1·65				
	0·0504	0·054	39·0	16·0	1·54	1·65	4·5	1·29	2·13 (ref. 9)
	0·0499	0·054	25·0	10·1	1·60				
	0·0588	0·054	25·0	8·9	1·66				
	0·0848	0·054	33·0	8·8	1·75				
	0·0685	0·054	33·0	10·8	1·62				
	0·0089	0·0054	7·3	2·0	1·61				

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* Provided by U.S. Geological Survey, Washington, D.C., U.S.A.

† Provided by H. J. M. Bowen, The University, Reading, England.

§ Sample Pt 3 (reference 9) provided by D. F. C. Morris, Brunel University, London, England.

portions of chloroform for about 5 min. The combined extracts were filtered and evaporated to dryness. The residue was dissolved in a mixture of nitric (5 ml) and perchloric (2 ml) acids and the solution boiled until white fumes of perchloric acid were evolved. After dilution of the solution with about 5 ml of distilled water, this procedure was repeated twice more before the final solution was cooled, transferred to a 50-ml separating funnel and diluted to 10–15 ml with distilled water. The palladium was finally extracted by shaking with 5 ml of dithizone solution for 30 or 45 min. The dithizone concentration was such that 25% of y would be consumed. A 3-ml aliquot of the organic phase was evaporated to dryness and counted (A).

For the standard, the same weight of palladium (y) was diluted to 10 ml in 0·05M sulphuric acid, extracted with the same dithizone solution, and the activity of a 3-ml aliquot of the organic phase determined as previously (A_s). The amount of palladium in the sample (x) was calculated according to the substoichiometric isotope-dilution equation

$$x = y\left(\frac{A_s}{A} - 1\right).$$

Kale. Before weighing the kale was dried for 24 hr at 80°. To the test sample in a 150-ml beaker a weight (y) of labelled palladium was added, followed by 5 ml of nitric acid and 5 ml of sulphuric acid. The mixture was heated until charring occurred and then a further 5 ml of nitric acid and 2 ml of perchloric acid were added and the solution was boiled until fumes of perchloric and sulphuric acids were evolved. This procedure was repeated, after dilution with distilled water, until the solution was colourless. The final solution was cooled and the palladium extracted as for the rock samples.

Platinum. To the test sample in a 100-ml beaker a weight of labelled palladium (y) was added, followed by 10 ml of *aqua regia*. The mixture was boiled gently until all the platinum had dissolved, then cooled, and the palladium was extracted as for the rock samples.

Reagent blanks. Known weights of labelled palladium (y) were added to the same quantities of reagents which had been used to dissolve each type of sample. The solutions were then treated in exactly the same way as the samples, the separations carried out and the weight of palladium in the reagents (x) calculated. In all cases no measurable amount of palladium was found.

To check for errors the ratio $x{:}y$ was varied for each sample and various sample weights were taken so that the lower limit of extraction could be checked. The results are given in Table IV.

CONCLUSION

The method has been shown to be capable of determining down to 3 ng of palladium. In our activation analysis method the smallest amount of palladium determined was 10 ng. Although the sensitivity of the activation analysis method could be increased, this appeared to be the limit under normal conditions, and therefore this isotope-dilution method compares very favourably with activation analysis.

The results obtained are in good agreement with our activation analysis results. In the case of the platinum sample it has been brought to our attention[10] that our activation analysis result may be low owing to self-shielding effects which we were unable to investigate because of the small amount of sample available. The large deviation between our results and the result reported by Killick and Morris[9] is attributed to inhomogeneity in the sample.

Although the samples tested contain a large variety of elements, no interference would be expected except from the products of their dissolution. Even with samples which might interfere, *e.g.*, those containing large amounts of mercury and gold, this interference would almost certainly be eliminated by dimethylglyoxime separation. Hence this method should be applicable to any type of matrix.

The conditions of formation of both the primary and secondary palladium dithizonate complexes, encountered in the development of this method, have been investigated and will be reported in a further paper.

Zusammenfassung—Eine radioaktive Isotopenverdünnungsmethode zur Bestimmung von Palladiumspuren wurde entwickelt. Sie beruht auf der Solventextraktion von Palladiumdithizonat aus saurer Lösung mit Hilfe einer unterstöchiometrischen Menge Dithizon in Tetrachlorkohlenstoff. Das Abtrennverfahren wurde auf die Bestimmung von Palladiumspuren in Platin, den Gesteinen W-1 und PCC-1 sowie einem biologischen Material (Kohl) angewandt. Palladiummengen bis herunter zu 3 ng wurden bestimmt.

Résumé—On a élaboré une méthode de dilution par isotope radioactif pour le dosage de traces de palladium. Elle est basée sur l'extraction par solvant du dithizonate de palladium d'une solution acide au moyen d'une quantité substoechiométrique de dithizone en tétrachlorure de carbone. On a appliqué la séparation à la détermination de traces de palladium dans le platine, les roches W-1 et PCC-1 et une matière biologique (chou vert). On a déterminé des quantités de palladium aussi faibles que 3 ng.

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L'UTILISATION DES MEMBRANES POUR L'INDICATION DU POINT D'ÉQUIVALENCE—VI

LA MEMBRANE DE PAPIER-PARCHEMIN IMPRÉGNÉE DE $BaSO_4$ POUR DES TITRAGES ACIDO-BASIQUES EN MILIEU NON AQUEUX

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Résumé—On présente une première tentative d'application de membranes inorganiques, faites de papier parchemin imprégné de précipités alcalinoterreux, comme électrodes indicatrices pour les titrages potentiométriques acide-base en milieux non aqueux. On peut titrer des mélanges d'acides et la marche du titrage est une fonction de la nature du solvant et de l'agent de titrage.

L'utilisation des électrodes-membranes comme électrodes indicatrices s'est de plus en plus développée durant les dernières années. Des membranes des types les plus différents ont trouvé des applications. Nous avons étudié antérieurement[1–4] les possibilités d'application des membranes en papier-parchemin imprégnées de précipités des cations alcalino-terreux au titrage en milieu aqueux des acides et des bases. On a remarqué entre autres, que pour ces types de membranes, la valeur maximale du potentiel de la membrane dépend de la solubilité du précipité formé dans les pores de la membrane: le potentiel croît à mesure que la solubilité du précipité diminue. Cette constatation nous a suggéré l'idée de l'application des électrodes-membranes de ce type à des titrages dans des milieux non aqueux, le fait étant connu que, dans certains milieux, par exemple l'alcool, la solubilité du précipité est diminuée.

A l'exception de l'électrode de verre, considérée comme un type spécial d'électrode-membrane, l'application des membranes à des milieux non aqueux a été, jusqu'à présent, très peu étudiée. Les travaux existants se réfèrent seulement à des membranes de nature organique, obtenues à partir des résines échangeuses d'ions.

Le premier travail paru dans ce domaine, dû à Bergin et Heyn,[5] concerne le comportement électrochimique dans l'ammoniac liquide et l'éthanol anhydre des membranes échangeuses de cations. En mesurant les potentiels de membrane, les auteurs ont établi certaines équations types par lesquelles on peut calculer les concentrations des cations Ag^+ et NH_4^+ dans un mélange de leurs sels, solubilisé en ammoniac liquide.

Gordievski et ses collaborateurs[6] ont montré la possibilité d'utilisation des électrodes-membranes ioniques pour la détermination de la concentration du LiCl dans l'alcool amylique. Ils ont calculé, à l'aide des données sur la répartition du LiCl entre l'eau et la phase organique, les coefficients d'activité du LiCl dans l'alcool amylique.

Les mêmes auteurs[7] ont utilisé pour la première fois les électrodes-membranes comme électrodes indicatrices pour des titrages potentiométriques acido-basiques dans des milieux non aqueux. Ils ont fait des titrages en milieu acide acétique anhydre, en utilisant une membrane cationique homogène. Les courbes obtenues pour le titrage de CH_3COONa 0,025*M* par une solution 0,1*M* de $HClO_4$ ont été comparées à celles obtenues pour les titrages avec l'électrode de verre et l'on constate qu'elles diffèrent fondamentalement. Le titrage de l'acide sulfurique par l'acétate de sodium présente un intérêt pratique. En milieu acétique, l'acide sulfurique est titré seulement comme monobasique.

Gordievski et ses collaborateurs[8] ont également étudié les fonctions d'électrode des membranes cationiques homogènes en méthanol et acétone.

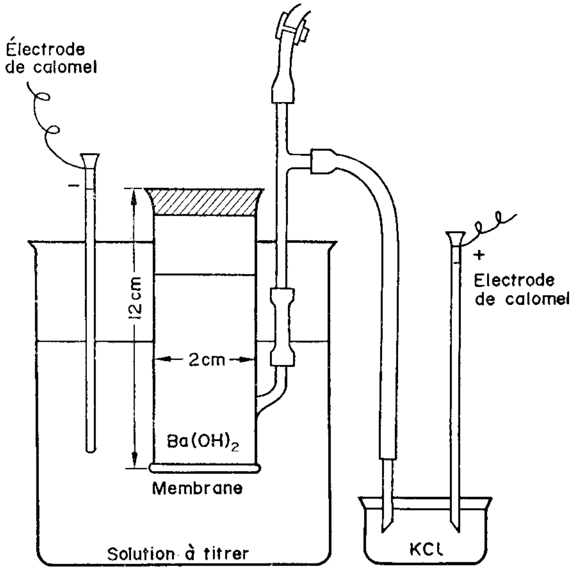

FIG. 1.—Récipient de titrage avec l'électrode indicatrice (la membrane) et l'électrode de référence.

A l'exception de l'électrode de verre, on n'a trouvé aucune indication dans la littérature sur l'utilisation dans des milieux non aqueux d'électrodes-membranes de de nature inorganique.

La première électrode-membrane que nous avons utilisée a été celle de papier-parchemin imprégnée de $BaSO_4$,[9] qui se forme par l'action concomitante de H_2SO_4 0,05*N* et $Ba(OH)_2$ 0,05*N*, situés de part et d'autre de la membrane. Le potentiel de membrane pour ce type de membrane dépend de la différence de pH créée entre les solutions interne et externe (Fig. 1). Un facteur absolument nécessaire pour maintenir les propriétés d'électrode de la membrane est la présence dans la solution externe des ions SO_4^{2-} et dans la solution interne des ions Ba^{2+}.

Considérant ces propriétés caractéristiques de la membrane de papier-parchemin-$BaSO_4$, nous avons pensé qu'elle est indiquée pour le titrage dans des milieux non aqueux de l'acide sulfurique, seul ou en mélange avec d'autres acides inorganiques ou organiques.

La détermination par titrage alcalimétrique de l'acide sulfurique à côté des acides inorganiques ou organiques, présente un grand intérêt pratique. En milieu aqueux, on titre l'acide sulfurique par voie potentiométrique en un stade seulement correspondant à l'acidité totale. Les mélanges d'acide sulfurique et d'autres acides minéraux ou acides organiques communs se comportent de manière similaire; il n'est donc pas possible d'analyser ceux-ci par titrage différentiel dans l'eau.

Plusieurs travaux de la littérature démontrent la possibilité d'exécuter des titrages différentiels des acides en milieu non aqueux ou semi-aqueux.[10–14]

Stuck[12] a effectué des titrages potentiométriques d'acide sulfurique en mélange avec d'autres acides en milieu méthanolique, en utilisant comme électrode indicatrice l'électrode de verre. Il a utilisé comme solutions de titrage une série d'amines, cyclohexylamine, monoéthanolamine, triéthylamine, pipéridine *etc.* Ses déterminations sont basées sur le fait qu'il réussit à titrer en deux stades l'acide sulfurique quand il se trouve seul en solution. En mélange avec d'autres acides minéraux, au premier point d'inflexion on titre l'acide minéral et la première acidité de l'acide sulfurique, le second point d'inflextion devant correspondre à la deuxième acidité de cet acide. Nous avons essayé d'exécuter les mêmes types de titrages en utilisant l'électrode-membrane comme électrode indicatrice.

L'électrode-membrane de papier-parchemin-$BaSO_4$, présente l'avantage d'une préparation très simple; elle ne nécessite pas d'équipement électronique parce qu'elle possède une résistance électrique beaucoup plus petite que l'électrode de verre. On atteint l'équilibre trois minutes au maximum après l'addition du réactif.

En parallèle, les titrages ont aussi été exécutés avec l'électrode de verre à titre de comparaison. Dans les deux cas, on a utilisé comme électrode de référence, l'électrode saturée de calomel (ESC).

En ce qui concerne le procédé de titrage, des précautions spéciales n'ont pas été prises. Tous les titrages ont été exécutés à la température ordinaire.

PARTIE EXPERIMENTALE

Titrage de l'acide sulfurique

La Fig. 2 présente le titrage de l'acide sulfurique 0,2*N* en milieu méthanolique au moyen d'éthanolamine 0,1*N* dans le même solvant. On remarque que, pour le titrage avec l'électrode-membrane, contrairement à celui exécuté avec l'électrode de verre, le saut du potentiel correspondant au premier stade de dissociation est plus petit que celui correspondant au second (Fig. 2).

Si l'on exécute le titrage avec une solution méthanolique de NaOH, on obtient un seul saut, correspondant à l'acidité totale tant dans le cas de l'électrode de verre que dans celui de l'électrode-membrane (Fig. 3).

Titrage de $H_2SO_4 + H_3PO_4$

En présence de l'électrode de verre, le titrage de l'acide phosphorique seul, en milieu méthanolique, ne révèle que la première dissociation si l'on opère avec de l'éthanolamine (en méthanol) (Fig. 4). En exécutant le titrage avec une solution méthanolique de NaOH, on obtient un saut correspondant au titrage de la deuxième acidité (Fig. 4).

En ce qui concerne le titrage du mélange des acides sulfurique et phosphorique, si l'on exécute le titrage avec une solution d'éthanolamine en présence de l'électrode de verre, on obtient un résultat surprenant: on titre seulement l'acidité totale de l'acide sulfurique (Fig. 5).

Dans le même mélange et avec le même agent de titrage, l'électrode-membrane révèle seulement la première dissociation de l'acide sulfurique (Fig. 5). Donc, avec la solution d'éthanolamine nous n'avons pas réussi à titrer ce mélange, bien que dans la littérature,[12] on affirme qu'en utilisant l'électrode de verre le titrage est possible.

Si l'on utilise comme solution de titrage la solution méthanolique de NaOH, en présence de l'électrode de verre, on titre au premier point d'inflexion l'acide sulfurique total, le second point d'inflexion correspondant au titrage de l'acide phosphorique jusqu'à sa deuxième acidité; on a obtenu le même résultat en effectuant le titrage en présence de l'électrode-membrane de papier-parchemin-$BaSO_4$, mais les sauts de potentiel sont plus petits (Fig. 6).

Titrage du mélange $H_2SO_4 + HCl$

Bien que, d'après les données existant dans la littérature,[12] ce titrage exécuté à l'électrode de verre

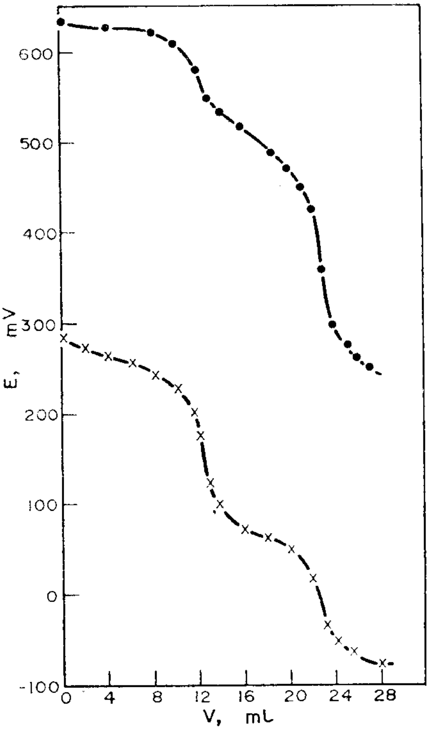

FIG. 2.—Titrage de H_2SO_4 0,2*N* par l'éthanolamine 0,1*N* en méthanol.
-x-x-x- électrode de verre
—·—·— electrode-membrane

et l'éthanolamine se déroule en deux stades, nous n'avons réussi à obtenir qu'un seul saut correspondant au titrage de l'acide chlorhydrique et de la première acidité de l'acide sulfurique. Dans le cas du titrage en présence de l'électrode-membrane, on enregistre aussi un seul saut de potentiel, assez petit, correspondant au titrage HCl + 1/2 H_2SO_4. Ceci s'explique par le fait que la membrane est perméable pour les ions Cl^-, de sorte que le potentiel de membrane diminue graduellement (Fig. 7).

La même situation se présente aussi dans le cas du titrage du mélange H_2SO_4 + $HClO_4$.

Titrage du mélange H_2SO_4 + $H_2C_2O_4$

Comme dans le cas du titrage du mélange H_2SO_4 et H_3PO_4 exécuté en présence de l'électrode de verre par une solution méthanolique d'éthanolamine, on titre seulement l'acide sulfurique en deux stades. Avec l'électrode-membrane on observe seulement le premier stade de dissociation de l'acide sulfurique, donc l'analogie avec le mélange H_2SO_4 + H_3PO_4 se maintient (Fig. 8).

Dans les deux cas, donc, l'acide oxalique ne peut pas être titré.

Si l'on exécute le titrage par la solution méthanolique de NaOH en présence de l'électrode de verre, on obtient deux sauts de potentiel, le premier correspondant aux deux acidités de l'acide sulfurique et le second à une seule acidité de l'acide oxalique (Fig. 9). En exécutant le titrage en présence de l'électrode-membrane, on obtient un résultat différent: le premier saut correspond au titrage des deux acidités de l'acide sulfurique et le second au titrage des deux acidités de l'acide oxalique (Fig. 9).

Etant donné que les sauts du potentiel que nous avons obtenus, surtout dans le cas du titrage avec l'électrode-membrane, étaient assez petits, nous avons cherché à les améliorer, en titrant par des solutions plus concentrées. Mais les résultats n'ont pas été meilleurs. Ainsi, dans le cas du titrage de l'acide sulfurique par de l'éthanolamine, nous avons réussi à accroître les sauts du potentiel, mais la reproductibilité du second saut a été plus faible. Dans le même but, nous avons aussi changé le solvant en utilisant un mélange de solvants comme l'acétone et l'éthylène-glycol (1:2).

Dans le cas du titrage de l'acide sulfurique en solution acétonique par la pipéridine en acétone + éthylèneglycol en présence de l'électrode de verre nous avous obtenu deux sauts nets du potentiel. L'électrode-membrane n'indique aucun saut à cause peut-être de sa perméabilité envers le mélange de solvants.

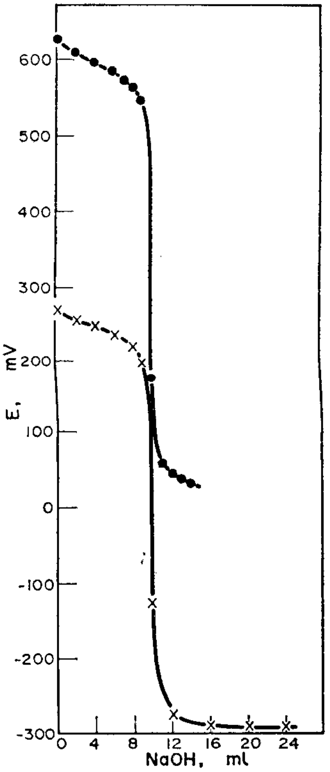

FIG. 3.—Titrage de H_2SO_4 0,2*N* par NaOH 0,2*N* en méthanol.
-×-×-×- électrode de verre
-·-·-×- électrode-membrane

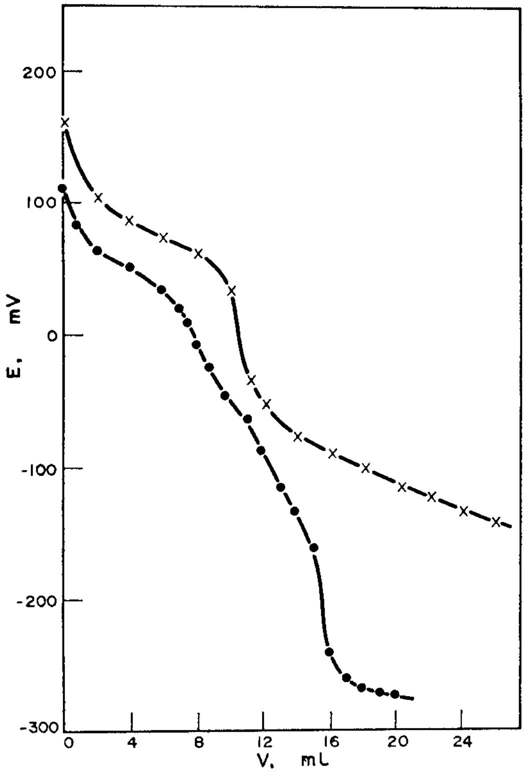

FIG. 4.—Titrage de H_3PO_4 0,1*N* en présence de l'électrode de verre.
-×-×-×- par l'éthanolamine 0,1*N*
-·-·-·- par NaOH 0,2*N*

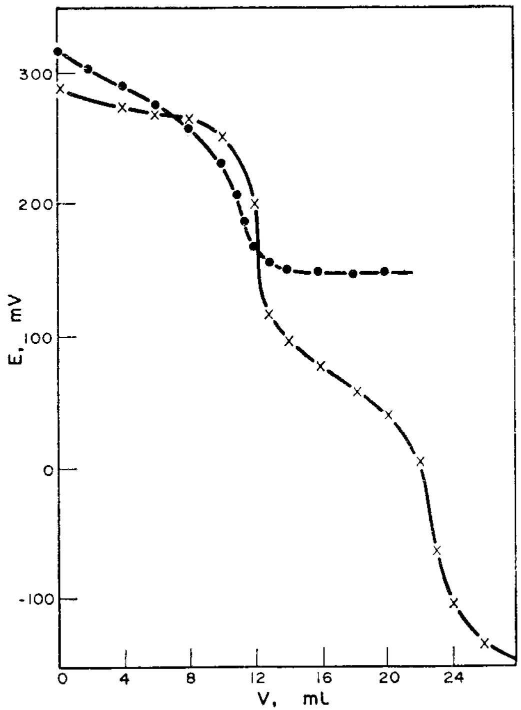

Fig. 5.—Titrage du mélange H_2SO_4 0,2*N* + H_3PO_4 0,1*N* par l'éthanolamine 0,1*N*. (Solvant méthanol).
–×–×–×– électrode de verre
–·—·–·– électrode-membrane

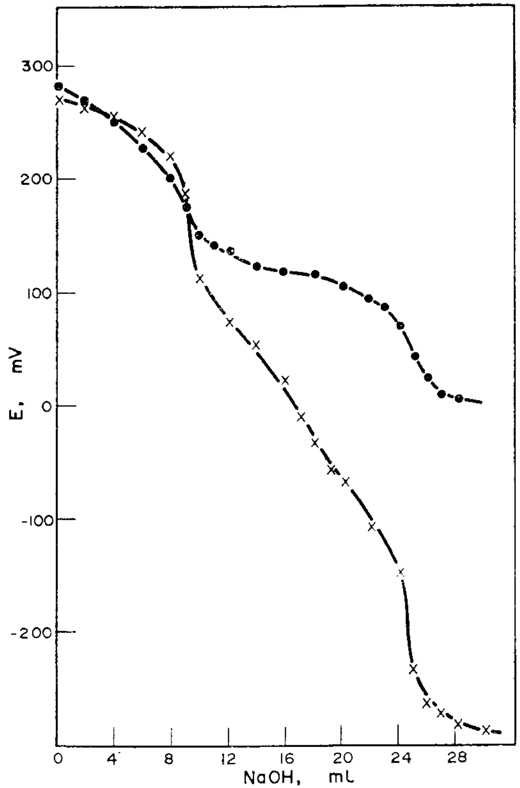

Fig. 6.—Titrage du mélange H_2SO_4 0,2*N* + H_3PO_4 0,1*N* par NaOH 0,2*N*.
–×–×–×– électrode de verre
–·–·–·– électrode-membrane

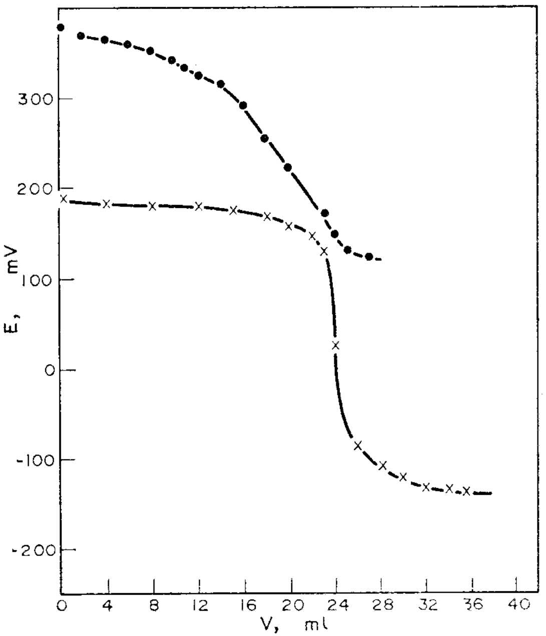

FIG. 7.—Titrage du mélange H_2SO_4 0,2*N* + HCl 0,1*N* par l'éthanolamine 0,1*N*.
-×-×-×- électrode de verre
-·-·-·- électrode membrane

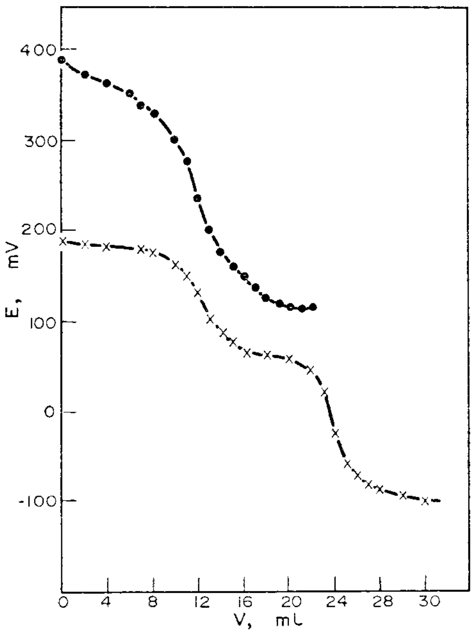

FIG. 8.—Titrage du mélange H_2SO_4 0,2*N* + $H_2C_2O_4$ 0,2*N* par l'éthanolamine 0,1*N*.
-×-×- électrode de verre
-·-·- électrode-membrane

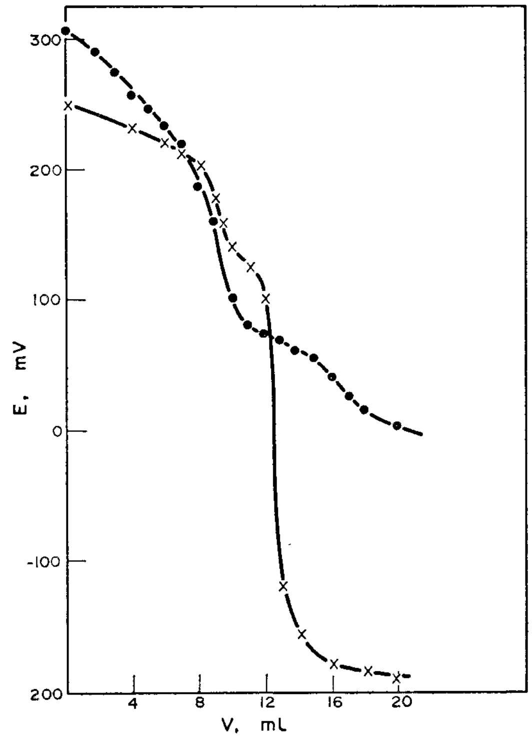

Fig. 9.—Titrage du mélange H_2SO_4 0,2*N* + $H_2C_2O_4$ 0,2*N* par NaOH 0,2*N*.

–×–×– électrode de verre

–·–·– électrode-membrane

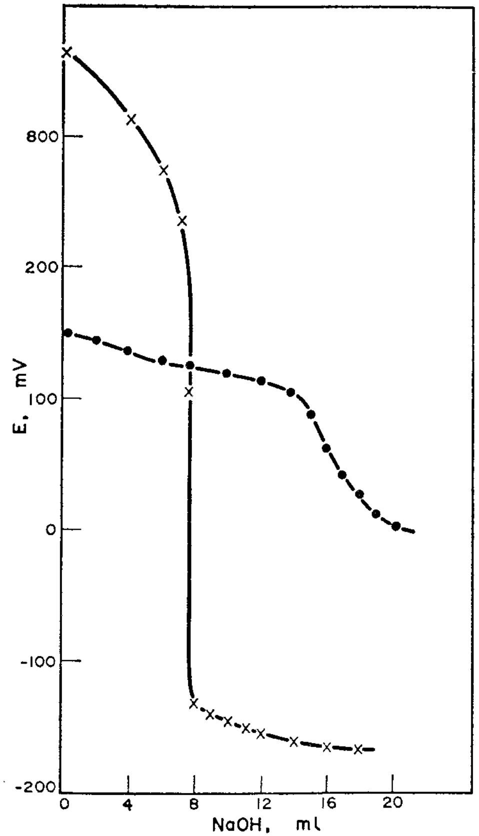

Fig. 10.—Titrage de H_2SO_4 0,2*N* (acétone) par NaOH 0,2*N* (acétone-éthylèneglycol).

–×–×– électrode de verre

–·–·– électrode-membrane

En titrant H_2SO_4 également dissous en acétone par une solution de NaOH (en acétone + éthylèneglycol), et bien que d'après les indications de la littérature[14] on doit obtenir deux sauts du potentiel, on n'en obtient qu'un seul pour l'électrode de verre aussi bien que pour l'électrode-membrane (Fig. 10). Nous spécifions que le saut correspond au titrage de la première acidité pour l'électrode de verre et au titrage total pour l'électrode-membrane.

CONCLUSIONS

(1) On peut utiliser l'électrode-membrane de papier-parchemin-$BaSO_4$, en milieu méthanolique, pour la détermination alcalimétrique par l'éthanolamine de H_2SO_4, des mélanges $H_2SO_4 + H_3PO_4$ et $H_2SO_4 + H_2C_2O_4$; dans le même milieu on peut déterminer, par NaOH en méthanol, H_2SO_4 et les mélanges $H_2SO_4 + H_3PO_4$ et $H_2SO_4 + H_2C_2O_4$.

(2) En milieu éthylèneglycol + acétone on peut déterminer H_2SO_4 par NaOH dans les mêmes solvants.

(3) Par comparaison à l'électrode de verre, pour le même système, l'électrode-membrane de papier-parchemin-$BaSO_4$, présente des comportements semblables ou différents, en le sens que les points d'équivalence correspondent quelquefois à des stades différents de neutralisation, ce qui démontre que dans ces cas une interaction d'un autre type a lieu entre la membrane et les composants de la solution.

Summary—A first attempt to apply inorganic membranes made from parchment paper impregnated with alkaline earth precipitates, as indicating electrodes for potentiometric acid-base titrations in non-aqueous media, is presented. Mixtures of acids can be titrated and the course of the titration is a function of the nature of the solvent and the titrant.

Zusammenfassung—Ein erster Versuch wird mitgeteilt, anorganische Membranen aus mit Erdalkaliniederschlägen getränktem Pergamentpapier als Indikatorelektroden bei potentiometrischen Säure-Basen-Titrationen in nichtwäßrigen Medien einzusetzen. Säuregemische können titriert werden; der Titrationsverlauf hängt vom Lösungsmittel und vom Titranten ab.

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ZWEI NEUE COMPUTERPROGRAMME ZUR BESTIMMUNG VON KOMPLEXBILDUNGSKONSTANTEN AUS POTENTIOMETRISCHEN UND SPEKTROPHOTOMETRISCHEN MESSUNGEN

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Zusammenfassung—VARIAT und SPANA, zwei neue Computerprogramme in FORTRAN V zur Bestimmung von Komplexbildungskonstanten aus potentiometrischen und spektrophotometrischen Messungen, werden beschrieben. Die beiden Programme sind so aufeinander abgestimmt, daß die Rechnung mit denselben Unterprogrammen möglich ist. Es werden verschiedene bei dieser Art von Analyse wichtige Punkte diskutiert und VARIAT wird mit anderen schon bekannten Programmen verglichen. Da die Konvergenz zu den richtigen Gleichgewichtskonstanten mit VARIAT besonders gut ist, genügt es, ohne eine graphische Vorbehandlung der Daten, grob geschätzte Anfangswerte für die Konstanten einzusetzen.

WÄHREND der letzten Jahre untersuchten wir in einer Serie von Arbeiten[1,2,3] verschiedene Systeme, in welchen ein Metallion M mit einem Liganden L in wäßriger Lösung eine größere Zahl von kinetisch labilen Komplextypen der allgemeinen stöchiometrischen Formel $M_aL_cH_z$ bildet. Daneben haben wir auch Gleichgewichtsmessungen in Lösungen durchgeführt, in welchen zwei verschiedene Liganden nebeneinander vorkamen und somit die Möglichkeit bestand, gemischte Komplexe der Formel $M_aL_cL_d'H_z$ zu finden.[4] Die letztgenannten Systeme sind oft so komplex, daß es möglich ist, die gemessenen Werte mit verschiedenen Sätzen von Gleichgewichtskonstanten ungefähr gleich gut zu deuten (vgl. z.B. zitat 5). In einem solchen Fall hilft es manchmal, zusätzlich spektrophotometrische Messungen heranzuziehen und zu prüfen, welche der Möglichkeiten sich durch die Spektren bestätigen läßt.

Bei den schon beschriebenen Systemen[1–4] konnten die Massenwirkungskonstanten nur mit Hilfe eines Digitalcomputers erhalten werden. Die dazu verwendeten Programme (in FORTRAN V) VARIAT (*Variat*ion von Konstanten) und SPANA (*Sp*ektren*ana*lyse) sollen hier beschrieben werden.

Bei der Auswertung von potentiometrischen sowie von spektrophotometrischen Messungen ist es unsere Aufgabe, einen Satz von I unbekannten Parametern $p_i(i = 1, \ldots, I)$ aus einer Serie von M Experimenten $(M \geqslant I)$ mit den Resultaten y_m [Gleichung (1)] zu bestimmen. Die $\alpha_{n,m}$ stellen N

$$y_m = f(\alpha_{n,m}, p_i) \tag{1}$$

weitere gemessene oder sonst bekannte Variablen dar, die zu bestimmenden Parameter p_i z.B. die Komplexbildungskonstanten k_i oder die molaren Extinktionskoeffizienten ε_i.

Als beste Werte für die p_i werden diejenigen betrachtet, für welche die gewogene Quadratsumme QS der Differenzen zwischen experimentellen und berechneten

y_m-Werten zu einem Minimum wird [Gleichung (2)] (Methode der

$$\mathrm{QS} = \mathrm{Min} = \sum_{m=1}^{M} g_m \cdot (y_m - f(\alpha_{n,m}, p_i))^2 \tag{2}$$

kleinsten Quadrate).[6] Für die Gewichte g_m sind die reziproken Varianzen der Werte y_m zu setzen.

Ist (1) eine lineare, explizite Beziehung zwischen y_m und p_i, dann erhalten wir ein System von I linearen Gleichungen, woraus mit Standardmethoden (z.B. Eliminationsverfahren[7] oder Matrixinversionstechnik[8]) die p_i in einem Schritt berechnet werden können. Ein Beispiel für einen linearen Zusammenhang zwischen y_m und p_i ist das Beer-Lambert'sche Gesetz. Das von uns entwickelte Programm SPANA verwendet die Matrixinversionstechnik, um die molaren Absorptionskoeffizienten in einem Gemisch von bis zu 20 Komplexen zu bestimmen.

Ist (1) nicht linear und explizit, dann müssen Iterationsverfahren angewendet werden, wobei über deren Konvergenz im allgemeinen Fall wenig vorausgesagt werden kann. Zwei Methoden sind zur Behandlung solcher Probleme häufig verwendet worden: Die Gaußsche Annäherung der kleinsten Fehlerquadrate[9–12] (im folgenden "Gauß" genannt) und das "Pit-mapping" nach Sillén.[13,14]

Nach "Gauß" wird die Beziehung (1) in eine Taylorreihe entwickelt und diese nach den ersten Ableitungen abgebrochen. Die Ableitungen können auf analytischem oder numerischem Weg erhalten werden. Aus der nun linearen Funktion können die k_i nach einem der oben beschriebenen Verfahren bestimmt werden. Die nach einer Iteration erhaltenen k_i werden ihrerseits als Ausgangswerte verwendet und der Prozess solange wiederholt, bis sich keine weitere Verbesserung mehr erzielen läßt.

"Pit-mapping" geht davon aus, daß QS in der Nähe des Minimums $\mathrm{QS}_{\mathrm{min}}$ die Gestalt eines $(I + 1)$-dimensionalen Paraboloids hat. Nach Haas *et al.*[11] kann deshalb (2) in der Nähe des Minimums in eine Taylorreihe entwickelt werden, die man nach dem dritten Glied abbricht. Sillén selbst[12] verwendet allerdings nicht die Differentialquotienten sondern die Differenzenquotienten, indem er die Konstanten um größere Beträge variiert und die Koeffizienten aus $1/2(I + 1)(I + 2)$ Werten von QS bestimmt. Nullsetzen der partiellen Ableitungen führt auch hier zu einem System linearer Gleichungen, welches am besten durch Matrixinversion gelöst werden kann.

Das Programm VARIAT

Das Programm VARIAT erlaubt die Berechnung von Massenwirkungskonstanten von Partikeln der allgemeinen Zusammensetzung $\mathrm{M}_a\mathrm{M}_b'\mathrm{L}_c\mathrm{L}_d'\mathrm{H}_z$($a, b, c, d \geqslant 0$; $z > 0$ für protonierte Komplexe, $z < 0$ für Hydroxokomplexe) aus potentiometrisch erhaltenen Titrationskurven. Es können bis zu 60 Punkte aus höchstens 10 verschiedenen Titrationskurven in einem einzelnen Problem verarbeitet werden. Als beste Konstanten werden diejenigen betrachtet, für welche die Quadratsumme QS der relativen Differenzen (bezogen auf den Äquivalenzpunkt EQ) zwischen experimentellem (OH) und berechnetem (OHB) Basenverbrauch zu einem Minimum wird [Gleichung (3)]. Über Unterschiede in den Gewichten sind keine

$$\mathrm{QS} = \mathrm{Min} = \sum_{M=1}^{m} \left(\frac{\mathrm{OH}_m - \mathrm{OHB}_m}{\mathrm{EQ}} \right)^2 \tag{3}$$

begründeten Aussagen möglich (vgl. zitate[11,12]), sie werden deshalballe gleich 1 gesetzt.

Das Programm wurde hauptsächlich dazu entwickelt, uns von der graphischen Vorbestimmung der Massenwirkungskonstanten freizumachen, denn dies braucht gewöhnlich vielmal mehr Zeit als die endgültige Auswertung mit Hilfe eines Digitalcomputers. Dafür ist es notwendig, daß die Konvergenz zum Minimum QS_{Min} auch bei größeren Abweichungen der geschätzten Konstanten von den richtigen Werten befriedigend ist. Wir dürfen die Funktion (1) nicht in eine Reihe entwickeln und nur einige Terme davon berücksichtigen, wie das in der unmittelbaren Nähe des Minimums möglich ist, sondern wir müssen die nicht lineare Gesamtfunktion und ein "trial and error" Verfahren verwenden. Um eine möglichst gute Konvergenz zu erhalten, wird die Annäherung der Massenwirkungskonstanten zunächst an kleineren Abschnitten einer Titrationskurve durchgeführt. Diese meistens aus 4–8 Titrationspunkten bestehenden Gebiete sind vom Programmbenützer so zu definieren, daß die in einem solchen Gebiet berechnete Quadratsumme auf Variationen dieser Konstanten besonders empfindlich ist. Sinngemäß sind getrennte oder überlappende Gebiete zu wählen, je nachdem ob die entsprechenden Komplexe in getrennten oder überlappenden Pufferzonen gebildet werden. Zur Definition der Gebiete können eine einzige oder mehrere Kurven herangezogen werden. Man erreicht so eine rasche Konvergenz zum Minimum und die Rechenzeit wird stark verkürzt.

VARIAT besteht aus einem fixen Teil, dem Hauptprogramm mit einer Serie von Hilfsprogrammen, und aus einem variablen Teil, dem Unterprogramm.

Das Hauptprogramm

Nach einigen Transformationen der Eingabegrößen wird mit den geschätzten Konstanten die Fehlerquadratsumme QS_1 (3) für das erste Gebiet G_1 berechnet. Anschließend wird k_1 mit einem vorgewählten Variationsfaktor VF_1 (gewöhnlich 1,2–2,0) multipliziert und das entsprechende QS_1' erhalten. Tritt Verbesserung ein ($QS_1' < QS_1$), dann wird k_1 weiter vergrößert, bis QS_1 bei $QS_{1,0}$ ein Minimum durchläuft (Abb. 1*b*). Damit nicht infolge eines zu klein gewählten Variationsfaktors allzuviele Iterationen durchgeführt werden müssen, wird nach drei Verbesserungen der Faktor automatisch vergrößert. Auf diese Weise sind selten mehr als fünf Iterationsschritte notwendig. Ist umgekehrt QS_1' nach der ersten Multiplikation größer als QS_1, dann wird k_1 durch VF_1 dividiert und darauf nach demselben Verfahren weiter verkleinert, bis das Minimum $QS_{1,0}$ erreicht ist. Mit dem so gefundenen Wert $k_{1,0}$ wird analog im Gebiet G_2 die Konstante k_2 angeglichen, usw., bis alle Konstanten der Reihe nach durchgerechnet sind. Ist der Variationsfaktor einer Konstanten gleich 1 gesetzt, so wird dieselbe nicht variiert. Die Berechnung bis zu diesem Punkt nennen wir einen "Durchgang". Die Faktoren werden nun alle verkleinert und ein neuer Durchgang mit der Berechnung von QS_1 gestartet. Dies wird fortgesetzt, bis die Zahl der Durchgänge einen festgesetzten Wert (gewöhnlich 4–6) erreicht hat. Jetzt werden die Gebiete G_i für alle Konstanten über das ganze experimentelle Material definiert und die einzelnen Fehlerquadratsummen QS_i werden durch eine einzige, QS, ersetzt.

Die Konstanten werden nun weiter variiert und QS verkleinert, bis die Rechnung aus einem der folgenden Gründe beendet ist:

(*a*) Die im Programm definierte maximale Zahl Durchgänge ist erreicht.

(*b*) QS ließ sich während eines ganzen Durchganges mit allen Kurvenpunkten nicht oder um weniger als 0,01 % verbessern und alle Variationsfaktoren haben den minimalen Wert VF_{min} erreicht. Die stete Bedingung $VF_i \geqslant VF_{min}$ sorgt dafür, daß die Verbesserungen nicht durch einen zu kleinen Variationsfaktor limitiert werden. Nach Ausgabe der Endresultate ist die Maschine zur Lösung einer neuen Aufgabe bereit, bis die definierte Zahl an Problemen erreicht ist.

Die Hilfsprogramme

Zu VARIAT gehören sieben Hilfsprogramme, LIGAND, QUADR, CUBIC, NEWRAP, MATIN, NULL und SUB76, welche die im Unterprogramm auftretenden Probleme zu lösen helfen.

LIGAND berechnet den Basenverbrauch einer mehrbasischen Säure LH_n in Abhängigkeit vom pH. QUADR liefert die Wurzel einer quadratischen, CUBIC diejenige einer kubischen Gleichung in X, mit der Einschränkung $0 < X \leqslant XMAX$. NEWRAP dient zur Bestimmung von zwei Variablen nach dem Newton-Raphson-Verfahren. MATIN errechnet die Lösungen eines Systemes von bis zu vier Gleichungen mit bis zu vier Unbekannten, wobei die Subroutinen NULL (Nullsetzen einer Reihe von Koeffizienten vor der eigentlichen Rechnung) und SUB76 (Inversion einer 4×4 Matrix) zur Anwendung kommen.

Das Unterprogramm

Das Unterprogramm dient zur Berechnung des Basenverbrauchs aus den Titrationsdaten und den geschätzten Konstanten mit Hilfe einer geeigneten Beziehung. Es wäre prinzipiell möglich, diese Gleichung so allgemein zu halten, daß alle Probleme mit demselben Unterprogramm gelöst werden können, doch scheint uns ein solches Vorgehen nicht optimal (vgl. Diskussion). Wir haben somit versucht, das Unterprogramm so weit zu vereinfachen, daß man es innerhalb kürzester Zeit aufstellen kann, wobei aber die Möglichkeit zur unabhängigen Konstantenwahl gewährt bleißt.

Ist die Titrationskurve eines Liganden auszuwerten, so besteht die ganze Subroutine darin, daß das Hilfsprogramm LIGAND aufgerufen wird. Bei der Titration eines Gemisches, das ein Metallion und einen Liganden enthält, ist das Gleichungssystem (4–7) zu lösen, wobei

$$\mathrm{CL_E} - \mathrm{CL_B} = \mathrm{CL_E} - \sum_j c_j [\mathrm{M}_a\mathrm{L}_c\mathrm{H}_z]_j = \mathrm{CL_E} - f(k_j, [\mathrm{M}], [\mathrm{LH}_i]) \tag{4}$$

$$\mathrm{CM_E} - \mathrm{CM_B} = \mathrm{CM_E} - \sum_j a_j [\mathrm{M}_a\mathrm{L}_c\mathrm{H}_z]_j = \mathrm{CM_E} - g(k_j, [\mathrm{M}], [\mathrm{LH}_i]) \tag{5}$$

$$\mathrm{CH} = \sum_j z_j [\mathrm{M}_a\mathrm{L}_c\mathrm{H}_z]_j + [\mathrm{H}] - [\mathrm{OH}^-] = h(k_j, [\mathrm{M}], [\mathrm{LH}_i]) \tag{6}$$

$$\mathrm{OHB} = \mathrm{EQ} \cdot \left(1 - \frac{\mathrm{CH}}{Z \cdot \mathrm{CL_B}}\right) \tag{7}$$

z die maximale Protonenzahl, die freigesetzt werden kann, CM und CL die totalen Konzentrationen des Metallions bzw. des Liganden und die Indices E und B experimentell bzw. berechnet bedeuten. Aus den Gleichungen (4)–(6) müssen die Parameter $[\mathrm{LH}_i]$, [M] und CH eliminiert werden. Das geschieht zweckmässigerweise so,daß man $[\mathrm{LH}_i]$ und [M] aus (4) und (5) bestimmt, damit aus (6) CH erhält und diesen Wert in (7) einsetzt. Gilt für alle Partikeln $\mathrm{M}_a\mathrm{L}_c\mathrm{H}_z$ $a \leqslant 1$ und $c \leqslant 2$ dann empfiehlt es sich, [M] aus (4) zu eliminieren und das Resultat in (5) einzusetzen. Für $a_{max} = 1$

und $c_{\max} = 1$ erhält man eine quadratische, für $a_{\max} = 1$ und $c_{\max} = 2$ (oder umgekehrt) eine kubische Gleichung. Diese haben eine einzige physikalisch sinnvolle Wurzel $0 < [\mathrm{LH}_i] \leqslant \mathrm{CL_E}$ und können direkt gelöst werden. Im Unterprogramm müssen wir nur die Koeffizienten der quadratischen bzw. kubischen Gleichung definieren und anschließend die entsprechenden Hilfssubroutinen aufrufen. Dabei können alle Gleichgewichtskonstanten beliebig definiert werden.

Im allgemeinen Fall können die Lösungen von (4) und (5) nach Umformen auf (8) und (9) gefunden werden. Es genügt, im Unterprogramm

$$\mathrm{CL_E} - \mathrm{TY} \cdot [\mathrm{LH}_i] - \sum_I \sum_J J \cdot \mathrm{T}(I, J) \cdot [\mathrm{M}]^I \cdot [\mathrm{LH}_i]^J = 0 \tag{8}$$

$$\mathrm{CM_E} - \mathrm{TX} \cdot [\mathrm{M}] - \sum_I \sum_J I \cdot \mathrm{T}(I, J) \cdot [\mathrm{M}]^I \cdot [\mathrm{LH}_i]^J = 0 \tag{9}$$

die Größen TX, TY und $\mathrm{T}(I, J)$ zu definieren, die Hilfssubroutine NEWRAP liefert die Lösung für [M] und $[\mathrm{LH}_i]$. $\mathrm{TX} \cdot [\mathrm{M}]$ und $\mathrm{TY} \cdot [\mathrm{LH}_i]$ berücksichtigen alle hydroxylierten bzw. protonierten Formen des Metallions resp. des nicht komplex gebundenen Liganden. In $\mathrm{T}(I, J) \cdot [\mathrm{M}]^I \cdot [\mathrm{LH}_i]^J$ sind alle Partikeln, die das Metallion und den Liganden im Verhältnis $I{:}J$ enthalten, zusammengefaßt.

Für Gemische mit zwei verschiedenen Metallionen und/oder Liganden, haben wir ein System von drei oder vier Gleichungen zum Darstellen der Totalkonzentrationen [vgl. (8) bzw. (9)]. Um die Funktionen aufzubauen, müssen wiederum die entsprechenden Koeffizienten im Unterprogramm definiert werden. Durch das Hilfsprogramm MATIN erhält man die Lösung dieses Gleichungssystems mit Hilfe einer Matrixinversionstechnik. Sind die Partikelkonzentrationen bekannt, so läßt sich mit Hilfe von zwei zu (6) und (7) analogen Gleichungen CH und OHB berechnen.

Im zweiten Teil des Unterprogrammes werden die molaren Konzentrationen der einzelnen Partikeln ermittelt. Interne Steuerung sorgt dafür, daß dies nur am Ende der Berechnung mit den endgültigen Konstanten geschieht.

Das Programm SPANA

SPANA berechnet aus Extinktionsmessungen die molaren Extinktionskoeffizienten ε_i von Komplexen, die nebeneinander in Lösung vorliegen. Die besten Werte ε_i erhält man bei der Bestimmung des Minimums der Funktion (10).

$$\mathrm{QS} = \sum_m (\mathrm{E}_m - \sum_i \varepsilon_i \cdot c_{i,m} \cdot d_m)^2 \tag{10}$$

Die für die Berechnung notwendigen Komplexkonzentrationen $c_{i,m}$ werden aus den Totalkonzentrationen und den Gleichgewichtskonstanten durch das gleiche Unterprogramm geliefert, das mit VARIAT zur Auswertung der Titrationskurve verwendet wurde. Danach werden die Matrixelemente errechnet, und die ε_i durch Inversion einer 20 × 20 Matrix (SUB 760) bestimmt. Wird, bedingt durch die Meßungenauigkeit, ein ε-Wert negativ, so setzt ihn der Computer gleich Null und führt die gesamte Rechnung nochmals durch. Nachdem die ε_i an einer Wellenlänge ermittelt worden sind, wird das gleiche Problem bei der nächsten Wellenlänge gelöst, bis man das ganze Spektrum erhalten hat.

Aus früheren Messungen bekannte ε-Werte können direkt eingegeben und bei der Berechnung berücksichtigt werden.

DISKUSSION

Unsere Programme VARIAT und SPANA erlauben die Analyse von Systemen, in welchen Komplexe der allgemeinen Zusammensetzung $M_aM_b'L_cL_d'H_z$ nebeneinander auftreten. Die Unterteilung von VARIAT und SPANA in ein Hauptprogramm, in ein Unterprogramm und in eine Serie von Hilfsprogrammen ist besonders vorteilhaft, da das Aufstellen des flexiblen Unterprogramms sich so ohne große Arbeit durchführen läßt, indem nur einige Koeffizienten definiert werden müssen.

Es wäre prinzipiell möglich, das Unterprogramm zur Berechnung der Partikelkonzentrationen so allgemein zu halten, daß alle Probleme damit gelöst werden können (vgl. z.B. zitate[15,16]), doch glauben wir nicht, daß dies sehr günstig ist, denn in einer allgemein gültigen Beziehung können die Konstanten nicht so unabhängig wie möglich voneinander definiert werden. Bei starker Korrelation wird gewöhnlich die Konvergenz nicht aufgehoben, jedoch die Zahl der notwendigen Iterationen gewaltig gesteigert und damit die Rechenzeit verlängert, es sei denn, die Auswirkungen der Korrelation werden durch eine zusätzliche Hilfsrechnung abgeschwächt.[14]

TABELLE I.—KONVERGENZ DER KONSTANTEN pk_2 AM BEISPIEL VON Cu^{2+} UND *N*-(2-DIMETHYLAMINOÄTHYL)-OXAMID[3]

Anzahl Durchgänge	pk_2 (A)	pk_2' (B)
0	−1,50	7,00
1	−0,46	6,07
2	−0,30	5,72
3	−0,37	5,59
5	−0,38	5,43
7	−0,38	5,41
10	−0,38	5,39

Im Fall A ist k_2 als Bruttokonstante ($k_2 = [M] \cdot [LH_3]/([H] \cdot [MLH_2])$), im Fall B als Einzelkonstante ($k_2' = [H] \cdot [MLH_2]/[MLH_3]$) definiert.

Tabelle I illustriert dies am Beispiel der Komplexbildung von Cu^{2+} mit *N*-(2-Dimethylaminoäthyl)-oxamid (ODA),[3] wobei gleichzeitig fünf Gleichgewichtskonstanten zu bestimmen sind. In (A) entspricht k_2 einer Bruttokonstanten ($k_2 = [M] \cdot [LH_3]/[H] \cdot [MLH_2]$), in (B) ist k_2' als Einzeldissoziationskonstante definiert ($k_2' = [H] \cdot [MLH_2]/[MLH_3]$). Im Falle (A) ist der endgültige Wert von k_2 nach drei Durchgängen praktisch erreicht, weitere Iterationen sind nur noch gelegentlich notwendig. Im Falle (B) ist auch nach zehn Durchgängen die Iteration noch nicht ganz abgeschlossen.

Zur Wahl der vernünftigen Definition einer Konstanten gilt folgender Grundsatz: Konstanten sollen so definiert werden,daß die Partikeln, aus denen der Komplex formal entsteht, in möglichst großer Konzentration vorliegen. Im Falle von ODA tritt MLH_3 in unseren Versuchen zu maximal 8% auf, sodaß es richtig ist, die Partikeln MLH_2 direkt aus M und LH_3 entstehen zu lassen (Bruttokonstante).

Verschiedene Autoren[13,17] weisen darauf hin, daß schon gute Näherungswerte nötig sind, damit mit Pit-Mapping Konvergenz zu den richtigen Parametern erzielt werden kann. Wenn wir die zu Beginn der Rechnung eingesetzten Konstanten nur ungenau kennen, besitzt die Quadratsumme (2) nicht mehr die Form eines mehrdimensionalen Paraboloids, wie das in Abb. 1*a* für $I = 1$ dargestellt ist. Sie muß durch die in Abb. 1*b* eingezeichnete Kurve wiedergegeben werden, denn bei großer Entfernung vom Minimum hat eine Veränderung der Konstanten keinen wesentlichen Einfluß mehr auf QS. Nach Pit-mapping kann nur 1*a* berechnet werden. Die in Abb. 1*b* eingetragenen Punkte liefern Parameter für eine kopfstehende Parabel, sodaß k_i im Laufe der Iterationen nicht dem besten Wert $k_{i,0}$ sondern den Werten $+\infty$ oder 0 zustrebt.

Als Ausweg bleibt die Möglichkeit, ein mehrdimensionales Netz von Konstantenkombinationen zu definieren und die Fehlerquadratsumme QS für jeden so bestimmten Punkt zu berechnen. Ist das Netz genügend fein, dann werden sicher ein oder mehrere Punkte im Hauptminimum liegen, anschließend können die besten Konstanten nach der Sillénschen Methode erhalten werden, wie dies von Leussing[18] beschrieben wurde. Die Dimension dieses Netzes ist gleich der Zahl der zu bestimmenden Konstanten, und wie leicht einzusehen, nimmt damit der Rechenaufwand exponentiell mit der Zahl der Parameter zu. Im Gegensatz dazu wächst dieser mit VARIAT sowie der Gausschen Methode in erster Näherung nur linear. Es läßt sich abschätzen, daß eine Berechnung nach[18] für ein System mit 7 Konstanten (wie in zitat 2) etwa 10^4 mal mehr Iterationen erfordern dürfte als die übrigen Verfahren und deshalb praktisch nur für relativ einfache Gleichgewichte in Frage kommt.

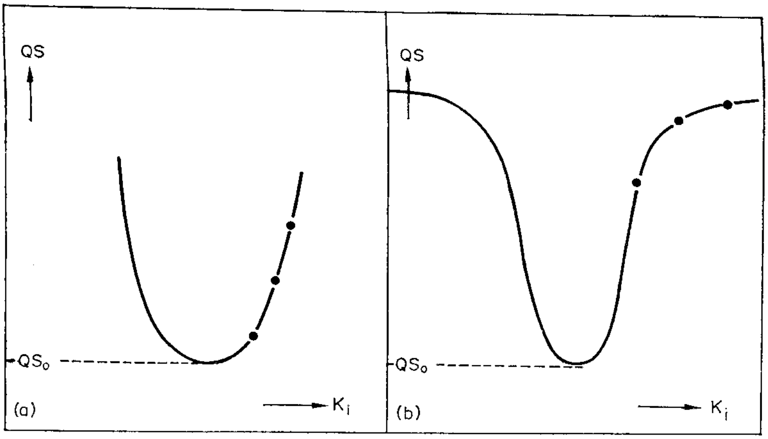

Abb. 1.—Quadratsumme QS als Funktion einer Konstanten k_i. (*a*) stellt einen Ausschnitt von (*b*) in der Nähe des Minimums QS_0 dar. Mit Pit-Mapping kann nur (*a*) berechnet werden, während SCOGS und VARIAT auch mit den in (*b*) eingezeichneten Punkten konvergieren.

Es ist hingegen schwierig vorauszusagen, wie gut die Konvergenz im Fall der Gausschen Näherung ist. Es lag deshalb nahe, die Arbeitsweise des kürzlich von Sayce[16] entwickelten und auf diesem Verfahren beruhenden Programmes SCOGS, das wie VARIAT die Bestimmung von Gleichgewichtskonstanten aus pH-Titrationskurven erlaubt, mit VARIAT zu vergleichen. Am Beispiel der Komplexbildung von Cu^{2+} und Diaminopropionsäure[19] waren die Konvergenzbedingungen für beide Programme sehr ähnlich, je nach Konstantenkombination tritt Divergenz bei Schätzungsfehlern von 0,7 bis 2,5 logarithmischen Einheiten auf.*

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* Die entsprechenden Messdaten sowie eine Kopie des Programms SCOGS wurden uns freundlicherweise von Prof. D. Perrin zur Verfügung gestellt.

Als Zweites untersuchten wir die Konvergenzbedingungen am System Cu^{2+}/N-(Dimethylaminoäthyl)-oxamid.[3] Dabei zeigte sich zunächst, daß mit SCOGS überhaupt keine Konvergenz der Partikelkonzentrationen erreicht wurde, wenn man zur Bestimmung der Konzentrationen mit dem für beliebige Probleme gültigen Unterprogramm COGSNR rechnet. Wir verwendeten deshalb SCOGS in Kombination mit einem speziellen Unterprogramm, das ähnlich wie die Unterprogramme von VARIAT von uns aufgestellt, aber natürlich an SCOGS angepaßt wurde.

Mit schon guten Anfangswerten der Konstanten ließen sich keine wesentlichen Unterschiede in den Resultaten und in der Rechenzeit feststellen (Tabelle II). Eine UNIVAC 1108 benötigte für beide Programme zwischen 8 und 10 Sekunden. Gehen wir jedoch von Näherungswerten aus, wie sie ohne graphische Vorbehandlung der Daten aus den Titrationskurven direkt abgeschätzt werden können, dann erhalten wir mit SCOGS keine oder nur äußerst langsame Konvergenz zu den richtigen Werten. VARIAT hingegen liefert auf Anhieb und mit fast derselben Rechenzeit das Endresultat (Tabelle II).

TABELLE II.—VERGLEICH ZWISCHEN SCOGS[16] UND VARIAT IN DER KONVERGENZ AM BEISPIEL DER KOMPLEXBILDUNG VON Cu^{2+} MIT N-(DIMETHYLAMINOÄTHYL)-OXAMID[3]

	gute Anfangswerte	Endwerte SCOGS	Endwerte VARIAT	schlechte Anfangswerte	Endwerte SCOGS	Endwerte VARIAT
pk_1	4,3	4,70	4,62	5,5	4,66*	4,62
pk_2	−0,4	−0,38	−0,38	−1,5	−0,33	−0,38
pk_3	8,4	8,44	8,44	9,0	13,92	8,45
pk_4	10,3	10,28	10,28	11,0	7,50	10,28
pk_5	2,9	2,99	2,97	3,5	5,84	2,97
ST		0,18%	0,175%		8,6%*	0,175%

Die Konstanten k_i sind wie folgt definiert: $k_1 = [M] \cdot [LH_3]/[MLH_3]$, $k_2 = [M] \cdot [LH_3]/([MLH_2] \cdot [H])$, $k_3 = [H] \cdot [MLH]/[MLH_2]$, $k_4 = [H] \cdot [ML]/[MLH]$ und $k_5 = [MLH_2] \cdot [MLH]/[M_2L_2H_3]$

* Endwerte und Standardabweichung ST nach 5 Zyklen.

Es scheint vielleicht ein Schönheitsfehler, daß VARIAT im Gegensatz zu SCOGS und anderen Programmen, die auf dem Gausschen Verfahren oder auf dem Pit-Mapping beruhen, keine direkte Angaben über die Genauigkeit der Massenwirkungskonstanten liefert. Ein Vergleich der mit SCOGS errechneten Standardabweichungen mit solchen die durch mehrfaches Wiederholen der Experimente erhalten wurden, zeigte jedoch, daß die ersteren bis viermal kleiner sind als aufgrund der Reproduzierbarkeit der Messungen zu erwarten wäre (vgl. auch zitat 20). Somit kann der durch Matrixinversion erhaltenen Standardabweichung keine allzu große Bedeutung zugeordnet werden und ein solches Verfahren liefert nicht mehr wesentliche Information als VARIAT.

Für unsere Zwecke interessiert eigentlich weniger die Standardabweichung der Konstanten, sondern die Genauigkeit, mit welcher die einzelnen Partikelkonzentrationen bekannt sind. Wie leicht abzuleiten ist, gilt in erster Näherung (11), d.h. der maximale

$$\sigma[M_aM_b'L_cL_d'H_z]_{\max} = \frac{Z \cdot \sigma_{OH}}{z \cdot EQ} \tag{11}$$

prozentuale Anteil ist bis auf einen bekannten Faktor Z/z für jede Partikel gleich genau bestimmt. Aus (11) folgt auch ein Kriterium zur Ausscheidung von Konstanten: Partikeln, deren maximale Konzentration nicht wesentlich größer als

$\sigma[M_aM_b'L_cL_d'H_z]_{max}$ ist, können nicht mit Sicherheit identifiziert werden und die entsprechenden Konstanten sind zu eliminieren. σ_{OH}/EQ liegt für eine sauber aufgenommene und gut erklärte Titrationskurve zwischen $1 \cdot 10^{-3}$ und $5 \cdot 10^{-3}$, d.h. Partikeln, deren Bildungsgrad nie mehr als *ca.* 1% beträgt, können nicht mit Sicherheit nachgewiesen werden.

Zusammenfassend können wir sagen, daß VARIAT und SPANA leistungsfähige und vielseitige Programme zur mathematischen Analyse von Komplexgleichgewichten darstellen. Im Gegensatz zu den in der Literatur beschriebenen Programmen ist man beim Arbeiten mit VARIAT auf keinerlei graphische Vorbehandlung der experimentellen Daten angewiesen. Mit dem Aufkommen immer rascherer Computer ist dies ein wesentlicher Punkt, da die reine Rechenzeit gewöhnlich nur noch eine untergeordnete Rolle spielt. Die Konvergenz ist sowohl bei überlappenden als auch bei getrennten Puffergebieten gut und rasch, wobei das von Sayce[16] beschriebene Programm SCOGS nur im ersten Fall als gleichwertig anzusehen ist. Dies liegt allerdings wohl weniger am Aufbau der entsprechenden Hauptprogramme sondern daran, daß wir mit VARIAT zur Berechnung der Partikelkonzentration flexible Unterprogramme verwenden. Das für die Spektrenanalyse entwickelte Programm SPANA ist so auf VARIAT abgestimmt, daß mit den gleichen Unterprogrammen gerechnet werden kann.

Eine genaue Bedienungsanleitung sowie ein Beispiel für die Eingabedaten mit der zugehörigen Berechnung kann von den Autoren erhalten werden.

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Summary—VARIAT and SPANA, two new computer programs in FORTRAN V for the calculation of complex stability constants from potentiometric and spectrophotometric data are oiscussed. The two programs were set up in a way that allows computation with the same set of subroutines. Several important points in this kind of analysis are discussed and VARIAT is compared with other computational methods. Because of the good convergence of VARIAT the starting values of the stability constants may merely be guessed, without preliminary graphical treatment of the data.

Résumé—VARIAT et SPANA, deux programmes d'ordinateur pour la détermination des constantes de stabilité des complexes métalliques à partir de mesures potentiométriques et spectrophotométriques, sont décrits. Les deux programmes furent accordés à fin, de permettre le calcul avec les memes sous-programmes. Différents aspects dans ce type d'analyse sont discutés et VARIAT est comparé avec d'autres programmes, précédemment décrits. Grâce à une très bonn convergence du VARIAT il suffit d'estimer les valeurs initiales des constantes sans qu'un traitement graphique préalable des données soit récessaire

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Das Hauptprogramm VARIAT

```
C     VARIAT
      DOUBLE PRECISION  S(20),C(20),U(20),HA,CV
      COMMON C,S,U,HA,CM,CMA,CL,CLA,EQ,MI,ND,WK,OHB,NKO
      DIMENSION  PH1(61),OH1(61),FA(60),HA1(60),CL2(60),CM2(60),EQ2(60),
     1CL01(11),CM01(11),EQ1(11),NPPK(11),SU(11),MA(100),J1(60),PK(20)
     2,CL02(11),CM02(11),S1(21),A(21),D(20),CL1(60),CM1(60)
     3,PH2(60),SU1(60)
    1 FORMAT(I2)
    2 FORMAT(38H VARIAT, KOMPLEXBILDUNGSKONSTANTEN AUS,20H PH-TITRATIONS
     1KURVEN)
    3 FORMAT (49H                                                 )
    4 FORMAT(1H//)
    5 FORMAT(2I2,3F6.3)
    6 FORMAT(           1X,I2,18H EINZELVARIATIONEN,4X,
     1 10H VOLUMEN =,F7.3,5X, 29H MINIMALER VARIATIONSFAKTOR =,F6.3,
     25X,6H PKW =,F6.3//)
    7 FORMAT(6E10.0)
   10 FORMAT(2E10.0)
   13 FORMAT(1X,I2,7X,4(E10.3,7X),F8.4,8X,I2,12X,F6.3)
   14 FORMAT(4H0NR.,5X,12H TOT. MET. 1,5X,12H TOT. MET. 2,5X,12H TOT. LI
     1G. 1,5X,12H TOT. LIG. 2,5X,
     212H AEQUIV.PKT.,4X,10HANZAHL KP.,4X,3H SU)
   17 FORMAT (45H0GLEICHGEWICHTSKONSTANTEN DES FREIEN LIGANDEN )
   21 FORMAT (36I2)
   22 FORMAT(F7.3)
   23 FORMAT (42H0GESCHAETZTE KONSTANTEN VARIATIONSFAKTOREN,1X,12HUND BE
     1REICHE)
   24 FORMAT(10(F7.3,1X)/10(F7.3,1X))
   25 FORMAT(48H0BERECHNETE KONSTANTEN  UND   VARIATIONSFAKTOREN,37X,8H
     1QUADSUM,4X,9H STANDABW)
   41 FORMAT(4H M =,I2,10X,14H KONSTANTE NR.,I2)
   54 FORMAT(1H+,78X,2(3X,E10.3))
   65 FORMAT(1H1)
   66 FORMAT(17H0BESTE KONSTANTEN,67X,8H QUADSUM,4X,10H STANDABW.)
   67 FORMAT(1H0,7X,15HTITRATIONSKURVE,40X,23H VERTEILUNGSKURVE      //)
   68 FORMAT(40H KUNR  KP    PH        OH       OHB   DELT,
     149HA    M  L  H    M  L  H    M  L  H    M  L  H ,
     230H    M  L  H    M  L  H      )
   69 FORMAT(36X,5HALPHA,5X,6(2(I2,1X),I2,4X)/)
   74 FORMAT(1H0,44X,47HM  L  H     M  L  H     M  L  H     M  L  H     ,
     120H M  L  H    M  L  H)
   75 FORMAT(46X,6(I2,1X,I2,1X,I2,4X)/)
   77 FORMAT (1H /)
   80 FORMAT(1X,I2,4X,I2,1X,F7.3,1X,3(1X,F7.4),2X,6(E10.3,2X))
   83 FORMAT(44X,6(E10.3,2X))
   94 FORMAT(15H DATEN NICHT OK)
   97 FORMAT(16H ZU VIELE KURVEN)
   99 FORMAT(22H ZU VIELE KURVENPUNKTE)
  107 FORMAT(20H ZU VIELE KONSTANTEN)
  108 FORMAT(I4)
  109 FORMAT(1X,10(I2,1H-,I2,3X)/1X,10(I2,1H-,I2,3X))
C     EINLESEN UND DARSTELLEN DER DATEN
      NP1=0
      READ 1,NP
      PRINT 2
      PRINT 4
```

```
   88 READ 3
      PRINT 3
      READ 3
      PRINT 3
      PRINT 4
      READ 5,NPAR,NEIN,VOL,VFMIN,PKW
      PRINT 6,     NEIN,VOL,VFMIN,PKW
      PRINT 4
      PRINT 14
      PKW=-PKW
      WK=10.**PKW
      NKH=1
      NKO=1
      NK=1
      NKP=1
      READ 1,ITEST
      IF(ITEST)93,61,93
   93 PRINT 94
      GO TO 87
   61 NPP=1
      READ 7,CMO1(NK),CMO2(NK),CLO1(NK),CLO2(NK),EQ1(NK),SU(NK)
      IF(EQ1(NK)) 9,9,8
    8 READ 10,PH1(NKP),OH1(NKP)
      IF(PH1(NKP))11,12,11
   11 NKP=NKP+1
      NPP=NPP+1
      GO TO 8
   12 NPP=NPP-1
      PRINT 13,NK,CMO1(NK),CMO2(NK),CLO1(NK),CLO2(NK),EQ1(NK),NPP,SU(NK)
      NPPK(NK)=NPP
      NK=NK+1
      IF(NK-11) 61,61,96
   96 PRINT 97
      GO TO 87
    9 PRINT 4
      NK=NK-1
  104 READ 22,S1(NKH)
      IF(S1(NKH))103,102,103
  103 NKH=NKH+1
      GO TO 104
  102 NKH=NKH-1
      IF(NKH-1) 15,16,16
   16 PRINT 17
      PRINT24,(S1(J),J=1,NKH)
   15 READ 22,A(NKO)
      IF(A(NKO))105,106,105
  105 NKO=NKO+1
      GO TO 15
  106 NKO=NKO-1
      IF(NKO-20) 100,100,101
  101 PRINT 107
      GO TO 87
  100 READ 22,(D(J),J=1,NKO)
      NPAR3=3*NPAR
      NKO2=2*NKO
      READ 21,(MA(J),J=1,NPAR3)
      READ 21,(J1(K),K=1,NKO2)
```

```
      READ 108,ITEST
      IF(ITEST)93,95,93
   95 PRINT 4
      PRINT 23
      PRINT24,(A(J),J=1,NKO)
      PRINT24,(D(J),J=1,NKO)
      PRINT 109,(J1(2*J-1),J1(2*J),J=1,NKO)
      PRINT 4
      PRINT 25
C     UMWANDLUNG DER EINGABEGROESSEN
      J=1
      DO 26 K=1,NK
      NPP=NPPK(K)
      DO 27 NPP1=1,NPP
      FA(J)=VOL/(VOL+OH1(J))
      PH2(J)=-PH1(J)
      HA1(J)=10.**PH2(J)
      CL1(J)=CLO1(K)*FA(J)
      CL2(J)=CLO2(K)*FA(J)
      CM1(J)=CMO1(K)*FA(J)
      CM2(J)=CMO2(K)*FA(J)
      EQ2(J)=EQ1(K)
      SU1(J)=SU(K)
   27 J=J+1
      IF(J-61) 26,26,98
   98 PRINT 99
      GO TO 87
   26 CONTINUE
      NKP=J-1
      DO 20 J=1,NKH
      S1(J)=-S1(J)
   20 S(J)=10.**S1(J)
      NKV=0
      DO 28 J=1,NKO
      A(J)=-A(J)
      IF(D(J)-1.)89,28,89
   89 NKV=NKV+1
   28 C(J)=10.**A(J)
C SETZEN DER INDICES FUER RECHNUNG
      ND=1
      NK=1
      NGES =0
      NPP=NPPK(NK)
C     ERSTE KONSTANTE EINZELVARIATIONEN
   56 NE=0
      QE=0.
      NG=J1(1)
      NG1=J1(2)
C     ERSTE KONSTANTE GESAMTGEBIET
   59 QC1=99E 30
   63 NVK=1
C     ZWEITE UND NAECHSTE KONSTANTEN
   49 CV=C(NVK)
      VF=D(NVK)
      IF(NGES) 90,90,91
   91 CV=CV*VF
   90 QE1=0.
```

```
      NE1=0
      IF(VF-1.) 32,30,32
C     VARIATION E I N E R  KONSTANTEN
   32 NVF=1
      NE1=NG1-NG+1
      DO 33 NI=1,20
      QC=0.
      MI=1
C     BERECHNUNG E I N E R  QUADRATSUMME
      DO 34 J=NG,NG1
      C(NVK)=CV
      CM=CM1(J)
      CMA=CM2(J)
      CL=CL1(J)
      CLA=CL2(J)
      EQ=EQ2(J)
      HA=HA1(J)
      CALL SUB
      OHB=OHB+SU1(J)
      DELTA=(OH1(J)-OHB)/EQ
      QC=QC+DELTA*DELTA
      IF(ND-30) 34,34,35
   34  CONTINUE
C     BESTIMMT OB QC IN E I N E R BESTIMMTEN RICHTUNG VERBESSERT WERDEN
      IF(QC1-QC)36,36,37
C     VERBESSERUNG DER QUADRATSUMME
   37 QC1=QC
      QE1=QC1
      NVF=NVF+1
      IF(NVF-4) 33,33,38
   38 NVF=1
      IF(VF-1.)39,33,40
   40 VF=1.+3.*(VF-1.)
      GO TO 33
   39 VF=1./(1.+3.*(1./VF-1.))
   33 CV=CV*VF
      NI=20
      PRINT 4
      PRINT 41,NI,NVK
      PRINT 4
C     UNTERSUCHT OB DIE RICHTUNG UMZUKEHREN SEI
   36 IF(NI-2) 42,42,30
   42 IF(VF-1.)30,30,43
   43 VF=1./VF
      CV=CV*VF*VF
      GO TO 32
   30 CV=CV/VF
C     ERHOEHT NUMMER DER ZU VARIIERENDEN KONSTANTEN
      IF(VF-1.)44,45,45
   44 VF=1./VF
   45 C(NVK)=CV
      D(NVK)=VF
      NVK=NVK+1
C     ENTSCHEIDET OB LETZTE KONSTANTE ODER NICHT
      IF(NVK-NKO)46,46,47
C     ENTSCHEIDET OB EINZELGEBIETE ODER GANZE KURVE
   46 IF(ND-NEIN)46,46,92
```

```
      92 NGES=1
         GO TO 49
 C       EINZELKONSTANTE
      48 QE=QE+QE1
         NE=NE+NE1
         NG=J1(2*NVK-1)
         NG1=J1(2*NVK)
         QC1=.99E30
         GO TO 49
 C       LETZTE KONSTANTE
      47 ND=ND+1
         DO50 J=1,NKO
      50 PK(J)=-LOG10(C(J))
         IF(ND-NEIN-1)51,51,52
      51 QC1=QE+QE1
         R=NE-NKV+NE1
         GO TO 53
      52 R=NKP-NKV
      53 PRINT 24,(PK(J),J=1,NKO)
         ST = SQRT(QC1/R)
         PRINT 54,QC1,ST
         PRINT24,(D(J),J=1,NKO)
         PRINT 4
         DO 55 J=1,NKO
         D(J)=1.+(D(J)-1.)/3.
         IF(D(J)-1.) 55,55,31
      31 IF(D(J)-VFMIN) 29,55,55
      29 D(J)=VFMIN
      55 CONTINUE
         IF(ND-NEIN-1)56,57,58
 C       ERSTES MAL GANZE KURVE VARIIERT
      57 NG = 1
         NG1=NKP
         QC2=.99E30
         GO TO 59
 C       ZUSAETZLICHE ITERATIONEN GANZE KURVE
      58 IF (ND-30) 60,60,32
      60 IF((QC2-QC1)/QC1-0.0001) 62,62,70
      70 QC2=QC1
         GO TO 63
      62 DO 64 J=1,NKO
         IF(D(J)-VFMIN) 64,64,63
      64 CONTINUE
         ND=31
         GO TO 32
 C       BERECHNUNG UND AUSGABE DER SCHLUSSRESULTATE
      35 IF(J-1) 71,71,72
      71 PRINT 65
         PRINT 66
         PRINT 24,(PK(I),I=1,NKO)
         PRINT 54,QC1,ST
         PRINT 4
         PRINT 67
         PRINT 68
         PRINT 69,(MA(I),I=1,18)
         IPAR =6
      76 IPA1=3*IPAR+1

         IPA2=3*IPAR+18
         IF(NPAR-IPAR) 72,72,73
      73 PRINT 74
         PRINT 75,(MA(I),I=IPA1,IPA2)
         IPAR=IPAR+6
         GO TO 76
      72 PRINT 77
         IF(J-NPP) 79,79,78
      78 NK=NK+1
         NPP=NPP+NPPK(NK)
         PRINT 77
      79 PRINT 80,NK ,J,PH1(J),OH1(J),OHB,DELTA,(U(I),I=1,6)
         IPAR =6
      84 IPA1=IPAR+1
         IPA2=IPAR+6
         IF(NPAR-IPAR) 81,81,82
      82 PRINT 83 ,(U(I),I=IPA1,IPA2)
         IPAR=IPAR+6
         GO TO 84
 C       ENTSCHEIDET OB ALLE PUNKTE BERECHNET SIND
      81 IF(J-NG1) 34,85,85
 C       ENTSCHEIDET OB WEITERE PROBLEME ZU LOESEN SIND
      85 NP1=NP1+1
         PRINT 65
         IF(NP-NP1) 87,87,88
      87 STOP
         END
```

Das Hauptprogramm SPANA

```
C     SPEKTRENANALYSE
C     EPSILONWERTE AUS KOMPLEXBILDUNGSKONSTANTEN UND EXTINKTIONEN
    1 FORMAT(//16H SPEKTRENANALYSE//)
    2 FORMAT (49H
    3 FORMAT(I2)
    4 FORMAT(2I4)
    7 FORMAT(F8.4)
    8 FORMAT(F7.3)
   22 FORMAT(6X,4(2X,I2),2X,I2/)
   23 FORMAT(2H  //)
   24 FORMAT(35H  K.N.     E EXP     E BER     DELTA E,
     1 8X,24H PARTIKELKONZENTRATIONEN//)
   26 FORMAT(1H+,1X,I2,3X,2(F8.5,1X)2X,F8.5)
   27 FORMAT(//22H WELLENLAENGE IN NM = ,I4//)
   30 FORMAT(16H PK-WERTE LIGAND,10(3X,F7.3)/16X,10(3X,F7.3))
   31 FORMAT(1H1)
   33 FORMAT(6I2)
   34 FORMAT(17H PK-WERTE KOMPLEX,2X,F7.3,9(3X,F7.3)/16X,10(3X,F7.3))
   40 FORMAT(16H QUADRATSUMME = ,E10.3,4X,31H RELATIVE STANDARDABWEICHUN
     1G = ,E10.3)
   44 FORMAT( 5H K.N.,5X,3H PH,8X,4H CM1,11X,4H CM2,11X,4H CL1,11X,4H CL
     12)
   48 FORMAT(28H DATEN NICHT OK IN KURVE NR ,I2)
   49 FORMAT( E10.0,I2)
   52 FORMAT(5E10.0)
   55 FORMAT(2X,I2,4X,F6.2,4(5X,E10.3))
   63 FORMAT(40X,7(1X,E10.3)/40X,7(1X,E10.3)/40X,6(1X,E10.3))
   72 FORMAT(40X,5(I4,13X))
   78 FORMAT(7X,9H PARTIKEL,12X,6H INDEX,4X,12H EPSILON UND,
     119H STANDARDABWEICHUNG,22H (WELLENLAENGE IN NM) /)
   79 FORMAT(1X,I2,2X,19H  M1  M2  L1  L2  H,6X,I2,6X,5(2E8.3,1X))
   84 FORMAT(45H ZU VIELE KURVEN,WELLENLAENGEN ODER PARTIKELN)
   87 FORMAT(12H EPSILON NR ,I2,3H = ,E10.3,13H BEI LAMBDA =,I4)
   92 FORMAT(16H ZU WENIG KURVEN)
   93 FORMAT(35H ZAHL EPSILON NICHT OK PARTIKEL NR ,I2)
   94 FORMAT(33H ZAHL BEKANNTE PARTIKELN NICHT OK)
   97 FORMAT(10F7.4)
  101 FORMAT(14H EXTINKTION = ,E10.3,15H BEI LAMBDA NR ,I2,
     110H KURVE NR ,I2)
  111 FORMAT(27H ZAHL PARTIKELN GLEICH NULL)
      COMMON C,S,U,HA,CM,CMA,CL,CLA,EQ,MI,ND,WK,OHB,NKO
      DOUBLE PRECISION C(20),S(20),U(20),E(20,20),BC(20,20),B(20,20), HA
      DIMENSION A(20,20),PS(20),NU(20),ECOR(20),M1(2
     10),M2(20),L0(20),L2(20),IH(20),ST(20,20),        E1(20,20),LAM(20),
     2  SUME(20),EPS(20),EBER(20),DELTA(20),PKO(20),EP(20,20),
     3EBEK(20,20),LOCH(20),D2(20)
      PRINT 31
C     SETZEN DER INDIZES
      NP1=0
      ND =31
      WK=1.E-14
      OHB=1.
      EQ=1.
      READ 3,NP
   28 MI=1
      IW1=1
```

```
      IW2=5
      NKH=1
      NKO=1
      NWEL=0
      IW=1
      NKU=1
      IP9=1
      D0=0.
      NLOCH=0
C     EINLESEN UND DARSTELLEN DER ALLGEMEINEN DATEN
      PRINT 1
      READ 2
      PRINT 2
      READ 2
      PRINT 2
      PRINT 23
      READ 4,LAMBDA,INC
   66 READ 8,PS(NKH)
      IF(PS(NKH))64,65,64
   64 NKH=NKH+1
      GO TO 66
   65 NKH=NKH-1
   69 READ 8,PKO(NKO)
      IF(PKO(NKO)) 67,68,67
   67 NKO=NKO+1
      GO TO 69
   68 NKO=NKO-1
   35 READ 33,M1(IP9),M2(IP9),L0(IP9),L2(IP9),IH(IP9),NU(IP9)
      IF(NU(IP9)) 32,32,17
   17 IP9=IP9+1
      GO TO 35
   32 NPAR=IP9-1
   13 READ 33,M1(IP9),M2(IP9),L0(IP9),L2(IP9),IH(IP9),NU(IP9)
      IF(NU(IP9)) 5,5,6
    6 IP9=IP9+1
      GO TO 13
    5 NPART=IP9-1
      NBEK1=NPAR+1
C     UMWANDELN DER ALLGEMEINEN EINGABEGROESSEN
      PRINT 30,(PS(J),J=1,NKH)
      PRINT 23
      PRINT 34,(PKO(J),J=1,NKO)
      PRINT 23
      DO 105 J=1,NKH
      PS(J)=-PS(J)
  105 S(J)=10.**PS(J)
      DO 106 J=1,NKO
      PKO(J)=-PKO(J)
  106 C(J)=10.**PKO(J)
C     EINLESEN DER SPEKTREN UND BERECHNEN DER KONZENTRATIONEN
      PRINT 44
      PRINT 23
   50 READ 52,CM,CMA,CL,CLA ,D
      IF(D-D0) 95,61,95
   95 READ 97,(ECOR(J),J=1,10)
      READ 97,(ECOR(J),J=11,20)
      D0=D
```

```
   61 IF(NWEL-IW+1)46,47,46
   46 NKU=NKU-1
      PRINT 48,NKU
      GO TO 29
   47 READ 49,PH,INDEX
      IF(PH) 53,54,53
   53 PRINT 55,NKU,PH,CM,CMA,CL,CLA
      PH=-PH
      HA=10.**PH
      CALL SUB
      DO 56 IP5=1,NPART
      IP9=NU(IP5)
   56 A(IP5,NKU)=U(IP9)
      D2(NKU)=0
      IW=1
   59 READ 7,E1(IW,NKU)
      IF(E1(IW,NKU)) 57,58,57
   57 E (IW,NKU)=(E1(IW,NKU)-ECOR(IW))
      IW=IW+1
      GO TO 59
   58 NKU=NKU+1
      IF(NKU-2) 60,60,61
   60 NWEL =IW-1
      GO TO 61
   54 IF(INDEX)50,51,50
   51 NKU=NKU-1
      IF(NBEK1-NPART) 21,21,62
   21 DO 42 IPB=NBEK1,NPART
      DO 43 IWB=1,NWEL
   43 READ 8,EP(IWB,IPB)
      READ 7,TEST
      IF(TEST) 88,42,88
   88 PRINT 93,IPB
      GO TO 29
   42 CONTINUE
      READ 7,TEST
      IF(TEST) 89,41,89
   89 PRINT 94
      GO TO 29
   41 DO 98 IW=1,NWEL
      DO 98 IK=1,NKU
   98 EBEK(IW,IK)=0.
      DO 36 IW=1,NWEL
      DO 36 IK=1,NKU
      DO 100 IPB=NBEK1,NPART
  100  EBEK(IW,IK)=EBEK(IW,IK)+EP (IW,IPB)*A(IPB,IK)*D2(IK)
      E(IW,IK)=E (IW,IK)-EBEK(IW,IK)
      IF(E(IW,IK)) 99,36,36
   99 PRINT 23
      PRINT 101,E(IW,IK),IW,IK
      E(IW,IK)=0.
   36 CONTINUE
C     AUFBAU DER MATRIX
   62 IF(NKU-NPAR) 90,90,91
   90 PRINT 92
      GO TO 29
   91 IF(NPART-19) 80,81,81
```

```
   80 IF(NWEL-20 )82,82,81
   82 IF(NKU-20)83,83,81
   81 PRINT 84
      GO TO 76
   83 DO 10 IW=1,NWEL
      PRINT 27,LAMBDA
  103 DO 37 IP1=1,NPAR
      DO 37 IP2=1,NPAR
   37 B(IP1,IP2)=0.
      DO 9 IP1=1,NPAR
      DO 9 IP2=1,NPAR
      DO 9 IK=1,NKU
    9 B(IP1,IP2)=B(IP1,IP2)+A(IP1,IK)*A(IP2,IK)*D2(IK)*D2(IK)
      DO 38 IP3=1,NPAR
   38 SUME(IP3)=0.
      DO 11 IP3=1,NPAR
      DO 11 IK=1,NKU
   11 SUME(IP3)=SUME(IP3)+E(IW,IK)*A(IP3,IK)*D2(IK)
      DO 12 I=1,NPAR
      DO 12 J=1,NPAR
   12 BC(I,J)=B(I,J)
      CALL SUB760(BC,NPAR )
      DO 39 IP4=1,NPAR
   39 EPS(IP4)=0.
      DO 14 IP4=1,NPAR
      DO 14 IP5=1,NPAR
   14 EPS(IP4)=EPS(IP4)+BC(IP4,IP5)*SUME(IP5)
      DO 85 IP5=1,NPAR
      IF(EPS(IP5)) 86,85,85
   86 PRINT 23
      PRINT 87,IP5,EPS(IP5),LAMBDA
      PRINT 23
      EPS(IP5)=0.
      NLOCH=NLOCH+1
      LOCH(NLOCH)=IP5
      EPS(20)=EPS(IP5)
      EPS(IP5)=EPS(NPAR)
      EPS(NPAR)=EPS(20)
      DO 102 IK1=1,NKU
      A(20,IK1)=A(IP5,IK1)
      A(IP5,IK1)=A(NPAR,IK1)
  102 A(NPAR,IK1)=A(20,IK1)
      NPAR=NPAR-1
      IF(NPAR) 110,110,103
  110 PRINT 111
      GO TO 109
   85 CONTINUE
  109 IF(NLOCH) 104,104,107
  107 IP5=LOCH(NLOCH)
      NPAR=NPAR+1
      EPS(20)=EPS(IP5)
      EPS(IP5)=EPS(NPAR)
      EPS(NPAR)=EPS(20)
      DO 108 IK1=1,NKU
      A(20,IK1)=A(IP5,IK1)
      A(IP5,IK1)=A(NPAR,IK1)
  108 A(NPAR,IK1)=A(20,IK1)
```

```
      NLOCH=NLOCH-1
      GO TO 109
  104 DO 45 IK1=1,NKU
   45 EBER(IK1)=0.
      QS=0.
      SUE=0.
      DO 15 IK1=1,NKU
      DO 16 IP6=1,NPAR
   16 EBER(IK1)=EBER(IK1)+EPS(IP6)*A(IP6,IK1)*D2(IK1)
       DELTA(IK1)=E(IW,IK1)-EBER(IK1)
      EBER(IK1)=EBER(IK1)+EBEK(IW,IK1)
      E(IW,IK1)=E(IW,IK1)+EBEK(IW,IK1)
      DELQ= DELTA(IK1)*DELTA(IK1)
   15 QS=QS+DELQ
      DO 161 IK2=1,NKU
  161 SUE=SUE+E(IW,IK2)
      R=NKU
      EQUER=SUE/R
      T=NKU-NPAR
      STQ=QS/T
      STR=SQRT(STQ)/EQUER
      PRINT 40,QS,STR
      PRINT 23
      DO 18 IP7=1,NPAR
      STKQ=STQ*BC(IP7,IP7)
      IF(STKQ) 19,20,20
   19 STKQ=-STKQ
   20 STK=SQRT(STKQ)
      ST(IW,IP7)=STK
      EP(IW,IP7)=EPS(IP7)
      LAM(IW)=LAMBDA
   18 CONTINUE
      PRINT 24
      DO 25 IK3=1,NKU
      PRINT 63,(A(IP7,IK3),IP7=1,NPART)
   25 PRINT 26,IK3,E(IW,IK3),EBER(IK3),DELTA(IK3)
      PRINT 31
   10 LAMBDA=LAMBDA+INC
      NP1=NP1+1
      PRINT 78
   77 IF(IW2-NWEL) 73,74,74
   74 IW2=NWEL
   73 PRINT 72, (LAM(IW),IW=IW1,IW2)
      PRINT 23
      DO 71 IP1=1,NPART
      PRINT 79, IP1,NU(IP1),(EP(IW,IP1),ST(IW,IP1),IW=IW1,IW2)
   71 PRINT 22,M1(IP1),M2(IP1),L0(IP1),L2(IP1),IH(IP1)
      PRINT 23
      IF(IW2-NWEL) 75,76,76
   75 IW1=IW1+5
      IW2=IW2+5
      GO TO 77
   76 PRINT 31
      IF(NP1-NP) 28,29,29
   29 STOP
      END
```

Die Hilfssubroutinen

```
      SUBROUTINE SUB76 (A760,N760)
      DOUBLE PRECISION A760(4,4)
    3 DO 764 K760=1,N760
      CM760=A760(K760,K760)
      A760(K760,K760)=1.0
      DO 765 J760=1,N760
  765 A760(K760,J760)=A760(K760,J760)/CM760
      DO 764 I760=1,N760
      IF(I760-K760) 762,764,762
  762 CM760=A760(I760,K760)
      A760(I760,K760)=0.0
      DO 763 J760=1,N760
  763 A760(I760,J760)=A760(I760,J760)-CM760*A760(K760,J760)
  764 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SUB760(A760,N760)
      DOUBLE PRECISION A760(20,20)
    3 DO 764 K760=1,N760
      CM760=A760(K760,K760)
      A760(K760,K760)=1.0
      DO 765 J760=1,N760
  765 A760(K760,J760)=A760(K760,J760)/CM760
      DO 764 I760=1,N760
      IF(I760-K760) 762,764,762
  762 CM760=A760(I760,K760)
      A760(I760,K760)=0.0
      DO 763 J760=1,N760
  763 A760(I760,J760)=A760(I760,J760)-CM760*A760(K760,J760)
  764 CONTINUE
      RETURN
      END
```

```
C    NULL ABGEAENDERT UND VERKLEINERT
      SUBROUTINE NULL(Q,R,T,P)
      DOUBLE PRECISION Q(4,4,4,4),R(4,4,4,4,4,4),T(4,4,4,4),P(4)
      DO 1 I=1,4
      DO 1 J=1,4
      DO 1 K=1,4
      DO 1 L=1,4
    1 Q(I,J,K,L)=0.
      DO 2 II=1,4
      P(II)=0.
      DO 2 JJ=1,4
      DO 3 I=1,4
      DO 3 J=1,4
    3 T(II,JJ,I,J)=0.
      DO 2 KK=1,4
      DO 2 I=1,4
      DO 2 J=1,4
      DO 2 K=1,4
    2 R(II,JJ,KK,I,J,K)=0.
      RETURN
      END
```

```
      SUBROUTINE LIGAND(C,U,HA,CL,EQ,ND,WK,OHB,NKO)
      DOUBLE PRECISION C(20),U(20),HA,PRO,SUML,SUMCH,WLHN
      PRO=1.
      SUML=1.
      SUMCH=NKO
      DO 1 I=1,NKO
      PRO=PRO*C(I)
      SUML=SUML+PRO/(HA**I)
      SUMCH=SUMCH+(NKO-I)*PRO/(HA**I)
    1 CONTINUE
      WLHN=CL/SUML
      CH=WLHN*SUMCH+HA-WK/HA
      OHB=EQ*(1.-CH/(NKO*CL))
      IF(ND-30) 2,2,3
    3 U(1)=WLHN
      DO 4 I=1,NKO
    4 U(I+1)=U(I)*C(I)/HA
    2 RETURN
      END
```

```
      SUBROUTINE QUADR(HA,A,B,C,X,XMAX)
      DOUBLE PRECISION A,B,C,X,HA,DIS
      PH=-LOG10(HA)
      DIS = B*B-4.*A*C
      IF (DIS) 1,2,3
    1 PRINT 4
    4 FORMAT(36H *FEHLER*  DISKRIMINANTE IST NEGATIV )
      PRINT 1000,PH
 1000 FORMAT(1H+,48X,5HPH = ,F6.3)
    2 X=-B/(2.*A)
      GO TO 5
    3 X=(-B-DSQRT(DIS))/(2.*A)
      IF (X) 6,6,8
    6 X=(-B+DSQRT(DIS))/(2.*A)
    5 IF(X) 7,7,8
    7 PRINT 9,X
    9 FORMAT (30H *FEHLER*  X NEGATIV ODER NULL ,5X,D10.3)
      PRINT 1000,PH
      X=1.E-20
      RETURN
    8 IF(X-XMAX) 10,10,11
   11 PRINT 12,X
   12 FORMAT(30H *FEHLER*  X GROESSER ALS XMAX , 5X,D10.3)
      PRINT 1000,PH
      X=XMAX
   10 RETURN
      END
```

```
      SUBROUTINE CUBIC(HA,A,B,C,D,Y,YMAX)
      COMPLEX DIS1,AK,BK,DK,B1K,EK,PK
      DOUBLE PRECISION A,B,C,D,Y,HA  ,A1,B1,DIS,A2,B2,Y1(3)
      PH=-LOG10(HA)
      A1=(3.*C/A-B*B/(A*A))/3.
      B1=(2.*(B/A)**3-9.*B*C/(A*A)+27.*D/A)/27.
      DIS=B1*B1/4.+A1**3/27.
      P=B/(3.*A)
      IF(DIS) 1,2,3
    3 A2=DCBRT(-B1/2.+DSQRT(DIS))
      B2=DCBRT(-B1/2.-DSQRT(DIS))
      Y=A2+B2-P
      GO TO 4
    2 Y=2.*DCBRT(-B1/2.)-P
      IF(Y) 5,5,17
   17 IF(Y-YMAX) 4,4,5
    5 Y=-DCBRT(-B1/2.)-P
      GO TO 4
    1 DIS1=DIS
      B1K=B1
      PK=P
      EK=2.
      AK=CCBRT(-B1K/EK+CSQRT(DIS1))
      BK=CCBRT(-B1K/EK-CSQRT(DIS1))
      Y1(1)=AK+BK-PK
      DK=-3.
      Y1(2)=-(AK+BK)/EK+(AK-BK)*CCBRT(DK)/EK-PK
      Y1(3)=-(AK+BK)/EK-(AK-BK)*CCBRT(DK)/EK-PK
      DO 8 I=1,3
      IF(Y1(I)) 8,8,9
    9 IF(Y1(I)-YMAX)  13,13,8
    8 CONTINUE
      PRINT 14,(Y1(I),I=1,3)
   14 FORMAT(37H *FEHLER*  KEINE VERNUENFTIGE LOESUNG ,3(5X,D10.3))
      PRINT 1001,PH
 1001 FORMAT(1H+,110X,5HPH = ,F6.3)
      GO TO 15
   13 Y=Y1(I)
      GO TO 11
    4 IF(Y) 7,7,6
    7 PRINT16,Y
   16 FORMAT(30H *FEHLER*  X NEGATIV ODER NULL,5X,D10.3)
      PRINT 1000,PH
 1000 FORMAT(1H+,48X,5HPH = ,F6.3)
      Y=1.E-20
      RETURN
    6 IF(Y-YMAX) 11,11,10
   10 PRINT 12,Y
   12 FORMAT(30H *FEHLER*  X GROESSER ALS XMAX,5X,D10.3)
      PRINT 1000,PH
   15 Y=YMAX
   11 RETURN
      END
```

```
      SUBROUTINE NEWRAP(HA,TX,TY,T,X,Y,XMAX,YMAX,MI,ND)
      DOUBLE PRECISION TX,TY,T(3,6),X,Y,F,G,FX,FY,GX,GY,XB,YB,DXY,DEL,
     1DEX,DEY,HA
      PH=-LOG10(HA)
      KONT=1
   27 DEX=0.
      DEY=0.
      IND=0
      GOTO (1,2),MI
    1 X=XMAX
      Y=YMAX
      KON=-1
      MI=2
      IF(ND-1) 36,36,2
   36 IMAX=0
      JMAX=0
      DO 37 I=1,3
      DO 37 J=1,6
      IF(T(I,J)) 38,37,38
   38 IF(IMAX-I) 39,40,40
   39 IMAX=I
   40 IF(JMAX-J) 41,37,37
   41 JMAX=J
   37 CONTINUE
    2 IF(KON) 3,3,4
    3 XB=TX*X
      FX=-TX
      FY=0.
      DO 5 I=1,IMAX
      DO 5 J=1,JMAX
      XB=XB+I*T(I,J)*X**I*Y**J
      FX=FX-I*I*T(I,J)*X**(I-1)*Y**J
    5 FY=FY-I*J*T(I,J)*X**I*Y**(J-1)
      F=XMAX-XB
    4 IF(KON) 6,10,6
    6 DXY=TX*X-TY*Y
      GX1=-TX
      GY1=TY
      DO 7 I=1,IMAX
      DO 7 J=1,JMAX
      DXY=DXY+(I-J)*T(I,J)*X**I*Y**J
      GX1=GX1-(I-J)*I*T(I,J)*X**(I-1)*Y**J
    7 GY1=GY1-(I-J)*J*T(I,J)*X**I*Y**(J-1)
      IF(KON) 9,9,8
    9 GX=GX1
      GY=GY1
      G=XMAX-YMAX-DXY
      GO TO 10
    8 FX=GX1
      FY=GY1
      F=XMAX-YMAX-DXY
   10 IF(KON) 11,12,12
   12 YB=TY*Y
      GX=0.
      GY=-TY
      DO 13 I=1,IMAX
```

```
      DO 13 J=1,JMAX
      YB=YB+J*T(I,J)*X**I*Y**J
      GX=GX-J*I*T(I,J)*X**(I-1)*Y**J
   13 GY=GY-J*J*T(I,J)*X**I*Y**(J-1)
      G=YMAX-YB
   11 DEL=FX*GY-FY*GX
      DEX=(-F*GY+G*FY)/DEL
      DEY=(-FX*G+F*GX)/DEL
      X=X+DEX
      Y=Y+DEY
      IND=IND+1
      IF(IND-50) 35,14,14
   35 IF(X) 15,15,16
   15 X=(X-DEX)/2.
      GO TO 2
   16 IF(XMAX-X)17,18,18
   17 X=(X-DEX+XMAX)/2.
      GO TO 2
   18 IF(Y) 19,19,20
   19 Y=(Y-DEY)/2.
      GO TO 2
   20 IF(YMAX-Y) 21,22,22
   21 Y=(Y-DEY+YMAX)/2.
      GO TO 2
   22 IF(ABS(F/XMAX)-0.0001)23,23,2
   23 IF(ABS(G/YMAX)-0.0001)24,24,2
   14 IF(KON) 25,26,26
   25 IF(KONT-3) 30,31,31
   30 KON=0
      GO TO 34
   26 IF(KONT-3) 32,31,31
   32 KON =1
      GO TO 34
   28 IF(KONT-3) 33,31,31
   33 KON=-1
   34 KONT=KONT+1
      X=XMAX
      Y=YMAX
      GO TO 27
   31 PRINT 29,X,Y
   29 FORMAT(37H *FEHLER*  RECHNUNG KONVERGIERT NICHT,2(5X,D10.3))
      PRINT 1001,PH
 1001 FORMAT(1H+,110X,5HPH = ,F6.3)
      X=XMAX
      Y=YMAX
   24 RETURN
      END
```

```
C     MATIN2  VERBESSERT AM  20.9.1969
C    SUBROUTINE ZUR BERECHNUNGEN VON PARTIKELN M1M2L1L2  MIT MATRIXINVERSIO
      SUBROUTINE MATIN(HA,Q,R,T,P,X,XMAX,MI,ND)
      DOUBLE PRECISION Q(4,4,4,4),R(4,4,4,4,4,4),T(4,4,4,4),P(4),X(4),
     1F(4),G(4,4),DX(4) ,HA
      DIMENSION XMAX(4),MAX(4),IN(4)
      PH=-LOG10(HA)
      KONT=1
      IND=1
      GO TO (1,102),MI
C    ERSTER DURCHGANG, SETZEN DER GROESSEN
    1 DO 3 I=1,4
    3 X(I)=XMAX(I)
      KON=-1
      MI=2
      IF(ND-1) 4,4,102
    4 DO 61 I=1,4
   61 MAX(I)=0
      DO 5 IP=1,4
      DO32 IP1=1,4
      IF(IP1-IP) 32,32,34
   34 DO70 IP2=1,4
      IF(IP2-IP1) 70,70,59
   59 DO 27 I=1,4
      DO 27 J=1,4
      IF(T(IP,IP1,I,J)) 18,16,18
   18 IF(MAX(IP)-I) 19,20,20
   19 MAX(IP)=I
   20 IF(MAX(IP1)-J) 21,16,16
   21 MAX(IP1)=J
   16 DO27 K=1,4
      IF(R(IP,IP1,IP2,I,J,K))  15,27,15
   15 IF(MAX(IP)-I) 17,88,88
   17 MAX(IP)=I
   88 IF(MAX(IP1)-J) 89,90,90
   89 MAX(IP1)=J
   90 IF(MAX(IP2)-K)91,27,27
   91 MAX(IP2)=K
   27 CONTINUE
   70 CONTINUE
   32 CONTINUE
    5 CONTINUE
      DO 62 I=1,4
      DO 62 J=1,4
      DO 62 K=1,4
      DO 62 L=1,4
      IF(Q(I,J,K,L)) 6,62,6
    6 IF(MAX(1)-I) 8,9,9
    8 MAX(1)=I
    9 IF(MAX(2)-J) 10,11,11
   10 MAX(2)=J
   11 IF(MAX(3)-K) 12,13,13
   12 MAX(3)=K
   13 IF(MAX(4)-L) 14,62,62
   14 MAX(4)=L
   62 CONTINUE
```

```
      NPA=4
      DO 23 I=1,4
      IF(MAX(I)) 22,22,23
   22 NPA=NPA-1
   23 CONTINUE
  102 DO 100 IP=1,4
      DO 100 IP1=2,4
      DO 101 I=1,4
      DO 101 J=1,4
  101 T(IP1,IP,J,I)=T(IP,IP1,I,J)
      DO 100 IP2=3,4
      DO 100 I=1,4
      DO 100 J=1,4
      DO 100 K=1,4
      R(IP2,IP,IP1,K,I,J )=R(IP,IP1,IP2,I,J,K)
  100 R(IP1,IP,IP2,J,I,K)=R(IP,IP1,IP2,I,J,K)
C    AUFBAUEN DER FUNKTIONEN UND DEREN ABLEITUNGEN
    2 IX=0
      DO 28 IP=1,NPA
      F(IP)=0.
      DO 24 J=1,NPA
   24 G(IP,J)=0.
      IF(MAX(4)) 26,26,25
   25 IMAX=MAX(1)
      JMAX=MAX(2)
      KMAX=MAX(3)
      LMAX=MAX(4)
      DO 29 I=1,IMAX
      DO 29 J=1,JMAX
      DO 29 K=1,KMAX
      DO 291L=1,LMAX
      IF(Q(I,J,K,L)) 292,291,292
  292 IN(1)=I
      IN(2)=J
      IN(3)=K
      IN(4)=L
      F(IP)=F(IP)+IN(IP)*Q(I,J,K,L)*X(1)**I*X(2)**J*X(3)**K*X(4)**L
      G(IP,1)=G(IP,1)+IN(IP)*I*Q(I,J,K,L)*X(1)**(I-1)*X(2)**J*X(3)**K*X
     1(4)**L
      G(IP,2)=G(IP,2)+IN(IP)*J*Q(I,J,K,L)*X(1)**I*X(2)**(J-1)*X(3)**K
     1*X(4)**L
      G(IP,3)=G(IP,3)+IN(IP)*K*Q(I,J,K,L)*X(1)**I*X(2)**J*X(3)**(K-1)*
     1X(4)**L
      G(IP,4)=G(IP,4)+IN(IP)*L*Q(I,J,K,L)*X(1)**I*X(2)**J*X(3)**K*X(4)**
     1(L-1)
  291 CONTINUE
   29 CONTINUE
   26 F(IP)=F(IP)-XMAX(IP)+P(IP)*X(IP)
      G(IP,IP)=G(IP,IP)+P(IP)
      DO 281IP1=1,NPA
      IF(IP1-IP) 30,281,30
   30 IMAX=MAX(IP)
      JMAX=MAX(IP1)
      DO 31 I=1,IMAX
      DO 311J=1,JMAX
      IF(T(IP,IP1,I,J)) 312,311,312
  312 G(IP,IP)=G(IP,IP)+I*I*T(IP,IP1,I,J)*X(IP)**(I-1)*X(IP1)**J
```

```
      G(IP,IP1)=G(IP,IP1)+I*J*T(IP,IP1,I,J)*X(IP)**I*X(IP1)**(J-1)
      F(IP)=F(IP)+I*T(IP,IP1,I,J)*X(IP)**I*X(IP1)**J
  311 CONTINUE
   31 CONTINUE
      DO 282IP2=2,NPA
      IF(IP2-IP) 7,282,7
    7 IF(IP2-IP1) 282,282,33
   33 IMAX=MAX(IP)
      JMAX=MAX(IP1)
      KMAX=MAX(IP2)
      DO 283I=1,IMAX
      DO 35 J=1,JMAX
      DO 351K=1,KMAX
      IF(R(IP,IP1,IP2,I,J,K)) 352,351,352
  352 F(IP)=F(IP)+I*R(IP,IP1,IP2,I,J,K)*X(IP)**I*X(IP1)**J*X(IP2)**K
      G(IP,IP)=G(IP,IP)+I*I*R(IP,IP1,IP2,I,J,K)*X(IP)**(I-1)*X(IP1)**J
     1*X(IP2)**K
      G(IP,IP1)=G(IP,IP1)+I*J*R(IP,IP1,IP2,I,J,K)*X(IP)**I*X(IP1)**(J-1)
     1*X(IP2)**K
      G(IP,IP2)=G(IP,IP2)+I*K*R(IP,IP1,IP2,I,J,K)*X(IP)**I*X(IP1)**J*
     1X(IP2)**(K-1)
  351 CONTINUE
   35 CONTINUE
  283 CONTINUE
  282 CONTINUE
  281 CONTINUE
   28 CONTINUE
      IF(KON) 48,49,50
   49 F(1)=F(1)-F(2)
      DO 60 I=1,NPA
   60 G(1,I)=G(1,I)-G(2,I)
      GO TO 48
   50 F(1)=F(1)-F(3)
      DO 63 I=1,NPA
   63 G(1,I)=G(1,I)-G(3,I)
   48 CONTINUE
C    SUBROUTINE FUER MATRIX INVERSION
      CALL  SUB76 (G,NPA)
      DO 37 I=1,NPA
   37 DX(I)=0.
      DO 36 I=1,NPA
      DO 87  J=1,NPA
   87 DX(I)=DX(I)-F(J)*G(I,J)
      X(I)=X(I)+DX(I)
      IF(X(I)) 40,40,41
   40 X(I)=(X(I)-DX(I))/2.
      IX=1
      GO TO 36
   41 IF(XMAX(I)-X(I)) 42,36,36
   42 X(I)=(X(I)-DX(I)+XMAX(I))/2.
      IX=1
   36 CONTINUE
      IND=IND+1
      IF(IND- 50) 38,38,39
   38 IF(IX) 43,43,2
   43 DO 44 I=1,NPA
      IF(ABS(F(I)/XMAX(I))-0.00001) 44,44,2
```

```
   44 CONTINUE
      GO TO 45
   39 IF(KON) 51,52,53
   51 IF(KONT-3)54,55,55
   54 KON=0
      GO TO 56
   52 IF(KONT-3) 57,55,55
   57 KON=1
      GO TO 56
   53 IF(KONT-3) 64,55,55
   64 KON=-1
   56 KONT=KONT+1
          DO 58 I=1,NPA
   58 X(I)=XMAX(I)
      IND1=1
      IND=1
      GO TO 2
   55 PRINT 46, (X(I),I=1,NPA)
   46 FORMAT( 37H *FEHLER*  RECHNUNG KONVERGIERT NICHT, 4(5X,D12.3))
      PRINT 1001,PH
 1001 FORMAT(1H+,110X,5HPH = ,F6.3)
      DO 47 I=1,NPA
   47 X(I)=XMAX(I)
   45 CONTINUE
      RETURN
      END
```

Beispiel einer Subroutine

```
C    LH4,LH3,MLH3,MLH2,MLH,ML,M2L2H3
C    EQ=4CL
C     C1=M*LH3/MLH3, C2=M*LH3/H*MLH2   C3=H*MLH/MLH2, C4=H*ML/MLH,
C     C5= MLH*MLH2/M2L2H3
      SUBROUTINE SUB
      COMMON C,S,U,HA,CM,CMA,CL,CLA,EQ,MI,ND,WK,OHB,NKO
      DOUBLE PRECISION C(20),S(20),U(20),HA
      DOUBLE PRECISION TX,TY,TN(3,6),X,Y
      ND=1    (siehe Bemerkung)
      IF(ND+MI-2) 9003,9003,9004
 9003 DO 9002 I=1,3
      DO 9002 J=1,6
 9002 TN(I,J)=0.
 9004 TX=1.+HA/S(1)
      TY=1.
      TN(1,1)=1./C(1)+1./(HA*C(2))*(1.+C(3)/HA+C(3)/HA*C(4)/HA)
      TN(2,2)=C(3)/HA*1./(HA*HA*C(5)*C(2)*C(2))
      XMAX=CL
      YMAX=CM
      CALL NEWRAP(HA,TX,TY,TN,X,Y,XMAX,YMAX,MI,ND)
      CH=X*(4.*HA/S(1)+3.)+X*Y*(3./C(1)+(2.+C(3)/HA)/(HA*C(2))) +3.
     1*TN(2,2)* X*X*Y*Y+HA-WK/HA
      OHB=EQ*(1.-CH/(4.*CL))
      ND=31   (siehe Bemerkung)
      IF(ND-30) 9000,9000,9001
 9001 U(1)=Y
      U(2)=X
      U(3)=X*HA/(S(1))
      U(4)=X*Y/(C(1))
      U(5)=X*Y/(HA*C(2))
      U(6)=U(5)*C(3)/HA
      U(7)=U(6)*C(4)/HA
      U(8)=U(5)*U(6)/C(5)
 9000 RETURN
      END
```

Bemerkung: Die beiden Befehle ND=1 und ND=31 werden nur im Zusammenhang mit SPANA verwendet, müssen aber beim Arbeiten mit VARIAT weggelassen werden.

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EXTRACTION WITH LONG-CHAIN AMINES—II*

EXTRACTION AND COLORIMETRIC DETERMINATION OF CHROMATE

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Summary—Highly selective extraction of chromate from slightly acidic solutions (0·1–0·2*M* sulphuric acid) with a chloroform solution of trioctylamine (Alamine 336-S) or trioctylmethylammonium chloride Aliquat 336-S) is described. Many metals such as iron, nickel, cobalt, copper, alluminium, zinc, are not extracted, even if present in large concentrations. Coextraction of vanadium(V) and uranium(VI) is prevented by addition of sodium chloride. Traces of extracted molybdenum are scrubbed with ammonium oxalate. Final determination of chromium is based on measurement of the absorbance of the extract at 445–450 nm.

DIRECT colorimetric determination of chromate or dichromate cannot be compared in sensitivity with the well known diphenylcarbazide reaction, but the latter suffers serious interference from iron, molybdenum, mercury, vanadium and large concentrstions of highly coloured cations. In addition the colour is not stable and fades very quickly.[1] Concentration of chromate into a small volume of a suitable solvent should compensate for this main disadvantage of lower sensitivity. Chromate can be extracted from acidic medium with isobutyl methyl ketone[2] and determined colorimetrically[3] or by flame-photometry.[4] Trioctylphosphine oxide has also been recommended for extraction of chromate, with final determination by the diphenylcarbazide reaction.[5] We have found that chloroform solutions of trioctylmethylammonium chloride or trioctylamine very smoothly extract dichromate from slightly acidic solutions (0·1–0·2*M*) of sulphuric acid. Moore[6] found that dichromate was similarly extracted from hydrochloric acid but did not pursue the matter, since his main concern was with uranium and plutonium. Uranium(VI) and molybdenum(VI) are also extracted. Many elements which are normally troublesome in the colorimetric determination of chromium are not extracted even in traces. For example we are able to determine 50 μg of chromium in the presence of 2 g of iron, *i.e.*, in the ratio 1:40000 (0·0025% Cr). We have also found very simple conditions for avoiding the coextraction of vanadium, uranium and molybdenum. The method is therefore very simple and selective enough for the determination of chromium in alloys, slags, minerals, *etc.*

EXPERIMENTAL

Reagents

The extractants were obtained from General Mills, Chemical Division, Kankakee, Illinois. Trioctylamine (TOA), marketed as Alamine 336-S, and trioctylmethylammonium chloride (TOMA)

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* Part I: *Talanta*, 1970, **17**, 801.

marketed as Aliquat S-336, were used as 5% solutions in chloroform (*i.e.*, about 0·1*M*), without further purification.

A 5 × $10^{-3}M$ solution of potassium chromate was prepared by dissolving 0·971 g of reagent grade substance, dried at 110° for 6 hr, in 1 litre of redistilled water. Solutions (0·05*M*) of various metals such as iron, copper, nickel, cobalt *etc*, were prepared from their reagent grade sulphates; 1*M* solutions of sodium chloride and sulphate, potassium nitrate and sulphuric acid were prepared from reagent grade chemicals, and so were saturated solutions of sodium chloride and sulphate.

Absorption spectra; influence of sulphuric acid

In a 150-ml separatory funnel 2 ml of 5 × $10^{-3}M$ potassium chromate, 1 ml of saturated sodium sulphate solution (for better separation of the phases) and 1–20 ml of 1*M* sulphuric acid were diluted exactly to 50 ml with redistilled water, and shaken for 2 min with a 5% chloroform solution of TOA, then let stand for separation of the phases. The organic extract was filtered into a 10-mm cell and the absorbance measured between 400 and 550 nm, against water. From Fig. 1 we see that the absorption maximum is at 445–450 nm and that variation of the amount of sulphuric acid (10–20 ml of 0·1*M*) in 50 ml of final solution (0·1–0·2*M* acidity) has only a very small influence on the position and height of the absorption maximum. Further experiments were carried out under these optimal conditions. It proved immaterial what volume of aqueous phase was used, between 50 and 200 ml.

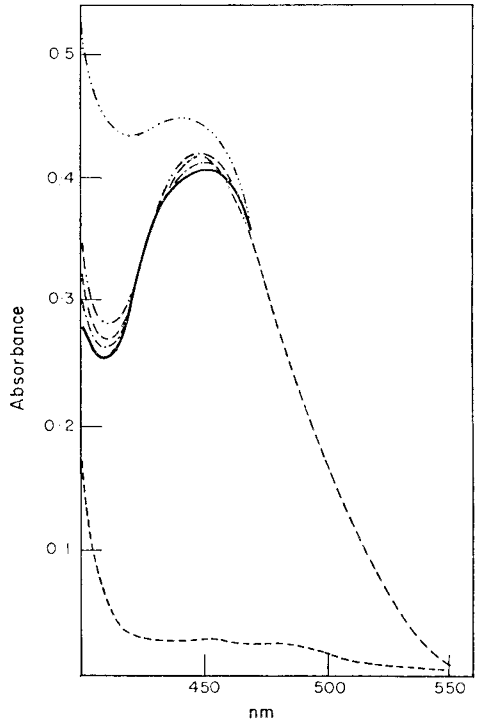

FIG. 1.—Influence of pH on the absorption spectrum of chromate.
2 ml of 5 × $10^{-3}M$ solution of chromium + 1 ml of satd. Na_2SO_4 solution + *x* ml of 1*M* H_2SO_4, diluted to 50 ml with water. Extracted with 5 ml of 5% TOA solution and measured against water at 450 nm in a 10-mm cell. H_2SO_4: – · · · · – 1 ml; · · – – – · · 5 ml; – – – – 10 ml; – · – · – 20 ml; ———— 40 ml; · · · · · · "blank".

Lambert-Beer law and stability of colour

Various amounts of 5 × $10^{-3}M$ chromium (0·5–5·0 ml in 0·5-ml steps) were mixed with 1 ml of saturated sodium sulphate solution and 10 ml of 1*M* sulphuric acid, diluted to 50 ml with water, extracted with 5 ml of 5% TOA solution and measured at 450 nm in a 10-cm cell. Concentrations of chromium from 0·1 up to 1·000 mg/50 ml obey the Lambert-Beer law. The colour is stable for at least two days. The molar absorptivity is 20 $l.mole^{-1}.mm^{-1}$.

Influence of anions

Sodium sulphate has a very good effect on phase separation. The influence of common anions in the presence of sodium sulphate was studied with 2 ml of $5 \times 10^{-3}M$ chromium, by the procedure described. The results are summarized in Table I.

Table I indicates that sodium chloride (up to 10%), sodium fluoride (up to 4%) and dipotassium hydrogen phosphate (up to 2%) do not effect the extraction of chromate. (Larger amounts of these salts were not examined.) Nitrates interfere seriously but 0·2% concentration (as potassium nitrate) is tolerated. Concentrations of nitrates higher than 3% make the extraction impossible. On the other hand the chromate can be stripped with a 5% potassium nitrate solution. Ammonium oxalate up to 0·2% has no effect on the extraction. Once extracted, chromium is inert towards an aqueous solution of oxalate. Acetate does not interfere.

TABLE I.—INFLUENCE OF ANIONS ON THE DETERMINATION OF CHROMATE (ABSORBANCE 0·395 IN ABSENCE OF ADDED SALT)

Salt	*A*	Salt	*A*	Salt	*A*
2 g NaCl	0·397	0·3 g NaF	0·399	0·5 g K_2HPO_4	0·394
5 g NaCl	0·393	0·5 g NaF	0·410	1·0 g K_2HPO_4	0·396
5 g NaCl	0·395	1·0 g NaF	0·398	0·1 g $(NH_4)_2C_2O_4$	0·394
0·1 g KNO_3	0·400	2·0 g NaF	0·405	0·3 g $(NH_4)_2C_2O_4$	0·379
0·2 g KNO_3	0·383	0·1 g K_2HPO_4	0·391	0·5 g $(NH_4)_2C_2O_4$	0·322
0·5 g KNO_3	0·169	0·2 g K_2HPO_4	0·395	1·0 g $(NH_4)_2C_2O_4$	0·275
1·0 g KNO_3	0·075				

Influence of foreign metals

Vanadium(V), uranium(VI) and molybdenum(VI) are extracted but many other metals are not. For example, 10 ml of 0·05*M* iron(III), cobalt(II), nickel and copper(II), treated under the same conditions, gave an absorbance of less than 0·004 in 5 ml of 5% TOA. In addition the presence of 10 ml of saturated sodium chloride solution prevents extraction of vanadium and uranium, and to a lesser extent that of molybdenum. The molybdenum extracted from 50 ml of solution containing 10 ml of saturated sodium chloride solution had an absorbance of 0·082 for 10 ml of 0·05*M* Mo, 0·039 for 5 ml and 0·008 for 1 ml, which means that small amounts of molybdenum up to 5 mg/50 ml could be tolerated. Larger amounts are coextracted and give high results for chromium. Molybdenum can easily be removed from the extract by washing it with dilute ammonium oxalate solution (see Table II).

Arsenic, antimony and selenium do not interfere if the acidity is properly adjusted before extraction. Manganese(VII) is easily extracted into TOMA but the colour fades rapidly. On extraction with TOA, manganese(VII) forms $MnO(OH)_2$. Manganese(VII) can be reduced selectively with oxalic acid, alcohol *etc.*, before extraction. Tungsten(VI) interferes but is normally removed, along with niobium and tantalum, during opening out of the sample.

Recommended procedure

To the solution containing 0·2–1·0 mg of chromium and other metals add 1 ml of saturated sodium sulphate solution, 10 ml of saturated sodium chloride solution, 10 ml of 1*M* sulphuric acid and dilute with water to about 50 ml. Extract with 5 ml of 5% TOA solution in chloroform, shaking for 2 min. Separate the organic layer and filter it through paper filter into a 10-mm cell and measure the absorbance at 450 nm, against water as a blank. Typical results are shown in Table II.

Determination of chromium in alloys

In a 250-ml tall beaker dissolve 0·1–1·0 g of the sample in a minimum amount of *aqua regia* and evaporate on the sand-bath nearly to dryness. Add 1–2 ml of sulphuric acid (1 + 1) and evaporate to white fumes. After cooling, add water and transfer (regardless of insoluble residue) to a 100–250-ml volumetric flask and fill to the mark. Take a suitable aliquot (2–25 ml) in a 100-ml beaker, add 0·2–0·5 g of potassium periodate, and boil the solution for few minutes. After cooling, transfer the solution and any insoluble residue into a 150-ml separatory funnel, dilute with 10 ml of 1*M* sulphuric acid and 3 ml of saturated sodium chloride solution and with water up to 50 ml. Extract the solution with 5 ml of 5% TOMA for 2 min, separate the chloroform phase and measure at 450 nm.

Some results are shown in Table III.

TABLE II.—DETERMINATION OF CHROMIUM(VI) (2ml OF $5 \times 10^{-3}M$, 0·520 mg) IN THE PRESENCE OF OTHER METALS

Metal	Added as*	Amount added g	A
—	—	—	0·394
Fe(III)	$NH_4Fe(SO_4)_2$	1	0·387
Fe(III)	$NH_4Fe(SO_4)_2$	2	0·393
Al + Ca	$Al_2(SO_4)_3 + CaCl_2$	2 + 1	0·393
Zn	$ZnSO_4$	2	0·396
Co + Cu + Zn	Sulphates	3	0·387
U(VI)	$UO_2(CH_3COO)_2$	1	0·385
V(V)	NH_4VO_3	1	0·398
Ti(IV)	H_2SO_4 soln.	0·138	0·390
Mo(VI)	50 ml of 0·05*N* soln.	0·240	0·452
	50 ml of 0·05*N* soln.	0·240	0·406†

* Water of crystallization is omitted.
† After scrubbing with water containing 0·2 g of oxalic acid.

TABLE III.—DETERMINATION OF CHROMIUM IN ALLOYS

Alloy	Composition, %	Cr present, % Cr	Cr found,* %
Fe–Ni	3·35 Fe, 87·45 Ni	9·10	8·98
Fe–Ni	10·70 Fe, 76·58 Ni, 3·62 S.	9·00	8·95
Ferrotitanium	40·4 Ti, 7·30 Al, 1·64 Mn 0·52 Cu, 0·12 V, 0·08 Nb 3·94 Si, 0·048 P, and Fe.	0·18	0·19

* Average of three determinations.

Acknowledgement—The authors wish to thank Mr. J. E. House (General Mills Inc., Minneapolis, U.S.A.) for providing samples of Aliquat and Alamine.

Zusammenfassung—Die hochselektive Extraktion von Chromat aus schwach sauren Lösungen (0,1–0,2*M* Schwefelsäure) mit Chloroformlösungen von Trioctylamin (Alamine 336-S) oder Trioctylmethylammoniumchlorid (Aliquat 336-S) wird beschrieben. Viele Metalle wie Eisen, Nickel, Kobalt, Kupfer, Aluminium und Zink werden nicht extrahiert, auch wenn sie in hoher Konzentration vorliegen. Die Mitextraktion von Vanadium(V) und Uran(VI) wird durch Zugabe von Natriumchlorid vermieden. Mitextrahierte Molybdänspuren werden mit Ammoniumoxalat ausgewaschen. Die Bestimmung von Chrom beruht schließlich auf Messung der Extinktion des Extrakts bei 445–450 nm.

Résumé—On décrit une extraction hautement sélective du chromate de solutions légèrement acides (acide sulfurique 0,1–0,2*M*) avec une solution chloroformique de trioctylamine (Alamine 336-S) ou de chlorure de méthyltrioctylammonium (Aliquat 336-S). De nombreux métaux tels que fer, nickel, cobalt, cuivre, aluminium, zinc, ne sont pas extraits, même s'ils sont présents en fortes concentrations. On évite la coextraction du vanadium (V) et de l'uranium (VI) par addition de chlorure de sodium. Des traces de molybdène extrait sont enlevées par lavage à l'oxalate d'ammonium. La détermination finale du chrome est basée sur la mesure de l'absorption de l'extrait à 445–450 nm.

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SHORT COMMUNICATIONS

Automatic determination of calcium and magnesium in water

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THE INDIVIDUAL determination of calcium and magnesium in water is very often more useful than a total hardness determination, both from the point of view of the maximum allowed concentration of magnesium in drinking water, and of the different effects of the two metals on the corrosion of metal pipes.

As far as we know the methods reported for the automatic colorimetric determination of calcium or of magnesium[1–6] are based on recording the absorbance at a suitable wavelength according to the specific reagent employed for each element, under different experimental conditions. In this paper a method is described for the automatic determination of both these elements with the same complexing agent and measurement of the absorbance at the same wavelength, with changes in the amounts of other complexing agents added to the solution.

The metallochromic agent, Eriochrome Black T (EBT), was chosen for its stability over long periods of time and its low cost. The Menon and Das procedure[7] was used, slightly modified and adapted for automation. EBT forms coloured complexes with both calcium and magnesium, but the absorptivity for magnesium is always much greater than that for calcium at the same pH and wavelength.

Menon, using solutions buffered at pH 9·5, measured the decrease in absorbance at 650 nm as a function of magnesium concentration, considering the calcium contribution to the absorbance at this wavelength to be negligible. On addition of MgEDTA to the solution all the calcium initially present as CaEBT complex was quantitatively converted into CaEDTA, and the equivalent amount of magnesium, displaced from the EDTA complex, formed MgEBT. From the difference in absorbance before and after addition of MgEDTA, the concentrations of both metals were obtained by successive approximations.

In our case we have measured at 571 nm, where an isosbestic point is observed for CaEBT and EBT. It is evident that under these conditions all the variations in absorbance are really proportional to the initial magnesium concentration, regardless of the amount of calcium in the solution.

Over the ranges 3–25 ppm of magnesium and 5–40 ppm of calcium the accuracy for both the elements was ±4%—better than the corresponding accuracy obtained by the manual method, which is about ±10%.[7]

PRINCIPLE OF THE METHOD

In Figs. 1*a* and 1*b* are shown some spectra of solutions containing EBT and calcium or magnesium respectively, at different concentrations. From these spectra isosbestic points for CaEBT and EBT at 571 nm and for MgEBT and EBT at 578 nm can be seen. In principle it would be possible to determine the former at 578 nm and the latter at 571 nm, avoiding any interference. From a practical point of view, however, this is to be disregarded owing to the very poor sensitivity for calcium at the magnesium isosbestic point and to the fact that measuring at two different wavelengths would require two spectrophotometers or the continual repositioning of the monochromator in a single instrument.

Using the same dye concentration in both the reference and sample cells, we have at any prefixed wavelength:

$$A = C_{\mathrm{Mg}}(\varepsilon_{\mathrm{Mg}} - f\varepsilon_{\mathrm{I}}) + C_{\mathrm{Ca}}(\varepsilon_{\mathrm{Ca}} - f'\varepsilon_{\mathrm{I}}) \tag{1}$$

where f and f', depending on the pH,[8–9] represent the number of complexing agent molecules bound to each magnesium or calcium ion respectively. A is the total absorbance, C the concentration, and ε the molar absorptivity of the species indicated by the subscript (I represents EBT, Ca and Mg represent CaEBT and MgEBT). Under our experimental conditions (pH = 10) it is very likely that f and f' are equal to unity.[10] At 571 nm

$$\varepsilon_{\mathrm{Ca}} = f'\varepsilon_{\mathrm{I}} \text{ and } A = C_{\mathrm{Mg}}(\varepsilon_{\mathrm{Mg}} - f\varepsilon_{\mathrm{I}}) \tag{1a}$$

We have found that equation (1*a*) holds for any excess of calcium as long as the concentration of free EBT allows magnesium to be present only as the MgEBT complex. Once the magnesium concentration has been determined, calcium is quantitatively displaced from the dye complex by addition of MgEDTA, according to:

$$\mathrm{CaEBT} + \mathrm{MgEDTA} \rightarrow \mathrm{CaEDTA} + \mathrm{MgEBT} \tag{2}$$

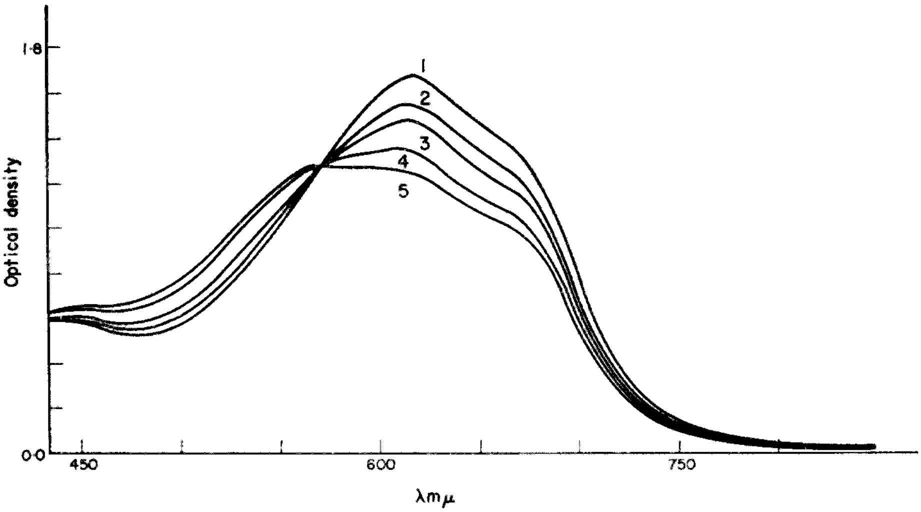

FIG. 1*a*.—Absorption spectra of EBT and CaEBT complex at pH 10.
EBT $0{\cdot}144 \times 10^{-3}M$ for all the curves.
* Ca: 0 ppm, curve 1; 10 ppm, curve 2; 20 ppm, curve 3; 40 ppm, curve 4; 50 ppm, curve 5.

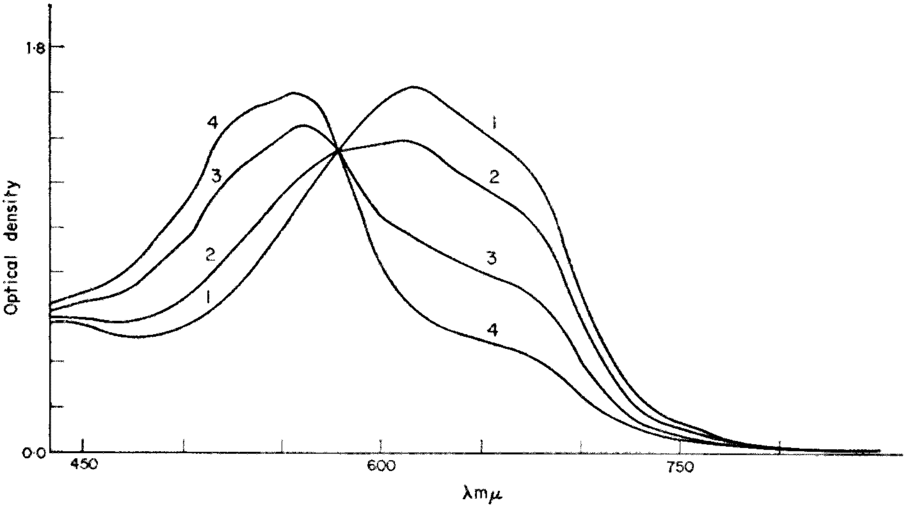

FIG. 1*b*.—Absorption spectra of EBT and MgEBT complex at pH 10.
EBT $0{\cdot}144 \times 10^{-3}M$ for all the curves.
* Mg: 0 ppm, curve 1; 2 ppm, curve 2; 6 ppm, curve 3; 10 ppm, curve 4.

By measurement of the increase in absorbance corresponding to the MgEBT obtained by this reaction, the concentration of calcium (in ppm) may be obtained with the same degree of accuracy as that of magnesium and with an amplification factor, with respect to its direct measurement at any wavelength with the exception of 571 nm, equal to: $\frac{\varepsilon_{\mathrm{Mg}} - \varepsilon_{\mathrm{I}}}{\varepsilon_{\mathrm{Ca}} - \varepsilon_{\mathrm{I}}}$.

Heavy metals, if present, affect to different extents the determination of magnesium and calcium. In the first case for instance, the presence of Cu(II) or Fe(II) causes a decrease in absorbance ($\varepsilon_{\mathrm{I}} > \varepsilon_{\mathrm{CuI}}$)

* All the concentrations reported are referred to the original concentration in the samples. The actual concentration in the optical cell was in each case 8 times more dilute.

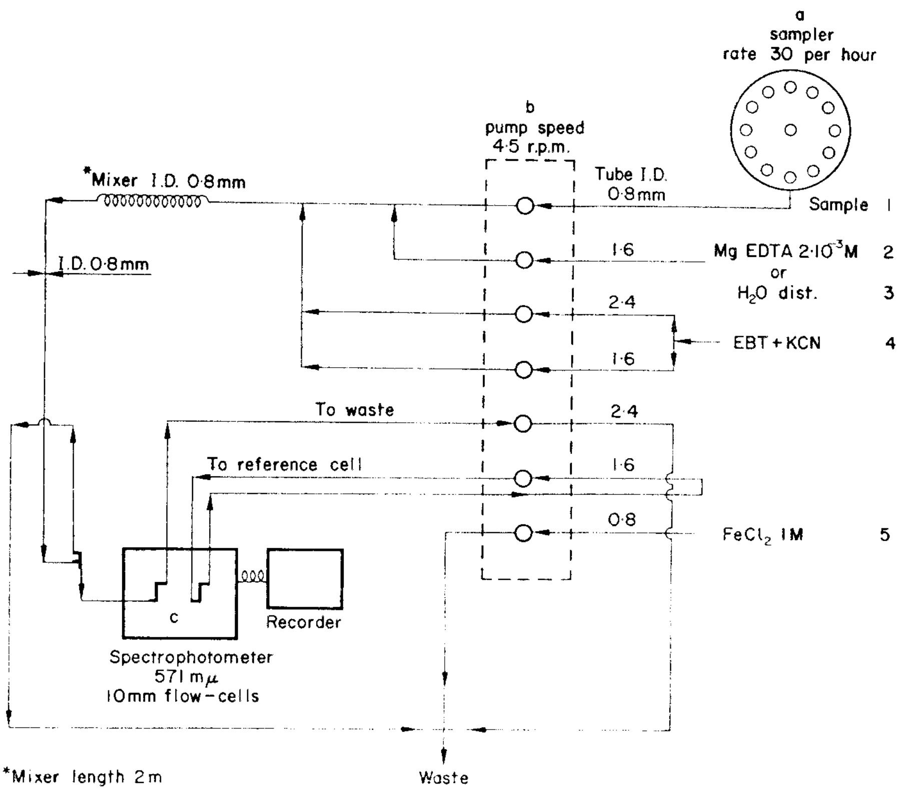

Fig. 2.—Diagram of automatic analyser.

which counteracts the increase due to magnesium, whereas Zn(II) has very little effect on measurements at 571 nm ($\varepsilon_{EBT} \sim \varepsilon_{ZnEBT}$) and so on. In the second case, on addition of MgEDTA, only Zn(II) displaces magnesium from MgEDTA, increasing the absorbance, while Cu(II) and Fe(II) still form the more stable CuEBT and FeEBT respectively.[11] For this reason, their presence must be masked by addition of cyanide to the solution to form the very stable cyano-complexes, which are stronger than the corresponding complexes with EBT or EDTA. The excess of cyanide can be removed afterwards by adding the waste solution to 1*M* FeCl$_2$ solution (see Fig. 2).

The choice of pH 10 as working condition is a compromise between the maximum formation of MgEBT and the minimum precipitation of Mg(OH)$_2$.

EXPERIMENTAL

Apparatus

In Fig. 2 the scheme for the automatic determination of magnesium and calcium is shown; *a* is a sampler for a hundred samples with variable operational programme, and *b* is an 8-channel precision peristaltic pump, both constructed in our laboratory; *c* is a non-scanning double-beam spectrophotometer adapted for two micro-cells ("Photocrom" built by Rastelli, Rome). The stability, the wavelength-setting precision and the half-intensity bandwidth (less than 1 nm at 571 nm for a slitwidth of 0·2 mm) of this low-cost instrument were satisfactory for the present purpose.

The sampler was programmed for 30 analyses per hr. After each sample (0·15 ± 0·009 ml) a 0·75-ml portion of pure water was pumped through the same channel in order to clean the tubing system. The scheme does not provide for the use of air bubbles for liquid segmentation and tube cleaning. It was found that the accuracy and precision were not improved by air-bubbling, and that with the system used a higher or lower concentration of determinant in the preceding sample had no effect on the value determined.

Solutions

All solutions except the sample were buffered at pH 10 with a borate buffer. The concentration of buffer in the solutions was adjusted to be about 0·1*M*. A variation in buffer concentration between

0·05 and 0·2*M* did not affect the results. The concentration of EBT was about 0·01%. Since the final concentration of EBT was the same in both sample and reference cells, equation (1*a*) was used for the calculation of concentration. The concentrations of the other reagents are given in Fig. 2.

The operating steps were: (1) pumping of reagents 1, 3, 4, 5 and determination of magnesium for all the samples, according to equation (1*a*) and a calibration curve; (2) pumping of reagents 1, 2, 4, 5 and determination of calcium from the difference in absorbance between steps 2 and 1.

RESULTS AND DISCUSSION

From the calibration curve, a slope of 0·014 absorbance units per 1 ppm of metal was found; the lowness of this value has mainly to be attributed to the fact that the magnesium concentrations are referred to the original concentration in the sample, while the concentration in the optical cell is only about 7% of this, in order to have an excess of EBT even when 40 ppm of calcium and/or magnesium are present in the sample.

Two criticisms may therefore be raised concerning sources of error; the low absorbance values and the effect of incorrect repositioning of the monochromator at the isosbestic point. As to the first point, improvements in electronics have enabled instruments to be constructed with very good stability of amplifiers and light intensities. Secondly, an error of 0·5 nm in wavelength was found to have very little effect on the results, since variation of the ratio of the molar absorptivities of calcium-EBT complex and free EBT with wavelength is small near 571 nm. For instance, with a solution containing 40 ppm of calcium and 3 ppm of magnesium, a 0·5-nm wavelength-setting error was calculated to cause an error of 10% or less in the magnesium result, depending on the bandwidth.

Table I reports the analyses of some relevant samples and shows that the relative standard deviation is about 4% (10 measurements for each set).

TABLE I.—ANALYSIS OF CALCIUM–MAGNESIUM MIXTURES

No.	Sample composition, ppm		*Ca found, ppm	Relative std. devn. for Ca, %	*Mg found, ppm	Relative std. devn. for Mg, %
	Ca	Mg				
1	10	3	9·5	5·0	3·1	3·0
2	40	3	40·9	5·0	3·2	7·0
3	30	5	30·5 (29·6)	3·2 (3·4)	4·8 (4·8)	3·1 (3·8)
4	15	15	14·5 (15·3)	3·7 (1·0)	15·7 (16·1)	1·7 (1·5)
5	5	25	4·5 (4·6)	3·8 (5·1)	24·2 (25·2)	2·2 (1·6)

* Average value from ten determinations.

The numbers in brackets refer to experiments with liquid segmentation.

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Summary—Magnesium and calcium may each be determined in water by an automatic spectrophotometric method. At 571 nm with an excess of Eriochrome Black T as metallochromic agent, the variation in absorbance is proportional to the magnesium concentration regardless of the calcium concentration. By addition of MgEDTA to displace the calcium from its CaEBT complex, this element may be determined at the same wavelength. For 3–25 ppm of magnesium and 5–40 ppm calcium, the standard deviation was about 4%. The apparatus is described.

Zusammenfassung—Magnesium und Calcium können beide in Wasser mit einer automatischen spektrophotometrischen Methode bestimmt werden. Die Extinktionsänderung bei 571 nm mit einem Überschuß Eriochromschwarz T als Metallfarbreagens ist proportional zur Magnesiumkonzentration, unabhängig von der Calcium-konzentration. Fügt man MgEDTA zu, um das Calcium aus seinem Komplex mit Eriochromschwarz T freizusetzen, so kann Calcium bei derselben Wellenlänge bestimmt werden. Bei 3–25 ppm Magnesium und 5–40 ppm Calcium betrug die Standardabweichung etwa 4%. Die Apparatur wird beschrieben.

Résumé—On peut doser le magnésium et le calcium dans l'eau par une méthode spectrophotométrique automatique. A 571 nm avec un excès de Noir Eriochrome T comme agent métallochrome, la variation de l'absorption est proportionnelle à la concentration en magnésium, sans tenir compte de la concentration en calcium. Par addition de Mg EDTA pour déplacer le calcium de son complexe Ca EBT, on peut déterminer cet élément à la même longueur d'onde. Pour 3–25 p.p.m. de magnésium et 5–40 p.p.m. de calcium, l'écart type est d'environ 4%. On décrit l'appareil.

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Analysis of platinum for certain elemental impurities by neutron activation

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THE PRESENCE of certain elemental impurities in platinum, even in trace concentrations, may seriously limit its catalytic characteristics. Several radiochemical procedures are currently reported for assay of Fe, Co, As, Se, Ru, Pd, Ag, Os, Ir and Au in platinum.[1–6] In the present work, platinum is simultaneously analysed for Ag, Ru, Co, Fe, Zn, Cd and Hg by a scheme based on their sequential separation by ion-exchange chromatography.

EXPERIMENTAL

Materials and pile irradiations

The matrix target was processed from analytical grade platinum chloride ($H_2PtCl_6 \cdot 6H_2O$), by reduction with formic acid at pH 1·5. A second platinum sample was a 0·5-mm diameter platinum wire of analytical standard grade. The monitoring standards were spectroscopically pure, and all other chemicals were of analytical grade purity. The ruthenium standard was prepared by the reduction of a ruthenium trichloride solution.

The ion-exchange resin used was the strongly basic Dowex-1 (X8, 100–200 mesh), freed from alcohol-soluble organic compounds, and successively washed with water and concentrated hydrochloric acid.

The neutron activation was carried out in UA-RR-1 at Inchas for 48 hr with a neutron flux of $1{\cdot}3 \times 10^{11}$ n/mm^2/sec. Test samples and standards were wrapped separately in aluminium foil (>99·95% pure) and subjected to the same neutron dose.

Radiochemical procedure

After a suitable cooling period, each sample is dissolved in 5–10 ml of *aqua regia*, then the solution is evaporated to dryness and the residue dissolved in concentrated nitric acid (5 ml). Aliquots of standardized carrier solutions of Ag, Ru, Co, Fe, Zn, Cd and Hg (50 mg each) are added. The separation and decontamination of the elements takes place simultaneously.

Silver. The nitric acid solution of test sample and added carriers is treated with 10 ml of hydrochloric acid (1 + 1), boiled, and the silver chloride precipitated is dissolved in excess of ammonia. Iron scavenger (5 mg) is added, and the iron(III) hydroxide is precipitated by addition of ammonia before further precipitation of silver as chloride.

Separation of the platinum. The hydrochloric acid solution, freed from silver, is treated with formic acid (5 ml), brought to pH 1·5 and boiled. Metallic platinum is filtered off and discarded. The formic acid is subsequently destroyed by boiling with nitric acid, excess of which is removed by repeated addition of concentrated hydrochloric acid and boiling.

Ruthenium, cobalt, iron, zinc, cadmium and mercury. The solution containing the residual elements is made 11–12*M* in hydrochloric acid (15–20 ml), and allowed to pass through an 8-mm column (flow-rate = 0·3 ml/min) containing about 20 g of Dowex-1 (chloride form). The column is successively treated with different concentrations of hydrochloric acid, hydrochloric acid–hydrofluoric acid mixture or nitric acid respectively (Fig. 1).

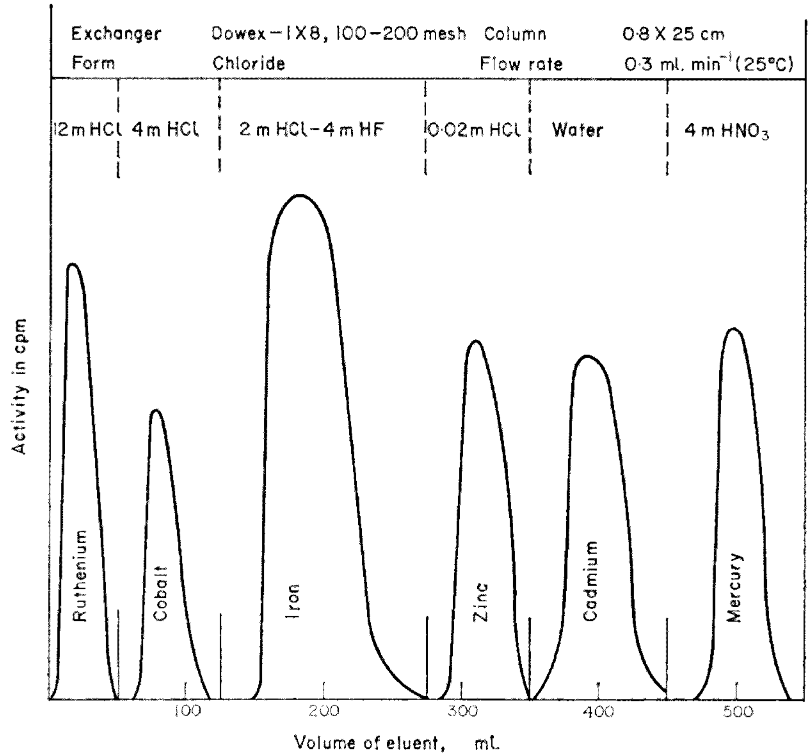

FIG. 1.—Separation of ruthenium, cobalt, iron, zinc, cadmium and mercury by ion-exchange chromatography.

Ruthenium. The concentrated hydrochloric acid effluent (50 ml) containing non-absorbable metal chlorides, including ruthenium, is concentrated. The solution is diluted to be 1:1 in hydrochloric acid, powdered zinc (500 mg) is added, and reduction is completed in 15–30 min. The metallic ruthenium formed is filtered off, repeatedly washed and dried.

Cobalt. The 4*M* hydrochloric acid eluates (75 ml) are concentrated by evaporation, then diluted and 5 mg of both iron and copper scavengers are added. The acid-insoluble sulphides formed on passage of hydrogen sulphide are separated and discarded. After removal of excess of hydrogen sulphide, iron is separated as iron(III) hydroxide and discarded. The solution containing cobalt is adjusted to pH 5·5, saturated with ammonium thiocyanate, and cobalt is extracted with diethyl ether, recovered from the organic layer with ammonium hydroxide (6*M*) and finally precipitated as the sulphide.

Iron. The 2*M* hydrochloric acid–3*M* hydrofluoric acid eluates (150 ml) are concentrated, made alkaline with ammonia, and the precipitated iron(III) hydroxide is dissolved in 9*M* hydrochloric acid. Iron is extracted by diethyl ether, stripped with water, precipitated as hydroxide and finally ignited to Fe_2O_3.

Zinc. The 0·02*M* hydrochloric acid eluate (75 ml) is concentrated, ammonium chloride is added (5 g) together with 10 ml of 2*M* sodium acetate, and the pH is adjusted to 6·5. Zinc is separated as

$Zn(NH_4)PO_4$ by the addition of 10% diammonium hydrogen phosphate solution to the hot solution. The precipitate formed is dissolved in hydrochloric acid and zinc is reprecipitated with ammonium phosphate.

Cadmium. To the water eluates containing cadmium (75–100 ml), iron scavenger (5 mg) is added, and the cadmium is complexed with excess of 4*M* ammonia. The precipitated iron(III) hydroxide is discarded, and cadmium is precipitated as the sulphide from slightly acid medium. The cadmium sulphide is dissolved in hydrochloric acid and iron scavenger is added and separated as hydroxide before the precipitation of cadmium as $Cd(NH_4)PO_4{\cdot}H_2O$.

Mercury. The 4*M* nitric acid eluates (75 ml) are concentrated and treated with excess of 10% sodium hydroxide solution to precipitate hydrated mercury(II) hydroxide. The precipitate is dissolved in hydrochloric acid, treated with hydrogen sulphide, and the mercury(II) sulphide formed from a warm dilute solution is dissolved in *aqua regia* and the excess of acid removed. The solution is made 8*M* in nitric acid and the mercury is extracted into ethyl acetate in the presence of a trace of chloride ions. It is stripped with 3*M* hydrochloric acid and finally precipitated as mercury(II) sulphide.

The radioactive preparations used as monitoring standards are separable in the same chemical forms as those in the analysed samples.

Radiation measurements

Activity measurements were carried out with a counting assembly including a scintillation head with an NaI(TI) crystal (40 × 25 mm) and a 100-channel analyser with a print-out facility.

RESULTS AND DISCUSSION

The separation of Co, Fe, Zn and Cd by ion-exchange chromatography is commonly used in analytical applications.[7–9] The scheme worked out for the determination of Ag, Ru, Co, Fe, Zn, Cd and Hg in platinum is based on their sequential separation by anion-exchange chromatography. The separation is due to differences in the overall stabilities of the anionic chloro-complexes of the metals in the systems used.[10] The decreasing concentration of hydrochloric acid (or mixed hydrochloric acid–hydrofluoric acid) in the eluents favours the sharp separation of the elements studied.[11]

The separation of the platinum matrix by reduction at an early stage eliminates the possible interference of $PtCl_6^{2-}$. This treatment also removes other noble metals such as ^{199}Au formed by β-decay of ^{199}Pt.

Separation of ruthenium by ion-exchange is not common.[12] Although the metal readily forms anionic complexes, it does so only to a limited extent in concentrated hydrochloric acid,[13,14] thus facilitating its direct elution by concentrated hydrochloric acid in the present system. Subsequent separation of the metal by reduction in an acid medium increases the efficiency of decontamination.

Sorption of Co, Fe, Zn, Cd and Hg on the ion-exchanges from 12*M* hydrochloric acid is expected in the light of the exchange behaviour of their chloro-complexes.[15–17] The order of elution could be predicted from the distribution coefficients listed in Table I. This is in accord with the reported stabilities of metal-ion complexes.[10]

Very high distribution coefficient values are observed for mercury(II), even in very dilute chloride solutions,[18–20] thus preventing its elution from chloride media.[21] The eluting action of nitrate (4*M* nitric acid) is attributed to the reduction in $[HgCl_4^{2-}]$ due to the decreased chloride concentration.

The results of the determinations carried out (Table II), are based on the scintillation gamma-ray spectrometric analysis of the characteristic photopeaks corresponding to the high-energy gamma-ray

TABLE I.—SEPARATION OF COBALT, IRON, ZINC AND CADMIUM*

Eluent	Distribution coefficient			
	Cobalt	Iron	Zinc	Cadmium
12*M* HCl	56	450	46	10·0
4*M* HCl	1·0	54	890	168
2*M* HCl/3*M* HF		1·0	450	87
0·02*M* HCl			1·5	31
Water				12·0

* Separation on the strongly basic anion exchanger, Dowex-1 X8, 100–200 mesh, by using different HCl or HCl–HF eluent concentrations.[25]

TABLE II.—DETERMINATION OF TRACE ELEMENTS IN PLATINUM*

Element	Isotope (n, γ)	$t_{1/2}$	Principal γ-energy, *MeV*	Σ_g† *mm*^{2}	Amount found, *ppm*‡	
					Sample 1	Sample 2
Silver	^{110m}Ag	260 d	0·66	0·76	31·7	23·3
			0·88		23·8	—
			others		—	19·0
Ruthenium	^{103}Ru	40 d	0·50	0·27	29·4	13·8
			0·61		19·3	16·5
					20·0	15·3
Cobalt	^{60}Co	5·25 y	1·17	3·7	0·26	0·04
			1·33		0·39	0·06
					0·91	0·08
Iron	^{59}Fe	45 d	1·10	$3·4 \times 10^{-3}$	32·3	19·4
			1·29		24·1	18·0
					21·7	16·2
Zinc	^{65}Zn	245 d	1·11	0·21	7·0	2·8
			0·51		—	1·3
			others		14·5	—
Cadmium	^{115m}Cd	43 d	0·48	0·013	17·4	4·8
			0·94		10·6	6·1
			1·30		11·1	—
Mercury	^{203}Hg	46 d	0·28	0·34	12·3	2·6
					12·3	5·1
					7·3	5·1

* About 100 mg of the neutron-activated Pt-targets have been used in each determination.

† The activation cross-sections per gram of element rather than the natural isotopic abundance and the microscopic activation cross-section.[26]

‡ Sample 1, powdered platinum was obtained from the platinum chloride by reduction, and sample 2 was the 0·5-mm wire. Results are corrected for self-shielding (4·5 and 4%, in samples 1 and 2 respectively).

lines of the respective radioisotopes. This is particularly important in silver determinations to eliminate the interference of ^{111}Ag ($E_\gamma = 0·34$ MeV) formed from elemental palladium.[22,23]

The interfering nuclear reactions affecting the determination of Zn, Cd, Ru and Hg are not expected to occur under the conditions used. The low cobalt concentrations in the samples analysed (<1 ppm), render insignificant the cobalt interference [due to the (n, p) process] in iron determinations. The results are corrected for self-shielding caused by the neutron flux attenuation in test samples.[24] The corrected results have a mean probable error of ±15%. This could be considerably decreased by repeated analysis and/or by the use of high integral doses of incident neutrons.

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Summary—Silver, ruthenium, cobalt, iron, zinc, cadmium and mercury are determined in platinum by neutron-activation analysis. The scheme developed requires the removal of the platinum matrix by reduction and the sequential separation of the elements by ion-exchange chromatography. The method is suitable for the simultaneous determination (at the ppm level) of these elements in milligram quantities of platinum.

Zusammenfassung—Silber, Ruthenium, Kobalt, Eisen, Zink, Cadium und Quecksilber werden in Platin durch Neutronenaktivierungsanalyse bestimmt. Bei dem entworfenen Trennungsgang wird die Hauptmenge Platin durch Reduktion entfernt und dann die anderen Elemente durch Ionenaustauschchromatographie getrennt. Das Verfahren eignet sich für die gleichzeitige Bestimmung der genannten Elemente (im ppm-Bereich) in Milligrammengen Platin.

Résumé—Argent, ruthénium, cobalt, fer, zinc, cadmium et mercure sont dosés dans le platine par analyse par activation de neutrons. Le schéma élaboré nécessite l'élimination de la matrice de platine par réduction et la séparation ultérieure des éléments par chromatographie par échange d'ions. La méthode convient à la détermination simultanée (au niveau de la p.p.m.) de ces éléments dans des quantités de platine de l'ordre du milligramme.

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Studies on the extraction and determination of metal salts with isobutyl methyl ketone—XIV*

Extraction of gold†

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SEVERAL reports have already been published on the extraction of gold(III) from hydrochloric acid solutions by means of isobutyl methyl ketone (IBMK). Gotô *et al.*[1] used 1, 3 and $6M$ hydrochloric acid, and Strelow *et al.*[2] used 0·1–$4M$ hydrochloric acid, but these experiments were confined to quite narrow ranges of the variable factors. Pinajian[3,4] covered a rather wide range of gold concentration

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† Paper read at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1969.

from 1·25 × 10^{-5} to 1·00 × $10^{-1}M$, and of hydrochloric acid concentration from 1 to 6*M*. There is no literature, however, on trace amounts of gold or extraction from mixtures of hydrochloric and other mineral acids. The present work remedies this deficiency.

EXPERIMENTAL

Reagents

Gold carrier stock solution (10 mg/ml). Prepared by dissolving about 10·6 g of chloroauric acid ($HAuCl_4 \cdot 4H_2O$, >99·2% purity) in 1 litre of a mixed solution (2*M*) of nitric and hydrochloric acids, and standardized gravimetrically.[5]

^{198}Au *tracer stock solution.* Prepared by diluting approximately 10 mCi of ^{198}Au activity in 100 ml of mixed solution (2*M*) of nitric and hydrochloric acids. The chemical form was $^{198}AuCl_3$ in a mixed solution (0·68*M*) of nitric and hydrochloric acids.

Gold carrier–^{198}Au *tracer solution.* Made by mixing various amounts (0–250 mg of gold) of the carrier stock solution with approximately 10 μCi of ^{198}Au tracer in a 100-ml beaker containing several ml of *aqua regia*, evaporating the mixture slowly to incipient dryness on a boiling water-bath, and then dissolving the residue in 50 ml of 2*M* hydrochloric acid.

Other reagents used were all of analytical-reagent grade.

Procedure

Ten ml of an acid solution containing a 2·00-ml aliquot of the gold carrier–^{198}Au tracer solution were shaken vigorously for about 1 min (240 shakes) with an equal volume of IBMK in a 100-ml separatory funnel. When the two phases had separated, equal aliquots of each were transferred into polyethylene tubes. The gamma-activity of the ^{198}Au in each aliquot was counted by means of a scintillation counter (1350 V, discrimination 35 μA). Samples from both phases of a given extraction were counted consecutively in the same geometry to minimize errors at the time of measurement.

The degree of extraction was calculated from the results after correction for the volume changes occurring on equilibration. Equilibrium was found to be reached within 15 sec. No temperature control was exercised, but the ambient temperature was fairly constant at 27 ± 2°.

RESULTS AND DISCUSSION

Extraction of gold(III) from hydrochloric acid solution

Under the experimental conditions given in the procedure, gold(III) in concentrations ranging from traces to 5·13 × $10^{-3}M$ was extracted with IBMK from hydrochloric acid solutions of various concentrations. The results are shown in Fig. 1.

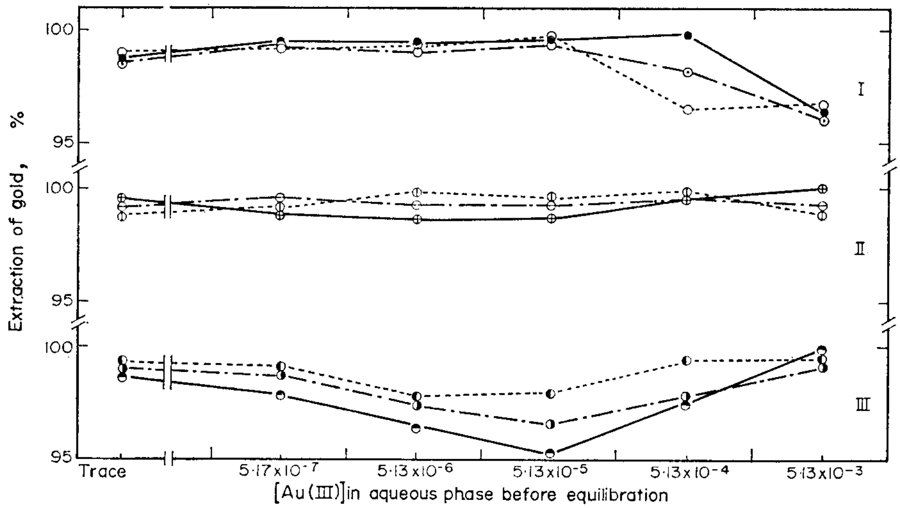

FIG. 1.—The extraction of gold(III) with isobutyl methyl ketone as a function of hydrochloric acid and gold concentrations

I; [···○···: 0·5*M*-HCl, ———○———: 1*M* HCl, —●—: 2*M*-HCl], II; [---⦶---: 3*M*-HCl, ———⊖———: 4*M*-HCl, ——⊕——: 5*M*-HCl], III; [---◐---: 6*M*-HCl, ———◑———: 7*M*-HCl, ——◒——: 8*M*-HCl]

TABLE I.—EXTRACTION OF GOLD FROM MIXED ACID SOLUTIONS

Acid	Concn. of acid,* N	Au(III),† M	R	Extraction of gold, %	Acid	Concn. of acid,* N	Au(III)† M	R	Extraction of gold, %
HCl + HNO$_3$	1 + 0	5·13 × 10^{-6}	1·01	99·$_0$	HCl + H$_2$SO$_4$	5 + 1	5·13 × 10^{-6}	1·08	100
	1 + 1	5·13 × 10^{-6}	1·00	99·$_8$		5 + 3	5·13 × 10^{-6}	1·12	99·$_5$
	1 + 3	5·13 × 10^{-6}	0·92	99·$_8$		5 + 5	5·13 × 10^{-6}	1·23	99·$_9$
	1 + 5	5·13 × 10^{-6}	0·80	99·$_4$		1 + 0	5·13 × 10^{-4}	1·01	98·$_2$
	3 + 0	5·13 × 10^{-6}	1·03	99·$_3$		1 + 1	5·13 × 10^{-4}	0·90	99·$_2$
	3 + 1	5·13 × 10^{-6}	0·98	99·$_9$		1 + 3	5·13 × 10^{-4}	1·03	98·$_0$
	3 + 3	5·13 × 10^{-6}	0·85	99·$_8$		1 + 5	5·13 × 10^{-4}	1·10	93·$_8$
	3 + 5	5·13 × 10^{-6}	0·75	99·$_2$		3 + 0	5·13 × 10^{-4}	1·03	99·$_8$
	5 + 0	5·13 × 10^{-6}	1·07	98·$_8$		3 + 1	5·13 × 10^{-4}	1·01	99·$_8$
	5 + 1	5·13 × 10^{-6}	0·98	99·$_7$		3 + 3	5·13 × 10^{-4}	1·04	99·$_9$
	5 + 3	5·13 × 10^{-6}	0·83	99·$_7$		3 + 5	5·13 × 10^{-4}	1·08	99·$_6$
	5 + 5	5·13 × 10^{-6}	0·71	98·$_7$		5 + 0	5·13 × 10^{-4}	1·06	99·$_6$
	1 + 0	5·13 × 10^{-4}	1·01	98·$_2$		5 + 1	5·13 × 10^{-4}	1·08	99·$_7$
	1 + 1	5·13 × 10^{-4}	1·00	100		5 + 3	5·13 × 10^{-4}	1·14	99·$_9$
	1 + 3	5·13 × 10^{-4}	0·92	99·$_8$		5 + 5	5·13 × 10^{-4}	1·24	97·$_0$
	1 + 5	5·13 × 10^{-4}	0·81	99·$_2$	HCl + HClO$_4$	1 + 0	5·13 × 10^{-6}	1·01	99·$_0$
	3 + 0	5·13 × 10^{-4}	1·03	99·$_8$		1 + 1	5·13 × 10^{-6}	0·85	99·$_7$
	3 + 1	5·13 × 10^{-4}	0·99	99·$_9$		1 + 3	5·13 × 10^{-6}	0·62	98·$_7$
	3 + 3	5·13 × 10^{-4}	0·84	99·$_8$		3 + 0	5·13 × 10^{-6}	1·03	99·$_3$
	3 + 5	5·13 × 10^{-4}	0·75	99·$_3$		3 + 1	5·13 × 10^{-6}	0·78	99·$_6$
	5 + 0	5·13 × 10^{-4}	1·06	99·$_6$		3 + 3	5·13 × 10^{-6}	0·55	99·$_6$
	5 + 1	5·13 × 10^{-4}	0·97	100		5 + 0	5·13 × 10^{-6}	1·07	98·$_6$
	5 + 3	5·13 × 10^{-4}	0·82	99·$_8$		5 + 1	5·13 × 10^{-6}	0·72	99·$_6$
	5 + 5	5·13 × 10^{-4}	0·72	99·$_2$		5 + 3	5·13 × 10^{-6}	0·41	98·$_3$
HCl + H$_2$SO$_4$	1 + 0	5·13 × 10^{-6}	1·01	99·$_0$		1 + 0	5·13 × 10^{-4}	1·01	98·$_2$
	1 + 1	5·13 × 10^{-6}	1·01	100		1 + 1	5·13 × 10^{-4}	0·96	99·$_2$
	1 + 3	5·13 × 10^{-6}	1·00	99·$_0$		1 + 3	5·13 × 10^{-4}	0·63	98·$_8$
	1 + 5	5·13 × 10^{-6}	1·00	91·$_9$		3 + 0	5·13 × 10^{-4}	1·03	99·$_8$
	3 + 0	5·13 × 10^{-6}	1·03	99·$_3$		3 + 1	5·13 × 10^{-4}	0·89	99·$_5$
	3 + 1	5·13 × 10^{-6}	1·02	99·$_8$		3 + 3	5·13 × 10^{-4}	0·55	98·$_9$
	3 + 3	5·13 × 10^{-6}	1·05	99·$_8$		5 + 0	5·13 × 10^{-4}	1·06	99·$_6$
	3 + 5	5·13 × 10^{-6}	1·07	90·$_0$		5 + 1	5·13 × 10^{-4}	0·87	99·$_9$
	5 + 0	5·13 × 10^{-6}	1·07	98·$_6$		5 + 3	5·13 × 10^{-4}	0·47	99·$_2$

* Acidity in the aqueous phase before equilibration.

† Concentration of gold in the aqueous phase before equilibration.

R = phase volume ratio, V_{aq}/V_{org}.

According to Pinajian,[4] the distribution coefficient of gold depends on the mutual variation of the concentrations of gold and hydrochloric acid, without a definite dependence on either alone. Figure 1 shows that gold(III) is approximately 99% extracted from 3-5*M* hydrochloric acid, irrespective of the gold concentration, but from 0·5–2*M* hydrochloric acid, the degree of extraction is still approximately 99% for traces up to $5 \times 10^{-5}M$ gold but decreases gradually with increasing gold concentration. In hydrochloric acid $>6M$, the degree of extraction decreases at around 5×10^{-6}–$5 \times 10^{-5}M$ concentration of gold.

Possible causes for the dependence of distribution of gold(III) on the gold concentration are dissociation of chloroauric acid in the IBMK phase or its polymerization in the aqueous phase.

Extraction of gold(III) from mixed acid solutions

Results for extraction of gold from mixed solutions of hydrochloric acid and nitric, sulphuric or perchloric acid containing gold(III) in $5{\cdot}13 \times 10^{-6}$ or $5{\cdot}13 \times 10^{-4}M$ concentration are shown in Table I.

The addition of 1–5*M* nitric acid, or 1–3*M* sulphuric or perchloric acid to 1–5*M* hydrochloric acid-solutions of gold caused no significant change in the extraction, but addition of 5*N* sulphuric acid lowered it slightly.

Gold(III) could not be extracted from nitric, sulphuric or perchloric acids either alone or mixed, because colloidal gold precipitated out between the aqueous and organic phases.

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Summary—The isobutyl methyl ketone extraction of gold(III) from hydrochloric acid or various mixtures of hydrochloric and other mineral acids was studied as a function of the gold concentration and the acid concentration. Gold (initial concentration up to $5 \times 10^{-3}M$) was quantitatively extracted (99%) from 3–5*M* hydrochloric acid. Addition of nitric acid in 1–5*M* concentration and sulphuric or perchloric acid in 1–3*N* concentration to the 1–5*M* hydrochloric acid solutions used had no effect.

Zusammenfassung—Die Extraktion von Gold (III) aus Salzsäure oder verschiedenen Mischungen von Salzsäure und anderen Mineralsäuren mit Isobutylmethylketon wurde in Abhängigkeit von der Gold- und der Säurekonzentration untersucht. Gold in einer Anfangskonzentration von höchstens $5 \cdot 10^{-3}M$ wurde quantitativ (99%) aus 3–5*M* Salzsäure extrahiert. Die Zugabe von Salpetersäure in Konzentrationen von 1 bis 5*M* und Schwefelsäure oder Perchlorsäure in Konzentrationen von 1–3*N* zu den 1–5*M* salzsauren Lösungen blieben ohne Einfluß.

Résumé—On a étudié l'extraction à la méthylisobutylcétone de l'or (III) à partir d'acide chlorhydrique ou de divers mélanges d'acide chlorhydrique et d'autres acides minéraux en fonction de la concentration en or et de la concentration en acide. L'or (concentration initiale jusqu'à $5 \times 10^{-3}M$) a été extrait quantitativement (99%) à partir d'acide chlorhydrique 3–5*M*. L'addition d'acide nitrique en concentration 1–5*M* et d'acide sulfurique ou perchlorique en concentration 1–3*N* aux solutions d'acide chlorhydrique 1–5*M* n'a pas d'influence.

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Liquid–liquid extraction behaviour of mercury(II) as chloride

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IN RECENT YEARS a good deal of interest has been shown in the neutron-activation determination of trace amounts of mercury in meteorites[1,2,3] and edibles.[4] Liquid–liquid extraction provides a quick and effective method of separation of mercury activity. Extraction of the chloro-complexes of various metals offers a very wide field for making such radiochemical separations. Most ions such as Fe(III), Ga(III), As(III) and Sb(V) which are extracted as chloro-complexes show high extraction at higher hydrochloric acid concentrations and poor or negligible extraction from acid more dilute than 1*M*. Mylius and Hüttner,[5] and West and Duff[6] pointed out that extraction of the mercury(II) chloro-complex is higher at very low molarity of hydrochloric acid. This difference in extraction behaviour would help in radiochemical separation of mercury(II) from other elements. In nuclear reaction studies there is a good chance of the mercury being contaminated with thallium and gold radioisotopes. Both gold(III) and thallium(III) show higher extraction as chloride at lower hydrochloric acid concentrations. A study has therefore been made of the factors which could possibly affect the extraction of mercury, such as hydrochloric acid concentration, temperature, concentration of Hg(II) and the presence of various anions. The difference in the behaviour of oxygenated and non-oxygenated organic solvents has also been investigated.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade. ^{203}Hg with a specific activity of 305 mCi/g was used as tracer; the isotope was obtained in the form of $Hg(NO_3)_2$ and the amount added was so small that any effect due to nitrate was insignificant.

Apparatus

The activity of ^{203}Hg in the aqueous and organic phases was determined by counting suitable aliquots on a flat 25 × 25 mm NaI(Tl) crystal scintillation counter. A special type of crystal head was mounted to hold the beakers. All counts were made under the 279-keV peak, with a single-channel analyser. Solid counting was purposely avoided because of the loss of mercury during sample preparation.

Analytical procedure

The aqueous and organic phases to be used were first equilibrated with each other; then 25 ml of the equilibrated organic phase were shaken with 24·95 ml of the equilibrated aqueous phase plus 0·05 ml of the tracer for a sufficient time to ensure complete equilibration. Equal aliquots of each phase were counted, and the distribution ratio and degree of extraction were calculated. The distribution ratios had a precision of ±5% and the precision of the degrees of extraction varied between ±1·7% and ±14%. Experiments were run in duplicate and the average values are reported.

All studies were made with the equilibrated solvents except the one with unequilibrated ethyl acetate for comparison. The effect of temperature, concentration of Hg(II) ions and presence of various anions was studied on the ethyl acetate system at a hydrochloric acid concentration of 0·0167*M*, around which the values have the best precision. The anions investigated were some of those which could suppress the extraction by masking, namely oxalate, tartrate and citrate, and nitrate was also studied to make sure that the concentration of nitrate furnished by the tracer did not affect the extraction. The temperature effect was studied by taking the same volume of the two equilibrated solvents, with the same amount of activity in each set. The two layers were shaken in a separatory funnel kept immersed in a constant-temperature water-bath, and a portion of the upper layer was removed for counting. The activity in the same volume of organic layer from sets at different temperatures gave a comparative idea of the temperature effect. This avoided cross-contamination of the layers, and taking the separatory funnel out of the thermostat.

RESULTS AND DISCUSSION

The dependence of the distribution ratio on acid concentration is shown in Fig. 1. With ethyl acetate, pentyl acetate and diethyl ether the degree of extraction increases with decrease in the molarity

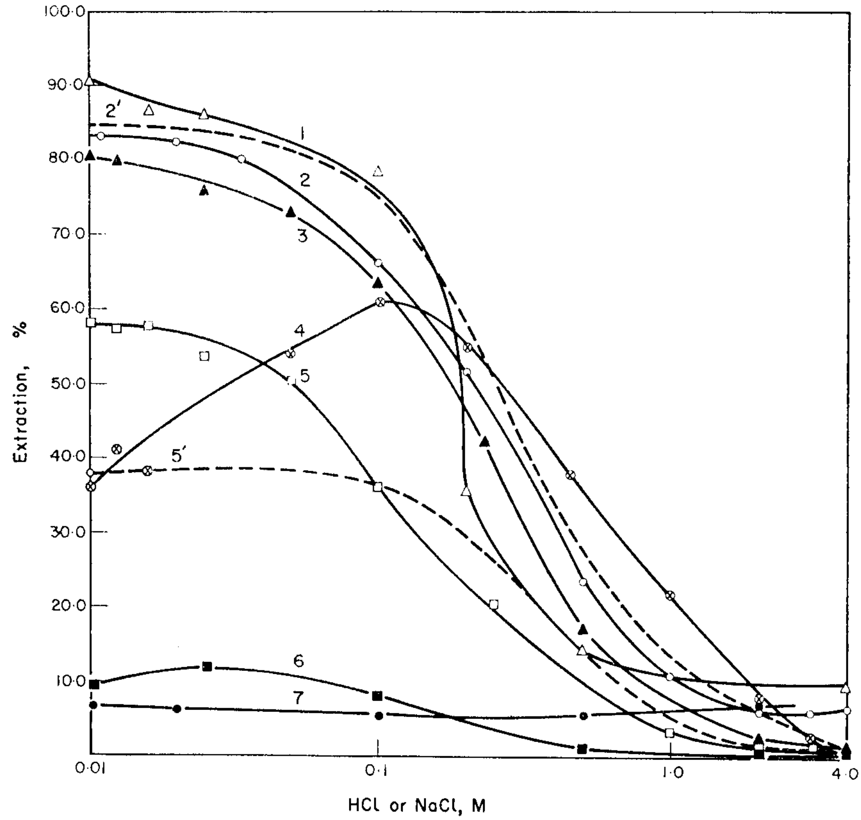

FIG. 1.—Extraction of mercury(II) from hydrochloric acid solutions in various organic solvents.

1, ethyl acetate (unequilibrated); *2*, ethyl acetate (equilibrated); *3*, pentyl acetate; *4*, nitrobenzene; *5*, diethyl ether; *6*, benzene; *7*, chloroform. For comparison the extraction curves from equivalent concentrations of sodium chloride are also shown (*2′*, equilibrated ethyl acetate *5′*, diethyl ether).

of the acid, with a tendency towards a limiting value. With nitrobenzene there is a maximum at around 0·1*M* hydrochloric acid. The two non-oxygenated solvents benzene and chloroform give very poor extraction. This clearly indicates that the oxygenated solvents are better solvents for the mercury chloro-complex than the non-oxygenated solvents.

The effect of temperature over the range 13–45° was negligible, and the concentration of Hg(II) ions had no effect on the extraction into ethyl acetate from 0·0167*M* hydrochloric acid. Nitrate, oxalate, tartrate and citrate in concentrations equimolar with the hydrochloric acid used had no effect.

The distribution ratios between water and ethyl acetate or diethyl ether were studied, with the chloride being supplied by sodium or barium chloride instead of hydrochloric acid. The results with sodium chloride are shown in Fig. 1, and those with barium chloride were similar. With ethyl acetate as solvent there is practically no difference in behaviour whatever the source of the chloride, but with diethyl ether the extraction is comparable only at chloride concentrations $>0{\cdot}1M$. At lower concentrations the extraction is much lower from barium or sodium chloride solutions than from hydrochloric acid.

This study provides a method of radiochemical separation of mercury(II) from a number of metals by extracting it into oxygenated solvent from $<0{\cdot}1M$ hydrochloric acid. The two serious interferences are from Au(III) and Tl(III).

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Summary—The solvent extraction behaviour of mercury(II) chloride with different organic solvents has been studied. The effect of acidity, temperature, concentration of Hg(II), and other anions has been studied. Radiochemical separations from ions such as Fe(III), Ga(III), As(III) and Sb(V) can be accomplished. Au(III) and Tl(III) interfere.

Zusammenfassung—Das Verhalten von Quecksilber(II)chlorid bei der Solventextraktion mit verschiedenen organischen Lösungsmitteln wurde untersucht. Der Einfluß von Acidität, Temperatur, Quecksilber(II)-Konzentration und von fremden Anionen wurde geprüft. Es können radiochemische Trennungen von Ionen wie Fe(III), Ga(III), As(III) und Sb(V) erreicht werden. Au(III) und Tl(III) stören.

Résumé—On a étudié le comportement à l'extraction par solvant du chlorure de mercure(II) avec différents solvants organiques. On a étudié l'influence de l'acidité, de la température, de la concentration en Hg(II), et d'autres anions. On peut réaliser des séparations radiochimiques d'ions comme Fe(III), Ga(III), As(III) et Sb(V). Au(III) et Tl(III) interfèrent.

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Differential titrimetric determination of mixtures of selenium and tellurium

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METHODS for the determination of mixtures of tellurium(IV) and selenium(IV) are important since these elements are associated in certain alloys and slags. Because of lack of selective oxidants or reductants, titrimetric methods are few and are generally based on selective reduction of either selenium or tellurium[1-8] or their separation by distillation.[9,10] Schrenk and Browning[11] determined tellurium(IV) in one aliquot by the dichromate–iron(II) method[12] and selenium plus tellurium in another aliquot by the permanganate–iron(II) method.[13] Johnson and Fredrickson[14] determined the total content by adding a known excess of sodium thiosulphate in 0·15–0·5*M* hydrochloric acid and back-titrating with iodine, and then determined tellurium alone in another aliquot by the same procedure but with 5*M* hydrochloric acid. Iron(III), copper(II), arsenic(V), silver(I) and thallium(III) seriously interfere. We have developed a method based on oxidation of Se(IV) and Te(IV) by permanganate in condensed phosphoric acid medium, followed by selective reduction of Te(VI). The advantages over the earlier methods are (*i*) both elements can be determined in the same aliquot; (*ii*) experimental conditions involve only simple visual indicator titrations and are not critical; (*iii*) the analysis takes only 10–15 min; (*iv*) iron(III), arsenic(V), silver, thallium(III), selenium(VI), uranium(VI), copper(II), nickel, potassium, sodium, aluminium and magnesium do not interfere.

EXPERIMENTAL

Reagents

Potassium permanganate, 0·05 *N*.
Selenium(IV), 0·02 *and* 0·05 *N*.
Tellurium(IV), 0·02 *and* 0·05 *N*.
Condensed phosphoric acid. Prepared as described earlier.[15]
The standard solutions were standardized by appropriate methods.[12,16,17]

Recommended procedure

To an aliquot containing tellurium(IV) and selenium(IV) add 1–5 ml of condensed phosphoric acid. Dilute to 25 ml with distilled water. Add a known and excessive amount of permanganate and titrate the excess after 3–5 min with a standard iron(II) solution, using ferroin as indicator (add 2–3 ml of 10*M* sulphuric acid if the indicator reaction becomes sluggish). After the iron(II) titration, add a known and excessive amount of arsenic(III) solution, and 0·4 ml of 0·1% osmic acid solution and titrate the unreacted arsenic(III) with permanganate. The first titration gives the amount of permanganate consumed for selenium plus tellurium, and the second indicates the amount of arsenic equivalent to the tellurium present.

RESULTS AND DISCUSSION

Permanganate–iron(II) procedure for determination of total content

It has already been reported[15] that the concentration of condensed phosphoric acid has a negligible effect on the oxidation of both selenium and tellurium when permanganate is added in excess, but the oxidation rate depends on the permanganate concentration. The permanganate oxidizes Se(IV) and Te(IV) to Se(VI) and Te(VI), the permanganate being reduced to Mn(III).

After the oxidation, titration with iron(II) reduces both Mn(III) and the excess of permanganate to Mn(II). If the concentration of permanganate and iron(II) are known, the difference between the volume of iron(II) equivalent to the total permanganate added and the volume of iron(II) used in the back-titration is equivalent to the selenium and tellurium present (provided no other reactive species are present).

Selenium oxidation. Aliquots of 0·0838*N* selenium(IV) were treated with 1·5–5 ml of condensed phosphoric acid, and diluted to 50 ml with water; various volumes of permanganate were added in excess and the unreacted permanganate was titrated with iron(II) at various intervals of time, ferroin or barium diphenylaminesulphonate being used as indicator. The results are shown in Table I.

TABLE I

Excess of KMnO$_4$,* %	[Se(IV)] found, *N*						
	Time, *min*	0	1	3	5	10	20
0		0·0207	0·0631	0·0780	0·0809	0·0828	0·0840
50		0·0696	0·0817	0·0833	0·0840	0·0840	0·0840
100		0·0735	0·0830	0·0840	0·0840	0·0840	0·0840
200		0·0821	0·0840	0·0840	0·0840	0·0840	0·0840

* On the basis of permanganate reduced to manganese(III) and selenium(IV) oxidized to selenium(VI).

Tellurium oxidation. Similar experiments showed that tellurium(IV) oxidation is rapid even with the reactants in stoichiometric proportion.

Oxidation of the mixture. Obviously if conditions are correct for selenium oxidation, tellurium will also be oxidized. This was confirmed by oxidation of mixtures of Se(IV) and Te(IV) in molar ratios ranging from 1:5 to 5:1. Results within 0·7% of theoretical were obtained in each case.

After the iron(II) titration, selenium(VI) and tellurium(VI) are present and a selective reductant has to be found for one of them. We tried hydrazine, hydroxylamine, ascorbic acid, iron(II), titanium(III), tin(II), chromium(II), arsenic(III) and antimony(III) and found that only arsenic(III) is selective for reduction of tellurium(VI), in the presence of osmic acid as catalyst. It has no action on selenium(VI).

Arsenic(III)-permanganate method for tellurium determination

Once arsenic(III) had been chosen for reduction of tellurium(VI) the problem was to determine the unreacted arsenic(III) in presence of the tellurium(IV) produced. It was found that arsenite could be titrated in 4–6*M* sulphuric acid in the presence of 0·4 ml of 0·1% osmic acid solution as catalyst, ferroin being used as indicator, without interference by tellurium(IV). Barium diphenylaminesulphonate does not work satisfactorily; at high acidity reduction of the indicator by arsenite is slow, whereas at lower acidities, although reduction of the indicator is sufficiently fast, some tellurium(IV) is also oxidized. With ferroin as indicator, if the sulphuric acid concentration is below 3*M*, although reduction of ferroin is fast some tellurium(IV) is oxidized; if the concentration of sulphuric acid is above 6*M* the reduction of ferroin is slow but if the titration is done slowly, no tellurium is oxidized. The indicator reactions are summarized in Table II.

From Table II, it can be seen that the catalytic effect increases with osmium tetroxide concentration, especially at higher acid concentrations, and that the best conditions are 4–6*M* sulphuric acid and 0·4 ml of 0·1% osmium tetroxide solution.

Aliquots of tellurium(VI) were treated with enough sulphuric acid to give an overall concentration of 4*M* on dilution to 50 ml. An excess of arsenite was added followed by 0·4 ml of 0·1% osmium tetroxide solution and dilution to 50 ml with water. Then 2 drops of 0·01% ferroin solution were added and the unreacted arsenite was titrated with standard permanganate, the titrant being added slowly towards the equivalence point. The permanganate is reduced to manganese(II). Results are given in Table III. The error is ±0·5% and the method can be used to standardize tellurium(VI) solutions.

When selenium(VI) was treated by this procedure no reduction by arsenite occurred provided the mixture was not allowed to stand for more than 1 min. A slow reduction occurred in longer periods (~2% in 5 min). If a small amount of condensed phosphoric acid is added, however, the reaction between arsenite and selenium is negligible even after 5 min.

When the procedure was applied to mixtures of selenium(VI) and tellurium(VI), correct results were obtained for the tellurium, showing that there was no induced reduction of the selenium.

The full procedure was then applied to mixtures of selenium(IV) and tellurium(IV). Representative results are given in Table IV.

TABLE II.—MIXTURES CONTAINING 2·50 ml OF ARSENIC(III) SOLUTION (≡ 3·38 ml OF PERMANGANATE) AND 3·00 ml OF TELLURIUM(IV) SOLUTION

$[H_2SO_4]$, *M*	Osmic acid (0·1 %), *ml*	$KMnO_4$ used, *ml*	Remarks
1·0	0·1	4·52	Reduction of ferroin by arsenite is rapid
1·0	0·2	4·51	
1·0	0.4	4·52	
2·0	0·1	4·46	
2·0	0·4	4·44	
3·0	0·1	3·84	Reduction of ferroin by arsenite is slow
3·0	0·4	3·72	Reduction fast, but higher titres are obtained
4·0	0·2	3·40	Indicator reaction satisfactory
4·0	0·4	3·38	Some fading of ferroin colour but remaining intensity is adequate
5·0	0·2	—	Colour of the ferroin discharged after addition of 1 drop of permanganate, colour reappeared slowly
5·0	0·4	3·38	No discharge of colour, but indicator reaction somewhat slow
6·0	0·2	—	Colour of ferroin discharged on adding permanganate, did not return
6·0	0·4	3·38	Reduction of ferroin by arsenite rather slow and titration must be done very slowly
8·0	0·2	—	Titration not possible
8·0	0·4	3·40	Titration to be done slowly, wait of 3–4 min after every addition of permanganate

TABLE III

Amount of tellurium(VI), *mg*		Amount of tellurium(VI), *mg*	
Taken	Found	Taken	Found
8·11	8·1	23·56	23·7
15·35	15·4	28·81	28·7
18·24	18·3	31·42	31·6
20·64	20·8	35·68	35·8

TABLE IV

Amounts taken, *mg*		Amounts found, *mg*	
Tellurium(IV)	Selenium(IV)	Tellurium(IV)	Selenium(IV)
3·64	8·62	3·63	8·60
4·98	1·96	5·00	1·96
5·24	5·24	5·24	5·26
6·16	2·48	6·14	2·50
8·12	1·52	8·16	1·51

Note. During the titration of unreacted arsenic(III) with permanganate, on addition of the first drop of permanganate nearly 50% of the ferroin colour will be discharged, but then remains the same until the end-point is reached.

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Summary—Methods are described for the differential titrimetric determination at room temperature of mixtures of selenium(IV) and tellurium(IV). The test solution in 0·75–3·5*M* condensed phosphoric acid medium is oxidized with an excess of permanganate and the unreacted permanganate is titrated with iron(II), with ferroin as indicator, to indicate the total content of selenium and tellurium present. Then 10–20 ml of 10*M* sulphuric acid, 0·4 ml of 0·1% osmium tetroxide solution and an excess of arsenic(III) are added to the same solution and the unreacted arsenic(III) is titrated with permanganate (ferroin as indicator) to indicate the content of tellurium.

Zusammenfassung—Verfahren zur differentialtitrimetrischen Bestimmung von Gemischen von Selen(IV) und Tellur(IV) bei Raumtemperatur werden beschrieben. Die Probelösung in 0,75–3,5*M* kondensiertem Phosphorsäuremedium wird mit einem Überschuß Permanganat oxidiert und das nicht verbrauchte Permanganat mit Eisen(II) und Ferroin als Indikator titriert; damit wird die Summe von anwesendem Selen und Tellur ermittelt. Dann werden zur selben Lösung 10–20 ml 10*M* Schwefelsäure, 0,4 ml 0,1% Osmiumtetroxidlösung und ein Überschuß Arsen(III) gegeben. Das nicht verbrauchte Arsen(III) wird mit Permanganat (Ferroin als Indikator) titriert; damit wird der Tellurgehalt ermittelt.

Résumé—On décrit des méthodes pour le dosage titrimétrique différentiel à température ordinaire de mélanges de sélénium(IV) et tellurium-(IV). La solution essai en millieu acide phosphorique condensé 0,75–3,5*M* est oxydée avec un excès de permanganate et le permanganate qui n'a pas réagi est titré au fer(II), avec la ferroïne comme indicateur, pour donner la teneur totale en sélénium et tellurium présents. Puis on ajoute à la même solution 10–20 ml d'acide sulfurique 10*M*, 0,4 ml de solution à 0,1% de tétroxyde d'osmium et un excès d'arsenic(III) et l'on titre l'arsenic(III) qui n'a pas réagi avec le permanganate (ferroïne comme indicateur) pour avoir la teneur en tellurium.

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Kinetic studies of xenon trioxide as an oxidant—I
Determination of alcohols

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N PREVIOUS PAPERS[1,2] we have indicated that the rate of xenon trioxide reactions with some organic acids and alcohols is affected by the pH of the solution and temperature. The time needed for reaction depends on the structure of the acid or alcohol being determined. In another paper[3] we have shown hat hydrogen peroxide can be determined by using it as a catalyst for the reaction of xenon trioxide with t-butanol.

In this work we will point out how a study of the kinetics of the reaction can be used to determine he optimum conditions for the analysis of some organic alcohols. We will show how certain catalysts or inhibitors can greatly speed up or slow down the time of analysis and how the kinetic study can be useful in predicting the limits of detection. In addition, a more complete understanding of the mechanism of the reaction will give the analyst a better insight into the problems that may be encountered when xenon trioxide is used as an oxidant.

EXPERIMENTAL

Apparatus

Spectrophotometer. A Cary Model 14, with matched quartz cells of 10-mm optical path, was used.

Reagents

Xenon trioxide. A standard solution was prepared by the hydrolysis of xenon hexafluoride.[4] The hydrogen fluoride was removed by vacuum distillation. Xenon trioxide was standardized by reduction with excess of sodium iodide and sodium thiosulphate titration of the iodine liberated.

Other reagent grade chemicals were used without further purification. Standard solutions were prepared by direct weighing and dilution to volume with triply distilled water.

Procedure

The alcohol and phosphate buffer were placed in one beaker and the xenon trioxide in a second. The volume in each beaker was either exactly 10 or 15 ml, so that on mixing, the total volume was xactly 25 ml. The initial xenon trioxide concentration was $2 \times 10^{-4}M$. The reaction was initiated by quickly mixing the two solutions and a portion of the mixed solution was at once transferred o a spectrophotometer cell. The reference cell contained the same concentration of alcohol and hosphate buffer solution. The change in absorbance of xenon trioxide at 200 nm was recorded as function of time.

RESULTS AND DISCUSSION

Kinetic study

The kinetic study was carried out first in order to obtain the optimum conditions for analysing he alcohols. The knowledge gained from this work greatly facilitated the analytical determinations.

The oxidation of alcohols by aqueous xenon trioxide is found to exhibit an initiation or induction eriod followed by a linear decrease in xenon trioxide concentration. The rate of reaction increases with increasing pH and is dependent on the type of alcohol present. At 25° the rate of reaction ncreases in the order n-butanol < n-propanol < methanol < ethanol < isopropanol as is shown in Table I by the values listed for the induction period (τ) and the time to reduce the xenon trioxide concentration to one-half its original value ($t_{\frac{1}{2}}$). Duplicate tests, run with deuterated methanol, give almost identical results to those for methanol.

TABLE I.—EFFECT OF pH ON THE RATE OF REACTION OF ALCOHOLS WITH XENON TRIOXIDE ($2{\cdot}4 \times 10^{-4}M$) AT 25°C

Alcohol	pH 3·1		pH 6·6	
	τ, *min*	$t_{\frac{1}{2}}$, *min*	τ, *min*	$t_{\frac{1}{2}}$, *min*
Methanol	1	19	<0·5	<0·5
Methanol*	1	19	—	—
Ethanol	<0·5	5	—	—
Isopropanol	<0·5	<0·5	—	—
n-Propanol	—	80	1·3	1·7
n-Butanol	—	100	1·8	2·8
t-Butanol	—	—	No reaction in 2 hr	

* Deuterated methanol (CD_3OH).

The solution remaining after the alcohol-xenon trioxide reactions are apparently complete, has been found to oxidize iodide to tri-iodide. This kinetic behaviour indicates that hydrogen peroxide may have been formed as one of the by-products. Hydrogen peroxide has also been found in the reaction of xenon difluoride with water and it has been suggested by Appelman[5,6] that the reaction of perxenate or xenon oxide with water may result in the formation of hydroxyl radicals which combine to form hydrogen peroxide.

An experiment was designed to measure both the decrease in xenon trioxide concentration and the increase in hydrogen peroxide in a reaction at 25°. The solution was buffered at pH 2·5 and excess of methanol ($MeOH/XeO_3 = 70$) was added. The change in xenon trioxide concentration was measured at 200 nm and the tri-iodide absorbance at 352 nm was measured periodically by removing 1-ml aliquots and quenching with and without ammonium molybdate as a catalyst. The tri-iodide concentration without a catalyst is a measure of the xenon trioxide concentration; with a catalyst it is a measure of both the xenon trioxide and hydrogen peroxide concentration. The hydrogen peroxide concentration is determined by subtracting the former value from the latter. A plot of the change in concentration of xenon trioxide and hydrogen peroxide with time is given in Fig. 1. From this plot it is seen that the hydrogen peroxide concentration increases quite rapidly and then levels off as a steady state is reached.

Free radical reactions are frequently autocatalytic and exhibit an induction period before the reaction begins. They are also inhibited by substances such as hydroquinone and catalysed by metal ions such as copper(II). Isopropanol does not react with xenon trioxide at pH 1·4 and reacts only very slowly at pH 2·2. The addition of a small amount of copper(II) perchlorate ($3 \times 10^{-6}M$) has no

TABLE II.—EFFECT OF Cu(II) AND HYDROQUINONE ON THE RATE OF REACTION OF ISOPROPANOL AND HEXAFLUOROISOPROPANOL WITH XENON TRIOXIDE ($3{\cdot}0 \times 10^{-4}M$) AT 20°C

pH	Alcohol	Alcohol, $10^{-2}M$	Additive	Additive, $10^{-6}M$	τ, *min*	$t_{\frac{1}{2}}$, *min*
1·4	Isopropanol	1·5	None	—	No reaction in 60 min	
1·4	Isopropanol	1·5	Cu(II)	3.0	No reaction in 60 min	
1·4	Hexafluoroisopropanol	1·5	None	—	7·0	9·2
2·2	Isopropanol	1·5	None	—	34·0	47·0
2·2	Isopropanol	1·5	Cu(II)	3·0	5·8	6·8
2·2	Hexafluoroisopropanol	1·5	None	—	6·5	7·7
2·2	Hexafluoroisopropanol	1·5	Hydroquinone	6·0	No reaction in 60 min	

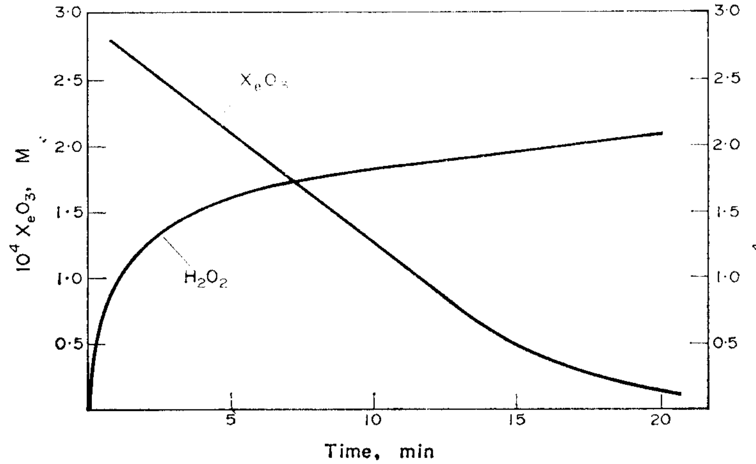

FIG. 1.—Reduction of 3·0 × $10^{-4}M$ XeO_3 by 2·1 × $10^{-2}M$ methanol and the production of hydrogen peroxide.

effect on the reaction at pH 1·4 but does accelerate the reaction at pH 2·2 (See Table II). Hexafluoroisopropanol reacts much faster than isopropanol at pH 1·4 and 2·2 as is shown in Table II. Since fluorine is a good electron-withdrawing group, the hexafluoro alcohol is a stronger acid than isopropanol. This fact along with the evidence of increasing rate with increasing pH suggests that the alkoxide ion rather than the alcohol may be the reactive species. When a small amount of hydroquinone (6 × $10^{-6}M$) is added the reaction with hexafluoroisopropanol is inhibited. Tertiary butanol will also inhibit the reaction of primary and secondary alcohols with xenon trioxide, and an analytical determination for alcohols, based on this discovery, is described in the next section.

The facts above give some evidence that these reactions may be occurring by a free radical mechanism with the generation of hydrogen peroxide as one of the products. Further experiments are in progress to determine this mechanism.

Determination of t-butanol

Tertiary butanol does not react with xenon trioxide at pH less than 6·6, but will do so at pH 7. An ester-like intermediate may be formed. Experiments to clarify the nature of this intermediate were carried out by Jaselskis and Warriner.[7] However, the reaction with t-butanol can be initiated by adding hydrogen peroxide as a catalyst.[3] The time of the initiation of the reaction (τ) depends on the concentration of hydrogen peroxide; as little as 1 × $10^{-6}M$ will initiate the reaction.

Rhodes and Blake[8] have found very slow reactions of tertiary alcohols with aqueous xenon trioxide. We have found that t-butanol will react in the presence of catalysts or at pH 7. At this pH the initiation time is directly proportional to the concentration of the alcohol as is shown in Table III. Tertiary butanol in amounts as low as 22 μg or 880 parts per milliard (ppM) may be determined.

Aqueous xenon trioxide is stable in acid solution but at pH 7 and in basic solutions it will disproportionate and decompose forming perxenate, lower oxides of xenon, oxygen, and xenon.[9] The rate of the reaction is dependent on the purity of the solution. In triply distilled water adjusted to pH 7 with phosphate buffer, xenon trioxide (2 × $10^{-4}M$) is reduced to about 90% of its original concentration in 30 min.

The increase in the reaction induction time as the molar ratio of xenon trioxide to t-butanol decreases gives further support to the formation of a stable ester-like intermediate which forms to slow the reaction. This ester-like intermediate prevents the formation of the more reactive lower oxides of xenon (such as XeO_2 or XeO) and hydrogen peroxide which are necessary for the reaction of t-butanol.

Determination of primary and secondary alcohols

A precise titrimetric method, using xenon trioxide, for the determination of primary and secondary alcohols is described by Jaselskis and Warriner.[10] The determination requires about 2 hr and is useful in detecting alcohols in amounts as low as 25 μg.

TABLE III.—DETERMINATION OF TERTIARY BUTANOL BY OXIDATION WITH XENON TRIOXIDE ($2 \times 10^{-4}M$)

Molar ratio XeO_3: t-BuOH	Initiation time, *min*	t-Butanol	
		Taken, *μg*	Found,* *μg*
200 : 12	3·75	22	25
200 : 20	5·0	37	33
200 : 40	10·0	74	76
200 : 80	16·2	148	147
200 : 120	23·1	222	222

* Calculated from polynomial regression analysis using an IBM 1130 computer.

If X = initiation time,

$$Y(\mu g) = 13{\cdot}4 + 0{\cdot}594X + 0{\cdot}72X^2 - 0{\cdot}0155X^3$$

and $Y(ppM) = 537 + 23{\cdot}8X + 29{\cdot}0X^2 - 0{\cdot}621X^3$

Tertiary butanol in amounts less than 40 μg is determined with a coefficient of variation of 4%, and less than 2% at higher concentrations.

A more sensitive and rapid method for determining primary and secondary alcohols in amounts as low as 2 μg has been developed by using the alcohols as catalysts for the reaction of t-butanol with aqueous xenon trioxide at pH 7. The initiation time of the reaction decreases with increasing concentration of the primary or secondary alcohol as is shown in Table IV. Without t-butanol the

TABLE IV.—DETERMINATION OF PRIMARY AND SECONDARY ALCOHOLS BY OXIDATION WITH XENON TRIOXIDE ($2 \times 10^{-4}M$). (MOLAR RATIO OF XeO_3:t-BuOH:Alcohol = 200 : 40 : x)

Alcohol	Molar ratio of alcohol, *x*	Initiation time, *min*	Alcohol	
			Taken, *μg*	Found,* *μg*
Methanol	12	7·5	9·6	8·2
	20	5·4	16	19
	40	2·9	32	31
Ethanol	2	6·7	2·3	2·3
	12	3·2	13·8	13·8
	20	2·2	23	23
	40	1·67	46	46
Isopropanol	2	9·38	3·0	3·0
	4	6·5	6·0	6·2
	12	4·33	18	17
	20	3·5	30	31
	40	2·45	60	60
None	0	10·0		

* Calculated from polynomial regression analysis using an IBM 1130 computer.

If X = initiation time,

for methanol: $Y_{(\mu g)} = 45{\cdot}1 - 4{\cdot}92X$

$Y_{(ppM)} = 1800 - 197X$

for ethanol: $Y_{(\mu g)} = 250 - 197X + 51{\cdot}9X^2 - 4{\cdot}18X^3$

$Y_{(ppM)} = 9980 - 7870X + 2070X^2 - 167X^3$

for isopropanol: $Y_{(\mu g)} = 196 - 80{\cdot}0X + 11{\cdot}1X^2 - 0{\cdot}512X^3$

$Y_{(ppM)} = 7860 - 320X + 445X^2 - 20{\cdot}5X^3$

Methanol, ethanol and isopropanol in amounts more than 20 μg are determined with a coefficient of variation of 10%; at lower concentrations the coefficient of variation decreases to 4%.

initiation time is too short to measure. A plot of the initiation time *vs.* the alcohol concentration shows that methanol differs from the other two alcohols. This may be explained by the difference in reaction of the oxidized products. Formic acid is much more rapidly oxidized by xenon trioxide than is acetic acid or acetone.

This method is very sensitive to trace impurities in the solution such as organic compounds which are easily oxidized by aqueous xenon trioxide. Amounts of hydrogen peroxide, copper(II) and iron(III) as low as 1–5 μg reduce the initiation time; nitrate in excess of 600 μg has a similar effect (probably due to the impurities). Halides (Cl^-, Br^-, I^-) in amounts greater than 1 μg interfere by increasing the initiation time. Phosphate, perchlorate, sulphate, and fluoride in amounts as high as 20 mg have no apparent effect on determinations. For precise results, the unknown solution should be run the same day under conditions identical to those used in obtaining values for known solutions.

Increased sensitivity for the determination of these alcohols may be obtained with higher concentrations of t-butanol. Higher molecular weight alcohols which react rather slowly, may be determined by adding less t-butanol with respect to xenon trioxide.

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Summary—A kinetic study of the oxidation of some alcohols by xenon trioxide has revealed the optimum conditions for analysis of these alcohols. The rate of reaction may be increased by adding a catalyst or by increasing the pH of the solution; it may be decreased by adding an inhibitor. The initiation time of the reaction is used to determine t-butanol in amounts as low as 22 μg or 880 parts per milliard (ppM). Primary and secondary alcohols which catalyse the reaction between t-butanol and xenon trioxide may be determined in amounts as low as 2·3 μg or 92 ppM. Tertiary butanol in amounts less than 40 μg is determined with a coefficient of variation of 4% while methanol, ethanol and isopropanol are determined with a coefficient of variation of 10% at the level of 25 μg or more. The precision in determination of t-butanol increases with increasing concentration, while for isopropanol, ethanol and methanol it decreases.

Zusammenfassung—Eine kinetische Untersuchung der Oxidation einiger Alkohole mit Xenontrioxid ergab die optimalen Bedingungen zur Analyse dieser Alkohole. Die Reaktionsgeschwindigkeit kann durch Zugabe eines Katalysators oder durch Erhöhung des pH der Lösung erhöht werden; durch Zugabe eines Inhibitors kann sie verringert werden. Die Anlaufzeit der Reaktion wird verwendet, um t-Butanol in Mengen bis herunter zu 22 μg oder 880 Teile pro Milliarde (ppM) zu bestimmen. Primäre und sekundäre Alkohole, die die Reaktion zwischen t-Butanol und Xenontrioxid katalysieren, kann man in Mengen bis herunter zu 2,3 μg oder 92 ppM bestimmen. Tertiär-Butanol wird in Mengen unter 40 μg mit einem Variationskoeffizienten von 4% bestimmt; für Methanol, Äthanol und Isopropanol beträgt er bei 25 μg oder mehr 10%. Die Genauigkeit der Bestimmung von t-Butanol steigt mit steigender Konzentration; bei Isopropanol, Äthanol und Methanol sinkt sie.

Résumé—Une étude cinétique de l'oxydation de quelques alcools par le trioxyde de xénon a révélé les conditions optimales pour l'analyse de ces alcools. La vitesse de réaction peut être accrue par l'addition d'un catalyseur ou en augmentant le pH de la solution; elle peut être diminuée en ajoutant un inhibiteur. Le temps d'amorçage de la réaction est utilisé pour déterminer le *t*-butanol en quantités aussi faibles que 22 μg ou 880 parties par milliard (p.p.M.). Les alcools primaires et secondaires qui catalysent la réaction entre le *t*-butanol et le trioxyde de xénon peuvent être déterminés en quantités aussi faibles que 2,3 μg ou 92 p.p.M. Le butanol tertiaire en quantités inférieures à 40 μg est déterminé avec un coefficient de variation de 4%, tandis que les méthanol, éthanol et isopropanol sont déterminés avec un coefficient de variation de 10% au niveau de 25 μg ou plus. La fidélité dans le dosage du *t*-butanol croît avec une concentration croissante, tandis que pour l'isopropanol, l'éthanol et le méthanol elle décroît.

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Determination of platinum and palladium in geological materials by neutron-activation analysis after fire-assay preconcentration*

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STUDIES of the geochemistry of platinum and palladium require analytical methods suitable for determining parts-per-milliard (ppM) levels of these elements. Palladium in G-1 and W-1 has been determined by activation analysis by Vincent and Smales,[1] Crocket and Skippen[2] and Crocket *et al.*[3] It has not been possible to determine platinum in rocks by activation analysis because of lack of adequate sensitivity and the difficulty of processing large samples chemically.

Fire assay provides a rapid method for the concentration of the noble metals from a large sample into a silver bead. Spectrographic methods for the analysis of fire assay beads have been developed by Barnett *et al.*,[4] Haffty and Riley,[5] Sarma *et al.*[6] and Dorrzapf and Brown.[7] Schnepfe and Grimaldi[8] and van Loon[9] analysed fire-assay beads by atomic-absorption methods. The procedure reported here applies activation analysis for the determination of platinum and palladium in the silver beads.

EXPERIMENTAL

Reagents

Standard solutions. Prepare standard stock solutions of platinum and palladium (1 mg/ml in 2% v/v hydrochloric acid) by dissolution of the metals or the ammonium chloro-salts. Prepare dilute solutions by dilution with 2% v/v hydrochloric acid.

Dimethylglyoxime. Prepare a 2% w/v solution of dimethylglyoxime in reagent grade alcohol.

Tin(II) chloride. Prepare a 10% w/v solution in 50% v/v hydrochloric acid. Add sponge tin.

Pt, Pd, Au and Ag carrier solutions. Prepare solutions containing 10 mg of the metal per ml in 2*M* hydrochloric acid.

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Platinum wash solution. Prepare a solution containing 1% tin(II) chloride and 1% silver chloride in 6*M* hydrochloric acid.

Fire assay preconcentration

Thoroughly mix 10–20 g of sample with 60 g of lead oxide, 25 g of sodium carbonate, 5 g of sodium tetraborate, and 3 g of flour. The recipe should be modified to suit the nature of the sample but the flux quoted is suitable for most silicates (see Bugbee[10] or Beamish[11] for specific details on fire-assay procedures). Prepare standards by evaporating 1 ml of a solution containing 2 μg each of platinum and palladium on silica and process as for the samples. Add one Herman inquart (approximately 100 mg of lead wire containing 2% silver) to samples, standards and blanks, and fuse for 1 hr at 950–1000°. Cupel the lead buttons obtained in the fusion.

Irradiation

Wrap the silver beads in aluminium foil and irradiate for 12–16 hr at a flux of 5×10^{10} n/mm^2/sec and allow to decay for at least 4 hr.

Radiochemistry

Dissolve the silver beads with nitric acid in disposable plastic beakers, add carriers (10 mg of Pd, 10 mg of Pt, and 10 mg of Au) and evaporate the solutions to dryness twice with *aqua regia* to achieve exchange of radioactive platinum, palladium, and gold with their carriers. Add 1 ml of hydrochloric and 0·5 ml of nitric acid, heat to dissolve the salts, and dilute to 20 ml. Add 2 ml of silver carrier, filter, discard the silver chloride precipitate, and repeat this step twice more. Add 15 ml of hydrochloric acid and a few drops of nitric acid to make the solution 4*M* in hydrochloric acid. Extract ^{198}Au and ^{199}Au with two 40-ml portions of ethyl acetate, rejecting the organic phase. Add 10 mg of gold carrier and extract again, repeating the extractions until the organic phase is colourless, and repeat. Dilute to about 100 ml so that the solution is 2*M* in hydrochloric acid. Add 5 ml of the dimethylglyoxime solution to precipitate palladium as the dimethylglyoximate. Centrifuge and reserve the supernatant liquid for the separation of platinum. Dissolve the palladium dimethylglyoximate in a few drops of nitric acid, dilute to 30 ml, and add 5 ml of the dimethylglyoximate solution to reprecipitate palladium. Centrifuge and wash the precipitate with 1*M* hydrochloric acid. Reject the washings and filter off the precipitate on a tared filter paper or glass fibre circle. Dry at 110° and weigh. Mount on an aluminium planchet and count. Transfer the supernatant liquid (from the first precipitation of palladium) to a 250-ml separatory funnel. Add 1 ml of the dimethylglyoxime solution and extract with 10-ml portions of carbon tetrachloride until the organic phase is colourless, rejecting the organic phase. Add 5 ml of hydrochloric acid to make the solution 3*M* in that acid. Add 1 ml of 5% hydroxylamine hydrochloride solution, 5 ml of 10% tin(II) chloride solution and allow to stand for a few minutes. Extract the platinum with two 30-ml portions of ethyl acetate. Wash the combined ethyl acetate extracts twice with 10 ml of the platinum wash solution. Reject the washings. Evaporate the ethyl acetate. Destroy organic material with nitric acid. Evaporate twice with *aqua regia.* Evaporate twice with a few drops of hydrochloric acid to drive off nitrates. Add 30 ml of 2*M* hydrochloric acid and heat. Add magnesium turnings to precipitate platinum metal. Heat to coagulate the precipitate. Filter on a glass fibre or Millipore circle. Mount on a planchet, using a Mylar cover. Count samples and standards on a NaI(Tl) crystal and qualitatively examine the gamma-ray spectrum for radiochemical purity. Because of the low concentrations of platinum and palladium found in rocks, beta-counting is required. Place planchets in the sample changer of a proportional beta-counter. Adjust the counting time and maximum counts to provide a statistically suitable number of counts, yet permitting a reasonable frequency of changes. Count platinum for 12 days, and palladium for 7 days or until counts approach background. After counting the platinum, remove the filter circle and precipitate, and treat with 10 ml of *aqua regia* and 1 ml of hydrofluoric acid in a 250-ml disposable beaker to dissolve the platinum. Evaporate to dryness on a steam-bath. Add 5 ml of *aqua regia* and heat to dissolve the salts. Add copper sulphate and cadmium sulphate to provide a final concentration of 0·5% of Cu and Cd and dilute to volume. Determine the chemical yield of platinum by atomic-absorption by the procedure of Schnepfe and Grimaldi.[8]

RESULTS AND DISCUSSION

Nuclear reactions

The nuclear reactions producing isotopes of platinum and palladium are shown in Table I. Crocket and Skippen[2] reported that the Ag/Pd ratio which produces a 1% interference is greater than 10000. ^{109}Pd formed by the irradiation of a 2-mg silver bead is calculated to be 2 ng of Pd (or 0·1 ppM on the basis of a 20-g sample). The subtraction of the palladium in the blank provides a

TABLE I.—NUCLEAR REACTIONS

Naturally occurring isotope	Abundance %	Nuclear reactions	Isotope produced	Activation cross-section, *barns**	Half-life
^{108}Pd	27·7	n, γ	^{109m}Pd	0·2	4·8 min
			^{109}Pd	12·0	13·5 hr
^{109}Ag	48·2	n, p	^{109}Pd	0·012(14·5)	13·5 hr
^{112}Cd	24·1	n, α	^{109}Pd	0·0013(14)	13·5 hr
^{235}U	0·71	n, f	^{112}Pd		21 hr
^{190}Pt	0·01	n, γ	^{191}Pt	150·0	3·0 days
^{192}Pt	0·78	n, γ	^{193m}Pt	2·0	4·4 days
			^{193}Pt	0·4	500 years
^{194}Pt	32·9	n, γ	^{195m}Pt	1·2	4·1 days
^{196}Pt	25·3	n, γ	^{197m}Pt	0·05	1·5 hr
			^{197}Pt	0·9	20 hr
^{198}Pt	7·2	n, γ	^{199m}Pt	0·03	14 sec
			^{199}Pt	4·0	30 min
^{200}Hg	23·1	n, α	^{197}Pt	0·0036(14·5)	20 hr
^{197}Au	100·0	n, p	^{197}Pt	0·0024(14·5)	20 hr

* Numbers in parentheses are neutron energies in MeV.

correction for the formation of ^{109}Pd from silver as well as for any palladium present in the fire-assay reagents.

The interference from ^{112}Cd(n, α)^{109}Pd can be considered to be negligible since the fire-assay preconcentration will eliminate Cd from the original sample, and the Cd/Pd ratio which produces a 1% interference is reported by Crocket and Skippen[2] to be greater than 10,000.

Crocket and Skippen[2] also reported that a U/Pd ratio of 180 would result in a 1% interference due to ^{112}Pd and ^{109}Pd produced as fission products of ^{235}U. Since uranium is not collected in the silver fire-assay bead, its presence in the original rock will not cause any interference in the determination of palladium. The decay results we obtained for palladium show only decay of 13·5-hr ^{109}Pd, indicating the absence of 21-hr ^{112}Pd from fission of ^{235}U.

In the determination of platinum, interference from the reactions ^{200}Hg(n, α)^{197}Pt and ^{197}Au(n, α)-^{197}Pt can be shown to be negligible from the data in Koch.[12]

The decay curve we obtained for platinum shows 20-hr ^{197}Pt, 4·1-day ^{195m}Pt, and 4·4-day ^{193m}Pt. The contribution of ^{193m}Pt is very small so that subtraction of the 4·1-day ^{195m}Pt component to resolve the decay curves results in a pure 20-hr component representing the decay of ^{197}Pt (Fig. 1).

Efficiency of fire-assay concentration

Frazer and Beamish,[13] Hoffman and Beamish[14] and Haffty and Riley[5] reported that the fire-assay procedure will efficiently collect platinum and palladium into a silver bead without significant losses. To verify the efficiency of the recovery, a tracer study was made by Simon and Millard.[15] Recoveries were greater than 90% for platinum and greater than 95% for palladium.

Blanks and contamination

Simon and Millard[16] applied fire-assay preconcentration to the determination of gold. They found significant gold in the reagents, hence no attempt was made here to determine gold simultaneously.

Blanks for palladium were found to vary from 5·7 to 10·6 ng with an average of 8·0 ng and a standard deviation of 1·3 ng. If the sensitivity limit is defined as three times the standard deviation of the blank, the detection limit is 4 ng of Pd or 0·2 ppM on a 20-g sample. Blanks for platinum varied from 4·0 to 7·6 ng, with an average of 4·9 ng and a standard deviation of 1·3 ng. The detection limit of platinum is 4 ng or 0·2 ppM on a 20-g sample. The foregoing detection limits apply only in the absence of extraneous activity in the final platinum and palladium precipitates. The practical limits are 0·5 ppM for each metal.

Yield determination

The palladium is obtained as the dimethylglyoximate, which forms a stoichiometric compound with palladium in a weighing form suitable for the chemical yield determination. Weighing of the

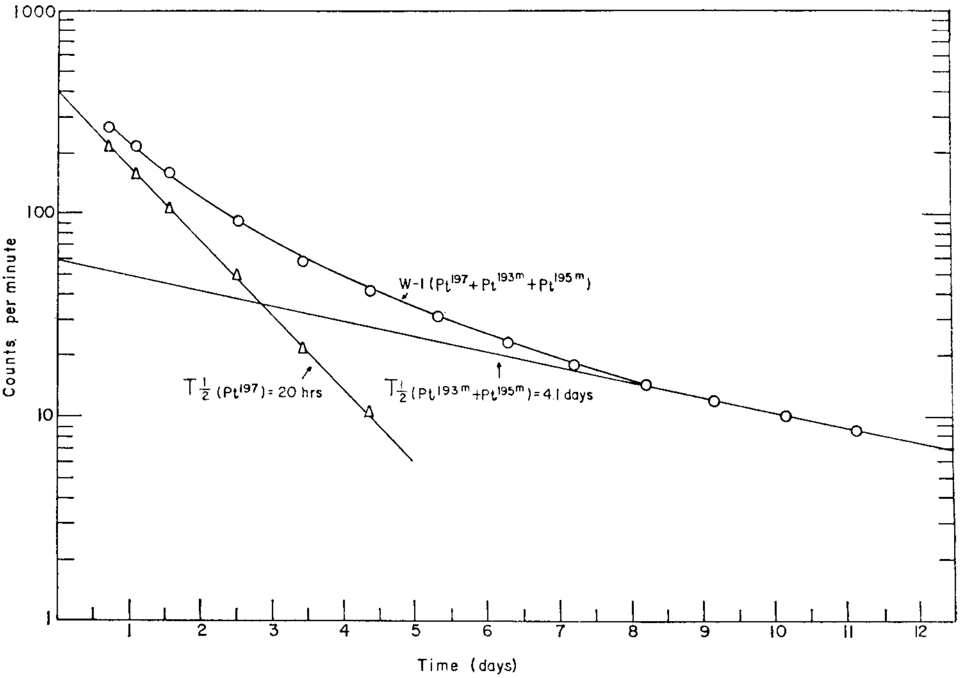

FIG. 1.—Resolution of ^{193m}Pt + ^{195m}Pt + ^{197}Pt beta-decay curve.

platinum precipitate can cause errors because the reduction of platinum by magnesium may result in various amounts of magnesium and tin being occluded in the precipitate. For this reason the platinum is dissolved and the yield is determined by atomic absorption. Yields were usually 60–90% for both platinum and palladium.

Application

The method was applied to the determination of platinum and palladium in seven U.S.G.S. standard rocks. The results are compared with those of others in Table II. The analyses by Crocket

TABLE II.—PALLADIUM AND PLATINUM CONTENT (ppM) OF STANDARD ROCKS

USGS sample		Sample weight,	Palladium		Platinum	
No.	Rock type	*g*	This method	Other methods	This method	Other methods
GSP-1	Grandiorite	25·9	<0·5	<4[5]	<0·5	<10[5]
PCC-1	Peridotite	26·9	3·6, 5·3, 5·1	7[5] (5·5)[7] (6, 6, 5, 5)[18]	5·7, 3·9, 6·7, 6·8	15[5], (10·5)[7] (11, 9, 10, 14)[18]
AGV-1	Andesite	22·7	<0·5	<4·0[5]	1·1	<10[5]
DTS-1	Dunite	22·8	<0·5	<4[5] (0·6, 0·8, 0·6)[7] (2, 2, 2, 1)[18]	1·7	(11, <10)[5] (4·9, 4·2, 2·1)[7] (4, 3, 5, 5)[18]
BCR-1	Basalt	20·0	<0·5	<4·0[5]	2·3	<10[5]
G-2	Granite	21·0	<0·5	<4·0[5]	<0·5	<10[5]
W-1	Diabase	20·0	12·2*	14[5], 11·5[3] (20, 17)[1] 15·8[2], 9[17] 15·4[7]	9·8†	9·2[6] (16, 22)[5] 14·9[7]

* Average of 12 determinations.
† Average of 6 determinations.

et al.,[3] Crocket and Skippen[2] and Vincent and Smales[1] for palladium in W-1 were obtained by neutron-activation analysis without preconcentration. Those by Grimaldi and Schnepfe[17] were by spectrophotometry after tellurium preconcentration. All other results were obtained by emission spectrography after fire-assay preconcentration.

The average palladium content of W-1 was found to be 12·2 ppM, based on 12 determinations ranging from 8·1 to 14·3 ppM with a standard deviation of 1·7 ppM. This value compares favourably with that of Grimaldi and Schnepfe[17] (9 ppM), and with that of Crocket *et al.*[3] (11·5 ppM).

The average platinum content of W-1 was found to be 9·8 ppM, based on 6 determinations ranging from 9·5 to 10·7 ppM with a standard deviation of 0·6 ppM. This compares favourably with the results of Sarma *et al.*[6] (9·2 ppM). Dorrzapf and Brown[7] obtained a value of 14·9 ppM by spectrographic analysis of a fire-assay bead.

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Summary—Fire-asay preconcentration followed by neutron-activation analysis permits the determination of as little as 0·5 ppM of platinum and 0·5 ppM of palladium on a 20-g sample. Platinum and palladium are separated with carriers and beta-counted. Results for the platinum and palladium content of seven U.S.G.S. standard rocks are presented.

Zusammenfassung—Schmelzanreicherung und nachfolgende Neutronenaktivierungsanalyse erlaubt die Bestimmung von 0,5 ppM Platin ond 0,5 ppM Palladium in einer 20 g-Probe. Platin und Palladium werden mit Trägern abgetrennt und ihre Beta-Strahlung gezählt. Ergebnisse für Platin- und Palladiumgehalt mehrerer Standardgestine von U.S.G.S. werden mitgeteilt.

Résumé—La préconcentration par voie sèche suivie de l'analyse par activation de neutrons permet la détermination de quantités aussi petites que 0,5 ppM de platine et 0,5 ppM de palladium sur un échantillon de 20 g. On sépare le platine et le palladium avec des entraîneurs et effectue le comptage beta. On présente les résultats pour la teneur en platine et palladium de sept roches étalons U.S G.S.

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Potassium thiocarbonate as a precipitant for platinum metals: N. K. KAUSHIK and K. N. JOHRI. (23 *November* 1970)

Investigation of the effect of metal ions on the quantitative reaction of potassium bromate with semicarbazide hydrochloride: M. J. M. CAMPBELL, R. GRZESKOWIAK and B. PERRETT. (23 *November* 1970)

Coulometric trace determination of chloride: A. CEDERGREN and G. JOHANSSON. (24 *November* 1970)

Talanta, 1971, Vol. 18, pp. iii to iv. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

The Determination of Hydrazino-Hydrazide Groups: HUGH E. MALONE. Pergamon, Oxford, 1970. Pp. xv + 393. £7. $18.75.

This is the most recent addition to the series of monographs dealing with the determination of functional groups. In this book all the methods which have been recommended for the analysis of hydrazines and hydrazides are outlined. These include methods based on the reducing properties of the group, its ability to release nitrogen, its electrochemical and polarographic properties and its ability to take part in a variety of colour reactions. In addition the use of hydrazines as analytical reagents is reviewed and the analysis of mixtures is discussed. This is a very comprehensive review and will be of value to all practising analytical chemists.

Marine Chemistry, Vol. 2: ed. DEAN F. MARTIN. Dekker, New York, 1970. Pp. xi + 451. $9.50. £4.10.

The second volume of this treatise on the chemistry of the sea is a collection of somewhat diverse dissertations, all however having a common ecological background. The cycles of various elements in the sea are discussed and their importance in maintaining our present environment is considered. In addition, material and energy transport processes are outlined and a simple model for the marine environment is proposed. As courses on chemical oceanography are now becoming available in universities, the interest in analytical problems associated with the sea is growing and this book can be recommended to the ever-increasing number of scientists involved in marine physics and chemistry.

H_2O: HAZEL ROSSOTTI. Oxford University Press, Oxford, 1970. Pp. 95. 24s.

Intended for 10–13 year old children, this little book can be wholeheartedly recommended to older children of any age up to 90 or more. It manages to convey an enormous amount of information about water and its chemical and physical properties in very short space, and connects these with their consequences for everyday life, by reference to phenomena within the child's own experience. The work is lavishly illustrated with excellent diagrams, and the instruction is supported by plenty of experiments that can be done with simple equipment that can be found in any kitchen. It is one of the best things of its kind since Tyndall's "Forms of Water".

Infrared Spectroscopy: Experimental Methods and Techniques: JAMES E. STEWART. Dekker, London, 1970. Pp. xiii + 636. £17.7.0. $36.50.

This is an authoritative text-book concerned with the experimental aspects of infrared spectrophotometry. The design and construction of various types of instrument is dealt with in some detail and the subject of interference techniques is included. The experimental methods of transmission, reflectance and emission spectrophotometry are described and there is a chapter dealing with the most recent innovations. In addition the book contains a considerable amount of general information useful to those interested in the design and operation of infrared spectrophotometers.

Analytical Chemistry: International Symposium Birmingham 1969: Plenary Lectures: INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY, AND SOCIETY FOR ANALYTICAL CHEMISTRY. Butterworths, London, 1970. Pp. vii + 95. £2.10.

These plenary lectures cover air pollution, stripping voltammetry, mixed ligand complexes, electron probe methods, organic microanalysis, and forensic science, and give a good cross-section of the great diversity of problems and techniques that the modern analyst has to deal with.

La Polarographie en Agronomie et en Biologie: PAUL NANGNIOT. Ducolet, Genbloux, Belgium, 1970. Pp. 392. B. Fr. 450.

A collection of methods for the polarographic determination of the most important trace elements in food, water, drinks, plants, soils and biological materials is accompanied by a similar collection for analysis of pesticides. Written by a well known authority in its field, this book is likely to prove extremely useful to practising analysts.

Publications received

uorescence Analysis: A Practical Approach: C. E. White and R. J. Argauer: Dekker, New York, 1970. Pp. x + 389. \$18.75. £8.18.0.

Written primarily for the working analyst, this is a collection of fluorescence methods covering the whole spectrum of application from indicators through reagents for metal ions to determination of organic species with native or induced fluorescence, and covers most fields of applied analysis, with special emphasis on agricultural and biochemical analysis.

e bepaling van Sporenelementen in Biologisch Materiaal door Neutronenactiveringsanalyse: P. van den Winkel. Koninklijke Vlaamse Academie van België, Brussel, 1970. Pp. 189. B. Fr. 500.

A collection of separation schemes for neutron-activation analysis of biological materials is accompanied by a consideration of preparation of standards, and of the methods of destroying organic matter. In spite of the unfamiliar language, most scientists will be able to extract the essential details without much recourse to a dictionary.

roceedings of the 3rd Symposium on Co-ordination Chemistry. Vol. 1: ed. Mihaly T. Beck. Akademia Kiado, Budapest, 1970. Pp. 525.

This is a collection of 48 papers presented at the symposium. Volume 2 will contain the texts of the plenary lectures and discussions on the papers in Vol. 1. The subject matter was limited to the chemistry of mixed ligand and outer-sphere complexes. The papers average about ten pages of typescript, are by a variety of authors, are mainly in English and have all the interest associated with collections of this sort.

Catalog of Standard Reference Materials: U.S. Department of Commerce, National Bureau of Standards. U.S. Government Printing Office, Washington D.C. Pp. 79. 75 cents.

This new edition of the NBS catalog incorporates changes which make it more readable and easy to use. Each class of standards is briefly placed in context (but no reference is made to appropriate Technical Bulletins) so that the whole provides a very convenient summary of all sorts of standards and standard materials.

Reprints of the following reviews published in Talanta are available from Learned Journals Division, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, or Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.

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SUMMARIES FOR CARD INDEXES

Recent developments in substoichiometric analysis: Jiří Starý and Jaromír Růžička, *Talanta*, 1971, **18**, 1. (Department of Nuclear Chemistry, Technical University, Praha 1, Břehová 7, Czechoslovakia.)

Summary—A review of recent developments in subtsoichiometric analysis is presented.

Studies on the extraction and determination of metal salts with methyl isobutyl ketone—XIII. Extraction of thorium and uranium: Norio Ichinose, *Talanta*, 1971, **18**, 21. (Department of Chemistry, Yamaguchi University, Yamaguchi-shi Japan.)

Summary—The work deals with the extraction of thorium or uranium from hydrochloric, perchloric, sulphuric or nitric acid solutions of various concentrations, or from mixed acid solutions, by means of isobutyl methyl ketone. When the extraction is made from 5–8M hydrochloric acid that is 10M in lithium chloride or from 7–8M hydrochloric acid that is 1M in magnesium chloride, uranium is extracted quantitatively (>99%), whereas thorium is hardly extracted at all.

Über die Genauigkeit und Anwendbarkeit der Röntgenfluoreszenz für die Bestimmung der Konzentration der Elemente Phosphor bis Uran in Lösung: B. Magyar, *Talanta*, 1971, **18**, 27. (Laboratorium für Anorganische Chemie, Eidg. Techn. Hochschule, Zürich, Schweiz.)

Summary—X-Ray fluorescence spectroscopy has been used for the determination in solution of elements of atomic number greater than 14. Interelement effects have been investigated, and the use of internal (neighbouring element) standards and of external standards has been compared. In dilute solutions (less than $5 \times 10^{-3}M$) matrix effects can be ignored. The sources of error and their effect on the choice of operating conditions and the optimum concentration range are discussed.

ДОСТИЖЕНИЯ СУБСТЕХИОМЕТРИЧЕСКОГО АНАЛИЗА В НАСТОЯЩЕЕ ВРЕМЯ:

Jiří Starý and Jaromír Růžička, *Talanta*, 1971, **18**, 1.

Резюме—Приведен обзор достижений в области субстехиометрического анализа в настоящее время.

ИЗУЧЕНИЕ ЭКСТРАКЦИИ И ОПРЕДЕЛЕНИЯ СОЛЕЙ МЕТАЛЛОВ С МЕТИЛИЗОБУТИЛКЕТОНОМ—XIII. ЭКСТРАКЦИЯ ТОРИЯ И УРАНА:

Norio Ichinose, *Talanta*, 1971, **18**, 21.

Резюме—Статья посвящена экстрагированию тория и урана из соляной, хлорной, серной или азотной кислотах различной концентрации, или из смешанных растворов кислот, с изобутилметилкетоном. При экстракции из 5–8M раствора соляной кислоты содержащего 10M хлорида лития, или из 7–8M раствора соляной кислоты содержащего 1M хлорида магния, уран экстрагируется количественно (99> %), в то время как торий почти не экстрагируется.

ТОЧНОСТЬ И ПРИМЕНИМОСТЬ МЕТОДА РЕНТГЕНОВСКОГО ФЛУОРЕСЦЕНТНОГО АНАЛИЗА В ОПРЕДЕЛЕНИИ КОНЦЕНТРАЦИИ ЭЛЕМЕНТОВ ОТ ФОСФОРА ДО УРАНА В РАСТВОРЕ:

B. Magyar, *Talanta*, 1971, **18**, 27.

Резюме—Метод рентгеновского флуоресцентного анализа применен в определении в растворе элементов имеющих атомный номер больше чем 14. Изучены межэлементные эффекты и сравнено использование внутренних (соседный элемент) и внешних эталонов. В разбавленных растворах (меньше чем $5 \times 10^{-3}M$) можно игнорировать матричные эффекты. Обсуждены источники ошибок и их влияние на выбор условый анализа и оптимальных пределах концентрации.

Substoichiometric determination of traces of palladium by radioactive isotope dilution analysis: G. B. BRISCOE and S. HUMPHRIES, *Talanta*, 1971, **18**, 39. (Department of Chemistry, The University of Aston in Birmingham, Gosta Green, Birmingham, 4, England.)

Summary—A radioactive isotope-dilution method for the determination of traces of palladium has been developed. It is based on the solvent extraction of palladium dithizonate from acid solution by means of a substoichiometric amount of dithizone in carbon tetrachloride. The separation has been applied to the determination of traces of palladium in platinum, the rocks W-1 and PCC-1 and a biological material (kale). Amounts of palladium down to 3 ng have been determined.

L'utilisation des membranes pour l'indication du point d'équivalence—VI. La membrane de papier-parchemin imprégnée de $BaSO_4$ pour des titrages acido-basiques en milieu non aqueux: C. LITEANU and MARIA MIOŞCU, *Talanta*, 1971, **18**, 51. (Chaire de Chimie Analytique de l'Université de Cluj, Roumanie.)

Summary—A first attempt to apply inorganic membranes made from parchment paper impregnated with alkaline earth precipitates, as indicating electrodes for potentiometric acid-base titrations in non-aqueous media, is presented. Mixtures of acids can be titrated and the course of the titration is a function of the nature of the solvent and the titrant.

Zwei neue Computerprogramme zur Bestimmung von Komplexbildungskonstanten aus potentiometrischen und specktrophotometrischen Messungen: TH. KADEN and A. ZUBERBÜHLER, *Talanta*, 1971, **18**, 61. (Institut für Anorganische Chemie der Universität Basel, Schweiz.)

Summary—VARIAT and SPANA, two new computer programs in FORTRAN IV for the calculation of complex stability constants from potentiometric and spectrophotometric data are discussed. The two programs were set up in a way that allows computation with the same set of subroutines. Several important points in this kind of analysis are discussed and VARIAT is compared with other computational methods. Because of the good convergence of VARIAT the starting values of the stability constants may merely be guessed, without preliminary graphical treatment of the data.

СУБСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ПАЛЛАДИЯ МЕТОДОМ РАЗБАВЛЕНИЯ РАДИОАКТИВНЫХ ИЗОТОПОВ:

G. B, Briscoe and S. Humphries, *Talanta*, 1971 **18**, 39.

Резюме—Разработан метод разбавления радиоактивных изотопов для определения следов палладия. Метод основан на экстрагировании дитизоната палладия субстехиометрическим количеством дитизона в тетрахлорметане из кислого раствора. Этот метод разделения был применен в определении следов палладия в платины, в горных породах W-I и PCC-I и в биологическом материале (кудрявой капусты). Определены количества палладия до 3 нг.

ИСПОЛЬЗОВАНИЕ МЕМБРАН ДЛЯ ОБНАРУЖЕНИЯ КОНЦА ТИТРОВАНИЯ—VI. ПРОПЫТАННАЯ $BaSO_4$ МЕБРАНА ИЗ ПЕРГАМЕНТНОЙ БУМАГИ ДЛЯ КИСЛОТНО-ЩЕЛОЧНЫХ ТИТРАЦИЙ В НЕВОДНОЙ СРЕДЕ:

C. Liteanu and Maria Mioşcu, *Talanta*, 1971, **18**, 51.

Резюме—Приведена первая попытка применить неорганические мембраны приготовленные из пергаментной бумаги, пропытанной осадками щелочных земель, в качестве индикаторных электродов для потенциометрических кислотно-щелочных титраций в неводных средах. Можно титровать смеси кислот, а ход титрования является функцией природы растворителя и титрованного раствора.

ДВЕ НОВЫХ ЭЛЕКТРОНОВЫЧИСЛИТЕЛЬНЫХ ПРОГРАММЫ ДЛЯ ОПРЕДЕЛЕНИЯ КОНСТАНТ КОМПЛЕКСООБРАЗОВАНИЯ НА ОСНОВЕ ПОТЕНЦИОМЕТРИЧЕСКИХ И СПЕКТРОФОТОМЕТРИЧЕСКИХ ДАННЫХ:

Th. Kaden and A. Zuberbühler, 1971, **18**, 61.

Резюме—Обсуждены VARIAT и SPAИA, две новых электроновычислительных программы в FORTRAN IV для рассчета констант комплексообразования на основе потенциометрических и спектрофотометрических данных. Две программы созданы так чтобы позволять рассчет используя ту же группу субрутин. Обсуждены некоторые точки важные для этого типа анализа и VARIAT сравнен с другими методами рассчета. Из-за хорошой конвергенции VARIAT исходные величины констант устойчивости можно только предполагать, без предварительной графической обработки данных.

Extraction with long-chain amines—II. Extraction and colorimetric determination of chromate: Jiří Adam and Rudolf Přibil, *Talanta*, 1971, **18**, 91. (Analytical Laboratory Institute of Geological Sciences, Charles University, Prague 2, Albertov 6, Czechoslovakia, and Analytical Laboratory, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—Highly selective extraction of chromate from slightly acidic solutions (0·1–0·2*M* sulphuric acid) with a chloroform solution of trioctylamine (Alamine 336-S) or trioctylmethylammonium chloride (Aliquat 336-S) is described. Many metals such as iron, nickel, cobalt, copper, alluminium, zinc, are not extracted, even if present in large concentrations. Coextraction of vanadium(V) and uranium(VI) is prevented by addition of sodium chloride. Traces of extracted molybdenum are scrubbed with ammonium oxalate. Final determination of chromium is based on measurement of the absorbance of the extract at 445–450 nm.

Automatic determination of calcium and magnesium in water: Sebastiano Impedovo, Angela Traini and Paolo Papoff, *Talanta*, 1971, **18**, 97. (Instituto Chimica Analitica, Universita' di Bari, Italy.)

Summary—Magnesium and calcium may each be determined in water by an automatic spectrophotometric method. At 571 nm with an excess of Eriochrome Black T as metallochromic agent, the variation in absorbance is proportional to the magnesium concentration regardless of the calcium concentration. By addition of MgEDTA to displace the calcium from its CaEBT complex, this element may be determined at the same wavelength. For 3–25 ppm of magnesium and 5–40 ppm calcium, the standard deviation was about 4%. The apparatus is described.

Analysis of platinum for certain elemental impurities by neutron activation: A. A. Abdel-Rassoul, H. K. El-Shamy and R. Madbouly, *Talanta*, 1971, **18**, 101. (Chemical Department, Ministry of Industry, Cairo, U.A.R.)

Summary—Silver, ruthenium, cobalt, iron, zinc, cadmium and mercury are determined in platinum by neutron-activation analysis. The scheme developed requires the removal of the platinum matrix by reduction and the sequential separation of the elements by ion-exchange chromatography. The method is suitable for the simultaneous determination (at the ppm level) of these elements in milligram quantities of platinum.

ЭКСТРАГИРОВАНИЕ АМИНАМИ С ДЛИННОЙ ЦЕПЬЮ—II. ЭКСТРАКЦИЯ И КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ХРОМАТА:

Jiří Adam and Rudolf Přibil, *Talanta*, 1971, **18**, 91.

Резюме—Описана высокоселективная экстракция хромата из слабокислых растворов (0,1 – 0,2*M* серной кислоты) раствором триоктиламина (Аламин 336-S) или триоктилметиламмоныйхлоридом (Аликват 336-S) в хлороформе. Ряд металлов так как на пример железо, никель, кобальт, медь, алюминий и цинк не экстрагируются, даже если присутствуют в больших концентрациях. Совместная экстракция ванадия(V) и урана(VI) предупреждается добавлением хлорида натрия. Следы экстрагированного молибдена удаляют оксалатом аммония. Конечное определение хрома основано на измерении светопоглощения экстракта при 445–450 нм.

АВТОМАТИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ И МАГНИЯ В ВОДЕ:

Sebastiano Impedovo, Angela Traini and Paolo Papoff, *Talanta*, 1971, **18**, 97.

Резюме—Кальци и магний в воде можно определять автоматическим спектрофотометрическим методом. При 571 нм, в присутствии избытка ериохромчерного Т в качестве металлохромного агента, изменение светопоглощения пропорционально концентрации магния не смотря на концентрацию кальция. Добавлением Mg ЭДТА для вытеснения кальция из его Са ЭЧТ-комплекса можно определять этот элемент при той же длины волн. Стандартная ошибка для 3–25 мкг (мл магния и 5–40 мкг) мл кальция равна около 4%. Описан прибор для проведения анализа.

ОПРЕДЕЛЕНИЕ СЛЕДОВ НЕКОТОРЫХ ЭЛЕМЕНТОВ В ПЛАТИНЕ МЕТОДОМ НЕЙТРОННО-АКТИВАЦИОННОГО АНАЛИЗА:

A. A. Abdel-Rassoul, H. K. El-Shamy and R. Madbouly, *Talanta*, 1971, **18**, 101.

Резюме—Серебро, рутений, кобальт, железо, цинк, кадмий и ртуть определены в платине методом нейтронноактивационного анализа. Разработанная схема основана на уклонении платиновой матрици путем восстановления, с последующим разделением элементов методом ионообменной хроматографии. Методом можно пользоваться для одновременного определения (при концентрации частей на миллион) этих элементов в миллиграммовых количествах платины.

Studies on the extraction and determination of metal salts with isobutyl methyl ketone—XIV. Extraction of gold: NORIO ICHINOSE, *Talanta*, 1971, **18**, 106. (Department of Chemistry, Yamaguchi University, Yamaguchi-shi, Japan.)

Summary—The isobutyl methyl ketone extraction of gold(III) from hydrochloric acid or various mixtures of hydrochloric and other mineral acids was studied as a function of the gold concentration and the acid concentration. Gold (initial concentration up to $5 \times 10^{-3}M$) was quantitatively extracted (99%) from 3–5*M* hydrochloric acid. Addition of nitric acid in 1–5*M* concentration and sulphuric or perchloric acid in 1–3*N* concentration to the 1–5*M* hydrochloric acid solutions used had no effect.

Liquid-liquid extraction behaviour of mercury(II) as chloride: S. N. TANDON and C. B. GUPTA, *Talanta*, 1971, **18**, 109. (Radiochemical Laboratories, University of Roorkee, Roorkee, (U.P.), India.)

Summary—The solvent extraction behaviour of mercury(II) chloride with different organic solvents has been studied. The effect of acidity, temperature, concentration of Hg(II), and other anions has been studied. Radiochemical separations from ions such as Fe(III), Ga(III), As(III) and Sb(V) can be accomplished. Au(III) and Tl(III) interfere.

Differential titrimetric determination of mixtures of selenium and tellurium: P. P. NAIDU and G. G. RAO, *Talanta*, 1971, **18**, 112. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—Methods are described for the differential titrimetric determination at room temperature of mixtures of selenium(IV) and tellurium(IV). The test solution in 0·75–3·5*M* condensed phosphoric acid medium is oxidized with an excess of permanganate and the unreacted permanganate is titrated with iron(II), with ferroin as indicator, to indicate the total content of selenium and tellurium present. Then 10–20 ml of 10*M* sulphuric acid, 0·4 ml of 0·1% osmium tetroxide solution and an excess of arsenic(III) are added to the same solution and the unreacted arsenic(III) is titrated with permanganate (ferroin as indicator) to indicate the content of tellurium.

ИЗУЧЕНИЕ ЭКСТРАКЦИИ И ОПРЕДЕЛЕНИЯ СОЛЕЙ МЕТАЛЛОВ С ИЗОБУТИЛМЕТИЛКЕТОНОМ—XIV. ЭКСТРАКЦИЯ ЗОЛОТА:

Norio Ichinose, *Talanta*, 1971, **18**, 106.

Резюме—Изучена экстракция метилизобутилкетоном золота(III) из соляной кислоты или из различных смесей соляной и других минеральных кислот в зависимости от концентрации золота и кислоты. Золото (начальная концентрация до $5 \times 10^{-3}M$) экстрагируется количественно (99%) из 3-5*M* соляной кислоты. Добавление азотной кислоты в коцентрации 1-5*M* и серной или хлорной кислоты в концентрации 1-3*M* к 1-5*M* растовре соляной кислоты не показало эффект на экстрагирование.

ПОВЕДЕНИЕ РТУТИ(II) В ФОРМЕ ХЛОРИДА ПРИ ЖИДКОФАЗНОЙ ЭКСТРАКЦИИ:

S. N. Tandon and C. B. Gupta, *Talanta*, 1971, **18**, 109.

Резюме—Изучено поведение хлорида ртути(II) при экстракции с различными органическими растворителями. Исследовано влияние кислотности, температуры, концентрации ртути(II) и других анионов. Удается провести радиохимические отделения от таких ионов как на пример Fe(III), Ga(III), As(III) и Sb (V). Au(III) и Tl(III) мешают определению.

ОПРЕДЕЛЕНИЕ СМЕСЕЙ СЕЛЕНА И ТЕЛЛУРА МЕТОДОМ ДИФФЕРЕНЦИАЛЬНОЙ ТИТРОМЕТРИИ:

P. P. Naidu and G. G. Rao, *Talanta*, 1971, **18**, 112.

Резюме—Описаны методы определения смесей селена(IV) и теллура(IV) при комнатной температуре методом дифференциальной титрометрии. Раствор пробы в 0,75-3,5*M* конденсированной фосфорной кислоте окисляют избытком перманганата а нереагированный перманганат титрируют железом(II), с использованием ферроина в качестве индикатора; эта титрация дает суммарное содержание селена и теллура в пробе. Затем добавляют тому же раствору 10-20 мл 10*M* серной кислоты, 0,4 мл 0,1%-тного раствора четырёхокиси осмия и избыток мышьяка(III) и нереагированный мышьяк титрируют перманганатом (с использованием ферроина в качестве индикатора), для определения теллура.

Kinetic studies of xenon trioxide as an oxidant—I. Determination of alcohols: ROBERT H. KRUEGER, STANISLAUS VAS and BRUNO JASELSKIS, *Talanta*, 1971, **18**, 116. (Department of Chemistry, Loyola University, Chicago, Illinois 60626, U.S.A.)

Summary—A kinetic study of the oxidation of some alcohols by xenon trioxide has revealed the optimum conditions for analysis of these alcohols. The rate of reaction may be increased by adding a catalyst or by increasing the pH of the solution; it may be decreased by adding an inhibitor. The initiation time of the reaction is used to determine t-butanol in amounts as low as 22 μg or 880 parts per milliard (ppM). Primary and secondary alcohols which catalyse the reaction between t-butanol and xenon trioxide may be determined in amounts as low as 2·3 μg or 92 ppM. Tertiary butanol in amounts less than 40 μg is determined with a coefficient of variation of 4% while methanol, ethanol and isopropanol are determined with a coefficient of variation of 10% at the level of 25 μg or more. The precision in determination of t-butanol increases with increasing concentration, while for isopropanol, ethanol and methanol it decreases.

Determination of platinum and palladium in geological materials by neutron-activation analysis after fire-assay preconcentration: J. J. ROWE and F. O. SIMON, *Talanta*, 1971, **18**, 121. (U.S. Geological Survey, Washington, D.C. 20242, U.S.A.)

Summary—Fire-assay preconcentration followed by neutron-activation analysis permits the determination of as little as 0·5 ppM of platinum and 0·5 ppM of palladium on a 20-g sample. Platinum and palladium are separated with carriers and beta-counted. Results for the platinum and palladium content of seven U.S.G.S. standard rocks are presented.

КИНЕТИЧЕСКОЕ ИЗУЧЕНИЕ ТРЁХОКИСИ КСЕНОНА В КАЧЕСТВЕ ОКИСЛИТЕЛЯ—I. ОПРЕДЕЛЕНИЕ СПИРТОВ:

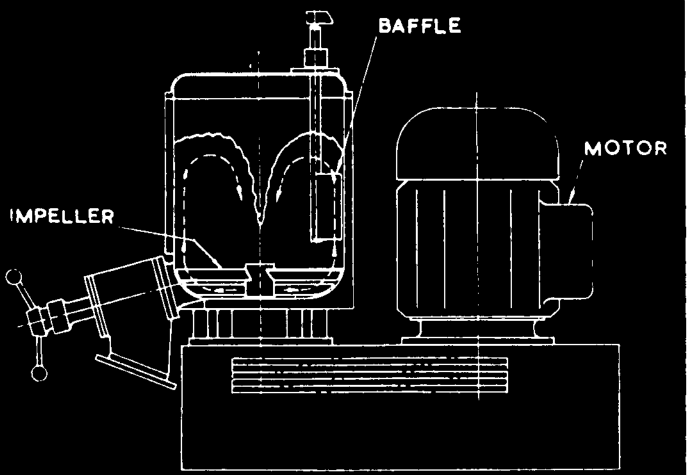
Robert H. Krueger, Stanisalus Vas and Bruno Jaselskis, *Talanta*, 1971, **18**, 116.

Резюме—Кинетическое изучение окисления некоторых спиртов трёхокисью ксенона выявило оптимальные условия для анализа этих спиртов. Скорость реакции можно повысить добавлением катализатора или повышением pH раствора, а уменьшать—добавлением ингибитора. Инициирующий период реакции использован для определения трет-бутанола при концентрациях 22 мкг или 880 частей на миллиард. Первичные и вторичные спирты, которые имеют каталитическое действие на реакцию трет-бутанола с трёхокисью ксенона, определили при концентрациях 2,3 мкг или 92 частей на миллиард. Трет-бутанол в количествах менее 40 мкг определили с коэффициентом вариации 4 %, а метанол, этанол и изопропанол—с коэффициентом вариации 10 % при 25 мкг или выше. Воспроизводимость определения трет-бутанола повышается с растущей концентрацией, но в случае изопропанола, этанола и метанола она снизуется с растущей концентрацией.

ОПРЕДЕЛЕНИЕ ПЛАТИНЫ И ПАЛЛАДИЯ В ГЕОЛОГИЧЕСКИХ ВЕЩЕСТВАХ МЕТОДОМ НЕЙТРОННО-АКТИВАЦИОННОГО АНАЛИЗА ПОСЛЕ КОНЦЕНТРИРОВАНИЯ СУХИМ ПУТЕМ:

J. J. Rowe and F. O. Simon, *Talanta*, 1971, **18**, 121.

Резюме—Концентрация сухим путем с последующим определением методом нейтронно-активационного анализа позволяет определить до 0,5 мкг/г платины и 0,5 мкг/г палладия в 20 г пробы. Платина и палладий разделены при помощи носителей и считана их бета-активность. Приведены содержания платины и палладия семь эталонных горных пород.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