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Talanta

An International Journal of Analytical Chemistry

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Aims and Scope

Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, French, or German; all papers have abstracts in these three languages and also in Russian. Special importance is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original papers short communications and reviews are refereed in the normal manner. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemists is welcomed by the Editor-in Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

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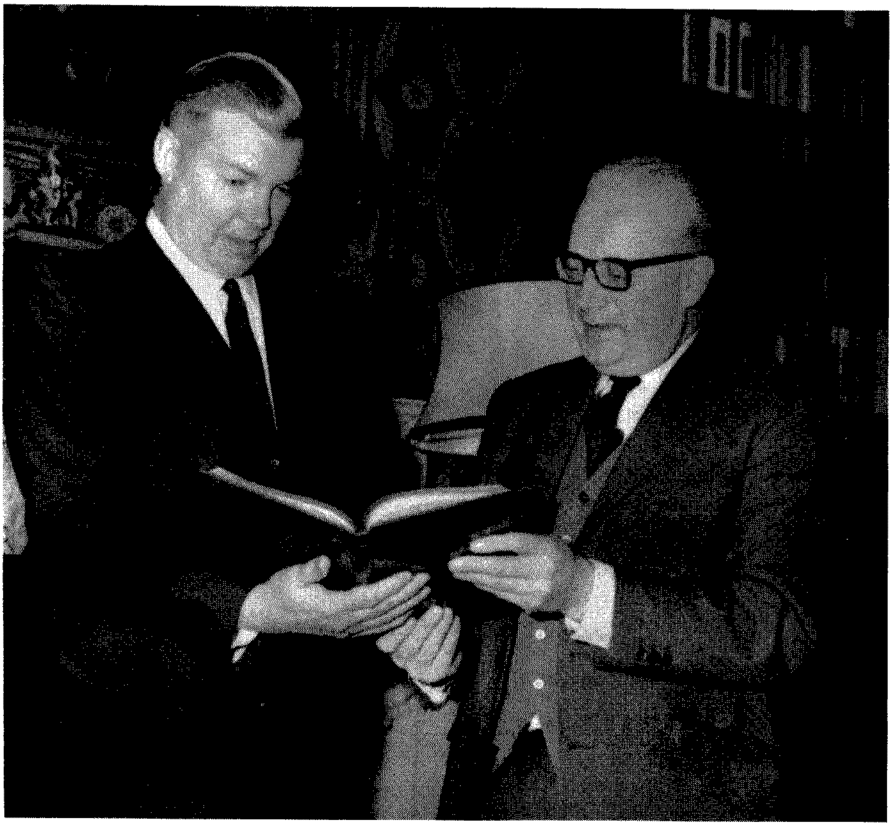

Dr. A. A. SMALES (Left) and Professor R. BELCHER (Chairman of the Advisory Board of *Talanta*) comment on some of the papers in the Smales Honour Issue (November 1968). The occasion was the presentation at Headington Hill Hall, Oxford, to Dr. SMALES of a leather-bound copy of the Honour Issue.

Those attending the presentation were—left to right—Mr. G. F. RICHARDS (Director, Pergamon Press), Dr. D. BETTERIDGE (Assistant Editor), Mrs. SMALES, Dr. SMALES, Professor BELCHER, Mrs. BELCHER, Dr. R. A. CHALMERS (Editor-in-Chief), Dr. M. WILLIAMS (Consulting Editor).

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LASZLO C. PASZTOR, Research Supervisor at the Graham Research Laboratory of Jones & Laughlin Steel Corporation, Pittsburgh, Pa., was born in Hungary. He graduated (1943) and received his MS (1954) from the University of Budapest and did further graduate work at the University of Pittsburgh. He joined J & L Steel Corporation in 1957 as a research chemist and his work has involved mainly analytical research and the application of analytical techniques to production, process and quality control problems. He was promoted to research supervisor in 1963. In 1962 and 1963 he served as an Overseas Member of the IUPAC, Working Committee on Automation. His publications have been mainly in the field of ferrous metallurgical analysis including papers on solvent extraction separations, spectrophotometric methods, isolation and determination of non-metallic inclusions in steels, and neutron-activation analysis. He received the Special Merit Award of the American Iron and Steel Institute in 1967.

YU. A. ZOLOTOV was born in 1932. He studied chemistry at Moscow University (1950–1955). In 1959 at the V.I. Vernadsky Institute of Geochemistry of the U.S.S.R. Academy of Sciences in Moscow, he was awarded the degree of Candidate of Chemical Sciences, and in 1965 that of Doctor of Chemical Sciences. At present he is vice-director of the Institute. Its scientific activity is in the field of solvent extraction of inorganic compounds and its use in analytical chemistry as well as the chemistry of complex compounds. His main interests are the theory of solvent extraction of chelate compounds and complex metallo-acids and the analysis of highly pure materials. In 1968 he published a monograph Solvent extraction of chelate compounds. Since 1963 he has been the vice-chairman of the Scientific Council on Analytical Chemistry of the U.S.S.R. Academy of Sciences.

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STUDIES ON METHYLTHYMOL BLUE—I

SEPARATION AND PURIFICATION OF METHYLTHYMOL BLUE AND SEMIMETHYLTHYMOL BLUE

TAKASHI YOSHINO, HARUMI IMADA, TADAYOSHI KUWANO and KATSUYA IWASA

(*Received* 25 *August* 1967. *Accepted* 5 *May* 1968)

Summary—The metallochromic indicator Methylthymol Blue was purified chromatographically with cellulose and ion-exchange resin columns. The monosubstituted product of the reaction, Semimethylthymol Blue, was also separated and purified, and can also be used for the colorimetric determination of metals. There are not marked differences between the infrared spectra of Methylthymol Blue and Semimethylthymol Blue. The purities of Methylthymol Blue and Semimethylthymol Blue finally obtained were above 97% and 90% respectively. In acidic medium Methylthymol Blue forms 1:1 greyish blue and 1:2 pure blue chelates with copper(II) whilst Semimethylthymol Blue forms only 1:1 orange chelates with bivalent metals. The molar absorptivities at 435 mμ are 1·89 ($\pm$0·03) $\times$ 10^4 for Methylthymol Blue at pH 5·00 and 1·76 ($\pm$0·03) $\times$ 10^4 for Semimethylthymol Blue at pH 5·45.

METHYLTHYMOL BLUE, 3,3′-bis-[*N*,*N*′-di(carboxymethyl)aminomethyl]thymolsulphonphthalein, MTB, has been already prepared and purified[1] by Körbl who introduced it as an excellent metallochromic indicator.[2] He pointed out[1] the existence of the monosubstituted product 3[*N*,*N*′-di(carboxymethyl)aminomethyl]thymolsulphonphthalein, but did not make mention of its utility. We have called it Semimethylthymol Blue, SMTB, after Semixylenol Orange,[3,4] and planned to separate SMTB from MTB and to investigate their usefulness, in the way in which we investigated Xylenol Orange, XO, and Semixylenol Orange, SXO.[4] This paper reports the results of this work.

Comparison of other workers' results[5–10] with ours suggests that any MTB which has been used till now has been of low purity, and there are some doubts about the composition of the chelates.[6–10] To resolve these inconsistencies it is necessary to obtain pure forms of the reagents and to investigate their physico-chemical properties.

EXPERIMENTAL

Reagents

MTB and SMTB. Stock solutions of MTB and SMTB were prepared by dissolving 79·3 mg (1×10^{-4} mole) of MTB or 63·0 mg (1×10^{-4} mole) of SMTB in 50 ml of 0·1*M* potassium nitrate. These solutions were standardized against standard sodium hydroxide solution potentiometrically. After standardization these solutions were diluted to 100 ml.

Metal ion solutions, $1 \times 10^{-2}M$. Prepared from analytical grade reagents and standardized by EDTA titration.[11]

Buffer solutions. pH 4–6: 1*M* acetic acid–1*M* potassium acetate; pH 7–10: 0·1*M* veronal–0·1*M* nitric acid.

Chromatography. Paper and cellulose chromatographic columns as described previously.[4]

Synthesis of MTB and SMTB

The synthesis was carried out by Körbl's method; 2 g of Thymol Blue, 1·5 g of iminodiacetic acid and a small amount of sodium hydroxide as catalyst were dissolved in 25 ml of glacial acetic acid, and 1 ml of 37% formaldehyde was added. The mixture was kept at 55° and the progress of the reaction was followed by paper chromatography with butanol–0·1% acetic acid solution. The

R_f of the sodium salt of MTB was about zero, of SMTB 0·16–0·60, and of unreacted Thymol Blue 0·87–1·00. If the reaction time is 4 hr the main product is SMTB and if 7–8 hr, MTB.

Separation and purification

After the reaction, glacial acetic acid was distilled off under reduced pressure. The residue, dissolved in a little water, was placed on a cellulose column 30 mm in diameter and 100 mm long and eluted with the top layer of a butanol–0·1 % acetic acid mixture. Three fractions were obtained as a result of this separation procedure; the first contained mainly Thymol Blue, the second SMTB and the third MTB and a little sodium iminodiacetate.

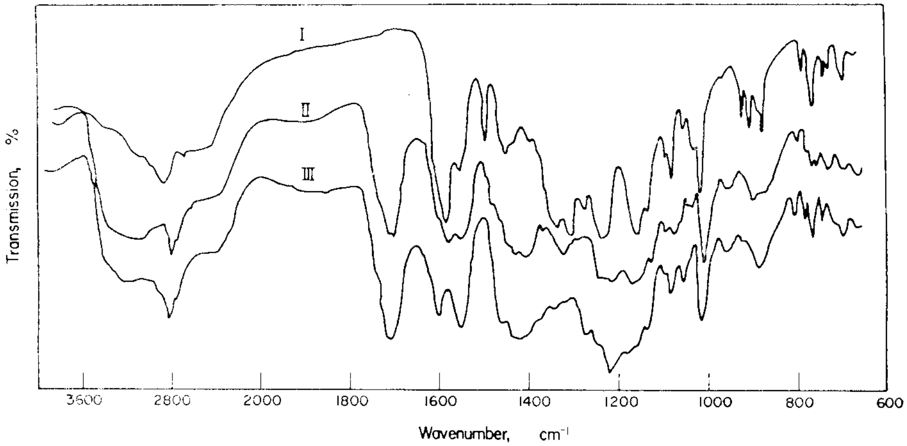

FIG. 1. Infrared spectra of Thymol Blue(I), Semimethylthymol Blue(II) and Methylthymol Blue(III).

It was not easy to separate sodium iminodiacetate from the sodium salt of MTB. There is a difference between the R_f values of their acid forms, so the crude MTB was converted into the acid form with a cation-exchange column (Diaion SK 1). After conversion, iminodiacetic acid and a small amount of SMTB were separated from MTB. These purification steps with both ion-exchange resin and cellulose columns were repeated several times until the MTB obtained finally had a purity >97%.

To complete the separation of Thymol Blue and SMTB, the crude SMTB which had been obtained in the first separation was chromatographed again on a cellulose column, and then SMTB was converted into its acid form by cation-exchange. The acid form of SMTB was further purified on a cellulose column and a cation-exchange column until the SMTB obtained finally had a purity >90%.

Analysis gave: for MTB, C 56·0%; H 6·2%; N 3·6%; theory requires C 56·0%, H 6·1%, N 3·5%; for SMTB, C 62·7%, H, 6·4%, N 2·1%; theory requires C 62·9%, H 6·1%, N, 2·3%.

The infrared spectra of MTB, SMTB and Thymol Blue were measured (Fig. 1). The infrared spectra of XO, SXO and Cresol Red are shown for comparison (Fig. 2).

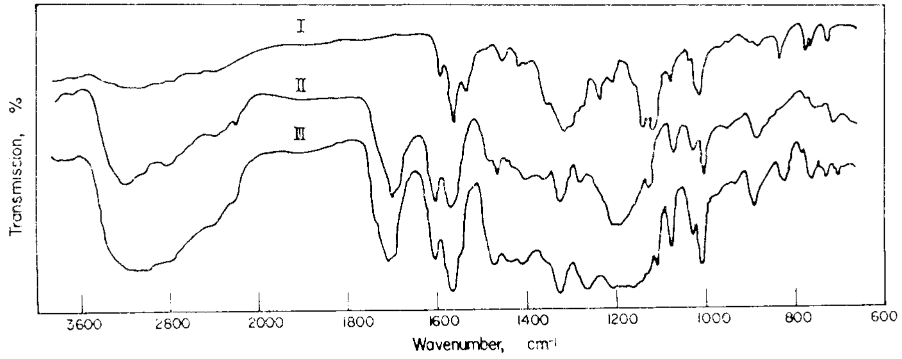

FIG. 2. Infrared spectra of Cresol Red(I), Xylenol Orange(II) and Semixylenol Orange(III).

pH Titration

The pH titration was run by the method described earlier.[4] The titration curves of MTB and SMTB were very similar to those of XO and SXO.[4]

Two clear inflection points were obtained at pH 5·1 and 8·7 for MTB and at pH 5·9 and 9·1 for SMTB. Three protons of MTB are titrated at the first inflection point and 2 of SMTB. One proton is titrated between the first and second points and this step was used to calculate the purity of MTB and SMTB. The dissociation constants of MTB and SMTB will be the subject of another paper.

Reaction with cations

MTB changed its colour from yellow to pure blue on reaction with copper(II) in acidic medium, and SMTB changed from yellow to orange on reaction with bivalent metals.

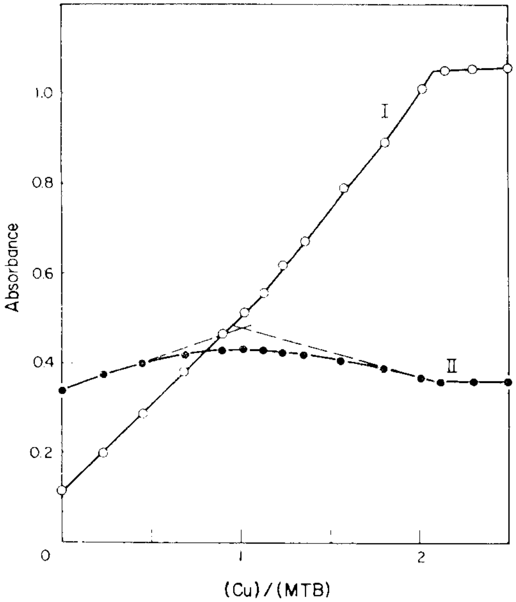

FIG. 3. Mole ratio studies of MTB–Cu complexes.
I: pH 6·08, 590 mμ; II: pH 6·08, 486 mμ.
[MTB] = 4 × 10^{-5} mol/l.

MTB was shown to form 1:1 and 1:2 (λ_{max} 590–595 mμ) complexes with copper(II) (Figs. 3 and 4), SMTB forms only 1:1 chelates, λ_{max} 515–540 mμ, with bivalent metals (Fig. 5).

On the assumption that breaks occurred at exact stoichiometric ratios, the concentrations of MTB and SMTB solutions were determined by the mole-ratio method, and were found to be equal to the value by pH titration.

The molar absorptivities at λ_{max}, 435 mμ, are 1·89 (±0·03) × 10^4 for MTB at pH 5·00 and 1·76 (±0·03) × 10^4 for SMTB at pH 5·45.

RESULTS AND DISCUSSION

The sodium salts of MTB and SMTB were converted into their acid forms because the latter are more stable, their purification can be more easily accomplished, and the concentrations determined more accurately by pH titration. Sodium ions act as catalyst in the reaction, therefore it is not strange that sodium ions promote decomposition.

The acid form of MTB obtained is very stable and can be kept for several months without decomposition. The aqueous solution of MTB, which is reported to be very unstable, can be kept for several weeks if the solution is kept acidic.

Our results for the properties of MTB were in general agreement with those of Körbl[5] but differed in detail.

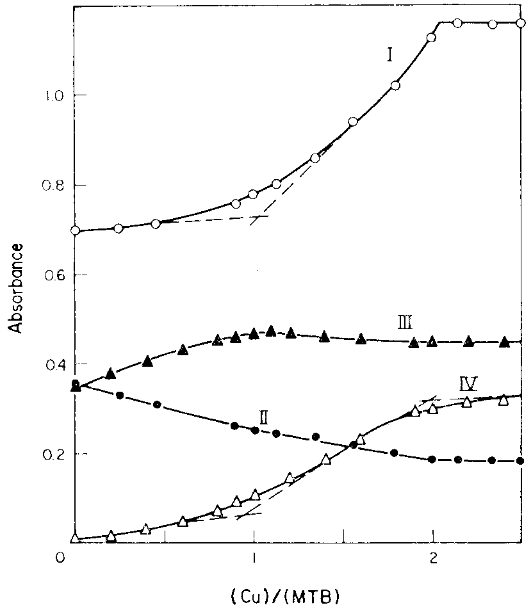

FIG. 4. Mole ratio studies of MTB–Cu complexes.
I: pH 8·25, 596 mμ; II: pH 8·25, 495 mμ;
III: pH 4·02, 496 mμ; IV: pH 4·02, 596 mμ.
[MTB] = 4 × 10^{-5} mol/l.

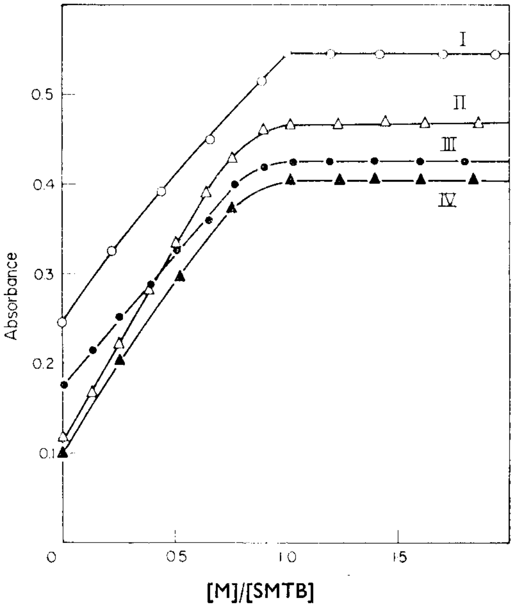

FIG. 5.—Mole ratio studies of SMTB–metal complexes.
I: Cu(II), pH 6·18, 515 mμ
II: Pb(II), pH 6·20, 537 mμ
III: Ni(II), pH 6·10, 518 mμ
IV: Co(II), pH 6·25, 540 mμ.
[SMTB] = 3·1 × 10^{-5} mol/l.

Cheng has reported 1:1 and 1:2 MTB-zirconium and 2:1 MTB-hafnium chelates,[6] and the 1:1 MTB-zirconium chelate has also been reported by Babko.[7] The close chemical similarity of zirconium and hafnium leads one to predict that they would react identically with MTB. The molar absorptivity values of MTB reported in all previous communications[4–10] are 70% below ours, so it can be assumed that previous preparations have contained many impurities which would affect determinations of stability constants, calibration curves, molar absorptivity, suitable pH region and absorption maximum.

The structure of SMTB was taken to be 3-[*N*,*N'*-di(carboxymethyl)aminomethyl]-thymolsulphonphthalein from the results of the pH titration curve, elemental analysis, the reaction with metals and the infrared spectra. The strong absorption in the infrared spectra at 1700 cm^{-1} is probably due to the *N*,*N'*-di(carboxymethyl)-aminomethyl group. SMTB has four dissociable protons, and undergoes two colour changes, and therefore contains one *N*,*N'*-di(carboxymethyl)aminomethyl group. This fact also becomes apparent from the composition of the SMTB complexes (Fig. 5).

The structure of MTB was taken to be 3,3'-bis-[*N*,*N'*-di(carboxymethyl)aminomethyl]thymolsulphonphthalein by similar arguments.

SMTB can be used as a metallochromic indicator or analytical reagent for the colorimetric determination of metals. SMTB is yellow below pH 5·5, orange at pH 5·5–9·0, and blue above pH 9·0. In acid medium its colour changes from yellow to blue on reaction with metals. Its utility at high pH is being investigated. SMTB was not so pure as MTB, but this difficulty will be overcome by further study.

The sample of MTB submitted for elemental analysis had been dried at room temperature under reduced pressure for a week. The results show that one mole of MTB contains two moles of water of crystallization. If SMTB was dried at 50° under reduced pressure for a day, no water of crystallization could be detected, but it seems likely that by analogy with SXO it is a monohydrate which easily loses water. The purities given above take the water of crystallization into consideration.

In the separation of XO and SXO,[4] the top layer of a butanol–10% acetic acid mixture was used, but was found to give poor separation of SMTB and Thymol Blue. This may be due to the isopropyl group which is present in SMTB but not in SXO.

From this and previous work, it is expected that most metallochromic indicators of the sulphonphthalein type, *e.g.*, XO, MTB, Glycine Thymol Blue and Glycine Cresol Red, are mixtures of several products and some starting material.

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Zusammenfassung—Der Metallfarbindikator Methylthymolblau wurde chromatographish mit Cellulose- und Ionenaustauschharzsäulen gereinigt. Das Monosubstitutionsprodukt der Reaktion, Semimethylthymolblau, wurde ebenfalls abgetrennt und gereinigt; es kann gleichfalls zur kolorimetrischen Metallbestimmung dienen. Es bestehen keine wesentlichen Unterschiede in den Infrarotspektren von Methylthymolblau und Semimethylthymolblau. Methylthymolblau und Semimethylthymolblau wurden schließlich in Reinheiten von über 97% bzw. 90% erhalten. In saurem Medium bildet Methylthymolblau ein graublaues 1:1- und ein rein blaues 1:2–Chelat mit Kupfer(II), während Semimethylthymolblau mit zweiwertigen Metallen nur orange 1:1–Chelate bildet. Die molaren Extinktionskoeffizienten bei 435 mμ sind 1,89(±0,03)·10^4 für Methylthymolblau bei pH 5,00 und 1,76(+0,03)·10^4 für Methylthymolblau bei pH 5,00 und 1,76(+0,03)·10^4 für Semimethylthymolblau bei pH 5,45.

Résumé—On a purifié chromatographiquement l'indicateur métallochrome Bleu de Méthylthymol au moyen de colonnes de cellulose et de résine échangeuse d'ions. On a aussi séparé et purifié le produit monosubstitué de la réaction, Bleu de Semiméthylthymol, et l'on peut également l'utiliser pour le dosage colorimétrique des métaux. Il n'y a pas de différences marquées entre les spectres infrarouges du Bleu de Méthylthymol et du Bleu de Semiméthylthymol. Les puretés du Bleu de Méthylthymol et du Bleu de Semiméthylthymol finalement obtenus ont été supérieures à 97 % et 90 % respectivement. En milieu acide le Bleu de Méthylthymol forme avec le cuivre(II) des chélates 1:1 gris-bleu et 1:2 bleu pur, alors que le Bleu de Semiméthylthymol ne forme que des chélates orangés 1:1 avec les métaux bivalents. Les coefficients d'absorption molaires à 435 mμ sont 1,89 ($\pm$ 0,03) $\times$ 10^4 pour le Bleu de Méthylthymol et 1,76 ($\pm$ 0,03) $\times$ 10^4 pour le Bleu de Semiméthylthymol à pH 5,45.

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AUTOMATED DETERMINATION OF TRACES OF MERCURY IN BIOLOGICAL MATERIALS BY SUBSTOICHIOMETRIC RADIOISOTOPE DILUTION

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Summary—Solid samples (1–2 g) are burned in oxygen in a flask containing radiomercury in dilute hydrochloric acid, in which the non-active mercury to be determined is immediately absorbed. All mercury is subsequently extracted by dithizone in carbon tetrachloride and then re-extracted into dilute hydrochloric acid. This aqueous phase is further analysed automatically (AutoAnalyzer, 20 samples/hr) as previously described. Liquids (up to 100 ml) are analysed in the same way but instead of being burned in oxygen are first oxidized with potassium permanganate in acid medium. Quantities between 2 and 0.00004 ppm Hg were determined in various materials. Results for international biological standards agreed well with values obtained by activation analysis: kale 0.159 ppm Hg (relative standard deviation 2%) and IAEA cereals 0.0435 ppm Hg (±5%). The new method is far more simple and rapid than activation analysis and just as sensitive; it is therefore more suitable for routine work. About 100 samples can be analysed per day.

THE increasing agricultural and industrial use of organic fungicides containing mercury has resulted in serious consideration being given to mercury poisoning in nature.

Most of these compounds are—or become—volatile, thereby ensuring effective distribution. In consequence, many laboratories throughout the world are actively engaged in investigating and screening a large variety of samples, collected in nature, for mercury contamination and toxicity, and provisionally FAO/WHO[1] has proposed a maximal permissible level of mercury in food (except fish or shellfish) corresponding to 50 ng total mercury per gram fresh weight. As the distribution coefficient between body fat and water may reach the value of 100 in the case of the most volatile organic mercury compounds, a maximal permissible level of such compounds in food must be even lower than 50 ng/g.

The analytical method suitable for this work must therefore be quantitative, very sensitive, highly selective, simple, rapid and suitable for routine work, and have very low and constant blank value.

Although often used for analysis of biological material, neither the micromethod of Stock,[2] nor the spectrophotometric dithizone[3] method can meet most of these requirements. Therefore "Activation analysis is at present probably the only method for determining mercury in biological materials in this concentration range"

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(Westermark).[4] Thousands of various biological samples are analysed by activation analysis, a method which has continuously been improved and nearly perfected.[1,5–8] Basically, however, destructive activation analysis is neither simple nor rapid. This is mostly because each sample analysed for mercury must be irradiated (48–72 hr), cooled (48–72 hr), chemically decomposed, and mercury separated (which includes electrolysis overnight). Finally the activity of the ^{197}Hg formed by irradiation must be measured. Activity measurements must be repeated after 4, 7 and 10 days. sometimes even after 21–28 days to ensure selectivity[4]).

We have developed an analytical procedure which requires less than one hour to complete. A substantial part of the procedure is performed automatically, using commercially available equipment (AutoAnalyzer) operating at a rate of 20 samples per hour. The method is based on isotopic dilution of a known amount of radiomercury (y) with an unknown quantity (x) of non-active mercury to be determined. To avoid the necessity of determining specific activities, substoichiometric separation[9] is used. When this is performed automatically as suggested by us[10,11] the following equation applies:

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

where A is the height of a standard peak, registered by a recording rate-meter connected to a scintillation detector, when a standard sample containing the quantity y of undiluted radiomercury is processed, and A_x is the height of a sample peak containing both the non-active mercury to be determined (x) plus the same amount of radiomercury as the standard sample.

In order that this equation be valid, the same quantity of mercury must always be reproducibly separated from each sample. This is achieved by use of a fixed, substoichiometric amount of zinc dithizonate in carbon tetrachloride. The non-active mercury to be measured competes for dithizone with the added radioactive mercury which also serves as a standard. The larger the amount of non-active mercury present, the lower will be the height of the sample peak (A_x).

This principle has already been experimentally verified.[10] The problem remained of finding a suitable method of decomposition for a wide variety of samples. The wet oxidation procedure[3,12] gave rather high blank values, and the concentrated acids could not be purified adequately. Moreover, this method is slow and requires frequent attention. Incomplete oxidation of fats may cause serious errors, as they are soluble in carbon tetrachloride, and by acting as solvents for the organomercury compounds prevent the achievement of isotopic equilibrium.

These difficulties were overcome by the use of the Schöniger oxygen flask. When the originally prescribed method[13] was used, serious losses of mercury could occur which were found to be due to the presence of reducing agents, resulting in incomplete extraction of the mercury by the dithizone. Towards the end of a combustion, quantities of reductants were found to be formed even when an excess of oxygen was still present. It is well known that iodide and sulphide, for example, prevent the extraction of mercury[14] and to remove these ions, small amounts of permanganate or hydrogen peroxide were added to the absorbing solutions, the former being preferable on account of its speed of reaction and its self-indicating properties. On the other hand,

TABLE I.—RECOVERY OF MERCURY FROM MANUAL DECOMPOSITION PROCEDURE.

A. Solid samples (oxygen-flask combustion)

Sample	Dry weight, *g*	Activity added,* *cpm*	After burning			Recovery, %
			Ashes *cpm*	Wire *cpm*	Solution, *cpm*	
Apple	1·0	21700	9	18	21500	99
Flour	1·0	22482	26	15	20415	91
Liver	0·5	23100	40	15	22300	96
Liver†	1·0	20214	1100	50	18910	94
Potatoes	1·0	40059	80	5	39981	100
Fish	0·5	22482	60	12	23200	102
Fish†	1·0	23100	18	20	22910	99
Meat	0·5	23100	42	8	22050	96
Kale	1·0	43291	40	21	41910	97
Egg	0·5	23100	9	18	23600	102
Flour‡	1·0	20214	50	10	12508	62
Apple‡	1·0	21700	30	30	7105	33
Kale‡	1·0	21646	8	16	5210	24

B. Liquid samples

Sample§	Volume, *ml*	Activity added,* *cpm*	Oxidant added	Solution, *cpm*	Recovery, %
Redistilled water	100	21646	none	22113	105
Redistilled water	100	21646	2 ml 0·02*M* $KMnO_4$	21100	98
Tap water	100	21646	none	10512	49
Tap water	100	21646	2 ml 0·02*M* $KMnO_4$	20824	96
Tap water	250	21646	4 ml 0·02*M* $KMnO_4$	21510	100
1 × $10^{-4}M$ KI	100	21646	none	5305	24
1 × $10^{-4}M$ KI	100	21646	2 ml 0·02*M* $KMnO_4$	21315	99
1 × $10^{-5}M$ Na_2S	100	21646	none	386	<2
1 × $10^{-5}M$ Na_2S	100	21646	2 ml 0·02*M* $KMnO_4$	21824	101
1 × $10^{-3}M$ Na_2S	100	21646	2 ml 0·02*M* $KMnO_4$	20315	94

* Based on mercury content in the sampler cup (containing 5·00 ml of 0·1*M* HCl)

† Oxidation purposely incomplete (deficiency of O_2). As much as 0·2 g of black ash left.

‡ No oxidant (10 ml of 0·1*M* H_2O_2 or 0·02*M* $KMnO_4$) added to the absorbing solution.

§ To each sample ^{203}Hg (0·1–0·2 μg) was added first, followed by 5 ml of 2·5*M* H_2SO_4, and potassium permanganate (see fourth column). Extraction with dithizone was then carried out as described for the absorbing solution.

hydrogen peroxide may be purified by dithizone extraction whereas permanganate may not.

Samples containing up to 30% of moisture may be burned in the oxygen flask, but those containing more water must be dried first as they will not ignite. Drying temperatures must not exceed 50° (to prevent volatilization of mercury compounds)[5] and in practice drying at 45° for 2–3 hr was usually sufficient, without causing any loss measurable by tracer techniques. Freeze-drying is also satisfactory.

Filter paper and cellophane were used in the preliminary experiments for holding the samples, but analyses on these materials alone showed that their mercury content was considerable, and all further work was done using pressed briquettes of powder samples or by attaching samples directly to the wire basket in the flask. Table I gives the results of experiments carried out to check the recovery of added radiomercury. Practically no activity was found either on the wire basket or in any remaining ash after the combustion.

The purpose of the preliminary dithizone extraction of the mercury is to achieve selectivity and a concentration step. The latter is important, as an initial absorption solution of about 100 ml must be reduced to 5 ml for sampling. Before extraction, any excess of oxidant (permanganate or hydrogen peroxide) must be removed by reduction with hydroxylamine. The destruction of dithizone with nitrite is fast, allowing a rapid back-extraction of mercury into the acid aqueous phase.

AUTOMATED ANALYSIS

The chemical reactions taking place in the AutoAnalyzer (see Fig. 1 in the previous communication[10]) comprise reduction of nitrite by hydrazine, pH adjustment and masking by a citrate-EDTA mixture, and solvent extraction of mercury by substoichiometric amounts of zinc dithizonate in carbon tetrachloride.

The separated organic phase to be assayed for gamma-activity is segmented by an aqueous solution containing acetic and hydrochloric acids before entering the flow-cell, thereby avoiding any tailing effect, or an increased background in the cell.[10]

The following compounds may be formed when mercury reacts with dithizone: $Hg(II)(HDz)_2$, $Hg(II)Dz$, $Hg(II)ClHDz$, and $Hg(I)HDz$. Although it was originally expected that $Hg(HDz)_2$ would be formed when mercury is reacted substoichiometrically with dithizone, recent experiments have shown that a compound with a mercury: dithizone molar ratio of 1:1 is being formed.[10,15] The choice between the last two possibilities mentioned is difficult—mercury can be reduced by hydrazine to the univalent state in hydrochloric acid, but on the other hand, the formation of Hg(II)Cl-HDz has recently been observed when bivalent mercury is reacted with a substoichiometric amount of dithizone.[16] These complexes are at present the subject of further study with ^{36}Cl in another laboratory. When zinc dithizonate is used in place of dithizone, (because of its greater stability with respect to time) it seems most likely that the following reaction occurs.

$$2\,Hg(II)Cl_2 + [Zn(HDz)_2]_{CCl_4} \rightleftharpoons 2[Hg(II)ClHDz]_{CCl_4} + Zn^{2+}$$

The solution to be sampled by the AutoAnalyzer also contains hydrochloric acid and sodium nitrite. The effect of varying the concentration of the latter was studied, and it was found that from 0·1 to 1·2 ml of a 0·5% solution could be added without affecting the final count-rate. A larger amount did interfere, as there was not sufficient hydrazine to remove the excess, and some zinc dithizonate was also decomposed. The effect of acid concentration was also investigated, and the optimum quantities were found to be 4 ml of 0·1*M* hydrochloric acid and 1 ml of 0·5% sodium nitrite solution for the back-extraction before sampling by the AutoAnalyzer.

The sensitivity of the method depends mainly on the activity of the radiomercury. At a sampling rate of 20 hr, the following ranges can be covered by suitable choice of the radiomercury concentration:

Mercury, *μg*	Specific activity of radiomercury, *Ci/g*
0·005–0·5	1·0
0·05–5	0·1
0·5–50	0·01

By decreasing the sampling rate to 10/hr, a five-fold increase in sensitivity may be achieved (or an increase in precision for the same sensitivity)—see Fig. 1. A standard radiomercury solution containing $0{\cdot}96 \times 10^{-7}$ g/ml was prepared in $0{\cdot}1M$ hydrochloric acid, and increasing portions of this were added to portions of zinc dithizonate in an "automatic radiometric titration." From the results it was found that 0·096 μg of mercury is more than sufficient to displace the zinc, and this quantity was added, to all samples.

A calibration was carried out with added quantities of non-active mercury and the expected isotope-dilution behaviour was found to be strictly obeyed. It is important to remember that the calibration is only valid as long as the pumping rates and the concentrations of the radiomercury and of the zinc dithizonate remain constant. The half-life of the radiomercury is 47 days which makes this the most important variable as the zinc dithizonate solution is stable for at least a year if kept in the dark and cold.

EXPERIMENTAL

Reagents

There are some differences between the solutions described here and those mentioned in the previous paper.[10] Unless otherwise stated, analytical reagent grade chemicals were used, and demineralized water was finally purified by double distillation in glass.

Radiomercury. An aqueous solution containing ^{203}Hg with a specific activity of 1 Ci/g was obtained from the Radiochemical Centre, Amersham, England, and 50 μl of this were diluted to 100 ml with $0{\cdot}1M$ hydrochloric acid. A standard mercury solution containing about 0·1 μg/ml in $0{\cdot}1M$ acid was prepared by further dilution. The formation of radiocolloids was prevented by the addition of 1% v/v of 0·5% sodium nitrite solution.

Carbon tetrachloride. The Merck *p.a.* product was used without further purification except for use with the very dilute solution of zinc dithizonate, when it was purified by shaking with displacement solution and stored in a refrigerator.

Dithizone solution, $10^{-4}M$. Prepared in carbon tetrachloride and purified.[3] The dilute solution ($10^{-5}M$) used for the pre-extraction was freshly prepared daily.

Zinc dithizonate solution. Prepared as follows. Dissolve 2 g of ascorbic acid in 25 ml of water in a 1-l. separatory funnel, add 150 ml of $1M$ acetic acid and 150 ml of $1M$ sodium acetate, and purify by dithizone extraction. Add 10 ml of $0{\cdot}1M$ zinc chloride, adjust the pH to about 5 with ammonia, add 300 ml of dithizone stock solution and extract for about 2 min. The separated filtered solution is stable for at least a year if kept cool.

Displacement solution. Dilute the aqueous phase from the zinc dithizonate preparation 10-fold and stabilize it by addition of 1% v/v of 2·5% hydrazine sulphate solution. The pH of this solution should be adjusted to 5–6; the solution is then kept in the refrigerator and may be used repeatedly for several months.

Dilute zinc dithizonate solution. Must be freshly prepared daily by diluting a suitable portion of the stock $5 \times 10^{-5}M$ $Zn(HDz)_2$ solution to 500 ml with cool purified carbon tetrachloride, shaking with displacement solution and running into the displacement flask which must then be completely filled up with displacement solution, and placed in melting ice, protected from light. The remainder of the displacement solution is run into a bottle and attached to the corresponding pump-tube.

Buffer and masking solution. Prepared by dissolving 20 g of citric acid in water, adding 100 ml of $1M$ sodium hydroxide and purifying by extraction. To this are added 50 ml of $0{\cdot}1M$ EDTA, and the whole is diluted to 1 litre.

Purification of reagents. Extract the aqueous solutions with 10 ml of stock dithizone solution, and wash with successive portions of carbon tetrachloride until no further colour appears. Filter the aqueous solutions to remove droplets of carbon tetrachloride. This procedure is applicable to the following reagents: hydrochloric acid, $0{\cdot}2M$; hydrazine sulphate, 2·5%; hydroxylamine hydrochloride, 20%; sulphuric acid, $2{\cdot}5M$.

Sodium nitrite, 5% solution. Purified with the zinc dithizonate solution, as dithizone itself is oxidized by nitrite. The 0·5% solution must be prepared twice daily.

Potassium permanganate solution, $0{\cdot}02M$. Cannot be purified by dithizone extraction. If a high blank is experienced, then hydrogen peroxide must be used instead.

Apparatus

Most of the apparatus has already been described.[10,22]

Combustion flask. A 5-l. flat-bottomed flask with a 40/35 standard taper socket has a 10-mm bore side-arm fused on about 40 mm below the joint. A rubber balloon about 50 mm long is attached to this arm. The sample-holder is a spiral of 1·2-mm nichrome wire (or resistor Kantal-P wire, m.p. 1430°) shaped into a rather flat basket about 20 mm in diameter, into which a briquette may be placed. The other end of the straight part of the wire (about 50 mm) is shaped into a hook, and hangs on a glass hook fused on to the end of the 40/35 standard taper stopper fitting the neck of the flask. Before use the flask is washed with dithizone solution and with dilute hydrochloric acid, and the wire basket is heated over a bunsen for a few minutes.

Analytical procedure

Powdered samples (flour, kale, cereals, *etc.*) are well mixed and about 1 g is taken for each analysis. Briquettes (diameter approx. 14 mm) are pressed and their exact weight is recorded. Samples containing more than approx. 30% of water are blended, weighed and dried for 2–3 hr at 45° This is satisfactory for most samples such as fish, apples, meat *etc.* As milk, eggs *etc.* must be dried for a longer time, freeze-drying in vacuum is more advisable to avoid losses of volatile mercury compounds. Again, briquettes are made of the dried samples. A teflon-covered magnetic stirrer (55 mm long, 10 mm diameter) is placed in the combustion flask and a rubber balloon is firmly attached to the side-arm. Then 70 ml of 0·2M hydrochloric acid and 10 ml of 0·1M hydrogen peroxide or 10 ml of 0·02M permanganate are added, followed by 1·00 ml of standard radiomercury solution (0·096 μg of mercury). The flask is then thoroughly flushed with oxygen. A paper fuse (3–10 mm) together with the briquette is placed in the wire basket, lit and immediately placed in the flask. The stopper is held firmly in position until the combustion is complete (approx. 20 sec), after which the flask is placed on the magnetic stirrer, which is operated fast enough to wash the inner surface of the flask with splashing solution. After 10–15 min all visible vapours are condensed and all combustion products absorbed. The flask is removed from the stirrer, the wire basket, with ash, is carefully removed and the flask is closed again with the glass stopper. The flask is tilted in order to rinse its upper part, but the acid must not enter the balloon. The flask is opened again, the balloon is removed and the absorbing solution is poured through the side-arm into a 250-ml separatory funnel. The flask is further rinsed twice with small portions of 0·1M hydrochloric acid which are also added to the funnel.

To the combined acid solutions are added 4 ml of 20% hydroxylamine hydrochloride solution (or enough to remove any pink colour if permanganate is used), and the solution is shaken and left to stand for 30 sec. About 4 ml of $10^{-5}M$ dithizone solution are then added, the mixture vigorously shaken for 30 sec and left for the phases to separate, during which time 4 ml of 0·1M hydrochloric acid are transferred (by pipette) to a 25-ml separatory funnel.

As much as possible of the organic layer is drained from the large to the small funnel, but the aqueous layer must not enter the bore of the stop-cock. The extraction is repeated with a second 4-ml dithizone portion and this extract is added to the first. Finally, in order to re-extract mercury from the organic to the aqueous phase, 1·00 ml of 0·5% sodium nitrite solution is added to the small funnel and it is vigorously shaken for at least 30 sec. The phases are left to separate, most of the lower layer is discarded, and at least 4·5 ml of the aqueous layer are transferred (by pipette) to the sampler cup and further analysed automatically. (Note: it should be realized that during *extraction* both dithizone portions must remain at least a little green. If not, either oxidants (which is most likely) or more than ~10 μg of mercury are present in the absorbing solution. During *re-extraction*, however, the combined dithizone extracts should be decolorized immediately and completely. It is therefore important always to use a freshly prepared 0·5% solution of sodium nitrite and to add it to the small funnel *immediately* before the re-extraction. Further, if for any reason this procedure is interrupted, the aqueous solutions containing hydroxylamine should not be kept longer than approx. 15 min, else there may be formation of radiocolloids (probably Hg, HgS or HgI_2) which might be adsorbed on the walls of the funnel. However, if the above procedure is followed exactly, mercury will always be quantitatively recovered.)

RESULTS AND DISCUSSION

The results of various analyses are summarized in Table II. For comparative purposes, two international biological standard materials were analysed—kale[17] and cereals, IAEA intercomparison number 66/11.[18] Although a sampling speed of 10/hr would have given a better precision, the faster rate was used as all routine screening was carried out at 20/hr. To avoid the "memory effect" mentioned below, only the last four out of five analyses are considered for each sample. The mercury content in kale was found to be 0·159 ppm, compared with 0·150 ± 0·008 ppm reported by Bowen.[17] For the cereals (IAEA) we found 0·0435 ppm with a 5% relative standard

TABLE II.—AUTOMATED DETERMINATION OF MERCURY IN BIOLOGICAL MATERIALS.

Material	Weight, *g* fresh	dry	A/A_x	Mercury content* (fresh weight) *ng*	*ppm*
Blank†	—	—	1·02	<2	—
Cereals IAEA	1·05		1·42$_5$	44	0·042
Kale (Bowen)[17]	1·04		2·60	166	0·159
Milk	5·22	0·584‡	1·26	28	0·005$_4$
White bread	2·70	1·080§		88	0·033
Flour	1·09		1·29	30	0·028
Apple (non-treated)	5·00	0·750‡	1·40	42	0·008$_4$
	5·10	0·765§	1·45	46	0·009$_2$
Apple	11·92	1·65‡	1·71	73	0·006$_6$
	7·40	1·12§	1·55	58	0·007$_8$
Egg (whole)	2·50	0·624‡	1·48	49	0·019$_6$
	2·07	0·518‡	1·41	43	0·020$_8$
Egg (white)	2·35	0·353§	1·31	32	0·013$_6$
	1·96	0·295§	1·29	30	0·015
Fish (plaice)	2·62	0·523‡	2·23	128	0·049
	2·74	0·547§	2·44	148	0·054
Beef	3·50	0·770§	1·63$_5$	66	0·019
Liver (beef)	2·11	0·535§	2·44	148	0·070
Fish bone flour	0·24¶		4·95	400	2·0
Filter paper W40	0·842		1·46	47	0·055
Filter paper S&S589	0·758		1·46	47	0·062
Cellophane	0·50		2·70	178	0·356
Blank**	—	—	<1·02	<2	—
H_2SO_4, Suprapur	9·2		<1·02	<2	<0·0002
H_2SO_4,*p.a.*	9·2		<1·02	<2	<0·0002
HCl, Suprapur	2·3		<1·02	<2	<0·001
HCl,*p.a.*	2·3		1·18	18	0·008
Demineralized H_2O	100		<1·02	<2	<0·00002
Tap H_2O	100		1·07	~4	~0·00004

* Each material was analysed 3–6 times. However, the table only lists typical individual results in order to demonstrate the relationship between sample weights and A/A_x ratios.

† Valid for all solid materials below (Schöniger combustion).

‡ Material dried by deep-freezing in vacuum (−20°C, 10 μbar, *ca.* 3 hr.).

§ Material dried in oven at 45°C max. for $\not>$3 hr.

¶ In order to facilitate the burning of fish bone flour, this sample was mixed with 25% dry milk powder.

** Valid for all liquid material below (permanganate oxidation).

deviation which compares favourably with the "most probable mean value" of 0·044 ppm (±0·0014 ppm) as calculated by the IAEA.[18] The wide range of values reported for this material is seen in the following list of values from several different laboratories (in ppm of mercury on a fresh-weight basis; number of determinations stated in brackets).

0·058	0·041	0·037	0·301	0·430	0·440	0·330	0·040	0·052	0·032	0·034	0·293	0·247
(6)	(6)	(6)	(5)	(2)	(6)	(3)	(6)	(6)	(6)	(3)	(3)	(6)

It is clear that the precision and sensitivity of our method are closely related to the sampling speed (Fig. 1) and to the specific activity of radiomercury used (Fig. 2). However, precision and sensitivity also depend markedly on the reagent blank. In order to keep the mercury content in all reagents below detectable level these must be purified by dithizone extraction (see *Reagents*). Blank values were established by frequently bracketting sample peaks by standard and blank peaks. This check was also

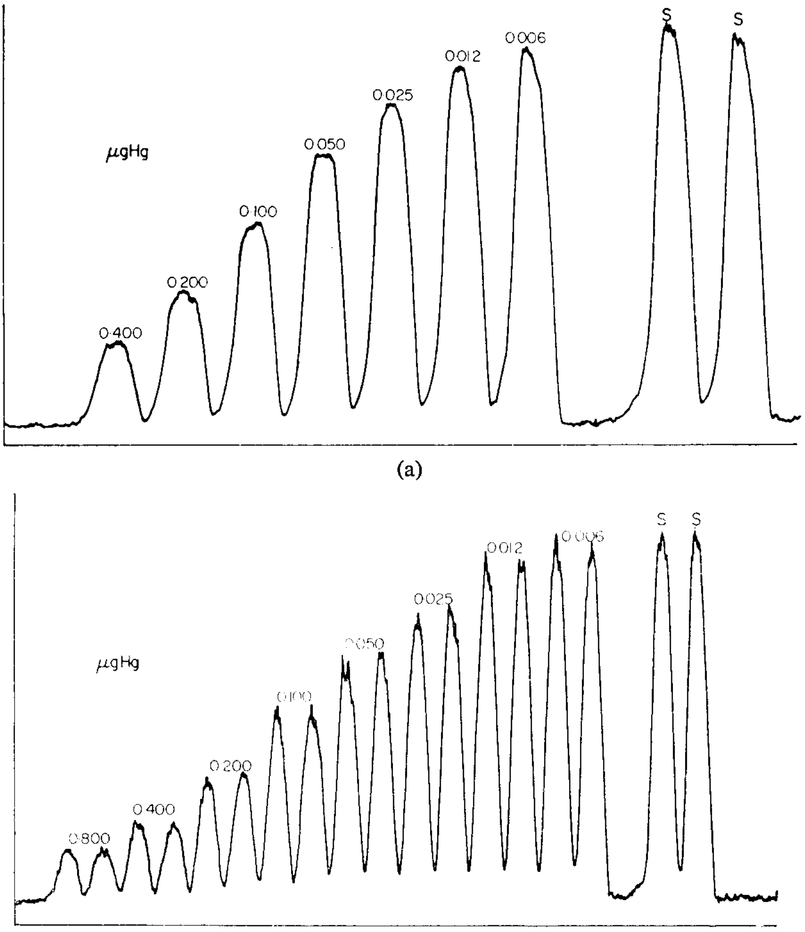

FIG. 1.—Calibration records for automated determination of traces of mercury; (*a*) 20 samples/hr; (*b*) 10 samples/hr.
The amounts of mercury refer to the whole content of the sampler cup, *i.e.*, the total content of mercury in a biological sample.

repeated whenever reagents or stock solution of radiomercury standard were replenished, or a new wire was used in the combustion flask. With a little cleanliness and care it was found quite easy to keep the reagent blank below the detectable limit, even in a normal radiochemical laboratory with unconditioned air. Besides careful purification of reagents and glassware with dithizone the main precaution taken was that *each* vessel, pipette, funnel, volumetric flasks, cylinder *etc.* was labelled and used strictly for the same operation every time.

The next factor influencing the precision is the "memory effect" as shown in Fig. 3. Here two standards, two blanks, five samples of cereal, five samples of kale, two standards, two blanks and two mercury samples were analysed consecutively. Clearly, the first cereal peak is influenced by the preceding blank as is the first kale peak by the last cereal peak, and so on. Thus, due to this carry-over, the first cereal peak gives the value 0·036 ppm mercury (the mean of the remaining four being 0·0435 ppm) and the first kale peak gives the value 0·128 ppm compared with the mean 0·159

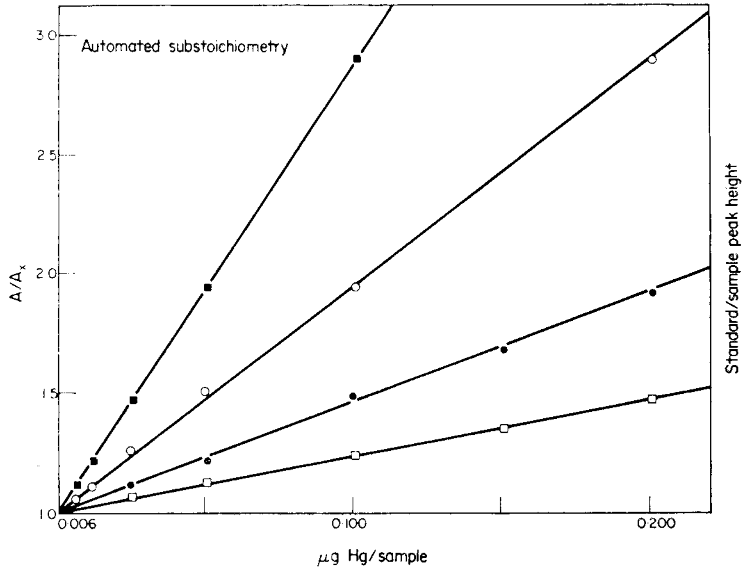

Fig. 2.—Calibration graphs.

	^{203}Hg added, μg	Zn(HDz)$_3$, *M*	Samples/hr
□	0·4	$2{\cdot}5 \times 10^{-7}$	20
●	0·2	$1{\cdot}2 \times 10^{-7}$	20
○	0·1 0·1	6×10^{-8} 3×10^{-8}	20 10
▲	0·05	3×10^{-8}	20

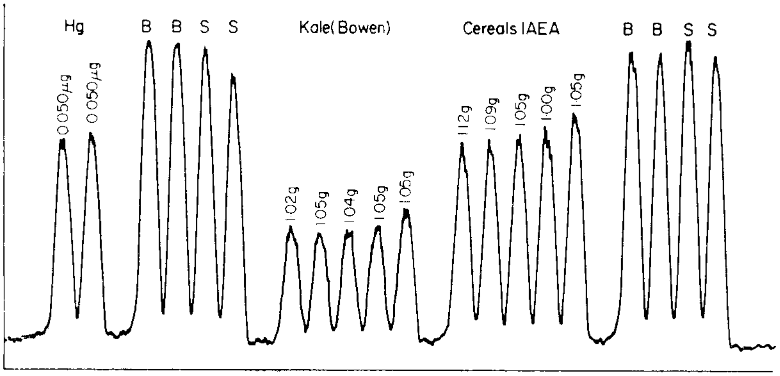

Fig. 3.—Automated analysis of international biological standard materials (20 samples/hr).

ppm of the remaining four. As the second peaks give the values 0·041 ppm Hg and 0·154 ppm respectively, obviously the first peak should be disregarded and used only as a preliminary one. This always applies when there are large differences between mercury contents of consecutively analysed samples. A minimum of three samples should therefore always be analysed for each material.

From the extraction constants and the values of redox potentials given in Table III it follows that this method is highly selective as only palladium and platinum might interfere. These elements, however, are unlikely to be present in biological materials

Table III.—Redox potentials[20] and dithizone extraction constants.[1]

Couple	E^0*, V	Metal ion	log K†	q‡
H_2O_2/H_2O	∼+1·7	Au^{3+}	>27	$>10^4$
MnO_4^-/Mn^{2+}	+1·51	Pd^{2+}	>27	$>10^4$
HNO_2/NO	+1·00	Pt^{2+}	>27	$>10^4$
$[AuCl_4]^-/Au$	+1·0	Hg^{2+}	26·8	$>10^4$
Hg^{2+}/Hg_2^{2+}	+0·92	Cu^{2+}	10·5	150¶
N_2H_2OH/N_2H_4	+0·73	Bi^{3+}	9·98	10^{-3}
$N_2H_5^+/N_2$	+0·67	Ag^+	7·18	$<10^{-4}$
$[PdCl_4]^{2-}/Pd$	+0·62	In^{3+}	4·84	$<10^{-4}$
I_2/I^-	+0·54	Zn^{2+}	2·3	$<10^{-4}$
SO_4^{2-}/SO_3^{2-}	+0·54	Cd^{2+}	2·14	$<10^{-4}$
$S_2O_3^{2-}/SO_3^{2-}$	+0·40	Sn^{2+}	2	$<10^{-4}$
Hg_2Cl_2/Hg	+0·33	Ni^{2+}	1·18	$<10^{-4}$
S^{2-}/S	+0·14	Pb^{2+}§	0·44	$<10^{-4}$

* In $1N$ acid medium, *vs.* hydrogen electrode.

† Logarithm of the dithizone extraction constant

‡ q is the distribution ratio of mercury between $1 \times 10^{-5}M$ H_2Dz in CCl_4 and $0{\cdot}2M$ HCl.

§ Other metals either have lower extraction constants than lead, or are not extracted at all.

¶ Although extracted with an *excess* of dithizone, copper will not interfere in the final *substoichiometric* determination of mercury, as according to the theory of substiochiometry,[9] the ratio of mercury to copper in the dithizone extract (as measured in the flow-cell) will be

$$\frac{[Hg(HDz)_2]_{org}}{[Cu(HDz)_2]_{org}} = \frac{10^{2\cdot68}[Hg^{2+}]}{10^{10\cdot5}[Cu^{2+}]}$$

in larger quantities than mercury. The following factors relevant to the analytical procedure are also responsible for this high selectivity.

(*a*) Mercury distils from the sample in the process of burning, leaving the bulk of inorganic substances in the ash.

(*b*) Sulphides and iodides are oxidized in the absorbing solution.

(*c*) Hydroxylamine reduces most of any gold present to the metal.

(*d*) Only mercury, platinum, palladium, copper and non-reduced gold are extracted by dithizone in carbon tetrachloride (platinum metals reacting slower than mercury). Of non-metals only iodine is extracted by carbon tetrachloride.

(*e*) Only metals are re-extracted into the aqueous phase containing hydrochloric acid and sodium nitrite.

(*f*) Even traces of gold will be reduced to the metal by the warm hydrazine sulphate solution in the AutoAnalyzer, where additional masking by EDTA is provided. This masking is really only a safety precaution, as any copper present cannot interfere in the substoichiometric determination of mercury (Table III).[9] Interference studies carried out as previously described[15] have shown that *e.g.*, gold, if present in the absorbing solution (or aqueous sample to be analysed) even in 1000-fold excess with respect to mercury, does not interfere (1 μg of gold in the sampler cup simulates the presence of 0·010 μg of mercury). The selectivity of the method is further confirmed by the good precision and accuracy of analysis of the kale sample which contains a wide variety of elements, most of which are present in a large excess relative to the mercury content.[17]

CONCLUSIONS

This method not only provides a new tool for reliable pesticide control, but also demonstrates that automated substoichiometric analysis possesses many advantages over activation analysis. This is especially true when traces of a single element must be determined routinely in complex materials. In such a case it is better to add a minute amount of a single radioisotope to the investigated material and to study its behaviour rather than to activate most of the elements present in the sample. The health hazard involved in handling isotopes is also much reduced.

Finally, two possible improvements of the present method should be mentioned.

(*a*) The wire basket could be heated electrically from outside the flask in order to avoid the necessary slow drying of wet samples (fish, meat *etc.*) at low temperature before burning. With such a device it should be possible to dry the samples quickly in the closed flask, already filled with oxygen, radiomercury and absorbing solution, without any losses of mercury. When dried sufficiently the samples would be ignited by further heating of the wire.

(*b*) The manual part of the procedure could be continuously checked for each sample by the use of a *two-detector system.* Here an additional scintillation detector would be located before the extraction coil and its integrated signal recorded together with the signal from the flow-cell detector by means of a two-pen recorder. As long as mercury is isolated from the analysed sample without loss during combustion or pre-extraction the standard and sample peak-heights from the additional detector must always be identical. Should any losses of mercury occur (because of some mistake in the manual operations this could be seen immediately from the recording. Besides this additional control the two-detector system offers some new and interesting possibilities in automated radiochemical analysis[21] and is therefore being further investigated by us.

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Zusammenfassung—Feste Proben (1–2 g) werden in Sauerstoff in einem Kolben verbrannt, der Radioquecksilber in verdünnter Salzsäure enthält, in der das zu bestimmende inaktive Quecksilber sofort absorbiert wird. Dann wird alles Quecksilber mit Ditnizon in Tetrachlorkohlenstoff extrahiert und in verdünnte Salzsäure reextrahiert. Diese wäßrige Phase wird dann, wie früher beschrieben, automatisch (AutoAnalyzer, 20 Proben pro Stunde) analysiert. Flüssigkeiten (bis 100 ml) werden ebenso analysiert, aber statt der Verbrennung in Sauerstoff zuerst mit Kaliumpermanganat in saurer Lösung oxidiert. Quecksilbermengen zwischen 2 und 0,00004 ppm wurden in verschiedenen Materialien bestimmt. Die Ergebnisse für internationale biologische Standards stimmten gut mit aktivierungsanalytisch erhaltenen Werten überein: Kohl 0,159 ppm Hg (relative Standard abweichung 2%) und Getreide der IAEA 0,0435 ppm Hg (± 5%). Die neue Methode ist viel einfacher und schneller als die Aktivierungsanalyse und ebenso empfindlich; daher ist sie für Routinearbeiten besser geeignet. Etwa 100 Proben können pro Tag analysiert werden.

Résumé—On brûle des échantillons solides (1-2 g) dans l'oxygène dans une fiole contenant du radiomercure en acide chlorhydrique dilué, dans lequel le mercure non actif à doser est immédiatement absorbé. Tout le mercure est ensuite extrait par la dithizöne en tétrachlorure de carbone puis extrait de nouveau en acide chlörhydrique dilué. Cette phase aqueuse est alors analysée automatiquement (AutoAnalyzer, 20

échantillons/h) comme décrit antérieurement. On analyse de la même manière des liquides (jusqu'à 100 ml) mais, au lieu d'être brûlés dans l'oxygène, ils sont d'abord oxydés au permanganate de potassium en milieu acide. On a dosé, dans divers produits, des quantités comprises entre 2 et 0,00004 ppm de Hg. Des résultats pour des étalons biologiques internationaux sont en bon accord avec les valeurs obtenues par l'analyse par activation: chou vert 0,159 ppm Hg (écart type relatif 2%) et céréales IAEA 0,0435 ppm Hg (± 5%). La nouvelle méthode est de beaucoup plus simple et rapide que l'analyse par activation et tout aussi sensible; elle est de ce fait plus convenable pour le travail de routine. On peut analyser environ 100 échantillons par jour.

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ION-EXCHANGE RESINS IN NON-AQUEOUS SOLVENTS—III

SOLVENT-UPTAKE PROPERTIES OF ION-EXCHANGE RESINS AND RELATED ADSORBENTS

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Summary—Solvent-uptake properties for several synthetic resins and common adsorbents were determined by the centrifugation method. Data are reported for eighteen different solvents, which include water and the common polar and non-polar organic solvents. The cation-exchange resins are of two varieties: the microreticular or gel type and the macroreticular or porous type. The latter resin being rigid and porous takes up all types of solvents, whereas the former resin, which relies on swelling of the resin matrix, does not take up the non-polar solvents. Data for the H^+ form and Na^+ form macroreticular resin are compared. Unsulphonated polystyrene-divinylbenzene polymers which possess similar micro- and macroreticular properties to the cation-exchange resins were also studied in the same solvents. The swelling properties of these non-polar resins are compared with each other and with the polar cation resins. Other adsorbents, which are frequently used as supports in chromatography were also examined in the same solvents. Several of these have large average pore diameters and surface areas like the macroreticular resin.

THE effects of water–organic solvent mixtures on the properties of ion-exchange resins, such as swelling, capacity, rates of exchange, solvent uptake, solvent preference, and bead fracture have been described.[1–3] In general, the properties, although different from those found in water, are not so seriously affected as to prevent the use of ion-exchange resins for separations with water–organic solvent eluting mixtures. In fact many standard separations of metal ions on anion and cation resins have been modified or improved, and in some cases are only made possible, by the addition of the organic solvent.[4]

Although numerous studies have been directed towards the separation of non-electrolytes, the eluting agents are usually aqueous or partially aqueous solutions often containing electrolytes.[5,6] Only recently has attention been turned to the use of completely non-aqueous or mixed solvents with very low concentrations of water. Cassidy and Streuli[7] studied the sorption of amides on the hydrogen form of a cation resin in acetonitrile and methyl alcohol, and Gordon[8] studied several other weak bases in acetonitrile. Tsuk and Gregor[9] separated several bases on specially designed resins with heptane and 1:1 dichloromethane–methanol. In this laboratory sorption studies have been made with nitroanilines and several other bases[10,11] in a wide variety of solvents. The goals in all of these studies, aside from application to separations, were to evaluate the behaviour of ion-exchange resins in anhydrous solvents.

Ion-exchange with conventional resins is frequently unsuccessful if anhydrous solvents of low polarity are used. The main difficulty is the inability of the resin matrix to swell sufficiently in the solvent. If the resin is not swollen or is only partially swollen, the ion-exchange rate-process or the penetration of the non-electrolyte or electrolyte into the resin will be curtailed. Therefore, in many of the cases where non-aqueous solvents of low polarity were studied, the resins used were preswollen (water-wet resins).[10,12,13] Actually, the measurements are then made in a water–organic solvent mixture. These types of ion-exchange resins are generally referred to as the gel type or microreticular resins. In polar solvents these resins will swell and usually contain 5–50 Å channel widths depending on the degree of cross-linking. If they are in the dry state or not swollen, the channel widths are practically non-existent, and the resins will remain in this condition when placed in a non-polar solvent.

More recently several resins have been synthesized which contain pores or channels several hundred Å wide. They are of the styrene–divinylbenzene copolymer type and differ only in their cross-linking and method of preparation. The result is a resin which is more rigid and porous than the microreticular resin. In essence, the channels or pores remain accessible even in the non-polar type of solvent. These resins have been designated as porous, macroporous, or macroreticular resins and are in other respects similar in properties to the microreticular resins.[14–16] More recently Gregor and co-workers[17,18] suggested an alternative type of resin which they have named "oleophilic ion-exchange resins". Their interesting approach is to introduce oleophilic groups into the resin structure to reduce its polarity. Consequently, the modified resin, which can be synthesized with anionic or cationic sites, is capable of swelling in solvents that do not solvate the sulphonate group.

As a part of a general programme on the performance of ion-exchange resins in non-aqueous and mixed solvents, data are reported here on the solvent-uptake properties of the macroreticular resins and compared to uptake data for the microreticular resins and typical adsorbents. Data for mixed solvents will be reported later. The potential practical aspects of these experiments were more insight into the use of resins in non-aqueous solvents as catalysts, in synthesis reactions, and as supports for various types of chromatographic separations.

EXPERIMENTAL

Solvents

Analytical grade solvents from common commercial sources were used, and dried by the following techniques. The alcohols were refluxed for 12 hr in the presence of the corresponding magnesium alkoxide (which was prepared by adding magnesium turnings to the alcohol in the presence of a small amount of ethyl bromide catalyst) and then distilled. Acetic acid was distilled, after 2 hr of refluxing, from triacetyl borate, which was prepared from acetic anhydride and boric acid. Ethyl acetate, n-butanol, hexane, and cyclohexane were treated with Linde Molecular Sieve 4A, 1·5-mm pellets. Benzene and acetonitrile were distilled from sodium and phosphorus pentoxide respectively. Nitromethane was fractionally distilled through a 1-m column of glass helices; carbon tetrachloride, chloroform, and isobutyl methyl ketone (IBMK) were used as received, from freshly opened bottles. Dimethylformamide and tetrahydrofuran were distilled from barium oxide and lithium aluminium hydride respectively. Dioxan was refluxed with sodium until a shiny surface was obtained on the metal, and then distilled, both operations being performed under nitrogen. All distillations were carried out at atmospheric pressure just before use of the solvents, moisture being excluded by calcium chloride drying tubes. Karl Fischer titration showed the water contents to be in the range 0·01%–0·10%, depending on the solvent.

Resins

Dowex 50S8, 100–200 mesh, hydrogen-form resin (D-50), Amberlite IR-120, 50–100 mesh, hydrogen-form resin (IR-120) and Amberlyst 15 hydrogen-form resin of random size but with an average of 20–30 mesh (A-15) were used. The A-15 was ground in a mortar and pestle and sieved and the 40–60 mesh fraction [U.S. Standard (A-15c)] was also studied.

The resins were initially backwashed with water to remove the very fine particles and then washed with a sodium citrate solution. Conversion back into the hydrogen form was performed by the passage of 1–2*M* hydrochloric acid. If the sodium form was desired, the resin was then washed with 1–2*M* sodium chloride. This was followed by extensive washing alternately with an 80% alcohol–20% water mixture and 100% alcohol, air-drying, and storage in a closed bottle. The A-15, which was received in toluene, was washed repeatedly with benzene and ethyl alcohol alternately, before the procedure given above.

Samples of the resin (40–50 g) taken in a weighing-bottle were dried in a vacuum oven at 95–105° and 5–9 mbar for 24–36 hr, and stored in a desiccator over phosphorus pentoxide. Storage studies and water contents by weight loss and Kral Fischer titration had already been made.[10]

The unsulphonated resins, polystyrene–8% divinylbenzene, 100–200 mesh (P-8D) and polystyrene–divinylbenzene copolymer, 20–60 mesh (XAD-1 and XAD-2) were used. Before use, they were extensively washed with water and alcohol and air-dried. Additional drying of the unsulphonated polymers was by the procedure used for the sulphonated resins.

Glass beads, 80–100 mesh (GB), molecular sieves A-5, 70–80 mesh, and activated coconut carbon, 60–70 mesh (CC) were obtained from Analabs, Inc. Silica gel, grade 62, 60–200 mesh (SG) was obtained from Grace Davison Chemical, and alumina, H-51, 20–80 mesh and F-20, 80–200 mesh from Aluminum Company of America. These adsorbents were not pretreated in any way except for drying. The drying technique used for the resins was also used for GB and CC, but the other adsorbents were dried in a muffle furnace at 425° for 12 hr. After cooling they were also stored in a desiccator over phosphorus pentoxide.

Procedure

The dried resin (~1·5 g) was weighed into an oven-dried 125-ml glass-stoppered flask. Freshly dried solvent (~25 ml) was rapidly added and the flask was stoppered, swirled and allowed to equilibrate for several days at 25 ± 1°. The resin and solvent were then quickly poured into a specially designed centrifuge tube which was constructed in the following manner. A 30 × 50 mm sintered glass crucible of coarse porosity was connected to a glass tube (50-mm diameter) which was closed at the bottom. The frit was 85 mm from the bottom of the tube. About 10 mm below the frit a 4·5-mm hole was made in the tube. The width and length of the centrifuge tube were patterned on the openings in the International Centrifuge Model PR-2 equipped with the Model 845a head. The side opening and the top of the crucible were stoppered immediately after the resin and solvent were poured onto the frit; most of the solvent had drained to the bottom chamber in about a minute. The tube was then centrifuged for 35 min at 300G (2000 rpm) and 25 ± 1° unless otherwise stated. The resin bed in all cases was less than 1·5–3 mm thick. After this, the resin was quickly divided in half and transferred to weighing-bottles (previously brought to constant weight) and weighed. To obtain the dry resin weight the weighing-bottles were placed in the vacuum oven at 95–105°and 6–9 mbar for 12–16 hr, cooled and weighed, the drying being repeated till constant weight was attained. The amount of solvent in or on the resin and the weight of dry and solvent-wet resin were thus obtained. The same procedure was used for the adsorbents. Details of the time studies are given in the discussion. The ion-exchange resins (sulphonated type) were in the hydrogen form unless otherwise stated. All the results are referred w/w to the dry resin (adsorbent).

RESULTS

The principal advantage of the macroreticular resin over the microreticular resin is that the former is capable of functioning even in the non-swelling type of solvent such as hexane or benzene[10,15] and therefore environmental conditions such as osmotic pressure are less important. Since the macroreticular resin is rigid and truly porous it is more capable of withstanding a large osmotic pressure, is more readily solvated owing to less resistance towards solvent uptake, and can be used in solvents of all polarities. In contrast, the microreticular type resin is very sensitive to environmental conditions and its performance would be largely dependent on its ability to swell in a particular solvent. The contrasting porous properties of the two types of resins are illustrated in Table I.

In essence, the macroreticular resin is acting like the zeolites or typical porous, non-swelling adsorbents such as alumina, silica and certain carbons. Consequently, a variety of these adsorbents which are often used as solid supports in chromatography were also studied for purposes of comparison. These substances vary in surface area from 5–10 m^2/g for glass beads (GB) to approximately 1700 m^2/g for the activated coconut carbon (CC). The alumina (F-20) and (H-51), molecular sieve (A-5), and silica gel-62 (SG) are intermediate in surface area. The average pore size, in contrast, is only large for SG and F-20, about 140 and 40 Å respectively. The others have pore sizes similar to the gel type resin except for the GB which are essentially non-porous.

Swelling or solvent uptake is conveniently determined by the centrifugation method. This method, which has been carefully evaluated by several researchers[20] and more recently by Parrish,[21] was used to evaluate the solvent uptake properties of the resin and adsorbents listed in Table I, in a variety of polar and non-polar solvents.

TABLE I.—APPROXIMATE SURFACE AREA AND AVERAGE PORE DIAMETER FOR SEVERAL RESINS AND ADSORBENTS[15,16,19]

Resin or adsorbent	Surface area *m²/g*	Average pore diameter, *Å*
Amberlyst-15 (A-15)*	42	290
Amberlyst-15-Na (A-15Na)†	‡	‡
XAD-1*	100	205
XAD-2†	300	90
Dowex 50X8 (D-50)§	¶	5–50
Amberlite IR-120 (IR-120)§	0·1	5–50
Polystyrene-divinylbenzene (P-8D)††	¶	5–50

* Sulphonated macroreticular resin.
† Unsulphonated macroreticular resin.
‡ Probably similar to A-15 hydrogen form.
§ Sulphonated microreticular resin.
¶ Probably similar to IR-120.
** Depends on degree of dryness.
†† Unsulphonated microreticular resin.

The more important experimental parameters involved in the centrifugation method are resin–solvent contact time before centrifuging, time of centrifuging, centrifugal field, volume of interstitial solvent, and effect of variation in particle size. The last two were evaluated by using glass beads as models of the resins and adsorbents to obtain an indication of the interstitial uptake.[20,21] The comparison of results for A-15, with its large and variable particle size, and for A-15c, with its smaller and more uniform size, gives an indication of the effect of particle size.

In order to examine the first three parameters, preliminary experiments on two ion-exchange resins, D-50 and A-15, were conducted with a polar (ethanol), a viscous (butanol) and a non-polar (benzene) solvent, and a fixed procedure based on reproducible results was established.

The first parameter, effect of time on centrifuging, was measured by determining solvent uptake after centrifuging for 5, 10, 20, 35, 60 and 120 min. A centrifuge field of 275 G was used and the two resins were kept in contact with the dry solvent for about three days before centrifugation. Resin and solvent were transferred to the centrifuge tube in such a manner that a small amount of liquid remained over the frit along with the resin, and the times quoted are those between turning the centrifuge on and off.

It was concluded that for the two resins in the alcoholic solvents the amount of solvent taken up was independent of centrifuge time, but for benzene there was a slight decrease in solvent uptake with increasing centrifuge time. For example, for the A-15 resin the uptake decreased from 0.365 g of solvent/g of dry resin at 5 min to 0.324 g/g at 120 min. A similar trend was observed for the D-50 resin in benzene.

The effect of contact time between dry solvent and resin before centrifugation was the second parameter studied and the results are shown in Table II. A centrifugation time of 30 min and a centrifugal field of 275 G were used. Control of the actual resin–solvent contact time is difficult since the resin is always in an atmosphere of solvent vapour during centrifugation. The times quoted are those of physical contact of resin with liquid.

TABLE II.—EFFECT OF RESIN–SOLVENT CONTACT TIME ON SOLVENT UPTAKE

Time, *min*	Solvent/dry resin, *g/g* Ethanol	Butanol	Benzene
5(D-50)	0·624	0·425	0·008
10	0·692	0·627	0·009
20	0·684		
30		0·676	
60	0·639	0·684	0·005
*	0·677	0·688	0·014
5(A-15)	0·837	0·814	0·324
10	0·847	0·907	0·343
20	0·850		
30		0·903	
60	0·859	0·900	0·324
*	0·848	0·909	0·330

* Several days for equilibration.

The effect of the centrifugal field was studied by measuring the solvent uptake for the D-50 and A-15 resins in the three solvents at 14, 100, 215, 335 and 755 G. A centrifuge time of 35 min was used. As the centrifugal field increases, the solvent uptake decreases very rapidly until the value 215 G is reached, and then the uptake changes only very slightly with increasing centrifugal fields. At the lowest field, 14 G, the apparent solvent uptake was expected to be high since the bottom portion of the centrifuged resin bed (1.5–3 mm at thickest) was visibly very wet with solvent. This was found for each of the two resins in the three solvents. As expected, the largest solvent uptake change at low fields was found for butanol.

The results for benzene are more difficult to use for the prediction of a general procedure for solvent uptake measurements. Since the uptake of benzene by D-50 is so low (about 15% by weight) and is probably due mostly to retention by the outer surface of the resin, trends with this solvent are not easily discernible. In the case of the A-15 resin, the trends for uptake of benzene appear to be more similar to ethanol than to butanol. A serious problem which occurred with benzene and was later observed with other non-polar solvents is the rapid change in weight with time on weighing the solvent-wet resin, caused by evaporation. Even with rapid transfer and weighing the experimental error is higher than with polar solvents. The overall error for polar solvents is about 2% and for non-polar about 7%. Since a wide variety of resins, adsorbents and solvents were to be examined, a contact time of several days, centrifuging time of 35 min, and a centrifugal field of 330 G were used to ensure reasonable accuracy.

Solvent uptake was then measured for a series of dried micro- and macroreticular ion-exchange and unsulphonated resins in a variety of dried solvents, and the results are shown in Table III. The ion-exchange resins are of the sulphonated type and are in the hydrogen form unless otherwise stated. The unsulphonated XAD-1 and XAD-2 resins have a high surface area and are highly porous and are similar to the sulphonated macroreticular resin A-15 in this respect. On the other hand, P-8D is similar, except for being unsulphonated, to the microreticular type resin, D-50 and IR-120.

TABLE III.—SOLVENT UPTAKE (*g* PER *g* OF DRY RESIN) FOR ION-EXCHANGE AND UNSULPHONATED RESINS

Solvent	Exchange resins					Unsulphonated resins		
	A-15	A-15c	A-15Na	D-50	IR-120	XAD-1	XAD-2	P-8D
Water	1·21	1·22	0·945	1·16	1·12	0·061	0·072	0·054
Methanol	0·815	0·823	0·585	0·701	0·674	0·488	0·699	0·050
Ethanol	0·848	0·892	0·586	0·677	0·663	0·507	0·719	0·062
n-Propanol	0·907	0·910	0·526	0·715	0·668	0·535	0·757	0·068
Isopropanol	0·892	0·907	0·461	0·604	0·559	0·509	0·721	0·131
n-Butanol	0·909	0·905	0·403	0·688	0·655	0·527	0·758	0·064
Dimethylformamide	0·828	0·908	0·609	0·601	0·551			0·810
Acetonitrile	0·553		0·493	0·288	0·255	0·688	0·743	0·171
Nitromethane	0·736	0·768		0·316	0·247	1·00	0·872	0·242
Tetrahydrofuran	0·830	0·852	0·390	0·591	0·496	1·05	0·736	0·808
Dioxan	0·848		0·467	0·040	0·126	1·21	0·960	0·881
Ethyl acetate	0·716		0·446	0·425	0·388	0·907	0·816	0·526
Acetic acid	0·905	0·936	0·809	0·570	0·505	1·872	1·00	0·218
Chloroform	0·842		0·619	0·387	0·357	1·59	1·22	1·40
Carbon tetrachloride	0·502	0·597	0·430	0·027	0·064	1·64	1·35	1·21
Benzene	0·330	0·346	0·316	0·014	0·054	0·993	0·779	0·724
Hexane	0·203		0·211	0·013	0·508	0·515	0·540	0·015
Cyclohexane	0·261		0·273	0·009	0·009	0·728	0·656	0·005
Isobutyl methyl ketone			0·324			0·818	0·745	0·124

A variety of typical adsorbents of high and low porosity was then examined and the results are reported in Table IV. These materials are not subject to swelling and therefore resemble the macroreticular resins.

The results in Tables II–IV represent an average of several measurements, usually 2–4, but as many as 10 for the resins with ethanol, butanol and benzene. As a control and check on the reproducibility, various measurements with ethanol and another solvent (a different one each time) were repeated for all the resins and adsorbents.

DISCUSSION

The theoretical approaches and models that are useful in describing swelling equilibria and solvent uptake are reviewed by Helfferich.[1] Using these models, it has been shown that the uptake of the solvent is determined by (*a*) the solvation tendency of the charged sites and counter-ions, (*b*) the tendency of the concentrated pore liquid to dilute itself, and (*c*) electrostatic repulsion between neighbouring fixed charges. To accommodate the solvent, the resin matrix must stretch. Swelling equilibrium is reached, therefore, when the swelling pressure, which tends to squeeze solvent out of the resin, balances the driving forces for the uptake of the solvent.

In non-aqueous solvents the extent of resin swelling is determined by the polarity of the solvent, the degree of cross-linking and the type of fixed ionic groups. For the macroreticular and microreticular resins the ability to take up solvent should be different since their swelling properties are not the same. The macroreticular resin with its rigid and porous structure should be more like the zeolites and other porous adsorbents; for these materials, solvent uptake, particularly for non-polar solvents, is not determined by their swelling ability but by the available space in their lattices.

In Table II, differences between the two types of ion-exchange resins, macroreticular A-15 and microreticular D-50, become apparent. For the more polar and less viscous ethanol, the amount of solvent taken up appears to reach a constant value at a faster rate for the A-15 resin than for the D-50 resin; 5 min contact time for A-15 and 10 min for D-50. The difference is more noticeable for the more viscous but less polar butanol (>10 min for D-50, <10 min for A-15).

TABLE IV.—SOLVENT UPTAKE PROPERTIES FOR TYPICAL ADSORBENTS

Solvent	Solvent/dry resin, *g/g*					
	GB	CC	SG	A-5	F-20	H-51
Water	0·019	0·622	1·26	0·505	0·346	0·459
Methanol	0·005	0·546	0·918	0·307	0·207	0·281
Ethanol	0·008	0·534	0·910	0·289	0·194	0·283
n-Propanol	0·014	0·579	0·950	0·277	0·213	0·318
Isopropanol	0·010	0·540	0·966	0·220	0·194	0·277
n-Butanol	0·016	0·539	1·00	0·244	0·184	0·256
Acetonitrile	0·010	0·497	0·916	0·249	0·202	0·280
Nitromethane	0·012	0·721	1·35	0·434	0·265	0·371
Tetrahydrofuran	0·001	0·463	0·923	0·086	0·132	0·273
Dioxane	0·015	0·425	1·19	0·262	0·241	0·358
Ethyl acetate	0·0002	0·519		0·219	0·128	0·273
Chloroform	0·001	0·806	1·48	0·087	0·231	0·468
Carbon tetrachloride	0·002	0·750	1·68	0·176	0·229	0·459
Benzene	0·002	0·494	0·954	0·145	0·141	0·303
Hexane	0·001	0·311	0·691	0·124	0·100	0·212
Cyclohexane	0·001	0·413	0·836	0·083	0·103	0·216

Unfortunately, very little research has been done on the kinetics of solvent uptake (resin swelling) or release (resin shrinking). Since no electric coupling is involved it would appear as a first approximation that the kinetics would be similar to those of non-electrolyte sorption. A very important complication is the expansion of the resin matrix. The necessity for expansion is illustrated by comparing the benzene uptake, Table II, for the A-15 and D-50 resin. The A-15 resin takes up the dry benzene freely, while the D-50 resin, which is dry and collapsed, remains virtually in this state when the solvent is added. This result is not surprising since it has already been shown in other studies with benzene and other non-polar solvents that non-electrolytes (amines) are not taken up by the dry D-50 resin but are by the A-15 resin.[10,15] These studies have also shown the more rapid attainment of equilibrium by the A-15 resin. In other studies the availability of the pores in the macroreticular type resin has been determined by measuring the kinetics of the exchange of H^+ and Na^+ for $(R)_4N^+$ ions and it has been found that the more porous the resin the more easily the larger tetra-alkyl ammonium salts are exchanged.[22]

Measurement of solvent uptake in other solvents, Table III, suggests several broad generalizations. The highly polar sulphonated type resin prefers water, the most polar solvent studied, over any other solvent. In all cases the solvent uptake is larger for the porous A-15 resin than for the gel-type and IR-120 resins. The largest difference occurs for the non-polar, non-oxygenated solvents in which the last two resins take up only traces of solvent whereas the A-15 resin takes up an appreciable amount. This is attributed to the A-15 resin retaining its effective porosity and rigid structure regardless of solvent, while the gel-type resins rely on expansion of the resin matrix. The ionic form of the resin plays an important role in solvent uptake for the A-15 resin. For the non-polar solvents benzene, hexane and cyclohexane the uptake is independent of the ionic form, at least for the H^+ and Na^+ forms, but the difference is the largest for the oxygenated solvents with their potential hydrogen-bonding properties, where the H^+ form resin takes up 1.5–2 times as much as the Na^+ form. The exceptions in which the difference is not nearly as large are water, where the uptake is large in both cases, and acetic acid, where the possibility of ion-exchange is an added complication. Attempts to correlate the swelling data with dielectric constant, solubility parameters, or acid-base properties of the solvents were not successful.

The effect of the highly polar sulphonate group on swelling is seen by comparing the results for XAD-1, XAD-2 and P-8D, which are unsulphonated polystyrene-divinylbenzene copolymers, with those for the sulphonated resins. The macroreticular XAD-1 and -2 are similar to the A-15 resin while the microreticular P-8D is similar to D-50. It is not surprising that all three resins, which are no longer polar, are virtually free from water-uptake. In contrast, however, only the XAD resins take up the hexane and cyclohexane; the extent of the uptake is also much larger than that found for the corresponding sulphonated resin. Benzene, on the other hand, being aromatic like the resin matrix, is taken up by all three resins. Another major difference between the resins occurs with the alcoholic solvents. The XAD resins take up the alcohols but the P-8D has only limited uptake for this type of solvent, in contrast to the sulphonated resins, which have a large uptake. The non-polar character of the XAD resins is still apparent since their alcohol uptake is less than that of the A-15 resin.

The differences in the XAD-1 and -2 resins are not uniform. XAD-2 has a higher uptake for the polar solvents, alcohols, water and acetonitrile, whereas XAD-1 has the higher uptake for the non-polar solvents. Acetic acid and nitromethane appear to be exceptions, but their properties are very dependent on their degree of dryness. Very dry nitromethane can exhibit non-polar properties;[23] wet acetic acid would become more polar. The average pore diameter of XAD-1 is much larger than that of XAD-2 and would be less dependent on the swelling of the resin, and could account for the preference for the non-polar solvent. In general, it appears that the swelling of the P-8D resin is influenced by London interactions between the resin and solvent. On the other hand, the XAD resins with their highly rigid and porous character remain highly porous in all solvents except water.

An interesting potential application for the XAD resins is as inert supports for reversed-phase chromatography. Many of the solvents taken up in large quantities, *e.g.*, non-polar solvents and isobutyl methyl ketone, are also frequently used as stationary phases in reversed-phase chromatography. The uptake of the IBMK is particularly interesting as this solvent is very useful for separation of many metal ions under a wide variety of eluting conditions. Similar resins have also been shown to be useful as column packings in gas-solid chromatography.[24,25]

The macroreticular resin will take up non-polar as well as polar solvents because of its highly porous and rigid character. Similarly, other adsorbents, which rely not on swelling but on sieve action, London interactions, hydrogen bonding, and other types of interaction, also take up the solvents. The results in Table IV show the similarity (in extent and type of solvent uptake) between these adsorbents and the macroreticular sulphonated and unsulphonated resins.

In general, the adsorbents which are typical column supports for adsorption and partition chromatography show a preference for the solvents of similar structure. All the adsorbents except glass beads have a large uptake of water, not surprisingly, since one of their practical uses is to remove water from gases and liquids. Silica gel has the highest uptake for all solvents. H-51, which is an experimental gel like alumina, falls between silica gel and F-20, the common activated alumina, in solvent uptake. The sieve properties of A-5 are apparent in the extent of uptake of several solvents. The results for D-50 and IR-120 in non-polar solvents are very similar to those for glass beads.

Glass beads have been frequently used as models for ion-exchange resins to demonstrate the amount of interstitial solvent uptake.[20,21] The solvent uptake by glass beads was virtually negligible in this study. Parrish has found that for a bed of equal spheres in random packing the saturation is equivalent to 2.5–3% of the total bed volume, and when the glass beads are centrifuged at 250–500 G the volume of water retained falls in this range.[21] He also found that on reduction of the surface tension the amount of interstitial water is even lower and concludes that this correction can often be neglected. The highest uptake of all the solvents in these studies was of water. That the other values are lower and random is probably due to the difference in surface tension properties of the solvents.

A large particle-size variation might cause a large error due to interstitial hold-up. This can be examined by comparing the results in Table III for the A-15 resin, which has a very large variation in particle size, with the 40–60 mesh A-15c. Although there is a slight tendency for the A-15c uptake to be larger it appears that the general effect is not a large one. A correction for interstitial hold-up was not made because the values for GB were generally so small, there was a wide range in surface tension, and the experimental error was probably larger than the correction.

The effect of pore size and surface area is important in chromatography and is responsible for several specific separation techniques; for example, molecular sieve and gel permeation chromatography. On the other hand, materials with large pores, particularly the synthetic resins, have only recently been considered in the chromatographic process. The actual effect of pore size is difficult to estimate because of the complications of swelling, and the various interactions that influence the uptake of solvent, all of which are in turn influenced by the composition of the resin or adsorbent. From the results reported here, it appears, *ceteris paribus*, that the larger the pore size the greater the solvent uptake.

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Zusammenfassung—Die Lösungsmittelaufnahme mehrerer synthetischer Harze und gebräuchlicher Adsorbentien wurde mit der Zentrifugiermethode bestimmt Für achtzehn verschiedene Lösungsmittel, darunter Wasser und die üblichen polaren und unpolaren organischen Lösungsmittel werden Daten mitgeteilt Die Kationenaustauschharze lassen sich in zwei Typen einteilen: solche mit feiner (Geltyp) und solche mit grober Netzstruktur (poröser Typ). Da ein Harz vom zweitenTyp starr und porös ist, nimmt es alle Arten von Lösungsmitteln auf; beim ersten Typ beruht die Lösungsmittelaufnahme auf dem Quellen des Harzgerüstes, daher werden die unpolaren Lösungsmittel nicht aufgenommen. Die Daten von grob vernetztem Harz in H^+-Form und Na^+-Form werden verglichen. In den selben Lösungsmitteln wurden auch nicht sulfonierte Styrol–Divinylbenzol–Polymere untersucht, die, ähnlich wie die Kationenaustauschharze, feine oder grobe Netzstrukturen aufweisen. Die Quelleigenschaften dieser unpolaren Harze werden miteinander und mit denen der polaren Kationenaustauschharze verglichen. Auch andere Adsorbentien, die häufig als chromatographische Träger verwendet werden, wurden in den selben Lösungsmitteln untersucht. Mehrere davon haben große mittlere Porendurchmesser und Oberflächen wie die Harze mit Grobnetzstruktur.

Résumé—On a déterminé les propriétés de fixation de solvant pour plusieurs résines synthétiques et adsorbants communs par la méthode de centrifugation. On rapporte des données pour dix huit solvant différents qui comprennent l'eau et les solvants organiques polaires et non-polaires communs. Les résines échangeuses de cations sont de deux types: le type microréticulaire ou gel et le type macroréticulaire ou poreux. La seconde résine étant rigide et poreuse fixe tous les types de solvants, tandis que la première résine, qui repose sur le gonflement de la résine-mère, ne fixe pas les solvants non-polaires. On compare les données pour les formes H^+ et Na^+ de la résine macroréticulaire. Les polymères polystyrène-divinylbenzène non sulfonés qui possèdent des propriétés micro- et macroréticulaires similaires à celles des résines échangeuses de cations ont aussi été étudiées dans les mêmes solvants. Les propriétés de gonflement de ces résines non-polaires sont comparées l'une à l'autre et avec les résines cationiques polaires. D'autres adsorbants, que l'on utilise fréquemment comme supports en chromatographie ont aussi été examinés dans les mêmes solvants. Plusieurs d'entre eux ont des diamètres moyens de pore importants et des aires superficielles comme la résine macroréticulaire.

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COULOMETRIC ASSAY OF THE PRIMARY STANDARDS POTASSIUM DICHROMATE AND AMMONIUM HEXANITRATOCERATE

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Summary—The high-precision coulometric titration apparatus of Eckfeldt and Shaffer (Leeds & Northrup Company) has been used for the precision assay of two primary standard materials for oxidation-reduction work. The purity found for NBS 136b Potassium Dichromate, 99.975%, standard deviation 0.002%, checks the earlier value of Marinenko and Taylor. Ammonium hexanitratocerate, if low in thorium, is also an excellent primary standard, two recent commercial preparations having purities of 99.972 and 99.984%, a higher standard deviation, 0.005%, reflecting a minor difficulty in end-point detection caused by platinum oxide formation on the indicating electrodes.

DURING the past fifteen years a curious and instructive controversy has arisen about the oxidation-reduction primary standard ammonium hexanitratocerate and in particular about the thorium present in various preparations of the compound, Ammonium hexanitratocerate was first proposed as a primary standard by Smith, Sullivan and Frank.[1] In a second paper, Smith and Fly,[2] using weight-burette titrations of NBS 40e Sodium Oxalate and NBS 83a Arsenic Trioxide, found for two commercial lots of ammonium hexanitratocerate a purity of 99·98%, the average standard deviation over five sets of analyses (two products, two primary standards, one product after storage for one year) being 0·010%. Commercial preparations of ammonium hexanitratocerate, however, were later shown to contain variable and often appreciable amounts of thorium: by Voigt[3] by measurement of the radioactivity, by Fassel[4] by emission spectrographic analysis, by Salutsky, Kirby and Quill[5] by separation and identification of the radium-224 daughter product of thorium. The problem is one of reconciling the reported high purity with a significant thorium content, as high in some lots as several parts per thousand.

Smith's original work[1] was done with small amounts of materials of which none remains. No lot numbers were recorded for the commercial preparations analysed by Smith and Fly[2] and again no material was preserved. Direct examination of the original materials is thus precluded but two recent papers throw light on the problem. Smith[6] subjected a batch of ammonium hexanitratocerate to a series of recrystallizations from concentrated nitric acid. The thorium in successive crops was determined by emission spectrographic analysis and neutron-activation analysis. The thorium content dropped very slowly; starting at 0·4%, it became successively 0·12, 0·041, 0·011 and 0·005% in four recrystallizations. In the other paper Fassel, Jasinski, DeKalb and Lucas[7] show that the failure to find thorium in earlier preparations may have resulted from misidentification of the lines of the spectra of cerium and of thorium. It is of course possible that the commercial preparations examined by

Smith and Fly[2] were free from thorium, either because the starting materials were fortuitously free from it or because these particular lots were the result of a sufficient number of recrystallizations not given other commercial lots. The present work makes it very certain that the purity determined by coulometric reductimetric titration falls with increasing thorium content. Given a thorium-free preparation, however, the reductimetric assay indicates a definite composition and a high purity which places ammonium hexanitratocerate on a par with potassium dichromate as a primary standard.

Constant current coulometry is one of the most precise techniques at the disposal of the analyst for determining the purity of materials. Precision of a few parts in 100000 has been obtained by several workers[8–13] and the method has been so successful that the coulomb has been proposed as the ultimate primary standard.[11,14]

In the work described here, apparatus for high precision constant-current coulometry has been assembled from commercially available components (Leeds & Northrup Company, Philadelphia, Pennsylvania; Eckfeldt and Shaffer[12]). The purity of NBS 136b Potassium Dichromate has been determined by coulometric titration with electrogenerated iron(II) and by comparison with the results of Marinenko and Taylor[10] a check obtained on the calibration and operation of the equipment. The purity of several preparations of ammonium hexanitratocerate has been determined by coulometric titration with electrogenerated iron(II).

EXPERIMENTAL

Measurement of current

A Leeds & Northrup Coulometric Analyzer (L & N 7960) was used as the source of constant current. The L & N 7960 has three output currents of approximately 64·3, 6·43 and 0·643 mA. Current was determined by measuring the voltage drop across a specially constructed and calibrated resistance of 19·99979 ohms (L & N 4025-B-S). Potential was measured with a Leeds & Northrup Potentiometer Facility (L & N 7555) consisting of a type K-5 potentiometer, a null detector (L & N 9834-1 D.C.), constant voltage supply (L & N 9878), and a Weston standard cell. Voltage regulators were used to eliminate fluctuations in the line voltage. Deviations of ±0·002% in the *IR* drop at maximum current flow could be detected with this arrangement. The manufacturer states[12] that the 7960 current source produces an appreciable a.c. ripple but that this falls within the integrating capabilities of the null detector.

The 4025-B-S resistor was immersed in a constant temperature bath of mineral oil, but even with the bath providing a heat sink, the temperature of the resistor rose with the passage of current. A temperature increase of about 1° occurred in the first few minutes of passage of maximum current (64·3 mA); the rate of temperature increase then slowed somewhat and after about 15 min the temperature reached a steady state 1·5° above the temperature of the bath. Most of the temperature increase took place during pretitration as described below, so the change in resistor temperature during an actual titration never amounted to more than a few tenths of a degree. Nevertheless each time the *IR* drop was measured, the temperature of the resistor was noted and the actual resistance calculated from temperature coefficients provided by the manufacturer:

$$R_t = 19{\cdot}9997[1 + 0{\cdot}000002(t - 25) - 0{\cdot}0000005(t - 25)^2]$$

Two Weston cells were used alternately. Each cell was calibrated every three months against a third, resident, cell in the Iowa State University Instrument Shop. This third cell was periodically calibrated against a fourth cell which was sent to the National Bureau of Standards for calibration at intervals of six months.

The type K-5 potentiometer was calibrated at the standardizing laboratory of the Leeds & Northrup Company. At the potentials measured no corrections were required.

Measurement of time

The L & N coulometric analyser is equipped with a synchronous timing motor and a counter reading directly in μequiv. To eliminate the consequences of possible variations in the frequency of the a.c. mains the counter may be driven by a frequency standard. A frequency standard (model

2005A) manufactured by American Time Products, Woodside, New York was used in this work. The frequency standard counter was calibrated by using the time signals of Radio Station WWV of the National Bureau of Standards. Six calibration runs were made over elapsed times ranging from 24 to 72 hr and agreed to within 1 ppm. The time calibration was checked periodically during the course of the work.

Measurement of mass

The standards of mass used were 1-g and 10-g class M weights calibrated by the National Bureau of Standards. Weighings were made on an Ainsworth TCX equal-arm balance to the nearest 0·01 mg. All weighings were made by substitution, that is, the empty sample boat and the calibrated weight of appropriate size were weighed together, the calibrated weight was removed, and sample was added to the boat until the weight was equal to the weight removed to within one milligram. Weighings were corrected to weight in vacuo, the density of potassium dichromate being taken as 2·69 and that of ammonium hexanitratocerate as 2·61 g/ml.

The weights of the materials titrated were chosen to require a sufficient number of coulombs to permit measurement to 1 in 100000 or better; 1-g samples of potassium dichromate (equivalent weight 49·0320) and 10-g samples of ammonium hexanitratocerate (equivalent weight 548·23) were used.

Titration cell, electrodes, electrolytes

Titrations were carried out in a cell similar to that of Eckfeldt and Shaffer.[12] The cell consisted of a 1-litre, tall-form beaker fitted snugly with a cover of polyethylene through which passed the generating, reference and indicator electrodes, shield tube, and nitrogen inlet tube. Cathode and anode were separated by two concentric shield tubes, the bottom of each being provided with ultrafine glass frits as shown in Fig. 1. The shield tubes are the essential feature of the Eckfeldt and Shaffer cell, and, as in their work, a head was maintained on the electrolyte in the intermediate bridge solution such that flow of this electrolyte was into both anolyte and catholyte, thus ensuring that no material was transferred out of either cathode or anode chamber.

The working cathode was a helix of platinum wire with a surface area of 2600 mm^2. The anode was a platinum foil with a surface area of 250 mm^2.

The catholyte consisted of 500 ml of a solution 0·20*M* in iron(III) perchlorate and 4·0*M* in perchloric acid. The anolyte, and also the electrolyte in the intermediate chamber, was a solution 1·0*M* in sodium perchlorate and 0·1*M* in perchloric acid.

Materials

Potassium dichromate. NBS 136b was dried at 110° for 24 hr and stored *in vacuo* over anhydrous magnesium perchlorate until analysed.

A 20-g sample of NBS 136b, weighed to the nearest 0·01 mg, was placed in an oven at 260° for 10 days and the loss in weight recorded. This material was stored over anhydrous magnesium perchlorate until analysed.

Ammonium hexanitratocerate. Six lots of ammonium hexanitratocerate were obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio, the materials having been manufactured at various times from 1952 to 1967; a seventh specimen (C in Table II) was prepared from basnaesite. Each specimen was dried at 70° for 24 hr and stored in a vacuum over anhydrous magnesium perchlorate.

Specimen C was prepared from a rare earth oxide concentrate obtained from the thorium-free mineral basnaesite, $CeFCO_3$. The rare earth oxide was partially dissolved in 2 l. of boiling nitric acid. The solution obtained was filtered and concentrated to 1 l. by boiling. The cerium(IV) in a small aliquot of the solution was determined by titration with iron(II) sulphate. The theoretical amount of ammonium nitrate was then added and ammonium hexanitratocerate caused to crystallize by cooling. The product was collected on a fritted glass funnel and washed with concentrated nitric acid. The ammonium hexanitratocerate obtained in this way was recrystallized five times from concentrated nitric acid and dried at 55° under vacuum for 48 hr.

Iron(III)perchlorate. Commercial samples were found to contain appreciable amounts of chloride and the iron(III) perchlorate used in the catholyte was prepared by dissolving individual 2-g portions of electrolytic iron (G. Frederick Smith Chemical Company) in 50 ml of 72% perchloric acid and heating to boiling. If the solutions were cooled quickly the resulting precipitate of ferric perchlorate was chloride-free.

Nitrogen. Commercial "prepurified" cylinder nitrogen was passed successively through scrubbers containing (1) distilled water; (2) vanadium(II) sulphate in 1*M* sulphuric acid over amalgamated zinc;[15] (3) alkaline permanganate (to ensure the absence of hydrogen sulphide sometimes generated in the preceding oxygen absorption scrubber); (4) a solution 0·20*M* in iron(III) perchlorate and 4·0*M* in perchloric acid (identical with catholyte).

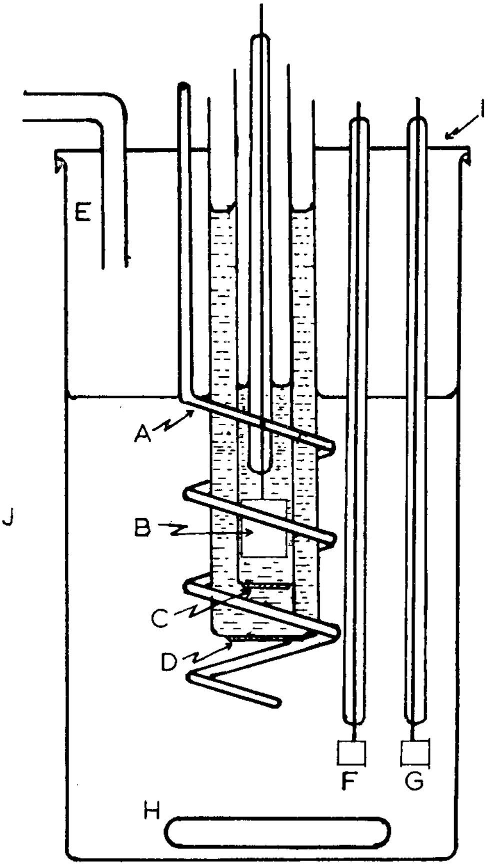

FIG. 1.—Coulometric titration cell.
A—Platinum cathode; *B*—platinum anode; *C*, *D*—ultrafine glass frits on bottoms of shield tubes; *E*—nitrogen inlet; *F*, *G*—indicator electrodes, either two platinum foils or a platinum foil and an S.C.E.; *H*—magnetic stirring bar; *I*—polyethylene cover; *J*—1-litre tall-form beaker.

Water. All solutions were prepared with distilled demineralized water, redistilled from alkaline permanganate.

Procedure

A sample was weighed to the nearest 0·01 mg into a platinum or glass boat by the substitution method. The boat was suspended by a platinum wire above the catholyte and held there while the pretitration was carried out and the major part of the iron(II) needed for the titration was generated. These three operations were carried out as follows. Nitrogen gas was bubbled through the catholyte for at least 1 hr; the nitrogen inlet tube was then raised above the catholyte and the flow of nitrogen reduced so that a small stream of nitrogen impinged gently on the surface of the catholyte. A small amount of the oxidizing agent (about 2 mg of potassium dichromate or 18 mg of ceric ammonium sulphate—about 40 μequiv) was added to the catholyte. The solution was stirred for about 5 min and the oxidizing agent titrated to well past the equivalence-point, the high current output of the constant current source being used. The procedure was repeated three times to ensure that any oxidizable or reducible impurities in the catholyte were removed. A fourth addition of oxidizing agent was then made to the catholyte and the titration carried out with the 0·643 mA output of the constant current source. The last pretitration was carried out by passing the current for short intervals, and after each, measuring the amperometric current in the end-point detection electrodes (see following section on end-point detection). The titration was carried beyond the end-point and the final reading on the counter was recorded. The counter was then reset to zero and iron(II) generated at 64·3 mA. This was continued until about 99·8 % of the iron(II) needed for the weight of sample taken had been generated. The reading of the counter was again recorded and the counter reset at zero. The boat and sample were lowered into the catholyte and after the sample had dissolved, the titration was continued with the 0·643 mA current and the same procedure for locating the end-point. Counter readings were then converted into seconds.

Weights of both potassium dichromate and ammonium hexanitratocerate were chosen so that about 20 mequiv were titrated, about 8 hr being required for the titration at 64·3 mA. During the titration the *IR* drop across the standard resistor was measured every 15 min or so. The temperature of the resistor was noted each time the *IR* drop was measured. The nominal value of the resistance was corrected to the temperature at which the *IR* drop was measured, as described above, and the current calculated. The thirty or so measurements of the current obtained during a given titration seldom varied by more than 8 parts in 100000, and the relative standard deviation of a set of values never exceeded 1 part in 100000. From the average value of the current and the number of seconds indicated by the standard frequency driven counter the number of coulombs passed at 64·3 mA was calculated. In a similar manner the number of coulombs passed at the lower current was determined by summing the counter readings for the current passed after the end-point in the pretitration and in approaching the end-point in the actual titration. The *IR* drop at the lower current was usually measured 7–10 times during each approach to an end-point. The precision of the measurement of the lower current was, of course, somewhat poorer, about 10 parts in 100000. However, only 0·1–0·2% of the total number of coulombs was passed at low current and the uncertainty introduced was negligible.

DISCUSSION

Current efficiency

The conditions for the electrogeneration of iron(II) with 100% current efficiency from iron(III) in sulphuric acid solution were determined by Marinenko and Taylor[10] who used the method of Lingane *et al.*[16,17] By the same method the conditions for 100% efficiency in the generation of iron(II) in perchloric acid solution were found to be similar. In a well stirred solution 4·0*M* in perchloric acid, and at the maximum current density used in this work, 23 μA/mm^2, the generation of iron(II) was complete as long as the concentration of iron(III) did not drop below about 0·02*M*. The initial concentration of iron(III) in all titrations was about 0·2*M* and, after generation of iron(II) almost equivalent to the amount of oxidant taken, about 20 mequiv, the concentration of iron(III) was 0·16*M*.

End-point detection

The end-point in the titration of potassium dichromate was determined amperometrically with the electrode pair S.C.E.–platinum (bright foil, 100 mm^2 total area). The platinum electrode was made 0·875 V positive to the S.C.E. by means of a Leeds & Northrup Electrochemograph. At this potential dichromate is not reduced, owing to the irreversibility of the dichromate-chromic couple, and no cathodic current flows before the end-point; iron(II) is oxidized, however, and the end-point is marked by the first current flow as indicated by the microammeter on the polarograph.

The end-point in a titration of dichromate is shown in Fig. 2. The end-point could easily be determined to the nearest 0·1 μequiv. Inasmuch as 1 g of potassium dichromate contains about 20000 μequiv the end-point was easily determined to the desired accuracy of 1 part in 100000.

The end-point detection system used in the titration of dichromate could not be used in titration of cerium(IV) with electrogenerated iron(II). At the applied potentials required to oxidize iron(II), cerium(IV) is reduced. A cathodic current, resulting from the reduction of the cerium(IV), flows before the end-point, and an anodic current due to the oxidation of iron(II) flows after the end-point. The microammeter records a continuous increase in current and the change from cathodic current to anodic current at the end-point is difficult to locate.

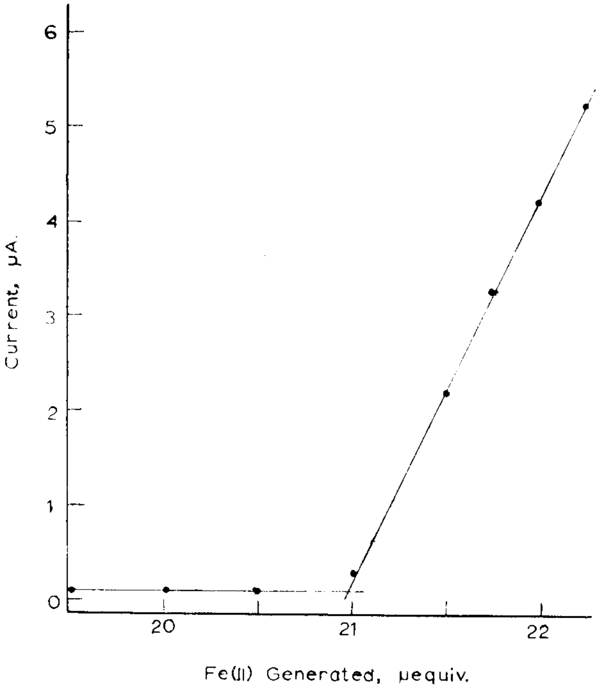

FIG. 2.—End-point in the titration of potassium dichromate with electrogenerated iron(II).
Indicating electrode system: 0·875 V *vs.* S.C.E. applied to a platinum foil 100 mm^2 in area.

The end-point detection system used in the titration of cerium(IV) was that of Stone and Scholten.[18] A potential of 100 mV was applied to two platinum electrodes, each 100 mm^2 in total surface area, a Leeds & Northrup Type E Electrochemograph being used to supply the potential and measure the current. The current before the equivalence-point accompanying the reduction of cerium(IV) decreased as the concentration of cerium(IV) decreased; beyond the equivalence-point the current accompanying the oxidation of the iron(II) formed increased with increasing iron(II). A typical end-point is shown in Fig. 3. The current fell to zero and remained at zero for about 2 µequiv before increasing. The equivalence-point was taken at point A, Fig. 3, the point at which a definite increase in the current was observed, and this point was used in both the pretitration and the titration proper.

As discussed in the next paragraph, the horizontal portion of the indicating current is caused by the reduction of platinum oxide on the surface of the indicating electrodes, this platinum oxide being formed just before the end-point by attack on the platinum by cerium(IV). It was hoped that the extent of formation and removal of this platinum oxide was the same in the two end-points used in each analysis. However, as will be seen in the results reported in Tables I and III, the standard deviation in the analysis of the ammonium hexanitratocerate is 2–2·5 times that in the analysis of the potassium dichromate and this probably results from the uncertainty in the end-point.

Platinum oxide formation as a complication in end-point detection. The existence of films of finely divided metallic platinum and of platinum oxide on bright platinum

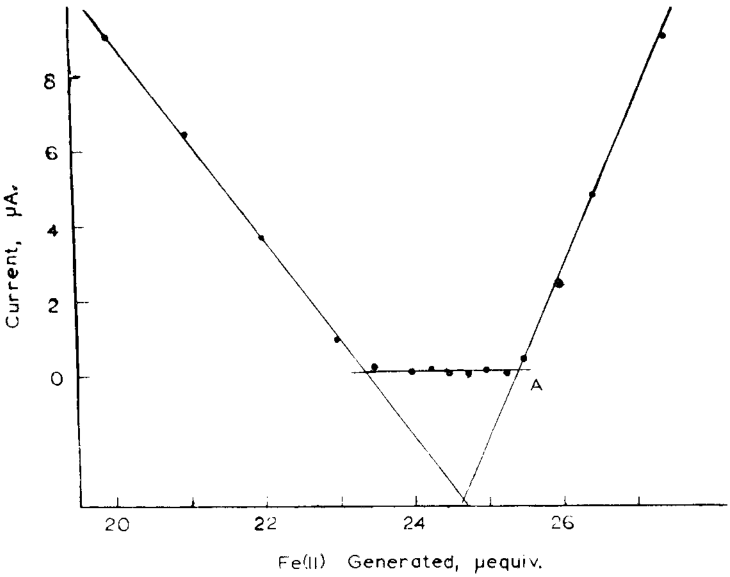

FIG. 3.—End-point in the titration of ammonium hexanitratocerate with electrogenerated iron(II).
Indicating electrode system: 100 mV applied to two platinum foil electrodes, each 100 mm^2 in area.

TABLE I.—COULOMETRIC ASSAY OF NBS 136b POTASSIUM DICHROMATE

Purity found, %	Other results, %
99·972*	99·98 Certificate value, National Bureau of Standards
99·977*	
99·975†	99·977 Marinenko and Taylor,[10] coulometric
99·974†	
99·977*	
99·974*	
Average 99·975	
Standard deviation 0·002	

* Sample added after 99·8 % of the iron(II) had been generated.
† Sample added immediately after pretitration.

TABLE II.—COULOMETRIC ASSAY OF NBS POTASSIUM DICHROMATE, SAMPLE DRIED 10 DAYS AT 260°C.

Purity found, %	
99·998	100·004
100·001	100·006
	Average 100·003

TABLE III.—COULOMETRIC ASSAY AND THORIUM CONTENT OF VARIOUS PREPARATIONS OF AMMONIUM HEXANITRATOCERATE

Specimen and source	Purity found, %	Thorium content as $(NH_4)_2Th(NO_3)_6$* *ppm*	Other work, %
A “Certified” Standard of Reference Grade† 1966	99·969	340	99·97 “Certified” value, G. Frederick Smith Chemical Company‡
	99·972		
	99·965		
	99·969		
	99·976		
	99·978		
Average	99·972		
Standard deviation	0·005		
B “Certified” Standard of Reference Grade† 1967	99·993	160	100·00 “Certified” value, G. Frederick Smith Chemical Company‡
	99·990		
Average	99·992		
C Prepared from basnaesite	99·987	<40§	
	99·982		
	99·980		
	99·988		
Average	99·984		
D “Reagent Grade”† 1952–1960	99·966	340	
	99·959		
	99·962		
Average	99·962		
E “Reagent Grade”† 1952–1960	100·022	140	
	100·030		
	100·026		
Average	100·026		
F “Reagent Grade”† 1952–1960	99·443	2,190	
	99·430		
Average	99·432		
G “Reagent Grade”† 1952–1960	98·705¶	7,900	
	98·668¶		
Average	98·686		

* Thorium analyses by V. A. Fassel.

† G. Frederick Smith Chemical Company, Columbus, Ohio.

‡ As determined by comparison with *NBS* 83b arsenic trioxide.[31]

§ Thorium content less than detection limit, 40 ppm of ammonium hexanitratothorate.

¶ Only 1-g samples because of limited amount of material.

surfaces has been demonstrated by various workers, in particular by Ross and Shain,[19] by Kolthoff and Nightingale,[20] by Anson,[21,22] and by Lee, Adams and Bricker.[23] In substance these papers report that the surface of bright platinum is oxidized to platinum(II) oxide by various strong oxidizing agents and the oxide reduced by iron(II) or iodide. Ross and Shain showed how this formation of oxide introduces an error into the titration of dichromate with iron(II) by delaying the potentiometric end-point, the size of the error, depending on the direction of titration, being governed by the speeds of formation and reduction of the oxide.

Some further experiments were made to confirm that the anomalous end-point behaviour observed in this work actually resulted from oxidation of the platinum indicating electrodes. It was found that the plateau observed at the end-point was extended by immersing the electrodes in a solution of cerium(IV) before using them in a titration; the plateau was reduced (to 1 μequiv) by immersing the electrodes in iron(II) sulphate, rinsing, and immediately using them in a titration already close to the end-point. Reduction in the area of the electrode resulted in a reduction of the length of the plateau; however this is not a solution to the problem, for the indicator current passed is also decreased and the lower slopes render the end-point less certain. Annealing the platinum foils before use and mounting them gently to avoid introducing surface strains or work hardening gave electrodes which did not function at all for a minute or so, the indicating current fluctuating widely but finally settling down and displaying the usual plateau; this surprising result indicates that the platinum oxide–platinum couple must be present for current flow, such a result being implicit in the work of Lee, Adams and Bricker.[23]

The length of the plateau observed, 2 μequiv in Fig. 3, makes it possible to calculate the amount of platinum oxidized, 195 μg; taking the atomic radius of platinum to be 0·129 nm and assuming a simple structure of eight platinum atoms at the corners of a cube, calculation indicates the platinum reacting to form oxide to be about 50 atoms deep.

Because the length of the plateau depends on the previous mechanical and chemical treatment given the electrode, an empirical approach to the problem was about all that could be made. The conditions before the end-point in the pretitration and in the actual titration were made as identical as possible. Point A of Fig. 3 was taken as the end-point on the assumption that all platinum(II) was reduced at this point in the pretitration and in the actual titration. Any platinum oxidized during the titration being at the expense of cerium(IV), an equivalent number of coulombs were presumably required to reduce the oxidized platinum so that in effect only cerium(IV) was titrated.

Sequence adopted during titration

The pretitration procedure was used to ensure that all iron in solution was present as iron(III), except for that generated beyond the end-point, and this was measured and taken into account in the calculations. Any other oxidizable or reducible impurities were presumably also removed by the pretitrations. Immediately after the pretitration the platinum indicating electrodes were raised above the solution and rinsed with a minimum volume of distilled deaerated water. After the major part of the iron(II) had been generated and the sample added and dissolved, the electrodes were again immersed and the titration completed. In this manner the electrodes were in contact with oxidizing agent for approximately the same length of time in the pretitration and in the actual titration.

For two reasons, about 99·8% of the iron(II) was generated before the sample was added to the catholyte. First, the only reaction at the cathode was thus the reduction of iron(III) and the back e.m.f. was thus constant during almost the entire generation and even the slight change in current which might result from a shift from the cerium(IV)–cerium(III) couple to the iron(III)–iron(II) couple was obviated. Secondly, reduction of nitrate, added necessarily in the titration of ammonium hexanitratocerate, was avoided. Nitrate is reduced slowly by iron(II) and, in this work with titrations which extended over 8 hr, the interference became serious if the sample were added immediately.

Actually, as shown in Table I, identical results were obtained in the analysis of potassium dichromate by adding the sample immediately and by deferring the addition until the iron(II) had been almost completely generated.

Platinum boats were used in the titrations of the potassium dichromate. Although an identical result was obtained in the one analysis in which the sample was carried in a glass boat, it is possible that platinum was being oxidized by the dichromate and reduced by iron(II) as the end-point was approached. Such oxidation and reduction is not detectable in this titration because no current flows in the indicating system until the end-point is passed. Glass boats were used in the titrations of ammonium hexanitratocerate.

Following the procedure outlined above, a second sample of potassium dichromate was sometimes titrated in the same solution, the end-point in the first titration becoming the pretitration end-point of the second. Titration of a third sample was not feasible owing to precipitation of potassium perchlorate which occluded dichromate to the extent of becoming yellow in color. A second sample of ammonium hexanitratocerate cannot be so titrated because of the reduction of nitrate (in trials, positive errors of 10% arose).

RESULTS

For the conversion of coulombs into electrochemical equivalents the current value of the faraday was used, 96487·0 ± 1·2 coulombs/equiv, as measured by Craig, Hoffman, Law, and Hamer[24] and corrected to the ^{12}C atomic weight scale.[9] The equivalent weights used, 49·0320 for potassium dichromate and 548·23 for ammonium hexanitratocerate, were calculated from the values of the 1961 Report of the International Commission on Atomic Weights.[25]

Results of six titrations of NBS 136b Potassium Dichromate, are given in Table I. The average, 99·975% is in good agreement with the value of 99·977% obtained by Marinenko and Taylor,[10] the standard deviation, 0·002%, being the same as theirs. This furnishes a check on the calibration of the L & N equipment and on the operation of the cell used. Three of the six titrations were carried out by direct titration, the other three by first generating 99·8% or so of the iron(II) before adding the sample; no difference was detected in the results.

The uncertainties in the atomic weights of potassium, ±0·001, chromium, ±0·001, and oxygen, ±0·0001 introduce an uncertainty of ±0·005 in the molecular weight of potassium dichromate (molecular weight, 294·192) or about 1·7 parts in 100000. The standard deviations of the analyses reported here and of those of Marinenko and Taylor[10] thus approach the uncertainty in the molecular weight of the potassium dichromate. The 0·024% unaccounted for in the coulometric assay must thus result from some impurity and not from errors in the atomic weights.

Svec and Conzemius have reported[26] from this laboratory a spark source mass spectrographic analysis of NBS 136b for eighty elements other than potassium, chromium and oxygen, dichromate, and hydrogen, lithium, and the rare gases. The impurities detected and measured semiquantitatively total only 55 ppma (parts per million atoms), sodium, rubidium, vanadium and iron accounting for 54 ppma. An equivalent weight was calculated on the assumption that sodium and rubidium replace potassium, that iron and vanadium replace chromium, and that vanadium is reduced from V(V) to V(IV) but the iron undergoes no change. Thus, for an amount of potassium dichromate corresponding to 10^6 atoms,

$$\text{Eq. wt.} = \frac{\text{total mass}}{\text{no. of electrons gained}}$$

$$= \frac{40\text{Na} + 6\text{Rb} + \left(\frac{2}{11} \times 10^6 - 46\right) \times \text{K} + \left(\frac{2}{11} \times 10^6 - 8\right)\text{Cr} + 7\text{V} + \text{Fe} + \left(\frac{7}{11} \times 10^6\right)\text{O}}{3\left(\frac{2}{11} \times 10^6 - 8\right) + 7}$$

$$= \frac{26744364}{545440} = 49{\cdot}0326$$

the symbols for the elements representing their atomic weights and the figure 10^6 meaning 1000000 (seven significant figures).

This value for the equivalent weight departs from the value for pure potassium dichromate, 49·0320, by 1·2 parts in 100000, less than the standard deviation of 2 parts in 100000 for the analyses reported, and also less than the uncertainty resulting from the uncertainties in the atomic weights. Thus, the impurities found do not account for the 240 ppm deficiency in the value obtained by coulometric assay.

The remaining impurity must most certainly be water. A determination of the water in NBS 136 Potassium Dichromate was made by Schwab and Wichers[27] who found 0·027 and 0·021 % water by a vacuum fusion–manometric method. Schwab and Wichers actually observed, under the microscope, bubbles in crystals of NBS 136. Further, Svec and Conzemius[28] found hydride clustering in the pre-spark mass spectrum of NBS 136b, indicative of water. We have confirmed by examination with the microscope that bubbles, presumably of mother liquor, are also present in the crystals of NBS 136b. Although the bubbles are not uniformly distributed, presumably the 1-g samples used were large enough for the inhomogeneity not to affect the coulometric assay. On prolonged heating of NBS 136b at 260° a weight loss of 0·019% was observed, the relatively large crystals being shattered in the process. Examination on a hot stage on a polarizing microscope showed that a phase change was occurring and that the bursting of the crystals released the occluded mother liquor. A change in the crystal structure of potassium dichromate, from triclinic to monoclinic, has already been reported.[29,30]

To establish that the weight loss at 260° was due to the loss of water and not the decomposition of potassium dichromate, the dried sample was also assayed by coulometric titration. The results given in Table II averaged 100·003%, slightly greater than expected, possibly because of slight decomposition at 260°.

Results of titrations of seven specimens of ammonium hexanitratocerate are given in Table III, together with the thorium content as obtained by emission spectroscopy and reported as ammonium hexanitratothorate.

The uncertainties in the atomic weights of nitrogen, ±0·00005, hydrogen, ±0·00001, and oxygen, ±0·00001, are overshadowed by the uncertainty in the atomic weight of cerium, ±0·01; thus, for ammonium hexanitratocerate, $\text{CeN}_8\text{H}_8\text{O}_{18}$, molecular weight 548·23, the total uncertainty in the $N_8H_8O_{18}$ portion is ±0·0023 and that in the cerium ±0·01 or about 2 parts in 100000.

The precision of the analysis of ammonium hexanitratocerate was somewhat poorer than that of the analysis of the dichromate, the standard deviation being 0·005%. This lower precision undoubtedly resulted from the difficulty in determining the end-point with high precision, as discussed above.

The specimens of ammonium hexanitratocerate designated **A** and **B** were obtained from the G. Frederick Smith Chemical Company in 1966 and 1967 as "Certified Standard of Reference" materials. The coulometric assays reported check the values of the Smith Company (Table III), the latter having been obtained[31] by weight-burette titrations of NBS arsenic trioxide and being reliable probably to 2 parts in 10000. The thorium in these samples, expressed as ammonium hexanitratothorate, added to the coulometric assay values gives 100·006 and 100·008%, respectively. Examination under the microscope revealed that the crystals of specimens **A** and **B** were small and poorly formed; occasional inclusions, presumably of mother liquor, were observed but they were far less frequent than in NBS 136b Potassium Dichromate.

As described above under *Experimental*, the preparation of ammonium hexanitratocerate from the rare earth oxide concentrate from basnaesite was straightforward and easy. The results of analyses of the materials obtained from the fourth and fifth recrystallizations were identical. Although the thorium in specimen **C** was below the detection limit of the emission spectrographic method, the assay, average 99·984%, indicated some 156 ppm of impurity present. Even so, this simple preparation is equal in purity to NBS 136b Potassium Dichromate and equally acceptable as a primary standard.

Specimens **D**, **E**, **F** and **G** were "reagent grade" materials, no claim having been made by the manufacturer that they could be used as primary standard materials. Specimens **D** and **E** are sufficiently pure to serve well as primary standard material but the lack of information as to the extent of the purification steps used makes it idle to speculate about them, although such speculation about **E** is especially inviting because of the high assay value together with appreciable thorium. Specimens **F** and **G** contain relatively large amounts of thorium and it is apparent that the oxidizing capacity falls off with increasing content of thorium as expected.

Because of recent advances in the technology of the rare earths, starting materials essentially free of thorium are now available commercially and future commercial preparations of ammonium hexanitratocerate should be essentially thorium-free[31] even without the numerous recrystallizations now known to be necessary for the elimination of thorium.[6] The present work leaves no doubt that ammonium hexanitratocerate is an excellent primary standard.

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Zusammenfassung—Das sehr genaue coulometrische Titrationsgerät von Eckfeldt und Schaffer (Leeds & Northrup Company) wurde zur genauen Prüfung zweier oxidimetrischer Primärstandards verwendet.

Mit der für das Kaliumdichromat NBS 136b gefundenen Reinheit von 99,975% mit der Standardabweichung 0,002% wurde der ältere Wert von Marinenko und Taylor nachgeprüft. Wenig Thorium enthaltendes Ammoniumhexanitratocerat ist ebenfalls ein ausgezeichneter Primärstandard: zwei neuere Handelspräparate haben Reinheiten von 99,972 und 99,984%, wobei die höhere Standardabweichung von 0,005% von einer geringfügigen Schwierigkeit bei der Endpunktsanzeige rührt, die auf der Bildung von Platinoxid auf den Indikatorelektroden beruht.

Résumé—On a utilisé l'appareil de titrage coulométrique de haute précision de Eckfeldt et Shaffer (Leeds & Northrup Co.) pour le dosage précis de deux produits étalons primaires pour travail d'oxydoréduction. La pureté trouvée pour le bichromate de potassium NBS 136b, 99,975%, écart type 0,002%, recoupe la valeur antérieure de Marinenko et Taylor. L'hexanitratocérate d'ammonium, s'il est à faible teneur en thorium, est également un excellent étalon primaire, deux préparations commerciales récentes ayant des puretés de 99,972 et 99,984%, un écart type plus élevé, 0,005%, reflétant une difficulté mineure dans la détection du point de fin de dosage due à la formation d'oxyde de platine sur les électrodes indicatrices.

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X-RAY FLUORESCENCE ANALYSIS OF TITANIUM ALLOYS*

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Summary—An X-ray solution method is proposed for determining major amounts of Mo, Sn and Zr in Ti alloys. The method utilizes adjacent elements in the periodic table as internal standards and has been successfully applied to levels of 3–10% Sn, 11–40% Mo and 6–20% Zr. The procedure involves three steps: dissolving the sample with a suitable acid mixture; adding the suitable internal standard at the concentration levels experimentally found to give optimum accuracy and precision; analysing the resulting solution mixture by X-ray fluorescence. Antimony was found to be a suitable internal standard for its adjacent element tin at a concentration ratio of 3:1 Sb:Sn. Niobium was successfully used for both its adjacent elements, molybdenum and zirconium, at 2:1 concentration ratios, Nb:Mo and Nb:Zr. A number of elements non-adjacent to tin, molybdenum and zirconium (i.e., copper, bromine, titanium, bismuth and tantalum) were experimentally found unsuitable as internal standards. Concentration factors of the internal standard and the adjacent elements sought were found to affect significantly the precision of analysis.

THE analysis of titanium alloys for molybdenum, tin and zirconium was requested at Crucible's Research Center. Ordinarily, if chemically pre-analysed standards and the right type of solid sample are available, the problem can be easily resolved by solid X-ray analysis. In this case, however, lack of both necessitated the use of an X-ray solution technique.

Direct X-ray measurements of the element sought in solution were tried first. This approach can overcome problems such as segregation, heterogeneity and effects due to a varying metallurgical history. However, it does not consider instrument variations, volume and density variations of the solution, bubbles that may appear during the measurement, variations of the foil thickness of the solution cup and absorption or enhancement effects that may be exerted among the various elements of a multicomponent system.

The use of internal standards was considered next.[1–5] During early experimental work, titanium and niobium appeared promising as internal standards. An investigation was therefore conducted to explore methods to improve precision and accuracy by selecting and comparing results obtained with different internal standards at varying concentrations.

EXPERIMENTAL

X-ray apparatus

A Siemens X-ray fluorescence spectrograph type "Crystalloflex IV" with an X-ray generator and control having a full-wave rectified power supply, voltage and current regulation up to 45 kV and 40 mA in air, and a high purity gold target, was used.

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Materials

Antimony solution, 20 mg/ml. Dissolve 20 g of pure antimony metal in concentrated hydrochloric acid and dilute with hydrochloric acid to 1000 ml.

Molybdenum solution, 50 mg/ml. Dissolve 50 g of pure molybdenum metal in 500 ml of hydrofluoric acid–nitric acid (1:1) mixture and dilute with distilled water to 1000 ml.

Niobium solution, 20 mg/ml. Dissolve 20 g of pure niobium metal in 200 ml of hydrofluoric acid–nitric acid mixture and dilute with distilled water to 1000 ml.

Tin solution, 20 mg/ml. Dissolve 20 g of pure tin metal in concentrated hydrochloric acid and dilute with hydrochloric acid to 1000 ml.

Titanium solution, 50 mg/ml. Dissolve 50 g of pure titanium metal in 500 ml of hydrofluoric acid–nitric acid (1:1) mixture and dilute with distilled water to 1000 ml.

Zirconium solution, 20 mg/ml. Dissolve 20 g of pure zirconium metal in 200 ml of hydrofluoric acid–nitric acid (1:1) mixture and dilute with distilled water to 1000 ml.

Procedure

Dissolve 1 g of sample in 20 ml of 1:1:2 hydrochloric–nitric–hydrofluoric acid mixture, added slowly, as the reaction is vigorous. Wash the sides of the beaker with water and add 4·5 ml of antimony solution (20 mg/ml) if the tin level is 3%, or 15 ml of the antimony solution if the tin level is 10%.

Add 10 ml of niobium solution (20 mg/ml) if the molybdenum and zirconium levels are below 12%, 40 ml if the molybdenum level is around 40%, and 20 ml if the zirconium level is around 20%. Evaporate the solution to approximately 25 ml, transfer it to a 50-ml plastic volumetric cup and dilute it to 50 ml with distilled water.

Prepare two sets of synthetic standards from standard titanium, molybdenum, tin and zirconium solutions to cover the ranges 2–6% Sn/9–13% Mo/4·5–7% Zr/balance Ti, and 10–16% Sn/39–45%-Mo/17–23% Zr/balance Ti, total metal weight 1·000 g. Add 5 ml of hydrochloric acid, 5 ml of nitric acid and 10 ml of hydrofluoric acid to each synthetic standard. Add antimony and niobium in the proportions used in the preparation of samples, and evaporate and dilute the solutions as just described. Fill the solution cup with sample, place it in the spectrograph, and measure the elements sequentially, starting with antimony, according to the following conditions.

Primary voltage 45 kV
Primary current 40 mA
Detector—scintillator
Detector voltage 525–560 V
Pulse-height analyser baseline 5 V
Pulse-height analyser channel-width 10 V
Preset counts 10^5
Crystal—LiF; 1st order K_α radiation
2θ values—Sb 13·48°, Sn 14·045°, Mo 20·34°, Nb 21·40°, Zr 22·55°

Measure the time needed to accumulate the preset count of 10^5, or the number of counts accumulated during a fixed time. Plot or count time-ratios of internal standard to element sought *vs.* concentration, to construct the calibration graphs, which are all linear. The molybdenum K_α radiation (2θ 20·34°) was used despite its proximity to the zirconium K_α radiation. No significant interference was found experimentally. If, however, interference *is* found experimentally, the molybdenum K_β line (2θ 18·07°) should be used.

RESULTS AND DISCUSSION

One of the difficulties encountered in a multi-component system, such as a titanium-base alloy, is the effect caused by interactions of the various elements present in the system. Figure 1 illustrates the factors involved in the system considered here and shows that absorption should be comparable for tin and antimony, and also for zirconium, molybdenum and niobium.

This was confirmed experimentally by establishing how uniformly these elements absorb when present alone and in a titanium matrix (Table I). Because methanol was used as a diluent for the antimony solution to prevent hydrolysis, count measurements were made on methanol and distilled water blanks at 2θ 13·48° and 14·05°,

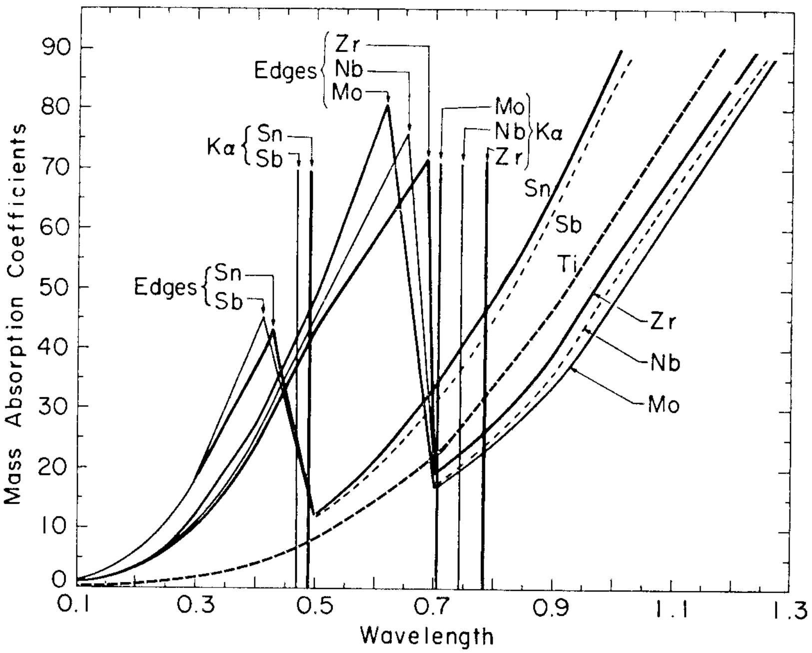

FIG. 1.—Data[6] to illustrate absorption effects in Ti–Mo–Sn–Zr alloy.

Element	Ti	Zr	Nb	Mo	Sn	Sb
At. no.	22	40	41	42	50	51
λK_{α_1}, *nm*	0·2748	0·0786	0·0746	0·0709	0·0491	0·0470
K absorption edge, *nm*	0·2497	0·0689	0·0653	0·0620	0·0425	0·0407

TABLE I.—X-RAY FLUORESCENCE ($K\alpha$) OF Nb, Sb, Sn, Mo AND Zr

Sample* composition, *mg/ml*	Count, *cps*				
	Nb	Sb	Sn	Mo	Zr
Nb, 2·0	8446				
Sb,† 2·0		4432			
Sn, 0·8			3292		
Mo, 3·0				9634	
Zr, 1·2					5669
Alloy, 6828,‡ 20			2655	7082	3729
Alloy, 6828 20 + Nb, 2 + Sb, 2	4078	3038	2064	4864	2495
Methanol blank		1719	1694		
Distilled water blank		1986	1724		

* Sample volume 50 ml.

† Volume adjusted with methanol to prevent hydrolysis.

‡ 4% Sn, 12% Mo, 6% Zr, 78% Ti.

the angles for antimony and tin K_α radiation. Blank readings for the other elements showed no appreciable differences between methanol and water. Titanium has an extremely poor sensitivity, compared with tin, molybdenum and zirconium, and gives less uniform absorption, which can cause serious errors, both in the accuracy and the precision of analysis. It was early found that accuracy improved when niobium was substituted for titanium as the internal standard for the determination of molybdenum, and this led us to examine the significance of the internal standard itself.

The results in Table II show satisfactory agreement for molybdenum and zirconium in duplicate samples of 6828 and 6829, but rather poor precision in almost all the tin results and in the molybdenum values for 6833 and 6834. The agreement with chemical methods[7,8] is satisfactory for molybdenum in 6828 and 6829 but there is room for improvement in the tin and zirconium results, and this led to the use of antimony as an internal standard. We felt that such a change was necessary to determine whether the internal standard itself played any significant role in analytical precision. Antimony was selected because it is next to tin in atomic number and has very similar properties. A set of synthetic standards was prepared, containing an arbitrary amount of 100 mg of antimony, giving an antimony/tin ratio of approximately 3:1 for samples 6828 and 6829, and 1:1 for 6833 and 6834. The results given in Table III show that the precision for 6828 and 6829 was improved considerably but was still poor for 6833 and 6834. We therefore investigated thoroughly the role of the concentration of the internal standard with respect to the element sought. For convenience, samples 6833 and 6834 were used. Antimony and niobium were added to a series of synthetic standards, to give the ratios Sb:Sn = 3:1; Nb:Mo = 1:1 and 2:1; Nb:Zr = 4:1 and 2:1.

TABLE II.—RESULTS FOR Mo, Zr AND Sn, WITH 200 mg OF Nb AS INTERNAL STANDARD

Sample	Mo, %		Zr, %		Sn, %	
	Chem	X-ray	Chem	X-ray	Chem	X-ray
6828	$11\cdot9$	$11\cdot7_3$	$5\cdot7_8$	$5\cdot8_5$	$3\cdot6_1$	$3\cdot6_8$
	—	$11\cdot7_3$	—	$5\cdot7_5$	—	$4\cdot1_0$
6829	$12\cdot0$	$11\cdot8_4$	$6\cdot0_2$	$5\cdot6_7$	$3\cdot6_1$	$3\cdot3_2$
	—	$12\cdot0_0$	—	$5\cdot7_0$	—	$3\cdot8_9$
6833	$40\cdot2$	$37\cdot6_7$	$20\cdot3$	$20\cdot2_0$	$13\cdot9$	$10\cdot2_0$
	$38\cdot5$	$38\cdot5_3$	$20\cdot7$	—	$10\cdot5$	—
6834	$42\cdot2$	$37\cdot4_8$	$19\cdot1$	$19\cdot6_6$	$12\cdot1$	$10\cdot5_0$
	$41\cdot0$	$38\cdot5_3$	$19\cdot0$	$19\cdot5_0$	$10\cdot6$	$10\cdot8_1$

TABLE III.—RESULTS FOR TIN, WITH ANTIMONY AS INTERNAL STANDARD

Sample	Sb:Sn	Sn, %
6828	3:1	$3\cdot9_2$
		$3\cdot8_9$
6829	3:1	$3\cdot8_2$
		$3\cdot9_0$
6833	1:1	$11\cdot1_2$
		$10\cdot8_6$
6834	1:1	$11\cdot8_0$
		$11\cdot5_9$

Table IV gives the results and shows that the 2:1 Nb:Mo ratio improves the molybdenum precision significantly. The Sb:Sn ratio of 3:1, found satisfactory for samples 6828 and 6829 (Table III), gave satisfactory precision for tin. The precision for zirconium indicated that improvement could be made.

Further tests were carried out with zirconium. First, pure refined zirconium metal was used to prepare synthetic standards; previously commercial zirconium metal had been used. Secondly, the sample concentration was halved (which should reduce interelement effects) and a 2:1 ratio Nb:Zr was used. The results obtained

TABLE IV.—EFFECT OF VARYING INTERNAL STANDARD CONCENTRATION

	Mo		Sn		Zr	
Sample	Nb:Mo	Mo, %	Sb:Sn	Sn, %	Nb:Zr	Zr, %
6833	1:1	40·7$_6$	3:1	11·3$_4$	2:1	23·9$_8$
		41·4$_6$		11·3$_1$		23·7$_7$
	2:1	40·3$_4$			4:1	22·9$_9$
		40·0$_7$				23·6$_7$
6834	1:1	43·3$_5$	3:1	12·1$_4$	2:1	23·6$_5$
		41·1$_2$		12·1$_0$		23·3$_2$
	2:1	41·2$_3$			4:1	22·7$_0$
		40·0$_8$				23·1$_8$

(6833—Zr 21·6$_9$ and 21·6$_7$%; 6834—Zr 21·0$_7$ and 20·9$_7$%) show some justification for using the resultant lower number of counts, and emphasize the important influence of concentration on accuracy and precision in X-ray solution analysis.

Adjacent elements, then, can be used satisfactorily as internal standards at suitable concentration ratios for tin, molybdenum and zirconium in a titanium matrix, primarily because of the similarity of absorption and of enhancement effects caused by the matrix elements.

Because no NBS samples were available, chemical procedures[7,8] were used to cross-check the X-ray methods. The X-ray and chemical results given in Table V summarize the agreement between the two methods. In general, the agreement is good; in most cases, the X-ray results are more precise than those of the chemical method, although which method is the more accurate is still uncertain and needs further examination.

TABLE 5.—COMPARISON OF CHEMICAL AND X-RAY SOLUTION METHODS

	Sn, %		Mo, %		Zr, %	
Sample	Chem	X-ray	Chem	X-ray	Chem	X-ray
6828-1	3·6$_1$	3·9$_2$	11·9	11·7$_3$	5·7$_8$	5·8$_5$
-2	—	3·8$_9$	—	11·7$_3$	—	5·7$_5$
6829-1	3·6$_1$	3·8$_2$	12·0	11·8$_4$	6·0$_2$	5·6$_7$
-2	—	3·9$_0$	—	12·0$_0$	—	5·7$_0$
6833-1	13·9	11·3$_4$	40·2	40·3$_4$	20·3	21·6$_9$
-2	10·5	11·3$_1$	38·5	40·0$_7$	20·7	21·6$_7$
6834-1	12·1	12·1$_4$	42·2	41·2$_3$	19·1	21·0$_7$
-2	10·6	12·1$_0$	41·0	40·8$_0$	19·0	20·9$_7$

Non-adjacent elements were also investigated as internal standards. Bromine was selected first because of the proximity of its atomic number to those of tin, molybdenum and zirconium, and also because of ease in preparation of synthetic samples and master solutions containing it. A non-adjacent transition element (copper) and elements, such as tantalum and bismuth, in the same families as niobium and antimony, were also tried as internal standards, but gave poor precision.

Reproducibility

The standard deviations for 3·6% tin, 12·4% molybdenum and 5·6% zirconium were 0·04%, 0·1% and 0·05% respectively (10 variates).

Conclusions

It is apparent from the experimental results obtained that internal standards, if properly used, correct for almost all the errors inherent in direct X-ray measurement.

Synthetic standards must be used to construct the working curves, and we wish to emphasize that X-ray fluorescence in solution analysis is recommended only when solid standards are not available, although it is an economical means of obtaining useful results and it answers many problems related to interelement effects and absorption phenomena for unusual alloys.

Zusammenfassung—Eine Röntgen-Naßmethode zur Bestimmung größerer Mengen von Mo, Sn und Zr in Titanlegierungen wird vorgeschlagen. Die Methode verwendet Nachbarelemente im periodischen System als innere Standards und wurde auf die Wertebereiche 3–10% Sn, 11–40% Mo und 6–20% Zr mit Erfolg angewandt. Das Verfahren geht in drei Stufen vor sich: Auflösen der Probe mit einem geeigneten Säuregemisch; Zugabe des inneren Standards in dem Konzentrationsbereich, der empirisch beste Genauigkeit und Richtigkeit liefert; Analyse der Mischlösung durch Röntgenfluoreszenz. Antimon wurde als geeigneter Standard für sein Nachbarelement Zinn im Konzentrationsverhältnis 3:1 Sb:Sn gefunden. Niob wurde für seine beiden Nachbarelemente Molybdän und Zirkonium im Konzentrationsverhältnis 2:1 Nb:Mo und Nb:Zr mit Erfolg verwendet. Eine Anzahl von Elementen, die zu Zinn, Molybdän und Zirkonium nicht benachbart sind (z.B. Kupfer, Brom, Titan, Wismut und Tantal) wurden im Experiment als innere Standards ungeeignet befunden. Es wurde festgestellt, daß die Konzentrationsfaktoren der inneren Standards und der gesuchten Nachbarelemente die Genauigkeit der Analyse wesentlich beeinflussen.

Résumé—On propose une méthode aux rayons X, en solution, pour doser des quantités importantes de Mo, Sn et Zr dans des alliages de Ti. La méthode utilise les éléments adjacents de la table périodique comme étalons internes et a été appliquée avec succès à des teneurs de 3–10% Sn, 11–40% Mo et 6–20% Zr. La technique comprend trois stades: dissolution de l'échantillon par un mélange acide convenable; addition de l'étalon interne convenable aux niveaux de concentration dont on a trouvé expérimentalement qu'ils donnet les justesse et précision optimales; analyse du mélange en solution résultant par fluorescence aux rayons X. On a trouvé que l'antimoine est un étalon interne convenable pour son élément adjacent l'étain avec un rapport de concentration 3:1, Sb:Sn. On a utilisé avec succès le niobium pour ses deux éléments adjacents, molybdène et zirconium, aux rapports de concentration 2:1, Nb:Mo et Nb:Zr. On a trouvé expérimentalement qu'un certain nombre d'éléments non adjacents à l'étain, au molybdène et au zirconium (par exemple, cuivre, brome, titante, bismuth et tantale) ne conviennent pas comme étalons internes. On a trouvé que les facteurs de concentration de l'étalon interne et des éléments adjacents examinés modifient de façon importante la précision de l'analyse.

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SPECTROPHOTOMETRIC EXTRACTIVE TITRATIONS—VI*

TITRATIONS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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Summary—The possibility of using PAN as a titrant in spectrophotometric extractive titrations has been investigated. Conditions suitable for the titration of zinc and of cadmium were found, with the aid of equations derived earlier and after investigation of the absorption spectra and pH- and reagent-dependence of the extraction of the chelates involved. For the purpose of spectrophotometric extractive titration of copper with PAN the formation and extraction of ion-association pairs $CuPAN^+ \cdot Br^-$ and $CuPAN^+ \cdot CNS^-$ were studied in detail. This titration was found to be highly selective. Dilute solutions of PAN in ethanol are much more stable than solutions of dithizone.

1-(2-PYRIDYLAZO)-2-NAPHTHOL, the dye introduced into analytical chemistry by Liu[1] and by Cheng and Bray[2] has to date been used almost exclusively as a metallochromic indicator or as an extractive chelating agent in spectrophotometric or colorimetric determinations of submilligram amounts of metals. Except for the spectrophotometric titration of copper with methanolic PAN solution for the dye purity control performed by Pease and Williams[3] no attempt to use this reagent as titrant is known. The high stability of the dye solutions mentioned by many authors[4–7] together with the high molar absorptivities of the metal-PAN complexes,[8] comparable with those of dithizonates, make the application of PAN as titrant in spectrophotometric extractive titrations attractive. This is the subject of the present paper.

Because PAN is known to react slowly with some metal ions, it was decided to titrate with ethanolic PAN solutions to obtain a much greater concentration of the reagent in the aqueous phase than would be obtained if the titrant solvent was chloroform, and to minimize the change in the volume of the chloroform phase. In order to make possible the use of the equations derived in Part V of this series[9] for calculation of the proper conditions for spectrophotometric extractive titrations, the conditional values of "extraction constants" under non-equilibrium conditions (*i.e.*, when PAN is initially present in the aqueous phase and the time of shaking with the organic solvent is too short for attainment of equilibrium) must be known. To obtain these values the pH- and reagent-dependence of the distribution of metals between the aqueous and organic phase were investigated, with PAN added to the aqueous phase as an ethanolic solution and with an equilibration time of 1 min.

It was intended to study spectrophotometric extractive titrations of cadmium, zinc, cobalt, nickel and copper with PAN. The preliminary experiments showed, however, that cobalt does not form the PAN chelate sufficiently quickly at any pH, and nickel does only at very high pH-values where very low selectivity is predicted. Therefore only investigations concerning cadmium, copper and zinc are described in the present paper. In all cases the metal–PAN complexes are extracted into chloroform.

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* Part V—*Talanta*, 1968, **15**, 771.

EXPERIMENTAL

Apparatus

Titration assembly. Absorbance was measured with a Unicam SP 600 spectrophotometer. Titrations were performed using the cells and cell-attachment similar to those described in Part I of the series.[10] To avoid manual shaking of the whole titration assembly after each addition of titrant, two mixers[4] were used, driven by two Igla motors in a serial circuit. The operation was further simplified by introducing a Vipo timer into the feed-circuit of the motors, so that the time of stirring the organic and aqueous phases was adjustable. A Multoscope electronic pH-meter equipped with antimony and calomel electrodes was used for measurement of pH.

Reagents

The common reagent solutions have been described previously;[10–12] only solutions and modifications not described earlier are listed below.

PAN. Ethanolic solutions of 1-(2-pyridylazo)-2-naphthol (Merck) were prepared by dissolving the appropriate amount in twice distilled ethanol in order to obtain $1–3 \times 10^{-4}M$ solutions.

Chloroform. In most cases purification through double distillation was quite satisfactory. Some batches of chloroform, however, caused trouble in the extraction of copper, probably because of the presence of decomposition products. In agreement with the findings of Berger and Elvers,[13] washing with sodium hydroxide and water before distillation removed this bad effect.

Buffer solutions. All buffer solutions were prepared from analytical-grade reagents and before dilution to final volume they were purified by adding one tenth of their final volume of 0·1% w/v ethanolic PAN solution, and after 1 hr, shaking with several 10-ml portions of chloroform until the last two extracts were colourless.

Procedures

Determination of molar absorptivity of PAN in ethanol. It is necessary for the simple calculation of titration results and for reagent purity control to determine the free reagent concentration. The simplest way is to measure the absorbance of the free reagent and to apply Beer's law. This requires the determination of the molar absorptivity at the wavelength of the measurement. To avoid purification of the reagent, the indirect method of Cooper and Kofron[14] was used. Into a series of 25-ml volumetric flasks were placed 1·00-ml portions of *ca.* $10^{-3}M$ ethanolic PAN solution together with an increasing amount of 10^{-3}—$10^{-4}M$ solution of metal ion (obtained by dilution of more concentrated solutions standardized by EDTA titration). The volume was made up to 5·00 ml with water and then to the mark with ethanol. As soon as the colour developed fully, the absorption spectra of the solutions were recorded in 10-mm cells. The molar absorptivity ε of PAN at the wavelength maximum—470 nm—was then calculated according to the formula

$$(\varepsilon_{\text{PAN}})_{470} = \frac{A_{\text{PAN}} - (A_1 - k \cdot A_2)}{n \cdot [\text{Me}]} \tag{1}$$

where A_{PAN} is the absorbance at 470 nm of solution containing PAN alone, A_1 is the absorbance at 470 nm of solution containing stoichiometrically less metal ion than PAN; A_2 is the absorbance of the same solution at the wavelength maximum of the PAN-chelate; k is the ratio of absorbances, at the wavelength maximum of the chelate and at 470 nm, of a solution containing an excess of metal ion; [Me] is the concentration of the metal ion in the solution and n is the number of PAN molecules in the chelate. In these experiments standardized solutions of copper ($n = 1$), cobalt ($n = 2$) and of nickel were used. In the case of nickel it was necessary to postulate $n = 1$ in order to obtain results consistent with those obtained for cobalt and copper. This composition of the nickel chelate (in ethanol) was confirmed by mole-ratio and continuous variation methods. The average value of the molar absorptivity of PAN in ethanol at 470 nm obtained from 15 independent measurement was $22{\cdot}16 \times 10^3$ l. mole^{-1} . cm^{-1}.

Effect of pH. The pH of 20 ml of aqueous solution containing 50 μg of copper or zinc as sulphates, or 50 ml of aqueous cadmium nitrate solution containing 100 μg of cadmium, was adjusted and measured, sulphuric acid, aqueous ammonia or borate–sodium hydroxide being used. The solutions were then transferred into 100-ml separatory-funnels containing 0·50 ml of $5{\cdot}00 \times 10^{-4}M$ ethanolic PAN. The chelates formed were extracted by vigorous 1-min shaking with 10 ml of chloroform. The extracts were drained into 10-ml volumetric flasks and diluted to the mark with chloroform. The absorbance of each extract was measured at 560 nm in 5-mm cells, against chloroform. In the case of cadmium the blank due to impurity of the sodium hydroxide was subtracted from the values obtained. Even though the extraction was performed with a substoichiometric amount of PAN, the extraction constant can be calculated from the results obtained. The ratios of A_{obs} to $A_{\max}$ (where A_{obs} is the

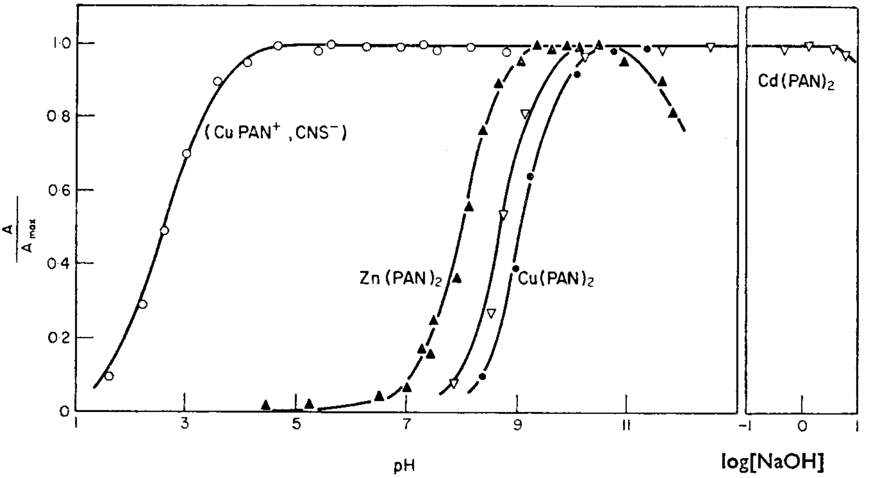

FIG. 1.—Effect of pH on the extraction of cadmium, copper and zinc with substoichiometric amount of PAN into $CHCl_3$.

absorbance of the extract obtained at a given pH and reagent concentration, and A_{max} is the maximum value of this absorbance), and the values of pH at which these ratios were measured, can be used to express the concentrations of individual species involved in the equation for the extraction constant

$$K_{ext} = \frac{[Me(PAN)_n]_{org}[H]^n}{[Me][HPAN]^n_{org}}. \tag{2}$$

The maximum concentration of the chelate in chloroform (corresponding to A_{max}) is equal to $1/n$ of the total concentration of PAN, c_{PAN}, in volume V_{org} of the organic phase:

$$\text{maximum } [Me(PAN)_n]_{org} = \frac{c_{PAN}}{n}. \tag{3}$$

The virtual equilibrium concentration of metal chelate is hence given by:

$$[Me(PAN)_n]_{org} = \frac{A_{obs}}{A_{max}} \cdot \frac{c_{PAN}}{n} \tag{4}$$

The virtual equilibrium concentrations of metal ion in the aqueous phase and that of unreacted PAN in the organic phase may then be calculated from the mass equilibria:

$$[Me] = c_{Me} - [Me(PAN)_n]_{org} \cdot \frac{V_{org}}{V} = c_{Me} - \frac{A_{obs}}{A_{max}} \cdot \frac{c_{PAN}}{n} \cdot \frac{V_{org}}{V} \tag{5}$$

where c_{Me} is the initial concentration of the metal ion in volume V of the aqueous phase and

$$[HPAN]_{org} = c_{PAN} - n[Me(PAN)_n]_{org} = c_{PAN}\left(1 - \frac{A_{obs}}{A_{max}}\right). \tag{6}$$

When applying these calculations to the case of zinc, the effect of complexation with hydroxide ion was taken into account.

As indicated in Fig. 1, the extraction of copper occurs only above pH 8, unless ions other than sulphate are present. Below this pH the violet copper–PAN complex remains in the aqueous phase. It was found, however, that the extraction takes place in more acidic solutions, if acetate, bromide, chloride, thiocyanate or phosphate is present. The effect of pH on the extraction of copper chelate into chloroform in the presence of $0{\cdot}001M$ thiocyanate is shown in Fig. 1, which summarizes the results of the extraction experiments.

Absorption spectra. The absorbance of the extracts was measured over the range 400–700 nm and the absorption spectra of pure PAN-chelates obtained. By comparing these spectra (Fig. 2) with that of a PAN solution in chloroform it may be concluded that spectrophotometric extractive titration of cadmium, copper and of zinc is best followed at the wavelength maximum of the chelates.

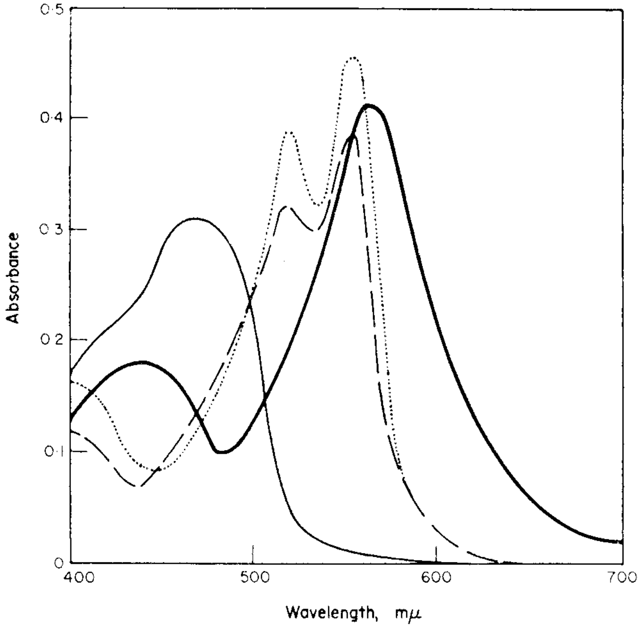

FIG. 2.—Absorption spectra of PAN and of its chelates in chloroform. Full line—PAN, broken line—cadmium chelate, dotted line—zinc chelate, bold line—$CuPAN^{+}{\cdot}CNS^{-}$.

Metal distribution curves. For the purpose of determination of extraction constants the pH- and reagent-dependence of the metal distribution were measured. In order to diminish the uncertainty in K_{ext} values obtained from pH-dependence measurements, because of insufficiently precise pH-measurement with the antimony electrode, the measurement of distribution ratios as a function of reagent concentration was undertaken at a pH fixed with buffers. Twenty ml of Britton-Robinson buffer of pH 6·80 containing 5·0 μg of zinc, or 20 ml of 0·05*M* sodium tetraborate (pH 9·24) containing 4·0 μg of cadmium were placed in 100-ml separatory-funnels containing various amounts of $10^{-3}M$ ethanolic PAN solution, and 10·0 ml of chloroform were added. After immediate 1-min shaking the organic phase was drained into 10-ml volumetric flasks and diluted to the mark with chloroform. The absorbance at λ_{max} of the chelate was measured in 5-mm cells against pure chloroform. The distribution of the metal chelates was calculated from the equation:

$$D = \frac{A_{obs}}{(A_{max} - A_{obs})} \cdot \frac{(20 + v)}{10} \tag{7}$$

where A_{obs} and A_{max} are as defined above and v is the volume of ethanolic PAN solution added. Because no independent determinations of the metal ion concentration in the aqueous phase were undertaken, there is some uncertainty in the value of D, especially for high D-values. By plotting log D vs. log [PAN] in the 10-ml extract, the number of PAN molecules involved in chelation was obtained. The values of the logarithm of the virtual extraction constant were calculated according to equation (8) (see Table I):

$$\log K_{ext} = \log D - n\,\mathrm{pH} - n \log [\mathrm{PAN}]_{org}. \tag{8}$$

To establish dependence of distribution of copper chelate on the salt concentration, (19·8 ml of salt solution of suitable concentration and 0·2 ml of $1 \times 10^{-4}M$ copper sulphate at pH 6 were placed in 100-ml separatory-funnels containing 0·5 ml of $5{\cdot}0 \times 10^{-4}M$ ethanolic PAN solution. Ten ml of chlorofrom were added and the solution shaken for 1 min. The extracts were drained into 10-ml volumetric flasks and made up to the mark with chloroform. The absorbance was measured in 5-mm cells at 565 nm against pure chloroform. Only in the case of potassium bromide and of ammonium thiocyanate was virtually quantitative extraction of copper-PAN chelate reached, so that only in these cases was the calculation of D according to equation (7) possible. Results of these experiments are plotted in Fig. 3.

TABLE I.—REAGENT DEPENDENCE OF THE EXTRACTION OF CADMIUM AND OF ZINC

log D_{Cd}	log $[\mathrm{HPAN}]_{\mathrm{org}}$	log $K_{\mathrm{exta}}^{\mathrm{CdPAN_2}}$	log D_{Zn}	log $[\mathrm{HPAN}]_{\mathrm{org}}$	log $K_{\mathrm{ext}}^{\mathrm{ZnPAN_2}}$
−0·32	−4·88	−9·04	−0·45	−4·50	−5·05
0·07	−4·64	−9·13	−0·21	−4·37	−5·07
0·49	−4·48	−9·03	−0·03	−4·28	−5·07
0·76	−4·40	−8·92	0·20	−4·17	−5·06
0·88	−4·33	−8·94	0·44	−4·08	−5·00
0·98	−4·30	−8·90	0·82	−3·88	−5·02
1·06	−4·24	−8·94	1·24	−3·68	−5·00
1·15	−4·18	−8·97			
1·33	−4·05	−9·05			
1·98	−3·80	−8·90			

Average log $K_{\mathrm{extr}} = -8{\cdot}98$ Average log $K_{\mathrm{extr}} = -5{\cdot}04$.

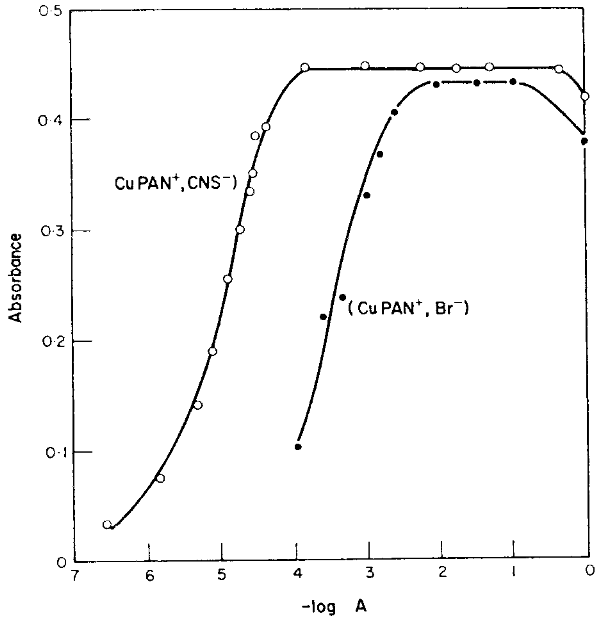

FIG. 3.—Effect of salts on the extraction of copper—PAN chelate.

RESULTS AND DISCUSSION

Cadmium

Under substoichiometric conditions, the extraction of cadmium begins above pH 7 and reaches its maximum above pH 10. Owing to the very low tendency of cadmium to form hydroxo-complexes, extraction takes place even in 2·5M sodium hydroxide medium. From distribution measurements (Table I) it is evident that two molecules of PAN are involved in chelation, so the extraction might be described by the equation

$$\mathrm{Cd^{2+}} + 2(\mathrm{HPAN})_{\mathrm{org}} = [\mathrm{Cd(PAN)_2}]_{\mathrm{org}} + 2\mathrm{H^+}. \qquad (9)$$

According to this equation the logarithm of the extraction constant was −8·98 from reagent-dependence, and −8·58 from pH-dependence measurements. From the average of these values and from the equations derived earlier,[9] the threshold pH for spectrophotometric extractive titration of μg amounts of cadmium (*i.e.*, *ca.* $10^{-7}M$ solutions) with PAN was calculated:

$$\mathrm{pH}_t = 2{\cdot}14 - \tfrac{1}{2}\log K_{\mathrm{ext}} - \log c_{\mathrm{Cd}} = 2{\cdot}14 + 4{\cdot}39 + 7 = 13{\cdot}53.$$

Procedure. Place 50 ml of slightly acidic sample solution (containing 2–10 μg of cadmium) in one of the titration cells and add 5–10 ml of $10M$ sodium hydroxide, followed by 10–15 ml of chloroform. In the second titration cell place 50 ml of redistilled water, and the amounts of sodium hydroxide and chloroform added to the sample solution. Equilibrate the chloroform with the aqueous phases by mixing for 2 min and measure the absorbance of the chloroform layers at 550 nm. Briefer equilibration leads to a slight turbidity at the start of the titration. Then tirate with $3 \times 10^{-4}M$ ethanolic PAN solution, adding precisely the same volume of titrant to both cells each time (*i.e.*, by simultaneous titration technique[12]). After each addition of titrant mix for 1 min, then wait approx. 20 sec and measure the absorbance as above.

The titration was quite satisfactory, if metal ions other than aluminium, gallium, molybdenum(VI), vanadium or cobalt were absent (see Table II). Cobalt(II) and (III) react with PAN in more acid solutions but under the conditions of titration do not. Many other metal ions interefere: some of them because of reaction with PAN, *e.g.*, zinc and manganese (in which case ascorbic acid was added to prevent air-oxidation), others by forming precipitates of hydroxides capable of adsorbing cadmium present, *e.g.*, lead, nickel, tin(II). The interference of many metals reacting with PAN may be avoided by extracting them with PAN at pH < 7, which might work for nickel, palladium, cobalt, zinc, copper, iron, indium and larger amounts of gallium. The interference of the other group of metals should be avoidable by adding a suitable auxiliary complexing agent, which should prevent the precipitation of hydroxides and the reaction of manganese with PAN. This auxiliary complexing agent must not, however, complex cadmium, otherwise the threshold pH for the titration will increase so that the titration will not be practicable. The search for such a complexing agent was not attempted.

TABLE II.—TITRATION OF CADMIUM

Cadmium present, μg	Cadmium found, μg	Difference, %	Other metals present, μg
10·0	10·1	+1	—
7·0	6·9	−1·4	—
6·0	6·3	+5	—
6·0	6·2	+3·3	110Ga, 100Mn(II)
5·0	5·1	+2	100Mo(VI)
5·0	4·9	−2	100V(V)
5·0	4·9	−2	30Co
4·0	3·0	−5	—
3·0	3·15	+5	—
2·0	2·1	+5	100Al, 100Ga

The interference of anions was not studied in detail, but it was noted that carbonate interferes seriously, as it prevents the formation of the cadmium-PAN chelate. To prevent the introduction of carbonate in the sodium hydroxide solution, only aged solutions of this reagent were used, in which the carbonate was already precipitated out. The titration in the presence of such sodium hydroxide yielded essentially zero blanks, and perhaps the metals reacting with PAN had been scavenged by the precipitate of sodium carbonate.

Zinc

After addition of ethanolic PAN solution to the solution of zinc salt the red zinc–PAN chelate is easily formed and rapidly extracted into chloroform over a relatively narrow pH range. Under substoichiometric conditions the reagent is most completely bound by zinc between pH 9·3 and 10·5%. Above this pH the hydrolysis of zinc ions suppresses the complex formation. Supposing that two PAN molecules are involved in formation of the zinc chelate, the pH-dependence experiments yielded $\log K_{\mathrm{ext}}^{\mathrm{Zn(PAN)_2}} = -5{\cdot}47$. According to the reagent-dependence experiments performed at pH 6·80, the value obtained was −5·04. By comparison of these values with the value −5·8 obtained by Nakagawa and Wada[15] and referred to by Starý[16] it may be concluded that the equilibrium displacement due to the addition of PAN to the aqueous phase is negligible and that the extraction of zinc occurs under conditions near to equilibrium.

In the prediction of conditions suitable for spectrophotometric extractive titration of zinc with PAN, the highest practicable pH value—10·5—was considered, as here the highest sensitivity is expected. At this pH value the formation of hydroxo-complexes of zinc is not negligible and must be taken into account. Instead of K_{ext} the conditional extraction constant K'_{extr},

$$K'_{\mathrm{ext}} = K_{\mathrm{ext}} \Big/ \left\{1 + \sum_{i=1}^{i=n} K_i[\mathrm{OH}]^i\right\}, \tag{10}$$

where $K_i = [\mathrm{Zn(OH)}_i]/[\mathrm{Zn}][\mathrm{OH}]^i$, must be used.[9] Using Lurye's values[17] for the hydrolytic constants, at pH 10·5 $\log K'_{\mathrm{ext}}$ is $\sim -9{\cdot}5$, so the lowest concentration of zinc which may be titrated with an error lower than 1% is given by the equation[9]

$$\log (c_{\mathrm{Zn}})_{\min} = 2{\cdot}14 - \tfrac{1}{2}\log K'_{\mathrm{ext}} - 10{\cdot}5 = -3{\cdot}6,$$

which represents 17 μg per ml of sample, and therefore the simultaneous titration method is not applicable. When lower concentrations of zinc were titrated, a positive error arose if the reagent was standardized according to Beer's law as described above. This disadvantage might be overcome, at least to some extent, by standardizing the PAN solution empirically by the extractive titration of a standard zinc solution.

Procedure. Place 9 ml of slightly acidic or neutral zinc solution containing 5–30 μg of zinc, in the titration cell containing 10–30 ml of chloroform. Add 1 ml of borate–sodium hydroxide buffer of pH 10·5. To the second cell add the same amounts of reagents, replacing the sample solution by redistilled water. Titrate with $5 \times 10^{-4}M$ ethanolic PAN, adding the titrant only to the cell containing the sample, and mixing for 1 min after each addition of titrant. Measure the absorbance at 555 nm and plot the absorbance *vs.* volume of titrant added. Then standardize the PAN solution by titrating 15 μg of zinc in the same manner. (It is essential that the buffer is thoroughly purified so that it does not contain any zinc.)

Some idea of the shape of the titration curve is obtained from the calculation of the B_{Zn} value:[9] under the conditions given,

$$B_{\mathrm{Zn}} = \frac{[\mathrm{H}]^2}{4K'_{\mathrm{ext}}c_{\mathrm{Zn}}{}^2} = \frac{10^{-21}}{4 \times 10^{-9.5} \times 10^{-10}} = 10^{-2}.$$

The titration curve for this value of B_{M} was calculated earlier.[9] The experimental titration curve was of the same shape. As a partial verification of the titration theory, the theoretical and experimental curves under unfavourable conditions for the titration

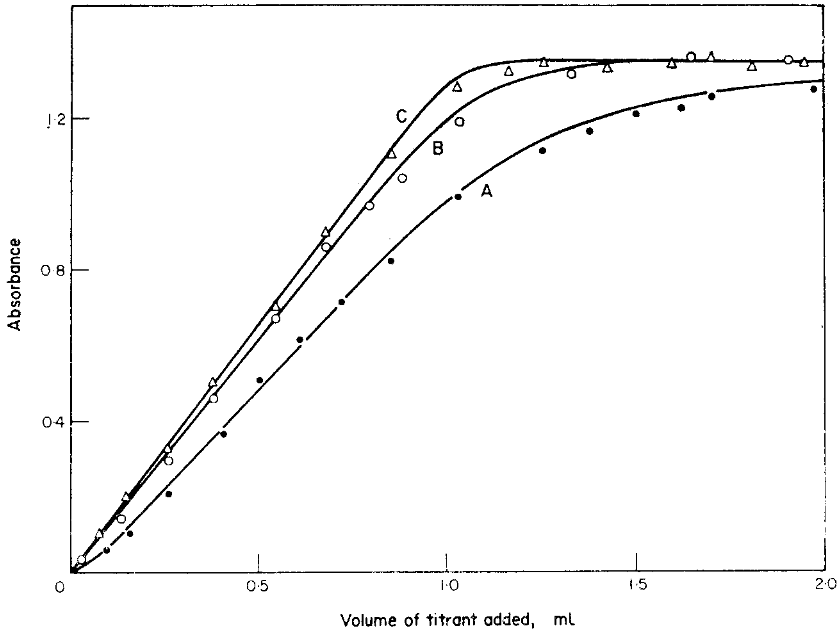

FIG. 4.—Titration of 6 μg of zinc with 1·83 × $10^{-4}M$ PAN.
Curve A—pH 7·1; curve B—pH 9·2; curve C—pH 10·5.
Full lines—theoretical curves; circles and triangles—experimental points.

TABLE III.—TITRATION OF ZINC IN THE PRESENCE OF DIETHANOLDITHIOCARBAMATE

Zinc present, μg	Zinc found, μg	Difference, %	Other metals present, μg
30·0	31·2	+4	—
20·0	19·8	−1	—
10·0	9·85	−1·5	—
10·0	10·8	+8	20Cu
9·0	9·27	+3	25Cu
8·0	8·45	+5·6	—
8·0	8·25	+3·1	120Pd, 100V(V), 111Al, 100Tl(I)
6·0	5·94	−1	111Al, 70Cu
6·0	6·03	+0·5	100Mo(VI), 100Hg(II)
6·0	5·91	−1·5	—
5·0	4·8	−4	—
5·0	5·05	+1	50Ag, 50Fe(III)

of zinc with PAN were compared; 6 μg of zinc were titrated with ~2 × $10^{-4}M$ ethanolic PAN at pH 10·5, 9·2 and 7·1. Equation (10) was used to calculate the conditional extraction constants. The agreement between theory and experiment is satisfactory (Fig. 4).

Because PAN reacts with many other metal ions under the zinc titration conditions, addition of auxiliary complexing agent was necessary for the procedure to be sufficiently selective. For this purpose 2 ml of 0·5% aqueous solution of potassium diethanoldithiocarbamate, synthesized according to Tulyupa *et al.*,[18] were added to the sample solution before the PAN titration. This masking agent prevented the interference of palladium, vanadium(IV), aluminium, thallium(I), silver, mercury(II), copper, iron(III), and molybdenum(VI) (Table III), but not of lead, cadmium, cobalt and bismuth. Lead and cadmium interfere by consuming the reagent after the end-point, so increasing there the slope of the titration curve. Their interference might be overcome by adding potassium iodide. Cobalt and bismuth prevent the reaction with PAN by adsorbing the zinc on their hydroxide precipitate and hence must be separated first.

From comparison of the titration of zinc with PAN and of zinc with dithizone,[12] it is evident that the latter is more sensitive and selective, and hence should be preferred. This is mainly due to zinc dithizonate having the higher extraction constant.

Copper

Copper(II) forms a violet chelate with PAN, which is easily extractable into chloroform above pH 8 (Fig. 2). As indicated by Shibata[19] and spectrophotometric extractive titration of copper with PAN at pH 10, the species extracted is $Cu(PAN)_2$. Below pH 8 the violet chelate formed is not extracted into chloroform, and is found, by the continuous variation method and by Pease and Williams,[3] to be a 1:1 complex. The fact that the chelate is not extractable may be explained by supposing that the copper is bivalent and the chelate positively charged, *cf.* Betteridge, Fernando and Freiser.[20] Formation of $CuPAN^+$ may be described by the equation

$$Cu^{2+} + (HPAN)_{org} = CuPAN^+ + H^+ \tag{11}$$

and the formation constant K_f':

$$K_f' = \frac{[CuPAN^+][H]}{[Cu][HPAN]_{org}}\,. \tag{12}$$

It was found that the chelate is extracted into chloroform if chloride, acetate, bromide or thiocyanate is also present, the violet colour of the chelate totally disappearing from the aqueous phase if proper amounts of bromide or thiocyanate are present. This may be explained by formation of the ion-pairs $CuPAN^+{\cdot}Br^-$ or $CuPAN^+{\cdot}CNS^-$, which pass into chloroform according to the equation:

$$CuPAN^+ + X^- = (CuPAN^+{\cdot}X^-)_{org};\ K_{ext}^{ass} = \frac{[CuPAN{\cdot}X]_{org}}{[CuPAN][X]} \tag{13}$$

where X^- denotes Br^- or CNS^-. The titration of copper with PAN, based on ion-pair formation, was tried, because the $CuPAN^+$ chelate is formed in more acidic solution than $Cu(PAN)_2$ chelate, and is thus more selective. In such a titration, the absorbance of the chloroform layer is given by the concentration of the (CuPAN·X) species in chloroform:

$$A = \varepsilon\,.\,l\,.\,[CuPAN{\cdot}X]_{org} \tag{14}$$

The volume of the titrant added may be normalized by introducing the equivalent ratio a

$$a = \frac{m_{PAN}}{m_{Cu}} \tag{15}$$

where m is the total amount (in moles) of the species denoted. The total amount of copper in the titration cell is $V\,.\,c_{Cu}$, where c_{Cu} is the initial concentration of copper in the solution titrated and V is the volume of the aqueous phase. During the titration the following mass equilibrium applies:

$$V \,.\, c_{\mathrm{Cu}} = \{[\mathrm{Cu}] + [\mathrm{CuPAN}]\} \,.\, V + [\mathrm{CuPAN{\cdot}X}]_{\mathrm{org}} \,.\, V_{\mathrm{org}} \tag{16}$$

supposing that all the ion-pair formed is extracted. Under the same supposition and by neglecting the dissociation of PAN in the aqueous phase (because of the low pH, and the high pK and partition coefficient of the reagent), the total amount of PAN in the titration cell is given by

$$m_{\mathrm{PAN}} = \{[\mathrm{HPAN}]_{\mathrm{org}} + [\mathrm{CuPAN{\cdot}X}]_{\mathrm{org}}\} \,.\, V_{\mathrm{org}} + [\mathrm{CuPAN}] \,.\, V. \tag{17}$$

Because the reaction described by equations (11) and (13) will not be quantitative under the conditions of the titration in general, it is necessary to take into account the effectiveness E of the consumption of PAN:

$$E = \frac{[\mathrm{CuPAN{\cdot}X}]_{\mathrm{org}} \,.\, V_{\mathrm{org}}}{m_{\mathrm{PAN}}} \,. \tag{18}$$

From equations (12)–(18) the following equation for the titration curve is obtained:

$$A = \varepsilon_{\mathrm{CuPAN{\cdot}X}} \,.\, l \,.\, E \,.\, a \,.\, c_{\mathrm{Cu}} \,.\, \frac{V}{V_{\mathrm{org}}} \tag{19}$$

$$a = E \,.\, a \,.\left\{1 + \frac{1}{K_{\mathrm{ext}}^{\mathrm{ass}}[\mathrm{X}]} \,.\, \frac{V_{\mathrm{org}}}{V} + \frac{[\mathrm{H}]}{K_{\mathrm{f}}' K_{\mathrm{ext}}^{\mathrm{ass}} [\mathrm{X}] c_{\mathrm{Cu}} \left(1 - Ea - \dfrac{EaV_{\mathrm{org}}}{K_{\mathrm{ext}}^{\mathrm{ass}}[\mathrm{X}]V}\right)}\right\}. \tag{20}$$

If K_{f}' and $K_{\mathrm{ext}}^{\mathrm{ass}}$ are known the titration curve can be constructed for the titration of copper in the presence of bromide or thiocyanate. The values of $K_{\mathrm{ext}}^{\mathrm{ass}}$ were obtained from the distribution experiments described above for bromide and thiocyanate. The K_{f}' values may be calculated from the literature data,[3,15,20,21] if it is realized that

$$K_{\mathrm{f}}' = \frac{[\mathrm{CuPAN}][\mathrm{H}]}{[\mathrm{Cu}][\mathrm{HPAN}]_{\mathrm{org}}} = \frac{K_{\mathrm{f}} \,.\, K_{\mathrm{HA}}}{q_{\mathrm{HA}}} \,, \tag{21}$$

where $K_{\mathrm{f}} = [\mathrm{CuPAN}]/[\mathrm{Cu}][\mathrm{PAN}^-]$ is $\sim 10^{16}$, the acid dissociation constant of PAN, K_{HA}, is $\sim 10^{-11 \cdot 2}$ and the distribution ratio of the reagent, q_{HA}, is $\sim 10^{5 \cdot 3}$ for the water–chloroform system. Hence $K_{\mathrm{f}}' = 10^{-0 \cdot 5}$.

There is, however, a more important way of utilizing equations (19) and (20) and the constants: it is the calculation of the pH and ligand concentration [X] needed to give an end-point error of $<1\,\%$. Taking it as before,[9] that the error is $<1\,\%$ if E is $>0{\cdot}99$ for $a = 0{\cdot}5$ and the titration is monitored at $\lambda_{\max}$ of the chelate, equation (20) may be transposed into an equation for the threshold pH as a function of ligand concentration. In the analytically significant case where $K_{\mathrm{ext}}^{\mathrm{ass}} \,.\, [\mathrm{X}]V/V_{\mathrm{org}} \gg 1$, equation (20) can be simplified by neglecting the second term in the main brackets, so obtaining the following formula for the threshold pH:

$$[\mathrm{H}]_t = K_{\mathrm{f}}' \,.\, K_{\mathrm{ext}}^{\mathrm{ass}} \,.\, [\mathrm{X}] \,.\, c_{\mathrm{Cu}} \,.\, 0{\cdot}0051 \tag{22}$$

$$\mathrm{pH}_t = 2{\cdot}292 - \log K_{\mathrm{f}}' \,.\, K_{\mathrm{ext}}^{\mathrm{ass}} - \log\,[\mathrm{X}] - \log c_{\mathrm{Cu}}. \tag{23}$$

From equation (23) the threshold pH for the titration of $10^{-6}M$ copper with PAN in the presence of $0{\cdot}01M$ bromide ($\log K_{\rm ext}^{\rm ass} = 3{\cdot}96$) was easily calculated:

$$\mathrm{pH}_t = 2{\cdot}292 - 3{\cdot}46 + 2 + 6 = 6{\cdot}8.$$

Similarly $10^{-6}M$ copper may be titrated in $0{\cdot}1M$ thiocyanate medium ($\log K_{\rm ext}^{\rm ass} = 5{\cdot}39$) at $\mathrm{pH} > 4{\cdot}4$.

Procedure. Place 30 ml of sample solution (containing 1–10 μg of copper) in one of the titration cells containing 10 ml of chloroform. In the second cell, place 10 ml of chloroform and 30 ml of redistilled water. Add 0·3 ml of $1M$ potassium bromide (or 3 ml of $1M$ ammonium thiocyanate) to both cells and adjust the pH to 7–8 (4·5–7 for thiocyanate) with isothermally distilled aqueous ammonia. Mix well with motor-driven mixers to saturate the aqueous phase with chloroform. Titrate with $10^{-4}M$ ethanolic PAN, by the simultaneous titration technique, mixing for 1 min after each addition of titrant. When the motors stop, wait ~20 sec for the organic phases to clarify and measure the difference in the absorbances of both titration cells at 565 nm. Plot absorbance *vs.* volume of titrant.

This procedure was successful: the titration curve breaks just at the equivalence point and then attains essentially zero slope. Variation of the time of mixing varies the shape of the curve at the break a little, but end-point location is not affected. In titrations at lower pH values, the slope of the titration curve after the equivalence point was higher than zero, and this also happened if the concentration of thiocyanate or bromide was decreased, as expected from the theory given above.

Aluminium, bismuth, iron(III), manganese(II), mercury, nickel, cobalt, cadmium, lead, palladium and vanadium(IV) in 100-μg amounts do not interfere, nor do 50-μg amounts of zinc and gallium ions. (Table IV). This high selectivity is due to the fact that at the pH chosen for the titration most of the ions mentioned react with PAN only slightly, if at all, or react with PAN much more slowly than does copper (especially iron, cobalt and nickel). According to the literature[5,6,8,16,22–24] it may be expected

TABLE IV.—TITRATION OF COPPER IN THE PRESENCE OF BROMIDE OR THIOCYANATE

Copper present, μg	Copper found, μg	Difference, %	Other metals present, μg
Bromide method			
10·0	10·2	+2	120 Pd
8·0	7·91	−1·1	—
6·0	6·3	+5	100 Pb
4·0	3·84	−4	100 Ni
2·0	2·0	0	—
1·0	1·06	+6	100 Al, 100 Fe(III)
Thiocyanate method			
10·0	10·12	+1·2	—
10·0	10·03	+0·3	100 Pb
8·0	7·96	−0·5	—
8·0	8·06	+0·6	100 Fe(III), 100 Pd, 100 Co
6·0	6·24	+4	100 Co, 50 Zn
6·0	5·95	−0·8	100 Ni, 100 V(V)
6·0	5·82	−3	100 Al, 100 Cd, 100 Bi
4·0	4·16	+4	100 Al, 100 Mn(II), 100 Bi
4·0	3·82	−4·5	100 Ni, 100 Pb
2·0	1·92	−4	—
2·0	1·97	−1·5	100 Pb, 100 Cd
1·0	1·01	+1	100 Cd, 100 Hg(II)
1·0	0·95	−5	16 Pd, 100 V(V)
1·0	1·06	+6	—

that some of the metal ions not investigated, such as uranium(IV), thallium(III), indium, titanium, silver and rare earths, will not interfere, because of partial extraction in the pH range used, screening effect of bromide or thiocyanate, much lower molar absorptivity, or poor extraction of their PAN chelates into chloroform.

Comparison of the PAN and dithizone[25] titrations shows that the PAN titration is more selective towards zinc and cadmium, and is not affected by presence of palladium or mercury, large amounts of which may cause serious difficulties in the dithizone titration. The highest permissible amounts of cobalt, nickel, bismuth, lead *etc.*, were not investigated, but it is believed that the PAN titration is at least as selective as the dithizone titration. Another advantage of PAN is the higher stability of even very dilute solutions of titrant. The dithizone titration is, however, more sensitive, as may be predicted both from the extraction constants and the molar absorptivities.

The influence of anions on the extraction of $CuPAN^+$ deserves further study. It was noted that sulphate does not form an association complex to any noticeable degree and that the results of Betteridge *et al.*[20] suggest that the hydroxide ion associates more readily than phthalate or acetate. Their data recast in the form above give $\log K_f' \,.\, K_{ext}^{ass}$ as 8·9.

Stability of dilute solutions of PAN

Many authors[4–7] have stated that methanolic or ethanolic solutions of PAN are very stable, but their statements concerned relatively concentrated solutions, *e.g.* 0·1%. In spectrophotometric extractive titrations, however, much more dilute solutions are used and must be stable. To investigate the behaviour of such dilute solutions, the concentration of ethanolic PAN solution was followed absorptiometrically over a 10-day period. Even $1{\cdot}69 \times 10^{-4}M$ ethanolic PAN solutions maintain constant absorbance during this period (and most probably for much longer).

Standardization of the same ethanolic solution by extractive copper titration during the same period showed there was no change in the content of active component in the solution of PAN. Standardization with other metal ions, however, may yield other results if the PAN is contaminated with metal impurity forming a less stable complex than that of copper, but more stable than that of the metal ion used for standardization. This difficulty was not met in the present experiments, but it is supposed that the presence of any metal impurity in the sample of PAN may be discovered by scanning the absorption spectrum of the ethanolic dye solution at wavelengths >500 nm.

CONCLUSIONS

It was confirmed that PAN is suitable for spectrophotometric extractive titrations, if added as ethanolic solution. A limitation is slow chelate formation. The main advantages are the high stability of very dilute solutions and, in some cases higher selectivity.

By studying the copper-PAN system the formation of extractable ion-pairs with bromide or thiocyanate was discovered. The theory of titration was extended to this case, and its application resulted in a highly selective titration procedure for copper.

Acknowledgements—The author thanks Mr. J. Králfor technical assistance in constructing the titration apparatus and Docent Dr. Ing. H. Leopold for his kind translation of foreign summaries.

Zusammenfassung—Es wurde die Möglichkeit der Verwendung von PAN als Titrationssubstanz bei spektrophotometrischen extraktiven Titrationen untersucht. Zwecks einfacher Berechnung der Konzentration des Reagens wurde der Wert des molaren Extinktionskoeffizienten des PAN in Ethanol ermittelt. Die Stabilität sogar sehr verdünnter PAN-Lösungen war weit grösser als die von Dithizon-Lösungen. Als Ergebnis der Untersuchung der Absorptionsspektren, der pH- und Reagens abhängigkeit des Extraktionen der betreffenden Chelate wurden, unter Verwendung früher abgeleiteter Gleichungen, die für die Titration von Zink und Cadmium geeigneten Bedingungen gefunden. Zur spektrophotometrischen extraktiven Titration des Kupfers mit PAN wurde die Bildung und Extraktion der Paare von Ionen-Assoziaten $CuPAN^+$, Br^- und $CuPAN^+$, CNS^- im Detail studiert. Diese Titration erwies sich als sehr selektiv.

Résumé—La possibilité de l'application de PAN comme substance de titrage pour le titrage spectrophotométrique et extractif fût examinée. À la fin d'une simple calculation des concentrations du réactif, la valeur du coefficient moleculaire du PAN en alcool fût établie. La stabilité même des solutions très diluées du PAN était plus grande que celle des solutions de dithizone. Comme résultant des investigations des spectres d'absorption, de la dépendance du pH et des réactives de l'extraction des chélates en question, on a trouvé les propres conditions pour le titrage du zinc et du cadmium, en appliquant des équations dérivées auparavant. Pour le titrage spectrophotométrique et extractif du cuivre a l'aide du PAN, la formation et extraction des paires des associations des ions, $CuPAN^+$, Br^- et $CuPAN^+$, CNS^- fût étudiée en détail. Ce titrage se montre très sélectif.

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VERWENDUNG MÄSSIG DISSOZIIERTER KOMPLEXE BEI SPEKTRALPHOTOMETRISCHEN BESTIMMUNGEN—I

ALLGEMEINE BETRACHTUNGEN

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Zusammenfassung—Bei der Bildung mässig dissoziierter Komplexe ist es möglich, lineare Eichkurven zu erhalten. Die Richtungskoeffizienten dieser Eichgeraden sind von der analytischen Ligandkonzentration abhängig. Die Abhängigkeit des Fehlers einer spektralphotometrischen Bestimmung bzw. einer photometrischen Titration von den Änderungen der analytischen Ligandkonzentration und der Beständigkeitskonstante wurde abgeleitet und diskutiert. Bei praktischen Analysen ist es günstig, bei möglichst hoher Ligandkonzentration zu arbeiten.

BEI SPEKTRALPHOTOMETRISCHEN Bestimmungen, denen die Bildung stabiler Komplexe zu Grunde liegt, kann eine vollständige Bindung des zu bestimmenden Stoffes im Komplex vorausgesetzt werden. Bei Ausnutzung dissoziierter Komplexe ist damit zu rechnen, daß die der Messung zugängliche Gleichgewichtskonzentration des Komplexes von der gesuchten, totalen Konzentration des zu bestimmenden Stoffes beträchtlich abweichen kann. Diese Abweichung ist von den Reaktionsbedingungen, d.h. auch von dem Verhältnis der reagierenden Stoffe abhängig.

Die Reaktion, die bei konstanten Bedingungen zur Bildung eines Komplexes M_aL_b führt, kann durch die schematische Gl. (1) und die entsprechende Beständigkeitskonstante K [scheinbare Bildungskonstante, Gl. (2)] beschrieben werden.

$$a\mathrm{M} + b\mathrm{L} \leftrightharpoons \mathrm{M}_a\mathrm{L}_b \tag{1}$$

$$K = \frac{[\mathrm{M}_a\mathrm{L}_b]}{(c_\mathrm{M} - a[\mathrm{M}_a\mathrm{L}_b])^a(c_\mathrm{L} - b[\mathrm{M}_a\mathrm{L}_b])^b} \tag{2}$$

Aus Gl. (2) folgt der Zusammenhang zwischen c_L, $[\mathrm{M}_a\mathrm{L}_b]$ und der gesuchten Konzentration c_M bei einem unveränderlichen K-wert (konstante Reaktionsbedingungen).

Titriert man das Anion L mit Kation M, wobei sich die Bildung des Komplexes ML_b photometrisch verfolgen lässt, erhält man eine mehr oder weniger stark gekrümmte Titrationskurve. Für die Tangente im Koordinatenursprung (d.h. $c_\mathrm{M} \rightarrow 0$) ergibt sich die Steigung [nach Gl. (9)[1]] nach Gl. (3).

$$k = \frac{c_\mathrm{L}{}^b}{c_\mathrm{L}{}^b + 1/K} \tag{3}$$

Diese Beziehung wurde zur Bestimmung von Extinktionskoeffizienten und K-Werten benutzt.[1] Ähnliche Aussagen erhielten Mandel und Depommier.[2] Sie beziehen sich jedoch nur auf die Abhängigkeit der Richtungskoeffizienten der Tangenten einer Jobschen Kurve von dem K-Wert des gebildeten Komplexes.

In der vorliegenden Arbeit werden Folgerungen aus Gl. (3) für spektralphotometrische Bestimmungen und zum Teil auch für die photometrische Titration diskutiert. Es ergibt sich die Möglichkeit, die bereits empirisch bekannten Grundsätze (z.B. Anwendung hoher c_L bei der Bildung dissoziierter Komplexe) mathematisch zu begründen und zugleich auf die Quellen systematischer Fehler hinzuweisen.

Einige in der analytischen Praxis häufig verwendete Komplexe[3] (z.B. von Arsenazo III mit UO_2^{2+} oder Th^{4+}) besitzen K-Werte, bei denen die Abhängigkeit der Richtungskoeffizienten der Eichgeraden von der verwendeten Ligandkonzentration bedeutend ist ($K < 10^6$ für ein Komplex ML).

Unter der Voraussetzung, daß ein einziger Komplex gebildet wird und die Gültigkeit des Lambert-Beer'schen Gesetzes in dem untersuchten Konzentrationsgebiet erfüllt ist, kann man die Einflüsse der Änderungen des Konzentrationsverhältnisses reagierender Stoffe bei konstantem K-Wert, und die Auswirkung einer K-Änderung (andere Ionenstärke, Temperatur, pH-Wert) auf die Analysenergebnisse untersuchen. Die Betrachtungen der entstehenden Fehler gelten für die pseudolinearen Teile der Eichkurven (vgl. unten).

Verwendete Symbole

$c_{M'}$, c_L	totale Metall-bzw. Ligand-Konzentrationen, molar
$[M_aL_b]$	Gleichgewichtskonzentration des Komplexes M_aL_b
K	Beständigkeitskonstante nach Gl. (2)
k	Richtungskoeffizient der Tangente im Koordinatenursprung
A	Extinktionsmodul
ΔA	Extinktionsmodul, gemessen gegen Blindansatz
$\varepsilon_{L'}$, $\varepsilon_{M_aL_b}$	molare Extinktionskoeffizienten
$\Delta\varepsilon_{M_aL_b}$	differentieller molarer Extinktionskoeffizient, vgl.[1]
$\Delta\varepsilon_{M_aL_b,\mathrm{eff}}$	effektiver differentieller molarer Extinktionskoeffizient, vgl.[1]
Δ,$\Delta\%$	Fehler bei einer c_M-Bestimmung

LINEARITÄT DER EICHKURVEN BEI SPEKTRALPHOTOMETRISCHEN BESTIMMUNGEN ALS FUNKTION VON K UND c_L

In Abb. 1 ist eine Eichkurve für die spektralphotometrische Bestimmung des Stoffes M bei Bildung eines mässig dissoziierten Komplexes ML_b schematisch abgebildet (Kurve 1). Für die Berechnung, ob ein Teil dieser Kurve (Anfang) als linear angesehen werden kann, bzw. wie lang dieser pseudolineare Teil in Abhängigkeit von den Reaktionsbedingungen ist, wird die Kurve unmittelbar in Koordinaten $[ML_b]$ gegen c_M dargestellt, denn es gilt:

$$\Delta A = k' \,.\, [ML_b] \tag{4}$$

Die Tangente der Kurve 1 in dem Koordinatenursprung (gerade OB) ist nach Gl. (3) durch Gl. (5) gegeben:

$$[ML_b] = \frac{c_L{}^b}{c_L{}^b + 1/K} \,.\, c_M \tag{5}$$

Eine Gerade, die gleichfalls von dem Ursprung ausgeht, jedoch einem um $\alpha_1\%$ niedrigeren Richtungskoeffizienten (Gerade OD, Abb. 1) besitzt, wird durch Gl. (5*a*) beschrieben:

$$[ML_b] = \frac{c_L{}^b}{c_L{}^b + 1/K} \cdot \frac{100 - \alpha_1}{100} \,.\, c_M \tag{5a}$$

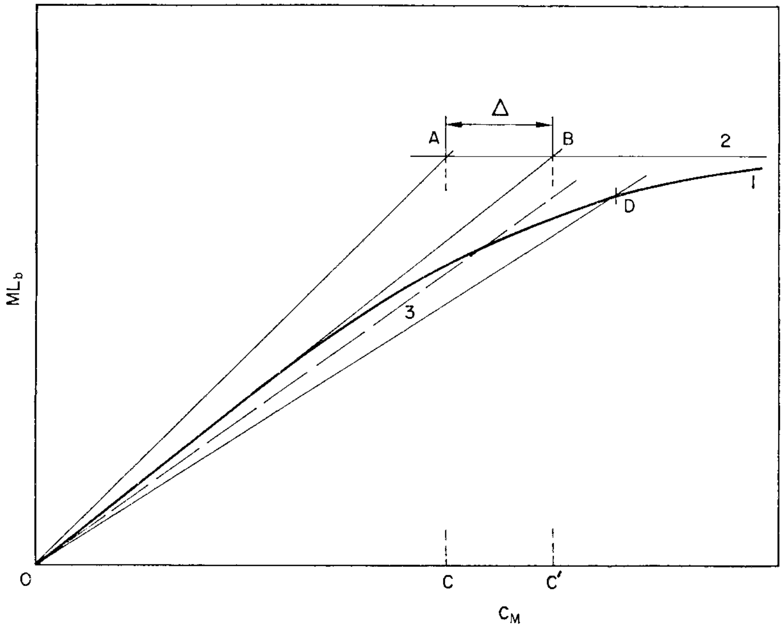

Abb. 1.—Photometrische Titrationskurve eines Ligands durch Kation bei Bildung eines dissoziierten Komplexes (schematisch).

Für die Kurve 1 folgt aus Gl. (2):

$$c_M = \frac{[ML_b]}{K(c_L - b[ML_b])^b} + [ML_b] \tag{6}$$

Aus den Gl. (5*a*) und (6) kann der Abschnitt OD (und der Maximalwert $[ML_b]_1$) der Eichkurve 1 ermittelt werden, in welchem die negativen Abweichungen der Extinktionen von der Tangente für $c_M \to 0$ niedriger bzw. gleich groß sind wie die gewählte Größe $\alpha_1\%$. Die auf diese Weise erhaltene Gl. (7) liefert einen Zusammenhang zwischen den Größen $[ML_b]$ (d.h. auch ΔA), K, b, c_L und α_1.

$$\frac{c_L{}^b}{c_L{}^b + 1/K} \cdot \frac{100 - \alpha_1}{100} \cdot \left[\frac{1}{K(c_L - b[ML_b])^b} + 1\right] - 1 = 0. \tag{7}$$

Für einen Komplex des Typus ML vereinfacht sich Gl. (7) zu (7*a*).

$$[ML]_1 = \frac{\alpha_1 \, . \, c_L(1 + Kc_L)}{\alpha_1 Kc_L + 100}. \tag{7a}$$

Für den horizontalen Ast der photometrischen Titrations kurve (Abb. 1, Kurve 2) gilt Gl. (8).

$$[ML_b]_{max} = c_L/b \tag{8}$$

Es ist also möglich, den nach (7*a*) berechneten quasilinearen Kurvenabschnitt auf den maximal erreichbaren Extinktionswert ΔA_{max} (für $[ML] = c_L$) zu beziehen, und als seinen Bruchteil in % auszudrücken:

$$\frac{\Delta A_1}{\Delta A_{max}} \, . \, 100 = \frac{[ML]_1}{c_L} \, . \, 100 = \frac{\alpha_1(Kc_L + 1)}{\alpha_1 Kc_L + 100} \, . \, 100\% \tag{9}$$

(Die Extinktion ΔA_1 ist der nach (7*a*) berechneten Gleichgewichtskonzentration $[ML]_1$ proportional).

Abbildung 2 zeigt die nach Gl. (9) berechneten quasilinearen Anteile der Eichkurven eines ML-Komplexes in Abhängigkeit von K, c_L ($1 \cdot 10^{-5}M$ und $1 \cdot 10^{-4}M$) und $\alpha_1\%$ (2; 5; 10%). Für kleine K-Werte nähern sich die quasilinearen Anteile der Kurven dem gewählten Wert $\alpha_1\%$ [Limes von Gl. (9) für $K \rightarrow 0$].

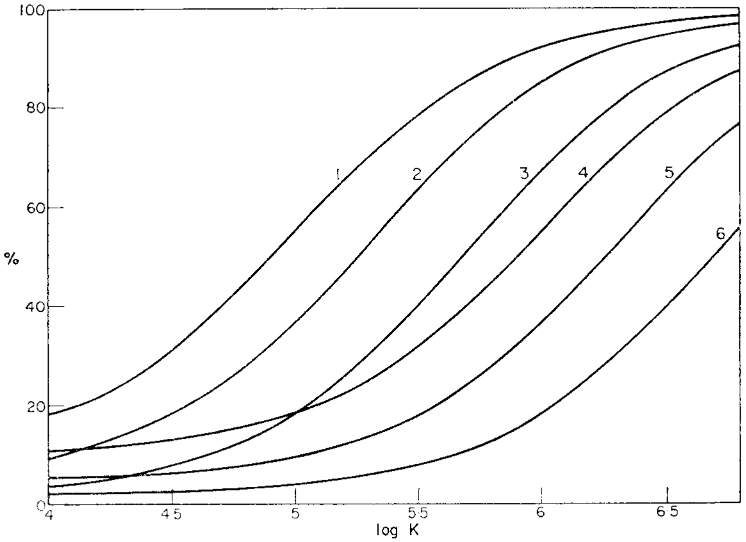

ABB. 2.—Linearität der Eichkurven bei Bildung eines Komplexes ML. $c_L = 1 \cdot 10^{-4}M$ (Kurven 1–3), $c_L = 1 \cdot 10^{-5}M$ (Kurven 4–6). $\alpha_1 = 10\%$ (Kurven 1 und 4), 5% (Kurven 2 und 5) und 2% (Kurven 3 und 6).

EXTRAPOLATIV BESTIMMTER SCHNITTPUNKT DER LINEAREN ÄSTE EINER PHOTOMETRISCHEN TITRATIONSKURVE

Die Verlängerungen der quasilinearen Äste der Titrationskurve 1 (Abb. 1, Kurve 2 und OB) schneiden sich in dem Punkt B, der irrtümlich als der Äquivalenzpunkt abgelesen wird. Der wahre Äquivalenzpunkt ist Punkt A. (Die Gerade OA entspricht einer quantitativen Komplexbildung. Bei der Bildung dissoziierten Komplexe ist sie experimentell nicht erreichbar.) Der Fehler $\Delta \equiv AB$ der photometrischen Titration soll als Funktion von K und c_L gedruckt werden.

Aus den Gl. (5) der Geraden OB und (8) der Kurve 2 folgt für den Abschnitt OC′:

$$OC' = \frac{c_L{}^b + 1/K}{c_L{}^b} \cdot \frac{c_L}{b} \tag{10}$$

Mit Rücksicht auf Gl. (9*a*)

$$OC = AC = BC' = \frac{c_L}{b} \tag{9a}$$

wird der gesuchte Fehler folgendermassen ausgedrückt:

$$\Delta = OC' - OC = \frac{c_L^{1-b}}{bK} \tag{11}$$

Der relative Fehler einer auf diese Weise ausgewerteten Titration (OC ≡ 100%) ist:

$$\Delta\% = \frac{100}{K \, . \, c_L{}^b} \, . \qquad (11a)$$

ABHÄNGIGKEIT DES FEHLERS EINER SPEKTRALPHOTOMETRISCHEN c_M-BESTIMMUNG VON c_L-ÄNDERUNGEN (ML-KOMPLEX)

Es werden die Folgen der durch die Bildung eines mässig dissoziierten Komplexes bedingten c_L-Abhängigkeit des Richtungskoeffizienten der quasilinearen Eichkurve für die Richtigkeit einer spektralphotometrischen c_M-Bestimmung betrachtet. Bei der c_L-Änderung kann es sich dabei z.B. um Alterung der benutzten Reagenzlösung handeln.

In Abb. 3 ist die Entstehung der Fehler bei der Verwendung der Eichgeraden OA (Ligandkonzentration c_L) für die c_M-Bestimmung bei einer Ligandkonzentration $c_L \, . \, (1 + \alpha_2/100)$ (Gerade OB) oder $c_L \, . \, (1 - \alpha_2/100)$ (Gerade OC) schematisch dargestellt.

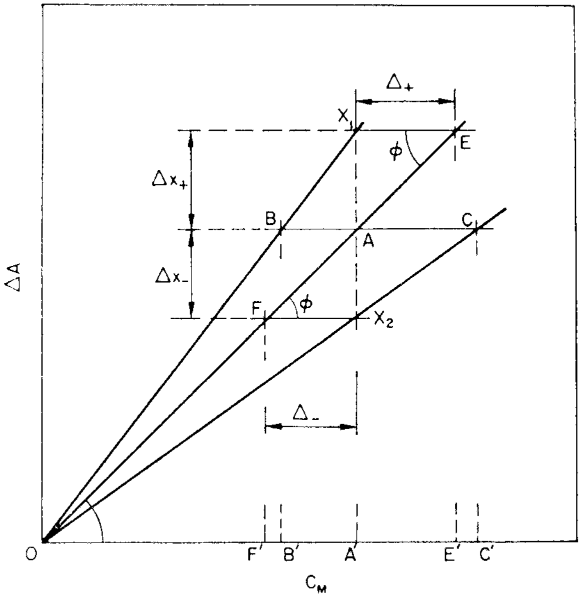

ABB. 3.—Entstehung von Fehlern bei einer c_M-Bestimmung (schematisch).

Die eingezeichneten Fehler Δ+ bzw. Δ− kommen wie folgt zustande: Zur Verfügung steht die Eichgerade OA (Abb. 3). Bei einer niedrigeren (höheren) c_L-Konzentration (bzw. K-Wert) sollte man jedoch mit den Eichgeraden OC bzw. OB arbeiten, da der gesuchten Konzentration c_M die Extinktionen X_2 bzw. X_1 entsprechen In Wirklichkeit werden aber mit Hilfe der Eichkurve OA die den Punkten F bzw. E entsprechenden Konzentrationen F' bzw. E' abgelesen.

Die Richtungskoeffizienten der Eichgeraden OA, OB, OC sind durch Gl. (3), (12), (13) gegeben:

$$k_{OB} = \frac{c_L \, . \, (1 + \alpha_2/100)}{c_L \, . \, (1 + \alpha_2/100) + 1/K} \qquad (12)$$

$$k_{OC} = \frac{c_L \, . \, (1 - \alpha_2/100)}{c_L \, . \, (1 - \alpha_2/100) + 1/K} \, . \qquad (13)$$

Aus Gl. (12) und (13) kann Gl. (14) für die Berechnung des Fehlers $\Delta\%$ einer photometrischen c_M-Bestimmung bei der c_L-Änderung um $\pm\alpha_2\%$ und gegebenen Werten von c_L und K abgeleitet werden.

$$\Delta\% = \frac{\alpha_2}{Kc_L \, . \, (1 + \alpha_2/100) + 1} \tag{14}$$

Es ist ersichtlich, daß bei kleinen c_L und K (z.B. $c_L = 1 \, . \, 10^{-5}M$, $K = 10^4$) die Größe des entstehenden Fehlers dem gewählten Wert von $\alpha_2\%$ nahe kommt. In Abb. 4 ist die K-Abhängigkeit des Fehlers [nach Gl. (14)] für den gebildeten Komplex graphisch dargestellt ($\alpha_2 = \pm 10\%$, $c_L = 1 \, . \, 10^{-5}M$; $5 \, . \, 10^{-5}M$ und $1 \, . \, 10^{-4}M$).

Zur Abl. der Gl. (14) und Gl. (16) werden die Dreiecke AEX$_1$ bzw. FX$_2$A (Abb. 3) betrachtet. Die c_L-Änderung wird durch den Faktor f^2 ausgedrückt

$$f' = 1 \pm \alpha_2/100 \, .$$

Somit gilt die Abl. auch für Gl. (16).

Die Abschnitte Δx_+, Δx_- können aus $k_{OA} \equiv \tan\phi$ (3); k_{OB} (12), (12a) und k_{OC} (13), (13a) berechnet werden:

$$k_{OB,OC} = \frac{f'c_L}{f'c_L + 1/K} \tag{12a), (13a}$$

$$\Delta x_+ = c_M \, . \left(\frac{f'c_L}{f'c_L + 1/K} - \frac{c_L}{c_L + 1/K} \right) .$$

Für die gesuchte Größe $\Delta_\pm$ folgt:

$$\Delta_\pm = \Delta x_\pm \, . \cot\text{an}\,\phi = \Delta x_\pm \, . \frac{c_L + 1/K}{c_L}$$

Nach Einsetzen für Δx, bzw. f' und Vereinfachen resultieren die Gl. (14) bzw. (16).

FEHLER EINER PHOTOMETRISCHEN c_M-BESTIMMUNG IN ABHÄNGIGKEIT VON ÄNDERUNGEN DES K-WERTES (ML-KOMPLEX)

Als Maß für die vom Reaktionssystem abhängige Beständigkeitskonstante K wird ein Faktor f eingeführt:

$$K' = f \, . \, K$$

Es ergibt sich dann aus Gl. (3) für den Richtungskoeffizienten der pseudolinearen Eichkurve Gl. (15).

$$k_{K'}, = \frac{c_L}{c_L + 1/fK} \tag{15}$$

Ähnlich wie durch Gl. (14) beschrieben (Einfluß der c_L-Änderung) kann der relative Fehler einer photometrischen c_M-Bestimmung im Bereich des pseudolinearen Verlaufes der Eichkurve in Zusammenhang mit f, K und c_L gebracht werden:

$$\Delta\% = 100 \, . \frac{f - 1}{fKc_L + 1} \tag{16}$$

In Abb. 5 sind die nach Gl. (16) berechneten Werte des Fehlers für $c_L = 1 \, . \, 10^{-4}M$ (Kurven 1–3) und $c_L = 1 \, . \, 10^{-5}M$ (Kurven 4–6), sowie gewählte f ($f = 2{,}0$ bzw. $0{,}5$—Kurven 1 bzw. 4, $f = 1{,}26$ bzw. $0{,}79$—Kurven 2 bzw. 5 und $f = 1{,}1$ bzw. $0{,}91$—Kurven 3 bzw. 6) in Abhängigkeit von K dargestellt.

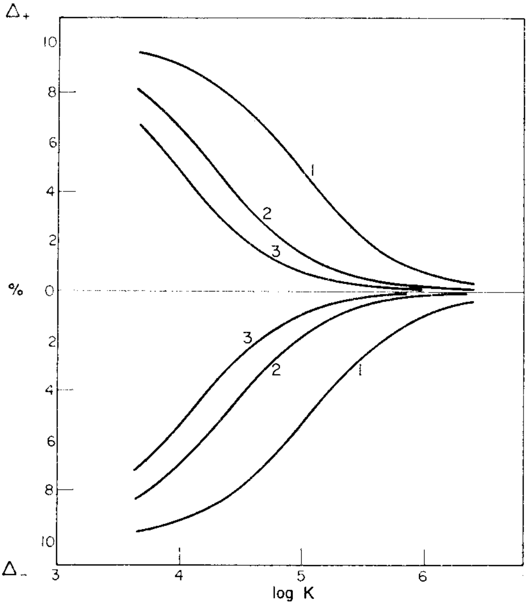

Abb. 4.—Fehler einer spektralphotometrischen c_M-Bestimmung bei einer c_L-Änderung um ±10%.
1—$c_L = 1 . 10^{-5}M$; 2—$c_L = 5 . 10^{-5}M$; 3—$c_L = 1 . 10^{-4}M$

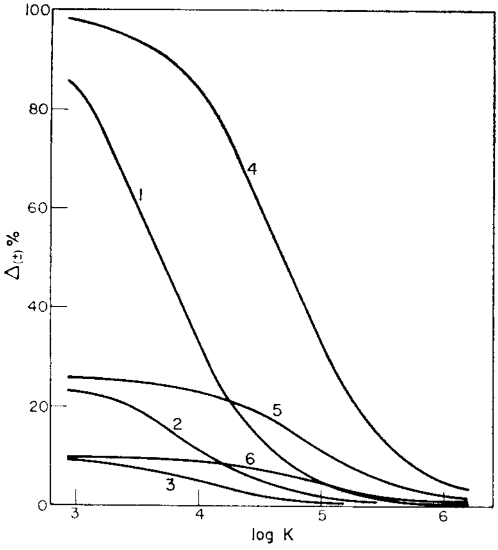

Abb. 5.—Fehler einer spektralphotometrischen c_M-Bestimmung bei einer Änderung von K.
$c_L = 1 . 10^{-4}M$ (Kurven 1–3), $c_L = 1 . 10^{-5}M$ (Kurven 4–6).
$f(\Delta_+)$ resp. $1/f(\Delta_-) = 2{,}0$ (Kurven 1 und 4); 1,26 (Kurven 2 und 5); 1,1 (Kurven 3 und 6).

DISKUSSION

Es wurde gezeigt, daß für verhältnismäßig dissoziierte Komplexe ($K_{ML} = 10^4$–10^5) besonders bei Anwendung hoher c_L-Werte bedeutende Teile der Eichkurven im Rahmen der gewählten Abweichung α_1% als pseudolinear angesehen werden können. Die Steigung der Eichgeraden ist aber c_L abhängig.

Als Eichgerade wird allgemein nicht die Tangente OB, sondern die Gerade 3 (Abb. 1) verwendet. Unter Berücksichtigung der Genauigkeit üblicher photometrischer Messungen ($\pm$1–2%) kann angenommen werden, daß die wahre Eichkurve 1 (Abb. 1) durch die Gerade 3 für Abweichungen bis zu 5% (α_1) ersetz werden kann.

Eine deutliche Krümmung der Eichkurve wird ab $\alpha_1 = 10\%$ bemerkbar. Bei $\alpha_1 = 2\%$ tritt kaum eine Differenz zwischen der Eichkurve und der Tangente im Koordinatenursprung auf.

Ein Beispiel für die Gültigkeit von Gl. (7*a*) stellt die Bildung des Barium-Komplexes von Sulfonazo III dar. In Tab. 1 sind die nach (Gl. 7*a*) berechneten und die früher[1] gemessenen Werte gegenübergestellt. Die Richtungskoeffizienten der Tangenten für $c_M \rightarrow 0$ der Eichkurven sind bei konstanten Reaktionsbedingungen merklich von c_L abhängig (vgl. die Werte von $\Delta\varepsilon_{ML,eff}$, Tab. I). Dadurch wird die Ermittlung des Äquivalenzpunktes von Titrationskurven durch Extrapolation der pseudolinearen Äste fehlerhaft.

TABELLE I.—LINEARITÄT DER EICHKURVEN BEI DER Ba^{2+}-BESTIMMUNG MIT SULFONAZO III (pH 2,8)

c_L	$\Delta\varepsilon_{ML,eff}$	ΔA*	ΔA†	ΔA‡
$2 . 10^{-5}$	$2{,}3 . 10^4$	0,2	0,095	0,170
$5 . 10^{-5}$	$3{,}2 . 10^4$	0,7	0,360	0,650
$1 . 10^{-4}$	$4{,}0 . 10^4$	1,6	1,1	1,8

* Merkliche Abweichung von der Tangente, experimentell nach Referat 1, Abb. 5

† Berechnete Grenze für $\alpha_1 = 5\%$

‡ Berechnete Grenze für $\alpha_1 = 10\%$

In Abb. 6 ist die Abhängigkeit des auf diese Weise entstandenen Fehlers $\Delta\%$ von K und c_L im logarithmischen Maßstab dargestellt. Für relativ dissoziierte Komplexe ist es bei üblichen c_L (bis $1 . 10^{-4}M$) unmöglich, durch Extrapolation der linearen Äste den wahren Äquivalenzpunkt auch nur ungefähr zu bestimmen ($\Delta\%$ 100 und mehr). Diese Tatsache darf besonders bei Komplexstudien, bei welchen die photometrische Titration oft zur grundlegenden c_L-Bestimmung, manchmal sogar auch zur Bestimmung der Komplexzusammensetzung dient, nicht ausser Acht gelassen werden. (Über die richtige Auswertung solcher photometrischen Titrationskurven wird in einer späteren Arbeit berichtet.)

Die merkliche c_L-Abhängigkeit der Richtungskoeffizienten der Eichgeraden ist eine mögliche Erklärung für die abweichenden Ergebnisse bei Benutzung neuer Reagenzlösungen. Der Gehalt des wirksamen Stoffes (Ligand) kann sogar in sonst reinen Präparaten um mehrere Zehner % voneinander abweichen. Die Ursache hierfür liegt in einem unterschiedlichen Wassergehalt oder einem unterschiedlichen Verhältnis von Salz zu freier Säure. Der bei einer c_M-Bestimmung entstehende Fehler für eine c_L-Änderung um $\pm 10\%$ ist aus Abb. 4 ersichtlich.

Es ist zweifellos günstiger die Bestimmung bei einem höheren c_L auszuführen. Bei

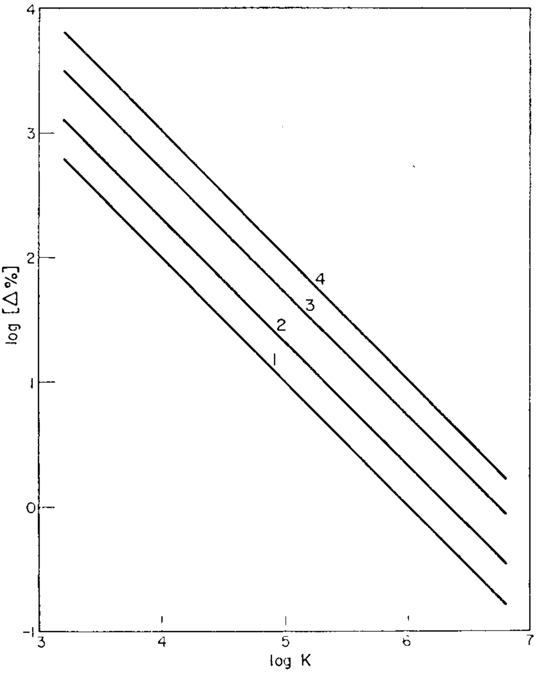

Abb. 6.—Fehler des extrapollierten Äquivalenzpunktes einer photometrischen Titration; ML-Komplex.
1—$c_L = 1 \,.\, 10^{-4}M$; 2—$c_L = 5 \,.\, 10^{-5}M$; 3—$c_L = 2 \,.\, 10^{-5}M$; 4—$c_L = 1 \,.\, 10^{-5}M$.

der Verwendung von Sulfonazo III für die Bariumbestimmung unter obigen Bedingungen sind die Ergebnisse bei einer gleichen relativen c_L-Änderung ($\alpha_2 = \pm 10\%$) mit einem Fehler von etwa ±2% bei $c_L = 1 \,.\, 10^{-4}M$, jedoch etwa ±7% bei $c_L = 1 \,.\, 10^{-5}M$, behaftet.

Während die Einflüsse der c_L-Änderungen durch Wahl einer genügend hohen Ligandkonzentration weitgehend behoben werden können, bereiten K-Änderungen wesentlich größere Schwierigkeiten. Bei einer Verdoppelung bzw. Halbierung der Konstanten ($f = 2{,}0$ bzw. 0,5, vgl. Abb. 5) betragen die Fehler mehrere Zehner %. Der Einfluß einer pH-Änderung (als Grund einer K-Änderung) kann an der Bildung eines ML-Komplexes aus dem Kation M^+ und Säure LH nach der Gl. (17) gezeigt werden.

$$M^+ + LH \rightleftharpoons ML + H^+ \tag{17}$$

Aus Abb. 5 ist der durch pH-Änderungen bewirkte Fehler in Abhängigkeit von K abzulesen: ±0,3 pH ($f = 2{,}0$ und 0,5); ±0,1 pH ($f = 1{,}26$ und 0,79); ±0,04 pH ($f = 1{,}1$ und 0,91). Bei niedrigen c_L-Konzentrationen und K-Werten zwischen 10^4 und 10^5 entstehen bereits bei einer schwierig kontrollierbaren pH-Änderung um 0,04 pH größere Fehler (über 5%).

Bei der Entwicklung einer neuen, oder bei der Optimierung einer bereits bekannten photometrischen Methode ist es daher notwendig, zuerst den K-Wert durch die Untersuchung der c_L-Abhängigkeit der Richtungskoeffizienten der Eichgeraden abzuschätzen. Diese Abschätzung kann auch mit einer nur ungefähr bekannten Konzentration der Reagens-Grundlösung durchgeführt werden.[1]

Tritt ein Einfluß der c_L-Änderung auf die Richtungskoeffizienten der Eichgeraden auf, sollten zuerst Bedingungen gesucht werden, bei welchen dieser Effekt ausbleibt, vor allem durch Erhöhung des K-Wertes (z.B. durch eine pH-Änderung). Anderenfalls müssen die Bestimmungen bei möglichst hoher totaler Ligandkonzentration und bei strengst standardisierten Reaktionsbedingungen (einschließlich Temperatur) ausgeführt werden.

Bei Berücksichtigung der diskutierten Ergebnisse dürften die günstigen Eigenschaften einer Reihe von Reagenzien, die relativ dissoziierte Komplexe bilden, auch in der analytischen Praxis Anwendung finden. Auf einige dieser Komplexbildner, die oft durch hohe Extinktionskoeffizienten und gute Selektivität ausgezeichnet sind, wird in einer nächsten Mitteilung eingegangen.

Für besondere Aufmerksamkeit und Interesse sind wir Herrn Prof. Dr. L. Sommer, Dr. Sc., aus der Universität Brno zu besonderem Dank verpflichtet.

Summary—The dependence of errors in photometric methods of analysis based on the formation of partially dissociated complexes is discussed, and the range of ligand concentrations for various errors is calculated. It is shown that the highest possible ligand concentration should be used in order to minimize the error in a determination.

Résumé—On discute de la dépendance des erreurs dans les méthodes photométriques d'analyse basées sur la formation de complexes partiellement dissociés, et calcule le domaine de concentrations en ligand pour diverses erreurs. On montre que la concentration en ligand la plus élevée possible devrait être utilisée afin de minimiser l'erreur dans un dosage.

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ON POTENTIOMETRIC TITRATION CURVES IN COMPLEXOMETRY

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Summary—An equation is given which describes the potential change during complexometric titration of metals with potentiometric end-point detection. The potential of the indicator electrode (*e.g.*, silver or mercury electrode) depends on the equilibrium of the reaction $MY + W \rightleftharpoons WY + M$, where W represents the indicator metal ion, and M the metal ion determined by titration with the ligand Y, forming 1:1 chelates. Introduction of the conditional stability constants and corresponding side-reaction coefficients facilitates the prediction of the limits of application of this type of titration as well as the optimum conditions for the determination.

POTENTIOMETRIC indication of a complexometric titration end-point with a silver or mercury electrode depends on the position of the equilibrium:

$$W + MY \rightleftharpoons M + WY \tag{1}$$

where W represents the indicator metal ion, M the titrated metal ion and Y the ligand used as a titrant—usually EDTA.

The first studies in this field were performed by Siggia, Eichlin and Rheinhart, who used the mercury-covered platinum electrode. Reilley and coworkers,[2–5] who have used the mercury electrode, have given many practical analytical directions and an equation which describes the potential changes in the course of titration, based on the assumption that the mercury complex is more stable than most other complexes. Fritz *et al.*[6] have mentioned that the shape of the curves must primarily depend on the relative stabilities of both complexes, *i.e.*, MY and WY. Strafelda,[7,8] who used a silver indicator electrode, has derived an equation which describes the changes of $[Ag^+]$ and therefore the potential—but it is difficult to predict directly the best titration condition. The simplified form of this equation is based on the assumption that the stability constant of the silver–EDTA complex is much lower than that of the titrated metal–complex.

Blaedel and Laessing[9] and Olsen and Adamo[10] have discussed the different shapes of the titration curves, and their applicability to end-point detection in automatic chelometric titrations.

Recently Hannema and den Boef[11,12] have explained the shape of potentiometric chelometric titration curves with emphasis on the successive titration of two ions with one ligand. However, we believe that the same analytically important conclusions may be more clearly understood on the basis of considerations derived on slightly different principles.

General equation for potential value

These considerations are based on the general principle of conditional constants.[13] The mass balances for metals M and W, and for the titrant Y are the following:

$$C_M = [M'] + [MY'] \tag{2}$$

$$C_W = [W'] + [WY'] \tag{3}$$

$$C_Y = [MY'] + [WY'] + [Y'] \tag{4}$$

where the primed symbols [M′] *etc.* represent concentrations of all indicated species not bound in a complex, and [MY′] and [WY′] represent the concentration sum of various complex species:

$$[MY'] = [MHY] + [MY] + [MOHY] \tag{5}$$

$$[WY'] = [WHY] + [WY] + [WOHY] \tag{6}$$

The corresponding stability constants are therefore the conditional ones:

$$K_{MY}' = \frac{(K^{M}_{MHY} \,.\, K_{HY}[H] + K_{MY} + K^{OH}_{MOHY} \,.\, K_{MY} \,.\, K_W[H]^{-1})}{\alpha_M \,.\, \alpha_Y} \tag{7}$$

$$K_{WY}' = \frac{(K^{W}_{WHY} \,.\, K_{HY}[H] + K_{WY} + K^{OH}_{WOHY} \,.\, K_{WY} \,.\, K_W[H]^{-1})}{\alpha_W \,.\, \alpha_Y} \tag{8}$$

where the real constants are named according to the accepted rules,[14] and α_M, α_W, α_Y are the side-reaction coefficients for the metal titrated, indicator metal and ligand respectively.

If the equilibrium (1) is considered in terms of the primed concentrations and conditional constants then

$$K = \frac{K_{WY}'}{K_{MY}'} = \frac{[WY'][M']}{[W'][MY']} \,. \tag{9}$$

The indicator electrode is sensitive to concentration [W] but not to $[W'] = \alpha_W[W]$. Substitution of $[WY'] = C_W - [W]\alpha_W$ gives

$$[W] = \frac{C_W K_{MY}'}{\alpha_W \left(K_{WY}' \dfrac{[MY']}{[M']} + K_{MY}'\right)} \,. \tag{10}$$

Then from the Nernst equation, the indicator electrode potential E is given by

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W K_{MY}'}{\alpha_W \left(K_{WY}' \dfrac{[MY']}{[M']} + K_{MY}'\right)} \tag{11}$$

This general equation presents the dependence of the electrode potential on the total concentration of indicator metal ion, C_W, its side-reactions, α_W, K_{WY}', conditional stability constants of both metal complexes, (K_{MY}', K_{WY}), and the primed concentrations ratio [MY′]/[M′] which indicates the progress of titration. If the concentration of the indicator ion is negligible compared with that of the titrated metal, $C_W \ll C_M$, then before the equivalence point the fraction titrated is $f = C_Y/C_M$, and

$$\frac{[MY']}{[M']} = \frac{f}{1-f}. \tag{12}$$

Appropriate potential equation when $0 < f < 1$

The detailed discussion of equation (11) is much easier when one of the two terms of the sum included in the brackets is neglected. Consider the case when

$$K_{WY}' \frac{[MY']}{[M']} < K_{MY}' \tag{13}$$

$$\frac{K_{MY}'}{K_{WY}'} > \frac{[MY']}{[M']}: \tag{14}$$

then the general equation (11) is simplified to the expression

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W}{\alpha_W} \cdot \tag{15}$$

In this equation the electrode potential depends exclusively on the indicator ion concentration and its reactions and does not change during titration.

This behaviour is observed as long as the condition given by (13) is valid. If the conditional stability constant of the titrated metal ion is greater than that of the indicator metal ion, then at the beginning of titration when $[MY']/[M']$ is <1, the first term in brackets in equation (11) is negligible compared to the second. Just before the equivalence point the ratio $[MY']/[M']$ rapidly increases, and the assumption expressed in equation (13) is no longer valid.

When

$$K_{WY}' \frac{[MY']}{[M']} > K_{MY}' \tag{16}$$

the potential is described by the equation

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W K_{MY}'[M']}{\alpha_W K_{WY}'[MY']} \tag{17}$$

or

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W K_{MY}(1-f)}{\alpha_M K_{WY} f} \tag{18}$$

Thus the potential of the indicator electrode depends not only on the indicator metal concentration, but also on the stability constants of both metal complexes, side-reactions of the titrated metal ion, and the fraction titrated. For given conditions of titration the potential value is expressed by

$$E = E' + \frac{RT}{nF} \ln \frac{(1-f)}{f} \tag{19}$$

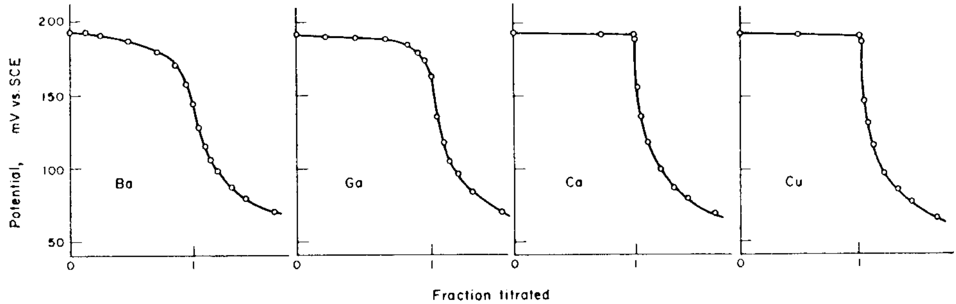
which is analogous with the curve for the titration of a weak acid with a strong base.

Then, in this instance, the $[MY']/[M']$ ratio favours the larger conditional stability constant in the region above $f = 0{\cdot}5$ in the vicinity of the equivalence point. However, at the very beginning of titration [MY′]/[M′] may be sufficiently small to make equation (15) the correct simplified equation.

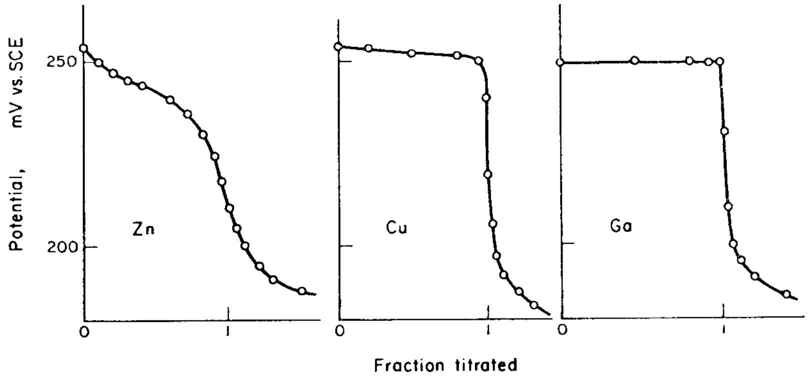
Thus, in the titration of any metal two simplified forms of equation (11) describe the course of the titration. The first part is given by equation (15), and the part just before the equivalence point by equation (17) or (18). In the intermediate region both terms in equation (11) are comparable and must be taken into account. This intermediate region is usually smaller than that corresponding to [MY′]/[M′] = 100.

The extent of each of these regions depends on the relative stabilities of the complexes. The more stable the indicator–metal complex, the greater the part of the titration curve described by equation (17) or (18). When the complex of the titrated metal is the more stable then equation (15) predominates.

This relationship may be demonstrated by the titration curves of several metals, the silver (Fig. 1a) or mercury (amalgamated on silver, Fig. 1b) indicator electrodes being used. All titrations using the silver electrode were performed in the same conditions (pH = 9·0—borax buffer, $C_M = 5 \times 10^{-4}M$, $C_{Ag} = 10^{-6}M$). The conditional stability constant for the silver-EDTA complex is then $10^{5.9}$, whereas the constants for the barium, gallium, calcium and copper complexes are $10^{6.4}$, $10^{7.6}$, $10^{9.3}$ and $10^{16.6}$ respectively. In the case of the mercury electrode the titrations were performed in 0·1M acetate buffer (pH = 3·0, $C_M = 2 \times 10^{-3}M$; $C_{Hg} = 10^{-5}M$), the conditional constant for Hg–EDTA complex being $10^{7.9}$ (the stability constant of the Hg–acetate complex being[14] $10^{8.4}$).



(a) Silver electrode, $C_M = 5 \times 10^{-4}M$, pH = 9·0 (borax buffer).



(b) Amalgamated electrode, $C_M = 2 \times 10^{-3}M$, pH = 3·0, 0·1M acetate buffer.

FIG. 1.—Titration curves for complexometric titrations.

For zinc, copper and gallium the constants are $10^{6\cdot0}$, $10^{8\cdot3}$ and $10^{11\cdot2}$ respectively. Thus for both electrodes only the relative values of the conditional stability constants govern the shape of the titration curve, which changes from that described by equation (17) to that described by equation (15).

The effect of side-reactions of the indicator metal ions, *i.e.*, the value of α_W, may be experimentally confirmed when silver electrode titrations are performed in the presence of variable amounts of chloride (Fig. 2). Under the conditions of titration no precipitation of silver chloride occurred. The initial potential values calculated from the corresponding side-reaction coefficients[14] $\alpha_{Ag(Cl)}$ are indicated with arrows on the left of Fig. 2. Except at the highest concentration of chloride the agreement of calculated and measured values is good.

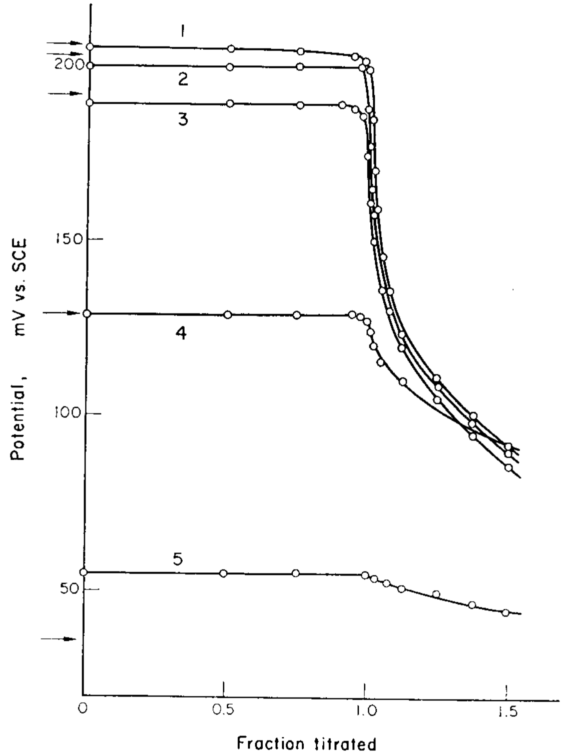


FIG. 2.—Effect of chloride ions on complexometric titration of $5 \times 10^{-4}M$ Ca^{2+}; silver electrode.
pH = 9·0, (borax), $C_{Ag} = 10^{-6}M$.
1—no chloride; 2—$10^{-4}M$ Cl^-; 3—$10^{-3}M$ Cl^-; 4—$10^{-2}M$ Cl^-; 5—$10^{-1}M$ Cl^-.

The titration curve after the equivalence point.

When considering the titration curve after the equivalence point, it is convenient to substitute in the general equation (11)

$$\frac{[MY']}{[M']} = K_{MY}'[Y'] . \qquad (20)$$

Then,

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W}{\alpha_W(K_{WY}'[Y'] + 1)} \tag{21}$$

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W}{K_{WY}[Y']\alpha_Y{}^{-1} + \alpha_W} \cdot \tag{22}$$

If the side-reaction coefficient α_W is negligible compared to $K_{WY}[Y']\alpha_Y{}^{-1}$, all titration curves coincide, and equation (22) may be expressed as

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W \alpha_Y}{K_{WY}[Y']} \tag{23}$$

or

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W \alpha_Y}{C_M K_{WY}(f - 1)} \cdot \tag{24}$$

This may be seen in Figs. 1 and 2, except the curve for $[\mathrm{Cl}] = 10^{-1}M$ in Fig. 2. In the latter case, at the point $f = 1{\cdot}5$, the value of $K_{AgY}[Y']\alpha_Y{}^{-1}$ is equal to $10^{2{\cdot}3}$, whereas α_{Ag} is equal to $10^{2{\cdot}8}$ and thus it is not possible to neglect its value. Obviously at very large values of f, which are not reached in practice, all curves will, with the limits of experimental error, follow a common curve, where the contribution of $(f - 1)$ is significant.

The equivalence point potential

For discussion of the potential changes during titration and of the precise determination of the end-point the potential value at the equivalence point must be known. This may be calculated from the relationship

$$[Y']_{eq} = [W']_{eq} + [M']_{eq}. \tag{25}$$

Substituting the corresponding stability constants and rearranging the equations, we obtain

$$E = E_W{}^0 + \frac{RT}{nF} \ln \frac{C_W}{\alpha_W} \sqrt{\frac{K_{MY}'}{K_{WY}'(K_{MY}'C_W + K_{WY}'C_M)}} \cdot \tag{26}$$

If in this equation we can assume that

$$\frac{K_{MY}'}{K_{WY}'} \geqslant 10 \frac{C_M}{C_W} \tag{27}$$

then the equivalence point potential is given by

$$E_{eq} = E_W{}^0 + \frac{RT}{nF} \ln \frac{\sqrt{C_W}}{\alpha_W \sqrt{K_{WY}'}} \cdot \tag{28}$$

This means that the potential at the equivalence point does not depend on the titrated metal ion and is the same (for given conditions) for all titrations performed with the same metal electrode.

If, conversely,

$$\frac{K_{MY}'}{K_{WY}'} \leqslant \frac{1}{10} \frac{C_M}{C_W} \tag{29}$$

the equivalence point potential is given by

$$E_{\mathrm{eq}} = E_{\mathrm{W}}{}^0 + \frac{RT}{nF} \ln \frac{C_{\mathrm{W}}\sqrt{K_{\mathrm{MY}}'}}{\alpha_{\mathrm{W}} K_{\mathrm{WY}}' \sqrt{C_{\mathrm{M}}}} \,. \tag{30}$$

The total potential change

The total change of potential during titration or the potential change in the vicinity of the end-point (*e.g.*, between $f = 0{\cdot}99$ and $f = 1{\cdot}01$)[8,11] may be used as a characteristic of the precision of titration. Consideration of two points close to the equivalence point may give a better evaluation of the precision attainable, but this procedure is complicated when the curve is asymmetric as is the case for a less stable indicator complex. In our studies we considered the potential difference between points $f = 0{\cdot}5$ and $f = 2{\cdot}0$. If conditions for a symmetric curve are fulfilled, *i.e.*,

$$K_{\mathrm{MY}}' < K_{\mathrm{WY}}' \tag{31}$$

the total potential change is equal to

$$\Delta E_{1/2,2} = \frac{RT}{nF} \ln \left(C_{\mathrm{M}} K_{\mathrm{MY}}'\right) . \tag{32}$$

The form of this equation is similar to that given by Tanaka and Nakagawa.[15] In their paper the log of the potentiometric sharpness index is also proportional to $\ln (C_{\mathrm{M}}K_{\mathrm{MY}}')$. Hannema and den Boef[11] show that the pM change at the end point is proportional to the same expression. In this discussion the proportionality factor changes when different f-values are considered, but the effect of the variables is the same. For an asymmetric curve when $K_{\mathrm{MY}}' > K_{\mathrm{WY}}'$ it seems that the best measure may be given by equation (33).

$$\Delta E_{1/2,2} = \frac{RT}{nF} \ln \left(C_{\mathrm{M}} K_{\mathrm{WY}}'\right). \tag{33}$$

Thus the concentration of the indicator metal ion influences only the absolute potential values, and not the magnitude of potential change during titration. If, however, the potential change between $f = 0{\cdot}5$ and $f = 1{\cdot}0$ had been calculated

$$\Delta E_{1/2,1} = \frac{RT}{nF} \ln \left(C_{\mathrm{W}} K_{\mathrm{WY}}'\right)^{1/2} \tag{34}$$

the potential change would have depended on the concentration of the indicator metal ion. By comparison of equations (33) and (34) it can be seen that the course of the titration curve is asymmetric unless $C_{\mathrm{M}} = C_{\mathrm{W}}$.

These conclusions are borne out by the experimental results (Fig. 3). In the titration of various concentrations of calcium, the silver indicator electrode being used, the conditional stability constants are $10^{10\cdot0}$ and $10^{6\cdot7}$ for the calcium and silver complexes respectively. The calculated and experimental potential changes between points $f = 0{\cdot}5$ and $f = 1{\cdot}2$ are given in Table I. The lowest titratable concentration of metal ion is independent of the conditional stability constant of this metal complex as long as it is greater than the corresponding constant for the indicator metal ion. Therefore we found it possible to titrate with reasonable accuracy with the silver indicator electrode, $10^{-5}M$ concentrations of calcium, zinc and copper. Their complexes have conditional stability constants greater than that of Ag–EDTA

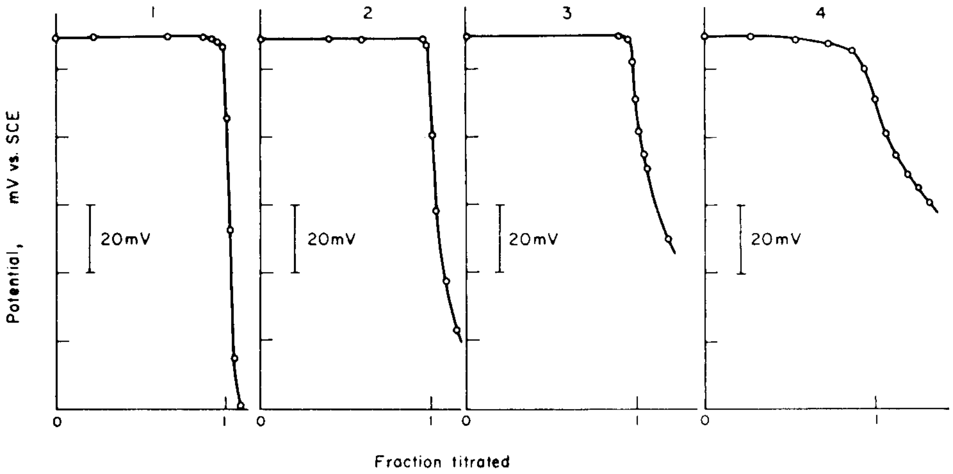


FIG. 3.—Titration curves for complexometric titration of calcium; silver indicator electrode.
pH = 9·7, (borax), $C_{Ag} = 10^{-6}M$.
1—$C_{Ca} = 2·5 \times 10^{-3}M$, 2—$C_{Ca} = 5 \times 10^{-4}M$; 3—$C_{Ca} = 1 \times 10^{-4}M$; 4—$C_{Ca} = 1 \times 10^{-5}M$.

complex, $10^{6·5}$. For barium, however, the constant decreases to $10^{6·8}$ which is comparable to the silver complex constant, and the titratable concentration cannot be smaller than $5 \times 10^{-5}M$.

In the case of the mercury indicator electrode in conditions where the stability constant of Hg–EDTA is $10^{8·5}$, zinc ($K_{ZnY}' = 10^{6·0}$) may be titrated at concentrations not less than $10^{-3}M$, and lead ($K_{PbY}' = 10^{7·3}$) not less than $10^{-4}M$, whereas copper ($K_{CuY}' = 10^{8·3}$) and gallium ($K_{GaY} = 10^{11·2}$) may be titrated at concentrations down to $10^{-5}M$.

TABLE I.—CALCULATED AND EXPERIMENTAL POTENTIAL CHANGE IN TITRATION OF DIFFERENT CONCENTRATIONS OF CALCIUM; SILVER INDICATOR ELECTRODE
(pH = 9·7)

C_{Ca}, M	Calc. ΔE, mV	Exper. ΔE, mV
$2·5 \times 10^{-3}$	140	140
5×10^{-4}	100	93
1×10^{-4}	60	60
1×10^{-5}	20	22

The effect of indicator ion concentration in asymmetric titrations

From equation (3) it follows that the potential change up to the equivalence point is related to the product of the indicator concentration and the indicator metal complex stability constant. If the value of K_{WY}' is not very large it is possible that for low concentrations of indicator metal $\Delta E_{1/2,1}$ is negative. This means that the potential from the beginning of titration is more negative than that at the equivalance point and therefore the break of the titration curve occurs after the equivalence point,

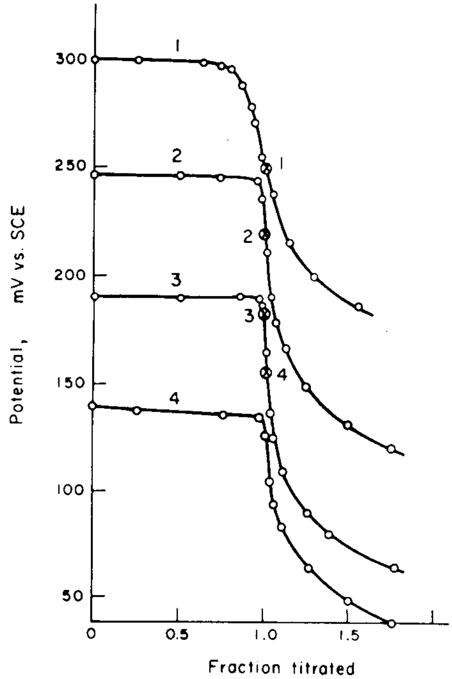


FIG. 4.—Effect of various concentrations of silver ions on titration curves of 5 × $10^{-5}M$ copper.
pH = 9·0, (borax)
1—$C_{Ag} = 10^{-4}M$; 2—$C_{Ag} = 10^{-5}M$; 3—$C_{Ag} = 10^{-6}M$; 4—$C_{Ag} = 10^{-7}M$.
Numbered points ⊗ indicate the corresponding theoretical equivalence points.

giving a systematic positive error. This may be seen from Fig. 4 where calcium was titrated in presence of decreasing amounts of silver indicator ions. Under these conditions K_{AgY}' is slightly greater than 10^6, and up to a concentration $C_{Ag} = 10^{-6}M$ a true equivalence point is obtained. In the titration at $C_{Ag} = 10^{-6}M$ the theoretical equivalence point is approx. 20 mV above the curve.

An important conclusion which follows is that the product $K_{WY}' \; C_W$ should be as close as possible to unity, but it should not be smaller. If no potential change occurs up to the equivalence point an extreme case of asymmetric curve is found, but the location of the end-point seems to be quite easy.

Acknowledgement—The authors are greatly indebted to Professor Wiktor Kemula, the Head of the Department of Inorganic Chemistry, University of Warsaw for his helpful comments and valuable discussions.

Zusammenfassung—Es wird eine Gleichung angegeben, die die Potentialänderung bei komplexometrischen Titrationen von Metallen mit potentiometrischer Endpunktsanzeige beschreibt. Das Potential der Indikatorelektrode (z. B. Silber-oder Quecksilberelektrode) hängt vom Gleichgewicht der Reaktion $MY + W \rightleftharpoons WY + M$ ab, wo W das Indikator-Metallion und M das durch Titration mit dem Liganden Y unter Bildung eines 1:1-Chelats bestimmte Metallion bedeuten. Die Einführung der Stabilitätskonstanten unter den betreffenden Bedingungen und entsprechender Nebenreaktionskoeffizienten erleichtert die Vöraussage der Anwendungsgrenzen dieser Titrationsart sowie der optimalen Bedingungen für die Bestimmung.

Résumé—On donne une équation qui décrit les changements de potentiel pendent le titrage complexométrique des métaux avec détection potentiométrique du point de virage. Le potentiel de l'électrode indicatrice (par exemple, électrode d'argent ou de mercure) dépend de l'équilibre de la réaction $MY + W \rightleftharpoons WY + M$, où W représente l'ion métal indicateur et M l'ion métal dosé par titrage avec le ligand Y, formant des chélates 1:1. L'introduction des constantes de stabilité conditionnelles et des coefficients de réaction secondaire correspondants facilite la prédiction des limites d'application de ce type de titrage ainsi que des conditions optimales du dosage.

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TERNARY COMPLEXES IN THE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF PLATINUM(IV)*

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Summary—A simple, rapid, reproducible, sensitive and selective method is proposed for the spectrophotometric determination of submicrogram amounts of platinum(IV) in aqueous media. The proposed method involves the formation of a ternary complex between the hexa-ammine–platinum(IV) cationic complex, and the counter-ion 2,4,5,7-tetrabromofluorescein ethyl ester. The reaction is instantaneous and the red ternary complex remains stable for *ca.* 1 hr. Beer's law is obeyed over the range 39–1170 ppM with molar absorptivity of *ca.* $8{\cdot}0 \times 10^4$ at 555 nm and pH 10. A relative standard deviation of 1·1% was found for the reproducibility of the method. Even without the use of masking agents, no interference is encountered from other noble metals except rhodium(III). Of 13 other cations and 8 anions tested, only iron(III) interferes.

THREE excellent review articles by Beamish[1–3] summarized and evaluated the published methods up to 1964 for the spectrophotometric analysis of platinum metal ions. In 1966, he published a book on the analysis of the noble metals.[4] Applications and modifications of some previously published methods have been reported since.[5–11] Five new spectrophotometric methods have been published between 1966 and May 1968.[12–16] Because relatively few spectrophotometric procedures for platinum have been published, more work in this field seemed desirable.

Up to 1966, Beamish recommended the use of the tin(II) chloride[17,18] and *p*-nitrosodimethylaniline[19] methods. However, neither method is truly selective, since the other platinum metals and gold(III) interfere seriously in both.[20] Furthermore, the tin(II) chloride method is not sensitive; its molar absorptivity[21] is only $8{\cdot}14 \times 10^3$.

One of the very selective spectrophotometric methods for the determination of platinum was described by Forsythe, Magee and Wilson in 1960.[22,23] The method involves formation of a ternary complex of platinum, pyridine and thiocyanate. Although this method is conditionally specific for platinum, it is not very sensitive since it is only applicable to a final concentration above 2·5 ppm of platinum(IV). The method is also quite involved and time-consuming.

In spectrophotometric analysis, ternary complexes are superior to binary complexes from the point of view of selectivity and sensitivity. In the formation of ternary complexes, the cation reacts not with one ligand species, but with two. It is thus possible for a much more absorbing organic envelope to be put around an ion than is usual. Consequently, the sensitivity and selectivity of such ternary systems are likely to be considerably superior to those of binary complexes.[24] West[24,25] has discussed this in more detail. He and his students have successfully applied the idea

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of ternary complex formation to the selective and sensitive determination of copper(II),[26,27] cyanides,[28,29] palladium(II),[30] and silver(I).[31,32] Recently, the present authors described another ternary complex system for the selective spectrophotometric analysis of trace amounts of silver(I).[33]

Several reagents have been examined briefly for their ability to form a coloured complex with platinum(IV) ions. It was found that 2,5,5,7-tetrabromofluorescein ethyl ester (TBFEE, Eosin, alcohol soluble, C.I. 45386) forms a red complex with platinum(IV) in the presence of ammonia buffer at pH 10. Higher concentrations of platinum, $\sim 10^{-3}M$, produce a red precipitate after the solution has stood for about 2 hr. With other buffer systems of the same pH (*i.e.*, 10), the red complex was not formed at all. These preliminary observations indicated the possibility of the formation of a platinum/ammonia/TBFEE ternary complex and also showed that TBFEE does not form a complex of the same colour with any other metal ion of the platinum metals or with silver(I) in the presence of ammonia buffer. Only gold(III) gave a light red colour, and this was not as intense as that of the platinum(IV) complex.

EXPERIMENTAL

Apparatus

Spectra were scanned with a Spectronic 505 recording spectrophotometer. Absorbance measurements at fixed wavelengths were made with a Unicam SP 500 spectrophotometer set at high constant sensitivity with a slit-width of about 0·05 mm. Matched glass cuvettes of 10·0-mm path-length were used.

Reagents

Ammonia-ammonium chloride buffer solution, pH 10, was prepared by mixing 35·5 g of ammonium chloride with 85 ml of ammonia solution (sp. gr. 0·9016) and diluting to 1 litre with twice distilled water.

Standard platinum(IV) solution, $10^{-3}M$, was prepared by dissolving 443·9 mg of ammonium chloroplatinate in $3M$ hydrochloric acid and diluting with twice-distilled water to 1 litre. This solution was then standardized by the formic acid procedure.[4,34] More dilute platinum(IV) solutions were prepared as needed by dilution.

2,4,5,7-Tetrabromofluorescein ethyl ester, TBFEE, $5 \times 10^{-4}M$, was prepared by dissolving 357 mg of TBFEE in 80% ethanol and diluting to 500 ml with 80% ethanol.

All other reagents were analytical reagent grade.

Procedure

A series of solutions was prepared containing 0·5–15 ml of $10^{-5}M$ platinum(IV), 5 ml of ammonia/ammonium chloride buffer solution and 2 ml of $5 \times 10^{-4}M$ TBFEE. The contents were diluted with twice-distilled water to 25 ml in volumetric flasks, mixed thoroughly and left for 10 min. The absorbance of the solutions was measured within the next hour, against a reagent blank, prepared similarly but containing no platinum, at 555 nm.

Preparation of the reagent TBFEE

The reagent used in this study was the Eosine a l'alcohol manufactured by Microcolor Laboratoires, L. Krall, Boulogne-sur-Seine, France, which was no longer available after our stock was depleted. Other Eosin brands marketed as alcohol soluble did not work at all, or gave rather poor sensitivity.

From thin-layer chromatographic studies, it was established that the French product was essentially 100% pure. The nuclear magnetic resonance and mass-spectroscopic investigations of the reagent showed it to be the potassium salt of 2,4,5,7-tetrabromofluorescein ethyl ester (TBFEE), C.I. 45386.

Instead of synthesis of the reagent, TBFEE, the feasibility of obtaining the same TBFEE reagent from other commercially available Eosin alcohol soluble dyestuffs was investigated. It was found that the Eosin, spirit soluble, obtained from British Drug Houses, gave the colour reaction with platinum(IV) in the presence of the ammonia-ammonium chloride buffer, but with a very low molar absorptivity of about 5000. This was attributed to impurities present in the B.D.H. Eosin.

In an attempt to purify the reagent chromatographically, about 200 mg of the B.D.H. Eosin, spirit soluble, was dissolved in a mixture of butanol, ethanol and twice distilled water in the ratio 80:20:10 (eluent). The mixture was passed through a chromatographic column packed with adsorption alumina. The first band was eluted, evaporated to dryness and dried at 60°. This product when dissolved in 80% ethanol gave the same colour reaction with platinum(IV) in the presence of ammonia-ammonium chloride buffer solution as the French Eosin had done, and the absorption spectrum of the reagent solution was identical with that of the French TBFEE solution, Fig. 1.

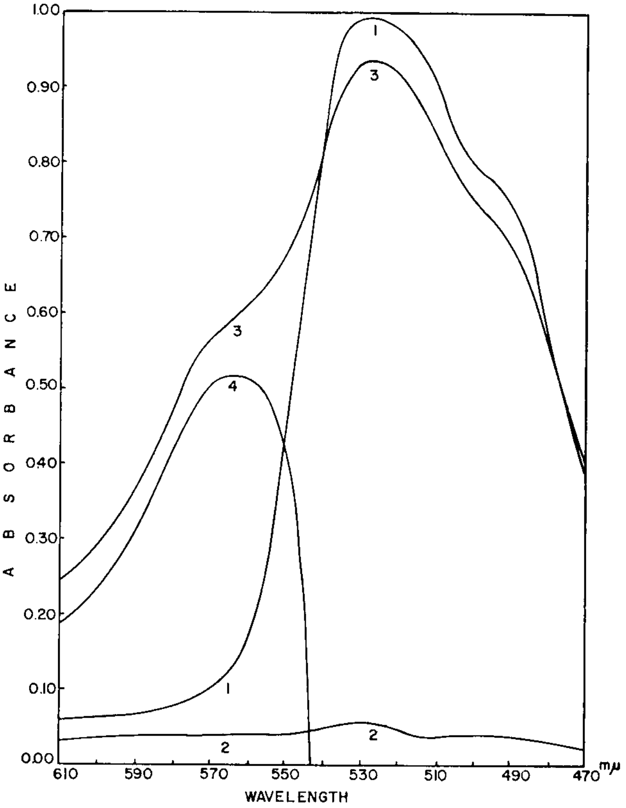

FIG. 1.—Absorption spectra.
1—TBFEE, in presence of borax; Pt/TBFEE, in presence of borax; NH_3/TBFEE (all give essentially the same spectrum): *2*—Pt/TBFEE *vs.* TBFEE, both in borax solution: *3*—Pt/NH_3/TBFEE: *4*—Pt/NH_3/TBFEE *vs.* NH_3/TBFEE.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectrum of 2 ml of $5 \times 10^{-4}M$ TBFEE per 50 ml of solution at pH 10 (borax buffer) shows an absorption peak at 525 nm with a shoulder at 495 nm, Fig. 1, Curve 1. The addition of 5 ml of $10^{-4}M$ platinum(IV) produces no significant change in colour or absorption spectrum.

The addition of 5 ml of ammonia/ammonium chloride buffer solution, pH 10, to the TBFEE solution produces no change in absorption spectrum, but addition of 5 ml of $10^{-4}M$ platinum(IV) solution changes the orange-yellow colour of this solution to red. The absorption spectrum shows a decrease in the absorption peak at 525 nm while a new peak is established at *ca.* 560 nm, Fig. 1, Curve 3. The maximum absorption is at 555 nm.

The order of addition of the reagents is not critical. However, the optimum order is platinum(IV) solution, buffer, TBFEE.

It was found that the red complex is formed only in the pH range 9–11, with maximum absorption at pH 10–10·5, Fig. 2. The colour reaction takes place instantaneously and the colour reaches a maximum after 10 min, after which it remains stable for about 1 hr and then fades gradually.

In the absence of the ammonia/ammonium chloride buffer no colour was produced. The absorbance was maximal when at least 3·0 ml of buffer solution were added. A 10–20-fold molar excess of TBFEE was required for maximum colour intensity.

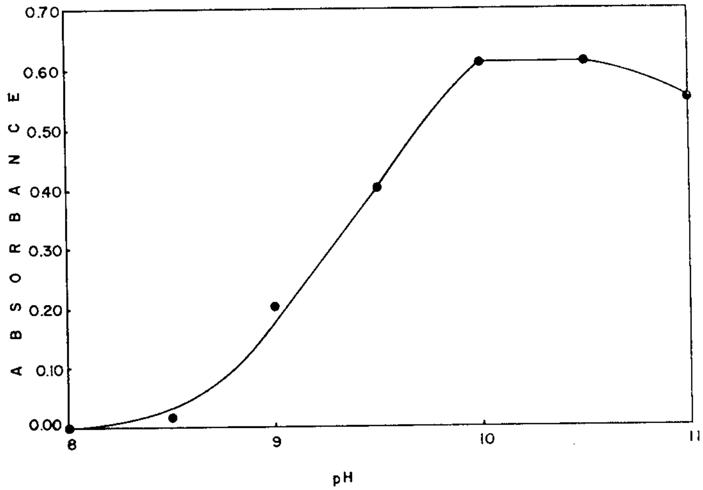

FIG. 2.—Effect of pH.

Effects of masking agents and extraneous ions

Only EDTA, fluoride and oxalate were examined as masking agents. It was found that EDTA cannot be used as a masking agent because the absorbance is decreased in the presence of 1000-fold molar excesses of EDTA over platinum(IV). On the other hand, fluorides and oxalates have no effect on the absorbance and can be used as masking agents, Table I.

The effect of the extraneous ions (20 cations and 8 anions) which may interfere either by reacting with the ammonia or with TBFEE were examined in the absence of any masking agents. The order of addition was similar to that in the recommended procedure, except that the foreign ion was added before the platinum(IV) and the acidic solution was then neutralized with 1*M* ammonia (pH test-paper). In the case of silver(I), the solution was centrifuged to separate the silver chloride before measurement of the absorbance. Iridium(IV), osmium(IV), palladium(II) and ruthenium(IV) also gave precipitates and these were centrifuged before the measurements of absorbance. The results obtained are summarized in Table I. Only iron(III) and rhodium(III) interfere seriously.

When rhodium(III) is present alone in solution, it does not form any coloured complex with the ammonia/TBFEE system, but when rhodium(III) and platinum(IV) ions are present together, the absorbance of the platinum complex is decreased as the amount of rhodium(III) increases. When rhodium(III) and platinum(IV) are present in equimolar quantities, the absorbance is less by 21% if the absorbance is measured after 10 min but by only 5 and 2% after 60 and 90 min respectively. Thus, the interference of rhodium(III) can be eliminated if it is present in equimolar quantity and the absorbance is measured after about 1 hr.

TABLE I.—INTERFERENCES

Ion added to Pt(IV) standard	Molar ratio ion:Pt	Absorbance *vs.* reagent blank	Difference
—		0·330	
Ag(I)	100	0·335	+0·005
Au(III)	10	0·400	+0·070
	1	0·340	+0·010
Ba(II)	100	0·328	−0·002
Ca(II)	100	0·330	0·000
Co(II)	100	0·340	+0·010
Cu(II)	100	0·328	−0·002
Fe(III)	10	0·190	−0·140
	1	0·250	−0·080
Hg(II)	100	0·250	−0·080
	10	0·310	−0·020
Ir(IV)	100	0·338	+0·008
K+	1000	0·330	0·000
Mg(II)	100	0·332	+0·002
Mn(II)	100	0·325	−0·005
Na+	1000	0·330	0·000
Ni(II)	100	0·335	+0·005
Os(IV)	100	0·332	+0·002
Pb(II)	100	0·340	+0·010
Pd(II)	100	0·338	+0·008
Rh(III)	100	0·050	−0·280
	10	0·130	−0·210
	1	0·260	−0·070
Ru(IV)	100	0·320	−0·010
Zn(II)	100	0·335	+0·005
Cl^-	10000	0·330	0·000
ClO_4^-	100	0·332	+0·002
CO_3^{2-}	1000	0·325	−0·005
$C_2H_3O_2$	1000	0·332	+0·002
$C_2O_4^-$	1000	0·330	0·000
F^-	1000	0·332	+0·002
NO_3^-	100	0·335	+0·005
SO_4	100	0·335	+0·005

Calibration curve

Beer's law is obeyed over the range 0·5–15 ml of $10^{-5}M$ platinum(IV)/25 ml or approximately 39–1170 ppM of platinum(IV) in the final solution, the molar absorptivity being $8·0 \times 10^4$ at 555 nm (ppM = parts per milliards).

Nature of the complex

The platinum(IV):ammonia ratio was investigated by the mole-ratio method,[35] using 2 ml of $5 \times 10^{-5}M$ platinum(IV) and 5 ml of $5 \times 10^{-5}M$ TBFEE in 50 ml of final solution. The ammonia concentration range was 5×10^{-5}–$5·0M$. The red complex was developed only when the ammonia was present in very large excess, *i.e.*, 1000-fold molar excess over platinum(IV). Further investigations would be needed to explain this finding. The platinum(IV):TBFEE ratio was investigated by both continuous variation[36,37] and mole-ratio[35] methods with $5 \times 10^{-5}M$ platinum(IV) and TBFEE and $5M$ ammonia. Both methods show a 1:4 platinum: TBFEE ratio, Figs. 3 and 4 through a 2:3 complex also appears to form.

TABLE II.—SPECTROPHOTOMETRIC METHODS FOR PLATINUM

Method	10^{-3} × Molar absorptivity	Wavelength *nm*	Interferences
Tin(II) chloride[21]	8·1	403	Platinum metals, AuCl$_4^-$, Cr(III), Ni(II)
Hexachloroplatinate[21]	11·5	262	Platinum metals and several transition metals
Potassium iodide[21]	11·9	495	AuCl$_4^-$, Bi(III), Cu(II), Fe(III), PdCl$_4^{2-}$, NaCl, Oxidizing agents
5-(*p*-Dimethylaminobenzylidene)-rhodanine[38]	23·0*	590	Ag(I), Au(III), Pd(II), Rh(III)
2,3-Quinoxalinedithiol[39]	25·6 26·4 27·5	599 585 624	Co(II), Cu(II), Ni(II), Rh(III), PO$_4^{3-}$
Dithizone[21]	29·6 30·0 31·6	260 710 490	Ag(I), Au(III), Hg(II), Pd(II) S^{2-}
p-Nitrosodimethylaniline[21]	67·0	525	Platinum metals AuCl$_4^-$, Co(II), Cr(III), Cu(II), Ni(II), I$^-$, SO$_4^{2-}$
TBFEE, ammonia	80·0	555	Fe(III) and Rh(III)
3,4-Diaminobenzoic acid[12]	114	715	Os(IV), Pd(II), Ru(IV)

* The molar absorptivity was calculated from the published data.

The complex therefore appears to be ternary rather than binary. It may be concluded that the platinum(IV) ion co-ordinates with six molecules of ammonia to form the hexa-ammine-platinum(IV) cationic complex which associates with four molecules of the counter-ion TBFEE, to form the ion-association system $[Pt(NH_3)_6]^{4+}$, 4[TBFEE$^-$].

The electrical neutrality of the platinum ternary complex was tested qualitatively by ion-exchange studies with anionic, cationic and neutral resins. In all cases, the red complex remained unchanged, confirming that the complex was uncharged.

Solvent extraction

Several water-immiscible solvents (amyl acetate, benzene, bromobenzene, carbon tetrachloride, chloroform, ethyl acetate, heptane, hexane, isoamyl alcohol, isobutyl methyl ketone, nitrobenzene, octane and toluene) failed to extract the ternary complex.

Reproducibility of the method

The relative standard deviation for solutions containing 2 ml of $5 \times 10^{-5}M$ platinum(IV), 5 ml of ammonia/ammonium chloride buffer solution and 2 ml of $5 \times 10^{-4}M$ TBFEE in 25 ml was found to be 1·1%.

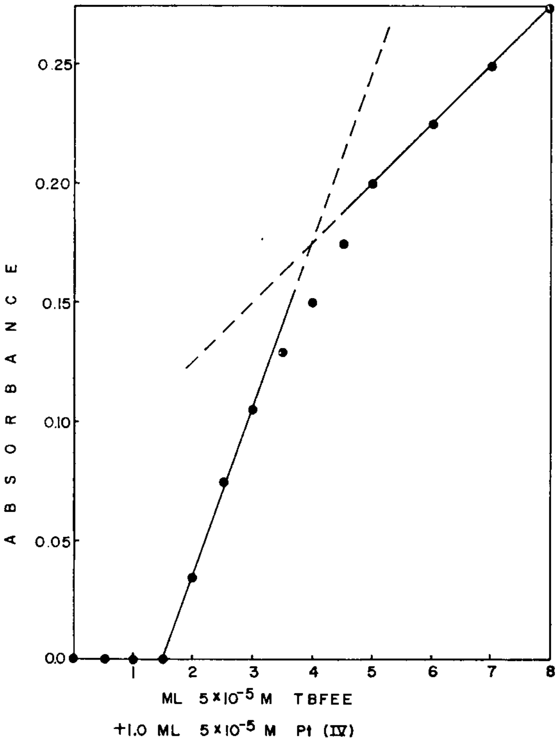

FIG. 3.—Continuous variation plot.
$5 \times 10^{-5}M$ Pt(IV); $5 \times 10^{-5}M$ TBFEE; $5M$ ammonia.

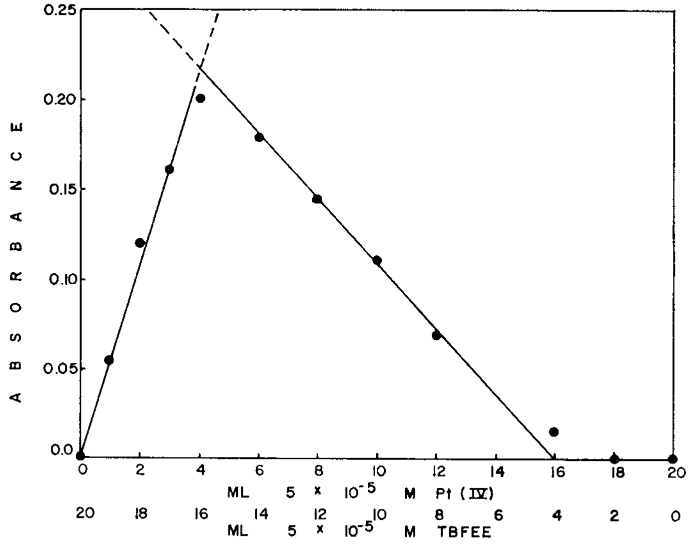

FIG. 4.—Mole-ratio plot, in presence of excess ammonia ($5M$).
$5 \times 10^{-5}M$ Pt(IV) and TBFEE; $5M$ ammonia.

The proposed method provides a simple, rapid, reproducible and highly sensitive and selective analytical procedure for the determination of trace amounts of platinum(IV) ions in aqueous solution, largely because of the formation of a ternary complex.

Gold(III) can be tolerated up to equimolar quantities without the use of masking agents. This level of tolerance may be improved in the presence of masking agents which have not yet been investigated. Similarly, the interferences of rhodium(III) and iron(III) may be eliminated.

Although the proposed method is pH sensitive to 0·5 pH unit, the ease of preparing the ammonia/ammonium chloride buffer system overcomes this limitation without the need to use a pH meter in adjusting the pH.

The column chromatographic purification of the commercially available Eosins is simple and efficient.

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Zusammenfassung—Zur spektrophotometrischen Bestimmung von Submikrogrammengen Platin(IV) in wäßrigen Medien wird eine einfache, schnelle, reproduzierbare, empfindliche und selektive Methode vorgeschlagen. Dabei wird ein ternärer Komplex zwischen dem kationischen Hexamminplatin(IV) und 2,4,5,7-Tetrabromfluorescein-äthylester als Gegenion gebildet. Die Reaktion geht momentan vor sich, der rote ternäre Komplex bleibt etwa 1 h stabil. Das Beersche Gesetz gilt im Bereich 39–1170 ppM mit einem molaren Extinktionskoeffizienten von 8,0 . 10^4 bei 555 nm und pH 10. Für die Reproduzierbarkeit der Methode wurde eine Standardabweichung von 1,1 % gefunden. Selbst ohne Maskierungsmittel findet man von den Edelmetallen außer Rhodium(III) keine Störungen. Unter 13 anderen Kationen und 8 Anionen, die untersucht wurden, störte nur Eisen(III).

Résumé—On propose une méthode simple, rapide, reproductible, sensible et sélective pour le dosage spectrophotométrique de quantités de platine(IV) de l'ordre du submicrogramme dans des milieux aqueux. La méthode proposée comprend la formation d'un complexe ternaire entre le complexe cationique hexammine-platine(IV) et l'ion opposé, ester éthylique de la 2,4,5,7-tétrabromofluorescéine. La réaction est instantanée et le complexe ternaire rouge reste stable pendant environ 1 h. La loi de Beer est suivie dans le domaine 39–1170 ppM avec un coefficient d'absorption moléculaire d'environ 8,0 × 10^4 à 555 nm et pH 10. On a trouvé un écart type relatif de 1,1 % pour la reproductibilité de la méthode. Même sans l'emploi d'agents de dissimulation, on n'a pas trouvé d'interférences de la part des autres métaux nobles à l'exception du rhodium(III). Des 13 autres cations et 8 anions essayés, seul le fer(III) gêne.

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SPECTROSCOPY IN SEPARATED FLAMES—V

THE ARGON- OR NITROGEN-SHEATHED NITROUS OXIDE–ACETYLENE FLAME IN FLAME EMISSION SPECTROSCOPY

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Summary—The separation of the premixed nitrous oxide–acetylene flame by sheathing with argon or nitrogen is described. The interconal zone of the hot, slightly fuel-rich flame exhibits low background and noise levels and an extended reducing atmosphere, providing better conditions for the excitation of atoms of elements which form refractory oxides. The limits of detection found for nine such elements are greatly superior to those obtainable in the conventional unsheathed flame under similar conditions.

In recent communications from this laboratory we have described the application of the fuel-rich separated nitrous oxide–acetylene flame in flame emission spectroscopy.[1,2] Pickett and Koirtyohann[3] have also shown that the premixed nitrous oxide–acetylene flame shows considerable promise in this field, despite its high background and noise levels. Separation of the secondary diffusion zone by a silica Smithells-type separator enables analytical emission in the hot, reducing interconal zone to be viewed without interference from the intense background radiation due to the OH radical and the reaction $CO + O \rightarrow CO_2 + h\nu$, which normally occur round it in the conventional flame. We have also found that the high noise levels obtained in the unseparated flame are suppressed in the separated flame. This flame thus possesses several advantages over the conventional flame for the determination by flame emission spectroscopy of elements which form refractory oxides in most hydrocarbon–air flames.

Mechanical separation of the secondary zone with a silica separator has, however, several disadvantages. Stable separated flames may only be supported over a limited range of fuel–oxidant mixture strengths. In addition, we have experienced some difficulty, when many organic solvents are nebulized, in maintaining a stable flame and preventing deposition of carbon on the walls and window of the separator tube. The modified burner described in this paper provides an alternative method of separation of a premixed nitrous oxide–acetylene flame, in which a stream of nitrogen or argon is driven vertically past the premixed nitrous oxide–acetylene flame burning at a circular slot. Access of atmospheric oxygen immediately above the primary zone is prevented, so that the secondary diffusion zone "lifts-off" and is supported higher up the flame where the partly combusted gases mix with the nitrogen. The hot, reducing interconal zone of the fuel-rich flame is thereby protected and extended in size. This paper describes the properties of this flame and its use in the detection by flame emission spectroscopy of a range of elements introduced into it as aqueous solutions of their salts.

EXPERIMENTAL

Apparatus

Unicam SP900A flame spectrophotometer and 0–10 mV Honeywell strip-chart recorder. The shielded burner arrangement employed replaces the conventional burner unit fitted to the commercial flame spectrophotometer and has been described previously.[4] The conventional meter type of burner head for air acetylene was replaced by a stainless steel head with a circular slot 0·75 mm wide and 11 mm internal diameter similar to that which has been described in a previous communication from this laboratory.[2]

Air, nitrous oxide and acetylene flow-rates were controlled by the cylinder reduction valves and rotameters fitted with needle valves (1–10 l./min, British Rotameter Co., Croydon, Surrey). These rotameters were calibrated in their normal operating positions by using a set of calibrated air rotameters and the conversion curves provided by the manufacturer. A conventional premixed nitrous oxide–acetylene flame was produced by first lighting a normal luminous fuel-rich air–acetylene flame (acetylene flow = 2·1 l./min, air flow = 6·6 l./min at a nebulizing pressure of 25 psig) and then gradually replacing the air with nitrous oxide *via* a T-piece and two rotameters (nitrous oxide flow = 4·0 l./min at an atomizer pressure of 15 psig). The nitrogen or argon flow was then started and the sheathing gas flow-rate set to about 15 l./min so that the secondary diffusion zone was "lifted-off" to a height of about 70 mm above the primary reaction zone. Finally, the acetylene flow-rate was adjusted to give a slightly fuel-rich flame with the best red zone (acetylene flow = 2·15 l./min with nitrogen sheathing and 2·12 l./min with argon sheathing). Sample solutions were aspirated into the flame by nitrous oxide *via* the indirect cyclone nebulizer of the SP900A flame spectrophotometer.

Reagents

Analytical grade metals or their salts were used where available to prepare stock solutions of suitable strength. These were diluted with distilled water to provide working strength solutions, except in the case of tungsten which was diluted with 0·2*M* hydrofluoric acid.

Molybdenum, 1000 *ppm.* Prepared by dissolution of ammonium molybdate in distilled water.

Aluminium, 1000 *ppm.* Prepared by dissolution of the metal foil in 1*M* hydrochloric acid.

Beryllium, 1000 *ppm.* Prepared by dissolution of the metal in the minimum quantity of *aqua regia* and dilution with distilled water.

Vanadium, 1000 *ppm.* Prepared by dissolution of the metal in 0·5*M* nitric acid.

Silicon, 50000 *ppm.* Prepared by dissolution of B.D.H. reprecipitated silica in the minimum quantity of hydrofluoric acid.

Tungsten, titanium, niobium and zirconium, 5000 *ppm.* Prepared by dissolution of the metal in the minimum quantity of hydrofluoric acid and dilution with distilled water.

RESULTS

Flame appearance

The conventional slightly fuel-rich nitrous oxide–acetylene flame supported at the slot burner described here exhibits the characteristic reducing "red feather" above the intense white–blue primary reaction zone. The pale blue–violet oxidizing secondary mantle, typical of most premixed air–hydrocarbon flames burning in air, surrounds this interconal zone. When the nitrogen sheathing gas is turned on, the secondary zone is "lifted-off" (separated) and is then supported about 70 mm above the burner where the nitrogen flow velocity is insufficient to prevent the access of atmospheric oxygen to the partly combusted gases of the interconal zone. The reducing interconal zone below this point can thus be viewed without interference from the background radiation of the secondary zone. The protective action of the nitrogen shielding also results in the production of a reducing interconal zone of extended dimensions. The red feather, which in conventional flames takes the form of a cone 30–40 mm high and 13 mm in diameter at the base, becomes a cylinder 120 × 16 mm. The intensity of the red CN emission band in this interconal zone also appears more intense in the separated flame. When argon is used instead of nitrogen, the dimensions of the interconal zone and the intensity of the CN red band are even further increased. Shielding with nitrogen or argon increases the overall height of the flame from approximately 320 to 400 mm.

Flame emission characteristics

Table I lists the main features of the background emission spectrum from the conventional and separated slightly fuel-rich nitrous oxide–acetylene flames. It is evident that the species responsible for the most intense background emission just above the primary zone in the conventional flame are OH, CO, NH, CN, C_2 and CH. In the argon- or nitrogen-shielded flame the background emission from OH and CO is suppressed owing to separation of the secondary zone. The reduction in background due to lifting-off of the continuum from CO + O is not as great with this flame as with separation of the air–acetylene flame,[5] possibly because the reaction $CO + O \rightarrow CO_2 + h\nu$ is not as favourable thermodynamically at the higher temperature. A slight reduction in the CH emission intensity is also observed on shielding, whereas the CN and C_2 background emission is considerably increased. These results agree with the visual observation of the "lifting-off" of the secondary oxidizing mantle, and also the extension and protection of the reducing atmosphere of the interconal zone which is achieved on separation. The background emission from all species is greater in the argon-shielded flame than in the nitrogen-shielded flame. This may be because nitrogen cools the flame more than argon, owing to their different thermal capacities and conductivities, and diatomic nitrogen molecules have a greater quenching effect on emission excitation than monoatomic argons.

It is difficult to state definitely which of these factors is of greater importance, but it seems unlikely that the effect could be due to differing amounts of oxygen present as an impurity in the two gases, as this would be unlikely to have the same effect on OH- as on CN-emission. Temperature measurements (above the primary zone) of the fuel-rich flame by the iron two-line method reveal that whereas argon-shielding reduces the temperature by about 150°, nitrogen-shielding reduces it by about 300°. This supports the explanation based on cooling effects.

The observed emission intensities for the flame species depend not only on concentration (if full thermal equilibrium prevails) but also on the temperature of the interconal zone and the volume of the flame from which radiation is received by the monochromator slit. Thus it is difficult to establish whether the increase in CN-emission on shielding is due to a higher concentration of CN in this flame, or to physical expansion of the reducing zone whereby radiation from a larger volume of flame plasma is received at the slit. Measurement of the background radiation in slightly fuel-rich shielded and conventional flames was made *via* a pinhole so that the monochromator could not accept the increase in radiation resulting from the greater height and width of the reducing zone in the shielded flame, and results similar to those in Table I were obtained. There is still the possibility, however, that the pinhole allows the monochromator to view the extended depth of this zone along the optical axis, and this difficulty cannot be overcome merely by quoting emission intensities per mm of flame diameter, since allowance must be made for self-absorption effects, and it is difficult to define the actual extent of the reducing zone.

Similarly, in border-line cases where the change in emission intensity on shielding is relatively small, it is difficult to separate the effect of actual concentration changes from that of the temperature reduction known to occur on shielding. This results in several species in Table I giving apparently anomalous results. For example, all of the C_2 (Swan) bands show an increase in emission intensity on argon-shielding, except that with shortest wavelength (436·52 nm) which shows a decrease. Since the effect

TABLE I

Wavelength, *nm*	Emitting species	Type of emission	Overall relative intensity in unshielded flame*	Relative intensities of lines in the three flames		
				No shield	Argon shield	Nitrogen shield
665·66	CN	Red system	2·5	100	382	147
650·23	CN	Red system	5·5	100	351	162
635·51	CN	Red system	9·5	100	346	185
619·12	C_2	Swan band	11	100	360	192
601·25	CN	Red system	14	100	270	160
587·76	CN	Red system	39	100	233	110
574·87	CN	Red system	27	100	422	198
563·55	C_2	Swan band	28	100	420	187
549·02	CN	Red system	30	100	231	119
536·50	CN	Red system	30	100	231	122
525·49	CN	Red system	29	100	219	132
516·52	C_2	Swan band	63	100	335	134
473·71	C_2	Swan band	170	100	122	69
460·61	CN	Violet band	160	100	141	72·5
444·0	CO	Continuum	105	100	57	35
436·52	C_2	Swan band	160	100	74	53
431·42	CH		220	100	84	35·5
425·0	CO	Continuum	110	100	64·6	38·5
422·5	CO	Continuum	110	100	83·3	42·1
421·60	CN	Violet system	1320	100	253	85·5
419·72	CN	Violet system	1080	†		
418·10	CN	Violet system	742	†		
416·78	CN	Violet system	512	†		
388·34	CN	Violet system	10000	100	268	102·3
387·14	CN	Violet system	5710	†		
386·19	CN	Violet system	3905	†		
359·04	CN	Violet system	1050	100	377	117
358·59	CN	Violet system	1020	†		
358·39	CN	Violet system		†		
343·5	CO	Continuum	92	100	28	12·7
336·00	NH		400	100	8·3	5·3
314·34	CH		‡	‡	100	82·3
308·90	OH	Band peak	6050	25000§	100	76
306·36	OH	Band head	5900		100	73
289·27	OH + NO	Partly β-NO system	380	100	7	5·1
282·90	OH	Band peak	510	100	4·5	3·0

* These values have *not* been corrected for the variation of instrumental sensitivity with wavelength.

† Relative intensities are not given for these peaks because they are the same as those quoted for the corresponding band-head.

‡ This peak could not be measured in the unshielded flame because of interference from the intense OH emission; in the argon-shielded flame the intensity ratio $CH_{314\cdot3} : OH_{308\cdot9} = 100:61$ was measured.

§ **The reduction on shielding is so enormous at this wavelength that this value for the relative emission from the unshielded flame can only be an approximate estimate.**

of a temperature drop on emission intensity is greater at shorter wavelengths, it is reasonable to assume that this example is a case of the temperature effect predominating. An effect of this type might explain why the CH emission at 431·4 nm decreases on shielding (when it would be expected to increase in the same way as C_2 and CN), and why certain of the CN peaks show an increase in intensity with argon-shielding but a decrease with nitrogen-shielding. However, it seems unlikely that this type of effect explains the very large decrease in NH emission on shielding of the slightly fuel-rich flame with either argon or nitrogen.

Figure 1 shows the variation in background emission intensity with acetylene flow-rate for the principal emitting species in the conventional and shielded flames. Measurements were made so that only radiation from the interconal zone was received by the slit. The sensitivity of the instrument was adjusted for each curve so that the maximum emission gave full scale deflection of the meter. Thus the curves show only the relative behaviour in the three flames. The shapes of the curves and the positions of the peaks are the important points illustrated, showing the net effect of change in flame temperature and in concentration of emitting species as the fuel flow changes.

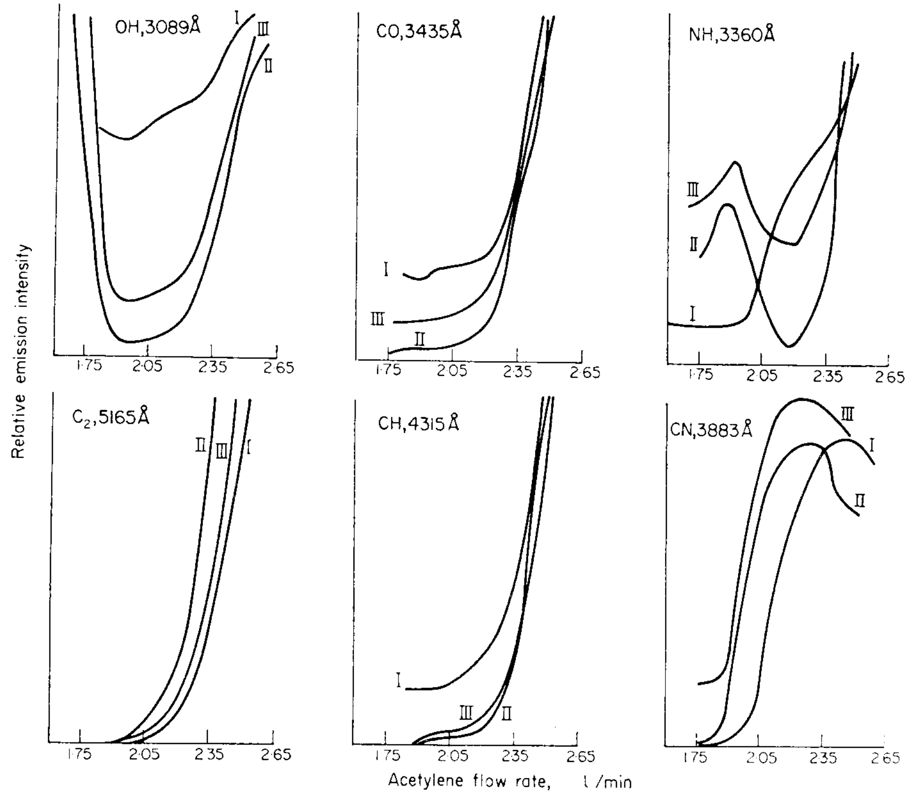

FIG. 1.—Effect of fuel flow-rate on relative emission intensity from the flame species in the nitrous oxide–acetylene flame.
I = Unshielded flame.
II = Nitrogen-shielded flame.
III = Argon-shielded flame.

The argon- and nitrogen-shielded flames produce curves almost identical in shape, confirming that the greater emission intensity obtained with argon is a purely physical effect (since all species are affected in the same way). For CN, C_2, CO and CH the curves for the shielded and unshielded flame are very similar except for the degree of fuel-richness at which certain features occur. Each of these species contains carbon, of which there is an increasing abundance as the flame is made more fuel-rich, so shielding of the flame probably has no effect except to require slightly less fuel-rich conditions to obtain the same emission (since shielding protects the reducing atmosphere from oxygen in the surrounding air), *cf.* results for CN and C_2. However, with

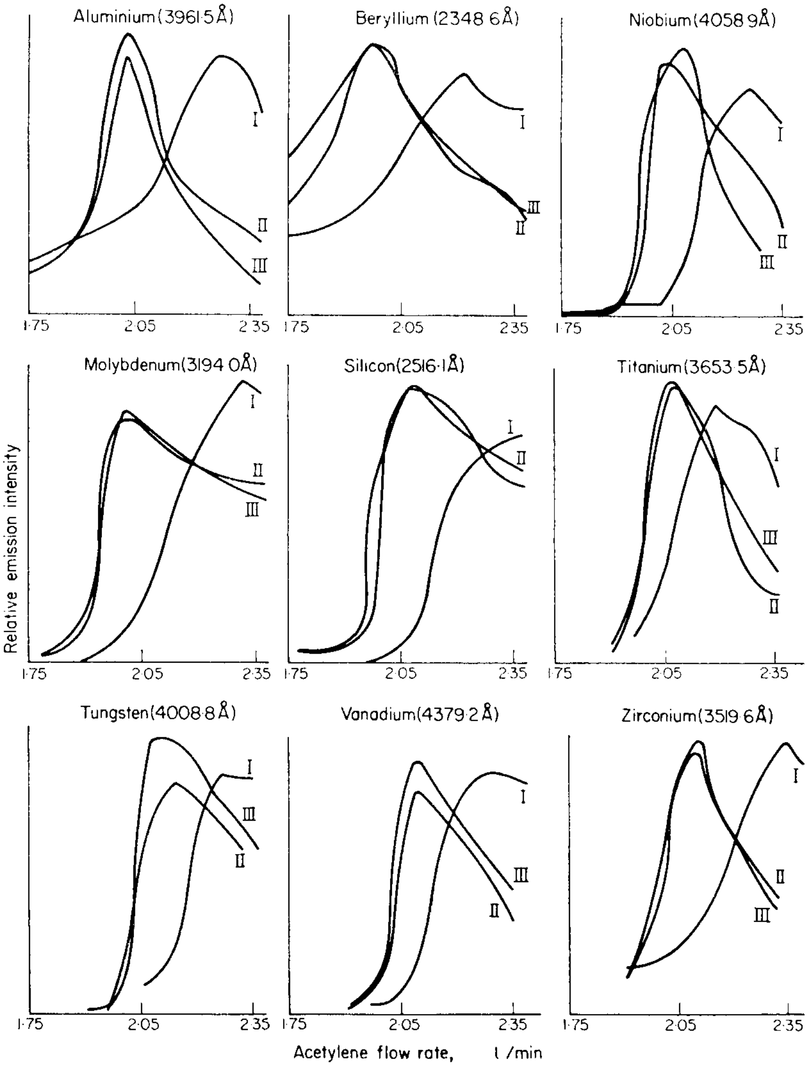

FIG. 2.—Effect of fuel flow-rate on relative emission intensity of elements introduced into the nitrous oxide–acetylene flame
I, II, III as in Fig. 1.

OH and NH emission, shielding the flame produces a curve of completely different shape. It is significant that these are the only two important species in the flame that do not contain carbon. The minimum in the OH curve for the unshielded flame becomes a very sharp trough on shielding. This may be because the trough arises from the OH emission from the inner cone of the flame (*i.e.*, from the OH formed by primary combustion) and in the ordinary flame this is masked by the much greater quantity of OH formed by secondary combustion at the outside of the flame. A similar effect is observed for NH.

Emission from elements in the flame

The atomic emission at 200–700 nm from elements introduced in aqueous solution into the conventional and separated nitrous oxide–acetylene flame was examined in the interconal region 5–25 mm above the primary reaction zone. The best line was chosen for each element and the variation in emission intensity at this wavelength was examined as the acetylene flow-rate was altered. The background emission in the separated flames was also studied. The results are illustrated in Fig. 2.

In general the atomic emission intensities increase rapidly as the mixture becomes fuel-rich, and the maximum intensity is obtained for each element in the slightly fuel-rich flame ($N_2O/C_2H_2 =$ *ca.* 1·90). The decrease on further flame-enrichment may be explained by the slightly lower temperature of the richer flames. In the unseparated flame maximum emission is not usually observed until the mixture is made richer ($N_2O/C_2H_2 =$ *ca.* 1·70). High noise levels were usually obtained with these fuel-rich conventional flames, and the maximum emission intensities were frequently lower than those obtained with the separated flames, especially with argon.

The relative intensities and detection limits for the strongest lines of the refractory elements investigated are shown in Table II.

In Fig. 3 the results from Table II for the emission in the shielded flames relative to the unshielded flame are plotted *vs.* wavelength, giving a surprisingly good linearity.

TABLE II

Element	Wavelength, *nm*	Relative emission			Detection limit, *ppm*		
		I	II	III	I	II	III
Al	396·15	100	87	197	0·4	0.04	0·02
Be	234·86	100	41	62·5	1·5	0·3	0·15
Mo	319·40	100	61	103	20	0·5	0·3
Nb	405·89	100	127	334	0·5	0·09	0·06
Si	251·61	100	43	96·5	60	10	6
Ti	365·35	100	128	206	7	1	0·5
	399·86	100	132·5	208	5	0·4	0·2
V	437·92	100	124	254	2	0·08	0·05
W	400·88	100	117·5	235	10	0·8	0·4
Zr	351·96	100	72	167	9	2	1·2

I = Ordinary nitrous oxide–acetylene flame.
II = Nitrogen-sheathed nitrous oxide–acetylene flame.
III = Argon-sheathed nitrous oxide–acetylene flame.

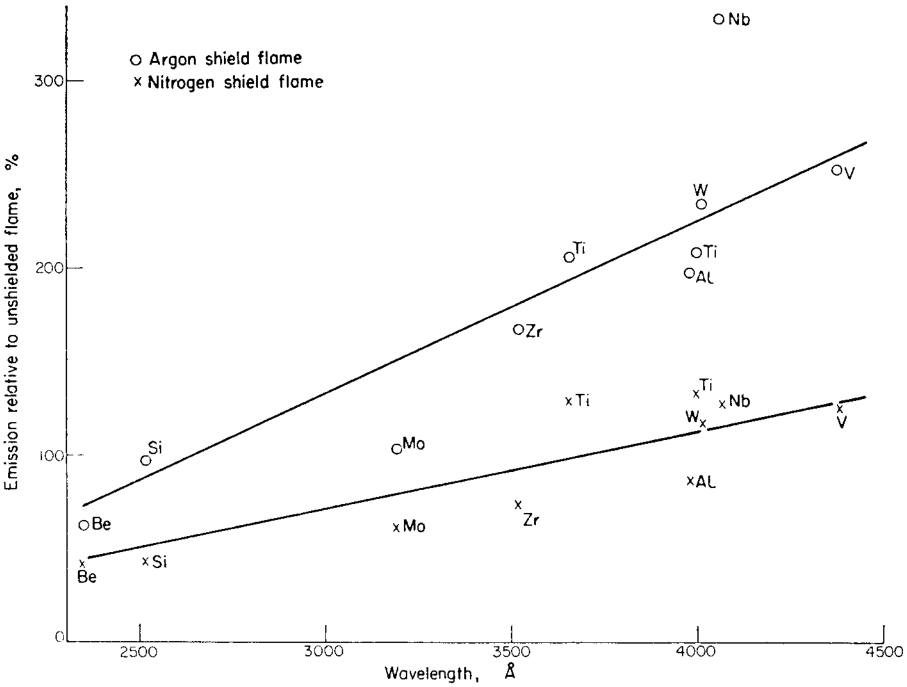

FIG. 3.—Relation between wavelength and intensity of emission of refractory elements relative to the unshielded flame in the nitrogen-and argon-shielded nitrous oxide–acetylene flames.

The theoretical importance of this is difficult to envisage since it must involve the effect of shielding on the temperature and the reducing character of the flame, but the graph is useful for predicting the enhancement to be expected for refractory elements on shielding.

CONCLUSIONS

Separation of the flame by gas-shielding instead of tube-separation has several advantages. There is no tube wall which the flame radiation must traverse, so contamination problems do not arise. The separated flame can be maintained for a wide range of mixture strengths, and organic solvents may safely be aspirated into the flame. High sensitivity is available for the detection of elements which form refractory oxides in most cooler, less reducing, conventional hydrocarbon–air flames. The lower background and noise levels, and the protective effect of inert gas-shielding on the reducing atmosphere, result in superior detection limits. The enhanced emission and lower background reduces the need for a high-resolution monochromator to obtain high signal to background ratios. The shielded nitrous oxide–acetylene flame is ideal for the atomic-emission spectroscopic determination of elements forming refractory oxides. The combination of high temperature, low background and ease of operation should also make this flame extremely useful for the determination of many other elements by atomic-emission spectroscopy.

Zusammenfassung—Die Abtrennung der vorgemischten Lachgas–Acetylen–Flamme durch Einhüllen mit Argon oder Stickstoff wird beschrieben. Die Zone zwischen den Kegeln der heißen, schwach überfetteten Flamme zeigt geringen Untergrund, geringeres Rauschen und einen großeren Bereich reduzierender Atmosphäre und bietet damit bessere Bedingungen für die Anregung der Atome von Elementen, die feuerfeste Oxide bilden. Die für neun solche Elemente gefundenen Nachweisgrenzen sind denen weit überlegen, die man unter ähnlichen Bedingungen in der üblichen nicht umhüllten Flamme erhält.

Résumé—On décrit la séparation de la flamme prémélangée protoxyde d'azote acétylène en gaînant à l'argon ou à l'azote. La zone interconique de la flamme chaude, légèrement riche en combustible, présente des faibles niveaux de fond et de bruit et une atmosphère réductrice développée, fournissant de meilleurs conditions pour l'excitation d'atomes d'éléments qui forment des oxydes réfractaires. Les limites de détection trouvées pour neuf tels éléments sont grandement supérieures à celles obtenues avec la flamme habituelle non gaînée dans des conditions similaires.

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SPECTROPHOTOMETRIC DETERMINATION OF TARTARIC ACID WITH β-NAPHTHOL

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Summary—Tartaric acid (50–800 μg) is reacted with β-naphthol (5 mg) in 90% sulphuric acid (2 ml) for 30 min on a steam-bath. The solution is cooled and diluted to 25 ml with 90% sulphuric acid and the absorbance is measured at 603 nm. Several absorption maxima are observed and the ratio and intensity of these depend on the concentration of acid during and after the reaction, and on the β-naphthol concentration. All tartaric acid isomers give essentially the same colour and absorbance. Interference studies are reported.

Tartaric acid and other compounds form various coloured products when heated with β-naphthol in concentrated sulphuric acid and these colour reactions have served as the basis for qualitative tests since the turn of the century.[1–3] However, this reaction has not apparently been used for the determination of tartaric acid, and this paper reports a detailed investigation of the necessary operating conditions.

EXPERIMENTAL

Reagents

Reagent grade chemicals were used without further purification. Tartaric acid solutions were prepared from Baker and Adamson fine crystal tartaric acid (*d*-tartaric acid) unless otherwise specified. β-Naphthol solutions were prepared by grinding crystals to a fine powder and dissolving this in sulphuric acid solution prepared from the concentrated acid (sp. gr. 1·8407–1·8437). Reactions were carried out by heating on a steam-bath for 30 min unless otherwise stated.

Apparatus

Small volumes of solutions were measured with Hamilton syringes (5 or 50 μl) which were calibrated coulometrically.[4]

Recommended procedure

Add the sample containing 50–800 μg of tartaric acid to a clean and dry 25-ml volumetric flask. Add 5 mg of freshly prepared β-naphthol in 2 ml of 90% sulphuric acid (see below for definition of concentration). Prepare a calibration curve and blank in the same manner, keeping constant the total amount of water added. Stopper the flasks and heat on a steam-bath for 30 ± 1 min. Remove from the steam-bath, cool in an ice-bath and dilute to volume with 90% sulphuric acid (or 100% for maximum sensitivity). Read the absorbance *vs.* blank at 603 nm and determine the concentration from the calibration curve.

RESULTS AND DISCUSSION

Spectra

In general, three absorption maxima were observed, at 603, 473 and 360–70 nm. These persisted under all conditions but varied in the ratios of the peak heights, as differently coloured solutions were obtained under varying conditions. A fourth peak occurred at 630–70 nm which became prominent as the final and initial concentrations of sulphuric acid were decreased and as the concentration of β-naphthol was increased. The peak at 360–70 nm occurred near the limit for the tungsten lamp and the slit was wide open for wavelengths near the peak. The wavelength of the peak was not constant and the blank exhibited a large absorption in this region; this peak was therefore not investigated in detail. It would perhaps prove useful for the ultraviolet determination of tartaric acid, a hydrogen lamp being used. Since the peak at 630–70 nm was not always present and was more subject to variation in its wavelength, it was not used either. The remaining peaks occurred at reproducible wavelengths for a given set of conditions and the one at 603 nm was by far the most sensitive and persistent, and was therefore preferred for quantitative measurements. A typical spectrum is shown in Fig. 1.

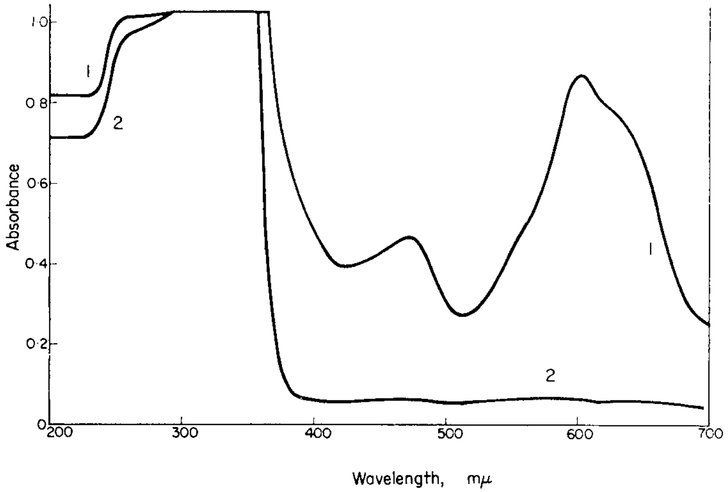

FIG. 1.—Absorption spectra
1. Tartaric acid (600 μg) reacted with β-naphthol (5 mg) by the recommended procedure and diluted to a final volume of 25 ml. Recorded *vs.* air.
2. Blank. Recorded *vs.* air.

Effect of acid concentration during the reaction

It early became apparent that the colour of the solutions depended on both the initial and final acid concentrations. Reactions were carried out in varying concentrations of sulphuric acid and results are summarized in Table I. The concentration refers to the volume ratio of acid to water, volume changes being ignored, *i.e.*, 90 ml of concentrated acid + 10 ml of water = 90% sulphuric acid. Tartaric acid (800 μg) was reacted with β-naphthol (5 mg) and then the volume was adjusted to 12·5 ml and a final acid concentration of 80%. Blanks were run for each initial acid concentration. No net colour change occurred in 50% acid and the colour changed from yellow-green to blue as the initial acid concentration was increased. An absorbance maximum was obtained at 90% acid for the 603 nm peak. The acid concentration during the reaction should therefore be kept at 90%.

Effect of final acid concentration

Tartaric acid (4·8 mg) and β-naphthol (30 mg) were reacted in 30 ml of 90% sulphuric acid. Then 1-ml aliquots were transferred to 5-ml volumetric flasks and

TABLE I.—EFFECT OF CONCENTRATION OF SULPHURIC ACID DURING THE REACTION

% H_2SO_4 in reaction	A_{603} nm	A_{473} nm	A_{360-70} nm	Colour
50	0	0	0	yellow
75	0·151	0·150	0·232	yellow-green
80	0·257	0·258	0·236	pale yellow-green
83	0·719	0·483	0·470	green
86	1·733	0·711	0·872	blue-green
90	2·155	0·765	1·276	dark blue-green
92	1·973	0·589	$2 > A > 1$	green-blue
95	1·312	0·373	1·020	deep blue
97	0·782	0·350	~1·1	blue
99·2	0·380	0·132	0·272	pale blue

Absorbances measured *vs.* the respective blanks.

diluted to volume with water and sulphuric acid to give the desired concentration of acid. A "stock" blank solution was run and 1-ml aliquots were diluted to acid concentrations corresponding to each sample. Results are given in Table II. Again the colour of the solution was dependent on the acid concentration. A plot of the absorbance *vs.* final acid concentration shows that the absorbance of the 603 and 630–70 nm peaks increased markedly at acid concentrations above 50% and was maximal at the greatest concentration of acid. The rate of increase was least at 99% acid, which would be favourable for greatest precision. While it is advantageous to dilute to volume with concentrated sulphuric acid, it is more convenient to dilute with the concentration used in the reaction; there is no great loss in sensitivity or precision. In this way, heat of mixing is minimized and the reaction volumes need not be the same (see below). The 630–70 nm peak was more prominent at the lower concentrations of acid. The other two peaks gave rounded maxima at 75–80% acid concentration.

TABLE II.—EFFECT OF FINAL ACID CONCENTRATION

Final % H_2SO_4	A_{630-70} nm*	A_{607} nm	A_{473-83} nm*	A_{350-70} nm†	Colour
18	0·047‡	0·061‡	0·248	0·779	yellow
50	0·200	0·221	0·502	0·915	reddish-yellow
75	0·900	0·827	0·707	1·171	green
90	1·265	1·282	0·620	1·103	blue-green
95	1·330	1·363	0·630	1·160	blue-green
99	1·345	1·386	0·584	1·070	green-blue

* Peak became less distinct as acid concentration increased.
† Peak became more pronounced as acid concentration increased.
‡ No peak.
All absorbances measured *vs.* blanks.

Effect of volume during reaction

Identical samples were run in 1, 2, 4, and 11 ml of 90% acid and were diluted with the same acid. The absorbances at 603 nm were 0·200, 0·170, 0·170, and 0·178 respectively, so the absorbance is not critically dependent on the volume during reaction. However, highest precision is attained if volumes are kept as nearly constant as possible, especially for volumes of 1 ml or less. This non-critical behaviour was in direct contrast to that observed for the fluorometric determination of malic acid with β-naphthol in which greater fluorescence was obtained with smaller reaction volumes.[5]

Time of reaction

A plot of absorbance *vs.* heating time is shown in Fig. 2. The reaction was initially rapid, as shown by the early appearance of the blue-green colour. Though the malic acid–β-naphthol reaction was complete in 30 min,[5] the tartaric acid-β-naphthol reaction apparently was not complete even after 1 hr. However, the reaction had slowed sufficiently after 30 min to allow good precision if the reaction was stopped at this time; the absorbance was about 75% of maximum so that loss in sensitivity was small. The precision should not be improved significantly by allowing the reaction to proceed for 1 hr, since the reaction rate at this point was approximately the same as that at 30 min.

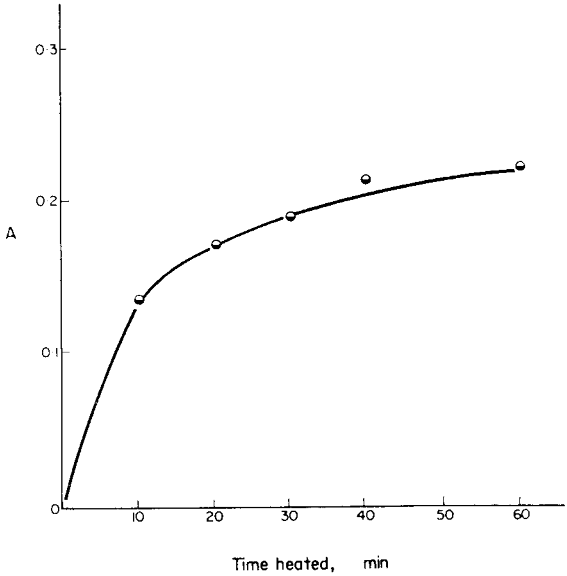

FIG. 2.—Effect of time of heating on absorbance.
Tartaric acid (400 μg) reacted with β-naphthol (2·5 mg) in 1 ml of 90% H_2SO_4 and diluted to final volume of 25 ml.

Effect of amount of β-naphthol

Tartaric acid (800 μg) was reacted with increasing amounts of β-naphthol in 5 ml of 90% acid. The absorbance was zero with about 800 μg of β-naphthol, and increased nearly linearly with increasing amounts of β-naphthol up to about a 10-fold excess (relative to a 1:1 stoichiometry) and then levelled off. A concentration of 5 mg or less of β-naphthol in 2 ml during the reaction is recommended (see below, stability study).

Stability of β-naphthol in sulphuric acid

The β-naphthol solutions go through a series of colour changes on standing. A freshly prepared solution of 2·5 mg of β-naphthol per ml of 90% sulphuric acid was initially dark yellow and became light yellow and then very pale yellow in about 1 hr. After 1 day, it was very pale grey, light grey after 3 days, and violet after 5 days. Identical tartaric acid solutions reacted with week-old and freshly prepared β-naphthol solutions had absorbances of 0·34 and 1·02, respectively. In addition, the wavelength of maximum absorption was shifted from 603 to 631 nm for the old solution. The β-naphthol solution appears to be stable for at least 8 hr.

A calibration curve prepared by using a fresh solution of 10 mg of β-naphthol in 2 ml of 90% acid yielded inconsistent results with a high blank reading, and sample readings much smaller than expected. The β-naphthol solution was initially orange, turned yellow in 30 min, green in 1–2 hr and dark green-grey in 3 days; *i.e.*, the green persisted. Tartaric acid reaction products were green. Thus, the concentrations of β-naphthol recommended above should not be exceeded.

Beer's law

A calibration curve prepared by the procedure described was linear from 50 to 800 μg of tartaric acid (final concentration 2 to 32 ppm) and passed through the origin. The calculated molar absorptivity under these conditions was $4{\cdot}79 \times 10^3$.

Effect of isomers of tartaric acid

Equal amounts of the *d*, *l*, and *dl* isomers gave the same absorbance reading at 603 nm. The meso isomer gave an absorbance about 5% less, but probably the acid was slightly impure or incompletely dried. The similarity of all isomers is in contrast to the results reported for the Fenton's reaction procedure in which the racemic acid gave half the colour intensity of the other isomers.[6]

Continuous variations study

A plot of mole fraction of tartaric acid *vs.* absorbance at 603 nm (Job's method)[7] gave a maximum at a 1:1 mole ratio of tartaric acid to β-naphthol. This is similar to the results obtained with malic acid.[5] Evidence has been presented that the malic acid rearranges and then condenses with the β-naphthol.[8,9] A similar mechanism may occur with tartaric acid. It is significant that when tartaric acid and β-naphthol were heated in separate solutions and then mixed, no colour resulted.

Interference studies

Results of investigations of materials which might be expected to interfere are given in Table III. Benzoic, oxalic and succinic acids caused a significant decrease in absorbance, but the colour of the solution remained essentially the same. Hence they appear to react with β-naphthol to give a colourless product. As seen above, the intensity of coloration is dependent on the amount of β-naphthol available for reaction with the tartaric acid. Citric acid did not interfere, but malic acid reacted with β-naphthol to give a yellow product. The colour of this product more than offset any loss of β-naphthol, causing a large positive interference. EDTA and iron(III) also appear to react slightly with β-naphthol to give a coloured product. The interference is not large and could be tolerated in some instances. Copper(II) evidently complexes the tartaric acid and prevents its reaction with β-naphthol.

Dextrose (800 μg), when reacted under the same conditions as in Table III but with no tartaric acid present, produced a dark green solution with an absorbance of 0·90 at 603 nm, and when heated with 2 ml of 90% sulphuric acid (no β-naphthol present), gave a light brown solution with an absorbance of 0·12. Thus, dextrose interferes markedly, mostly by reaction with β-naphthol but partly by charring when heated with the high concentration of sulphuric acid. Albumin (800 μg), treated as was dextrose, exhibited no charring and produced a light yellow solution in the presence of β-naphthol (absorbance = 0·072). Proteins would therefore be expected to interfere slightly when present in the same amounts as the tartaric acid.

TABLE III.—EFFECT OF FOREIGN SUBSTANCES ON COLOUR INTENSITY

Substance	$A_{603\text{ nm}}$	Colour	Error, %
—	0·405	blue-green	
Benzoic acid	0·349	blue-green	−14
Citric acid	0·402	blue-green	−1
EDTA	0·441	green	+9
Malic acid	0·735	deep green	+82
Oxalic acid	0·330	blue-green	−19
Succinic acid	0·359	blue-green	−11
Copper(II)	0·107	very pale blue-green	−74
Iron(III)	0·436	dark blue-green	+8

Tartaric acid (800 μg), β-naphthol (5 mg) and foreign substance (800 μg) treated according to procedure and diluted to 50 ml.

Since tartaric acid is often separated before chemical analysis, many of these interferences can be avoided. Precipitation as lead tartrate is a common method of separation.[10] Usually, after separation, the precipitate is shaken with water which is then saturated with hydrogen sulphide to precipitate lead sulphide and release the tartrate. The excess of hydrogen sulphide could then be boiled off. Brief studies suggest that it may not be necessary to eliminate the lead from the precipitate in the present method. A suspension of lead tartrate was prepared and 0·04 ml transferred by pipette to give a sample containing the equivalent of 800 μg of tartaric acid. The sample was run through the recommended procedure. The sample dissolved and gave the typical blue-green solution on heating, with the same spectrum as obtained with tartaric acid. On two separate days, absorbances of 0·99 and 0·70 were obtained, compared to 0·97 for a tartaric acid sample. It appears that under proper conditions, the lead tartrate precipitate will give the same results as tartaric acid. It is likely that a longer heating period will be required to ensure complete reaction of the tartrate. In any case, standards prepared in the same manner as the sample would be required. A more detailed investigation is suggested. Tartaric acid can also be separated by ion-exchange chromatography.[11]

Nitrates should be absent because in the presence of the sulphuric acid they cause charring of β-naphthol. Flasks should not be dried by rinsing with acetone since it has been demonstrated that acetone forms an 8:1 molecular compound with tartaric acid in aqueous solution;[12] any traces of acetone remaining would be likely to interfere.

Zusammenfassung—Weinsäure (50–800 μg) wird mit 5 mg β-Naphthol in 2 ml 90% Schwefelsäure 30 min auf dem Dampfbad umgesetzt. Die Lösung wird gekühlt, mit 90% Schwefelsäure auf 25 ml aufgefüllt und die Extinktion bei 603 nm gemessen. Mehrere Absorptionsmaxima werden beobachtet; ihr Verhältnis und ihre Intensität hängen von der Säurekonzentration während und nacht der Reaktion und von der Konzentration an β-Naphthol ab. Alle Isomeren der Weinsäure geben im wesentlichen dieselbe Färbung und Extinktion. Über Störungsuntersuchungen wird berichtet.

Résumé—On fait réagir l'acide tartrique (50–800 μg) avec le β-naphtol (5 mg) dans l'acide sulfurique à 90% (2 ml) pendant 30 mn au bain-marie bouillant. La solution est refroidie et diluée à 25 ml par l'acide sulfurique à 90% et l'on mesure l'absorbance à 603 nm. On observe plusieurs maximums d'absorption et le rapport et l'intensité de ceux-ci dépendent de la concentration de l'acide pendant et après la réaction, et de la concentration en β-naphtol. Tous les isomères de l'acide tartrique donnent essentiellement les mêmes coloration et absorbance. On rapporte des études d'interférences.

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APPLICATION OF A DEMOUNTABLE WATER-COOLED HOLLOW-CATHODE LAMP TO ATOMIC-FLUORESCENCE SPECTROMETRY

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Summary—A demountable water-cooled hollow-cathode lamp has been investigated as a primary source in atomic fluorescence spectrometry. The discharge current ranged from 300 to 500 mA, and the flowing argon pressure between 0·4 and 4 mbar. Sensitivities ranging from 0·03 to 2 μg/ml were obtained for 12 elements. The performances of the hollow-cathode lamp and those of the customary metal vapour discharge lamps for thallium, indium and gallium are compared. The role of the narrowness of the exciting lines in increasing the signal-to-scattering ratios is stressed.

ATOMIC-FLUORESCENCE spectrometry, which resembles atomic-emission and atomic-absorption spectrometry, is now an analytical tool in its own right. A detailed discussion of the theory and investigation of the parameters involved can be found in the works of Winefordner *et al.*[1,2], Jenkins[3] and Dagnall *et al.*[4] As in atomic absorption, the two basic parameters involved are the excitation source and the means of atomization.

The problem of atomization in both techniques is similar, but the excitation source plays a rather different role. Because of the linear dependence of the fluorescent signal on the intensity of the excitation source, the brightness of the primary source seems to be more essential than the width of the emitted lines. Successful results have been obtained with conventional metal vapour discharge lamps, which are unsuitable for atomic-absorption measurements.[5]

Unfortunately, few lamps are commercially available, although the possibility of making analytical use of the "overlapping" lines of different elements could extend the range of their applicability.[6] Also a continuum with sufficient intensity in the narrow frequency range of the absorption lines has proved useful in exciting the fluorescence of several elements.[7,8] However, some limitations and difficulties are probably to be expected in the use of this source, because of the low energy output in some frequency intervals and a less favourable signal-to-noise ratio.

From a theoretical point of view, sharp line sources should prove to be ideal, provided sufficient energy can be concentrated in the exciting lines.

Commercially available high-intensity hollow-cathode lamps as developed by Sullivan and Walsh[9] gave satisfactory results only for nickel and silver.[10,11] On the basis of the results presented in the literature, the most promising and attractive source seems to be the microwave excited electrodeless discharge tubes described by Dagnall *et al.*[12–15] owing to the intensity and narrowness of the emitted resonance lines, and the stability of the output signal.

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Recently, some 17 elements were reported by Dinnin[16] to fluoresce when excited by a demountable hollow-cathode lamp. The experience gained in our laboratory with this type of source[17,18] has led us to investigate the applicability of a demountable water-cooled hollow-cathode lamp, working at high energy, for atomic-fluorescence measurements. This paper presents preliminary results obtained for 12 elements.

EXPERIMENTAL

Apparatus

The experimental set-up previously described[6] and schematically represented in Fig. 1 was used during the present investigation.

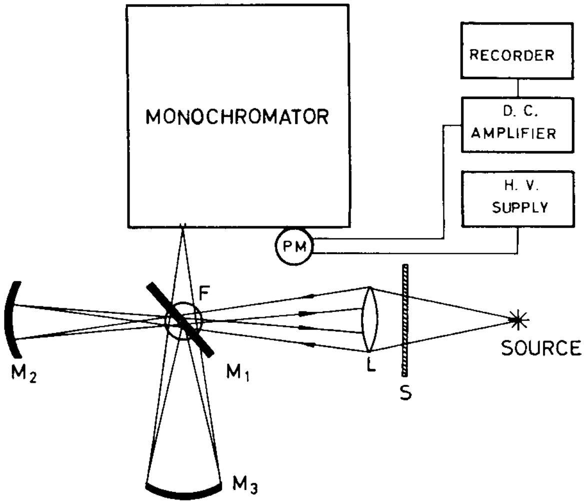

FIG. 1.—Layout of the experimental set-up.
S: shutter
L: condensing lens
F: flame
M_1: plane rotatable mirror
M_2, M_3: concave mirrors

Lamp. Figure 2 shows a sketch of the hollow-cathode lamp, specially designed and made in our laboratory for uranium isotopic analysis[18] and successfully used for atomic-absorption studies.[19] The lamp is made of a water-cooled stainless-steel hollow-cathode holder and a brass body holding a copper tubing (anode.) Two glass cylinders, with their extremities cemented to the anode block and to a brass ring, constitute the water-cooled lamp body. For the glass to metal seal a low vapour pressure resin (Torr seal—Varian Co.) was used. Neoprene O-rings ensure vacuum-tight joints between the optical window and the anode block and between the lamp body and the cathode holder. Two copper tubes soldered to the anode block connect the lamp to the vacuum system and to the gas supply line. The gas stream in front of the optical window very effectively prevents the darkening of the window by metal vapour scattered from the cathode. A disc of mica covers the cathode holder in such a way that only the cathode mouth is exposed to the discharge, so increasing the emission intensity and stability.

The lamp was energized by currents ranging from 200 to 500 mA. The flowing gas was argon at a pressure from 0·4 to 4 mbar, depending on the physical properties of the element investigated. The unique design of the lamp, which incorporates conical nickel cathodes, allows for a rapid interchanging of cathodes, without the necessity to disassemble the lamp. Moreover, reproducible and uniform cathode cooling permits steady discharge conditions to be reached in about 10 min.

Most of the elements introduced into the nickel cathodes were in the form of metal discs (6 mm diameter, 2 mm thickness), but for gallium and thallium, gallium oxide and thallium(I) sulphate were pressed onto the bottom of the cathode. Cathode preparation and lamp conditioning have been described.[17]

Flame. All tests were carried out with a total consumption Hetco burner and with an air-hydrogen flame. This is not necessarily the most efficient burner but the investigation of the optimum atomization conditions was not in the scope of the present paper.

Procedure

Light from the hollow-cathode lamp was reflected with a plane mirror on a 10-μm slit of the monochromator. Operating conditions (lamp current and gas pressure) were adjusted for each element until stable discharge conditions and maximum intensity were reached. Once the intensity of the analytical line reached a stable value, the mirror was taken off and the flame lit, the slit being opened to 400 μm. A d.c. amplifier was used, and the recorder zeroed with the lamp shutter closed and with water aspirated into the flame. Then the shutter was opened and the signals for water (A) and sample solution (B) were recorded. Finally the lamp was shuttered and the signal due to thermal emission from the sample (C) was recorded. The net fluorescent signal is $B - (C + A)$.

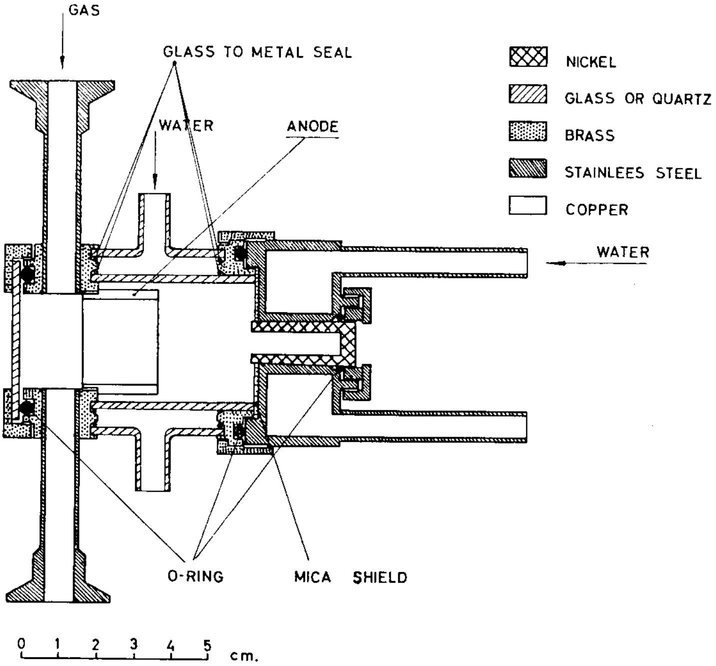

FIG. 2.—Sketch of the water-cooled hollow cathode lamp.

RESULTS AND DISCUSSION

For a better evaluation of the hollow-cathode lamp, fluorescence measurements were also performed, whenever possible, for each element with the corresponding metal vapour discharge lamp. Unfortunately the limited number of discharge lamps available restricted the comparison to thallium, indium and gallium. Table I summarizes the results obtained and the experimental parameters. The sensitivity data reported in the table show clearly that a hollow-cathode lamp working at high current discharge provides an excellent source to excite the fluorescence of the elements considered.

Moreover, the limits of detection of gallium, indium and thallium are better than or of the same order of magnitude as those obtained with the discharge lamps, despite the greater intensity of the latter.

The superiority of the sharp-line source over the broad-line source becomes more evident if the intensities of both sources as well as the fluorescence to noise ratios are considered. Emission intensities of both sources were recorded by limiting the projection of the discharge pattern on the 10-µm slit of the monochromator to 1-mm height, and measuring the fluorescence signals from 10 µg/ml solutions of each element. In the evaluation of the emission intensities the real pattern of the discharge as produced by both sources was not taken into account. In fact, while the hollow cathode lamp produced a luminous spot about 6 mm high, that from the discharge lamps extended beyond the 20-mm slit height. In other words, assuming a flame diameter of about 10 mm, flame volumes from 10 (Ga) to 50 (In) times larger were irradiated by the discharge lamps. Results obtained are summarized in Table II.

Table I.—Sensitivity data and operating conditions

Element	Analytical line, *A°*	Lamp current, *mA*	Slit, *µm*	Detection limit,* *µg/ml*	
				DHCL	Philips
Ag	3281	300	400	0·03	—
Co	2407	500	400	0·3	—
Cr	3579	500	400	1	—
Cu	3247	500	400	0·1	—
Fe	2483	500	400	2	—
Ga	4172	500	400	1	2
In	4511	500	400	0·3	0·5
Mg	2852	200	400	0·03	—
Mn	2795	500	400	0·05	—
Ni	3415	500	400	1	—
Pb	4057	500	400	1	—
Tl	3776	300	400	0·1	0·1

* Values are referred to that concentration which produced a signal due to fluorescence twice as large as the variations in the noise signal.

Table II.—Relative intensities of hollow-cathode and discharge lamps

Element, 10 *µg/ml*	Intensity of the exciting lines, *µA*	Intensity ratio *a/b*	Fluorescence intensity *µA*	Fluorescence intensity ratio, *a/b*	Intensity of scattering, *µA*	Fluorescence-to-scattering ratio
Tl	*a* 46·5	18·25	*a* 13·5 . 10^{-3}	6·43	*a* 34·5 . 10^{-3}	*a* 0·39
	b 2·55		*b* 2·1 . 10^{-3}		*b* 1·8 . 10^{-3}	*b* 1·17
Ga	*a* 28·05	40·4	*a* 3·6 . 10^{-2}	2·4	*a* 12·6 . 10^{-2}	*a* 0·286
	b 0·705		*b* 1·5 . 10^{-2}		*b* 0·2 . 10^{-2}	*b* 7·5
In	*a* 27·45	9·92	*a* 33 . 10^{-3}	13·2	*a* 38 . 10^{-3}	*a* 0·8
	b 2·79		*b* 2·5 . 10^{-3}		*b* 2 . 10^{-3}	*b* 1·25

a Philips metal vapour discharge lamp
b Demountable hollow-cathode lamp.

These results seem conclusively to indicate that the sensitivities obtained with the two types of excitation sources are not to be attributed to the output intensities but mainly to the difference in the scattering values produced. This is to be expected because for a given monochromator band-width, if it is assumed that exciting radiation of the same order of magnitude is effectively absorbed in all cases by ground-state atoms in the flame, any unadsorbed energy in the frequency range of the monochromator will contribute only to the scattering, and this will decrease in the order continuum > broad-line > sharp-line source. It seems to be preferable to have at disposal, in atomic fluorescence as well as in atomic absorption, line excitation sources with half-widths narrower than that of the absorbed line.

CONCLUSIONS

A demountable water-cooled hollow-cathode lamp working at high energy can be effectively used as excitation source in atomic-fluorescence spectrometry. However, this is not because a hollow cathode, even at high discharge current, can rival in intensity the most intense light sources used in atomic-fluorescence investigations, but mainly because of the much more favourable fluorescence-to-scattering ratios. Lamp stability is quite satisfactory and the time loss in interchanging the cathodes and subsequent stabilization is reduced to a minimum. Moreover, no difficulty in cathode preparation and exciting conditions were encountered for the elements investigated in the present work. On the other hand some difficulty in obtaining high intensity output from some other elements would probably limit the applicability of such a source, since fluorescence intensity is directly related to the excitation intensity.

It is concluded that it is strongly advisable that any excitation source providing a spectral energy chiefly concentrated in resonance lines, should emit these lines with a half-width smaller, as in atomic-absorption technique, than that of the absorbing lines.

Zusammenfassung—Eine demontierbare wassergekühlte Hohlkathodenlampe wurde als primäre Lichtquelle bei der Atomfluoreszenzspektrometrie untersucht. Der Entladungsstrom lag bei 300–500 mA, der Druck des strömenden Argons bei 0,4–4 mbar. Für 12 Elemente wurden Empfindlichkeiten von 0,03-2 μg/ml gefunden. Für Thallium, Indium und Gallium wurde die Arbeitsweise der Hohlkathodenlampe mit der üblichen Metalldampf-Entladungslampen verglichen. Nachdruck wird auf die Schärfe der Anregungslinien gelegt, was das Signal-Streuungs-Verhältnis verbessert.

Résumé—On a étudié une lampe à cathode creuse refroidie à l'eau, démontable, comme source primaire en spectrométrie de fluorescence atomique. L'intensité de décharge est comprise entre de 300 et 500 mA, et la pression de l'argon en flux se situe entre 0,4 et 4 mbar. On a obtenu des sensibilités allant de 0,03 à 2 μg/ml pour 12 éléments. On a comparé les performances de la lampe à cathode creuse et celles des lampes à décharge à vapeur métallique usuelles pour le thallium, l'indium et le gallium. On fait ressortir le rôle de la finesse des raies excitatrices sur l'accroissement des rapports signal-lumiere diffusée.

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PRÜFUNG DER FLAMMENPHOTOMETRISCHEN ANIONENSTÖRUNG—I

UNTERSUCHUNG DER ALUMINIUMSTÖRUNG

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Zusammenfassung—Zur Deutung der Anionenstörung wurde die Emissionsvermindernde Wirkung des Aluminiums bei Calciumlösungen untersucht. Die Messungen wurden in einer turbulenten H-O-Flamme bei verschiedenen Höheneinstellungen durchgeführt. Die Meßergebnisse bestätigen die Bildung eines Ca-Al-Komplexes mit dem Atomverhältnis 1:2. Nach unserer Meinung ist die Anionenstörung durch Gleichgewichtserscheinungen in der Gasphase zu erklären.

Die flammenphotometrischen Eigenschaften der Anionen wurden von zahlreichen Verfassern untersucht. Die Anionen üben nämlich einen Einfluß auf die Reaktionen in der Flamme aus[1] und können in bedeutendem Maße die Metallemission vermindern. Dieser Einfluß wird gewöhnlich als Anionenstörung bezeichnet. Mit der Untersuchung dieser Erscheinung beschäftigten sich u.a. Alkemade und Mitarbeiter,[2,3,4] Schuhknecht und Mitarbeiter,[5] Margoshes und Vallee[6] usw. Die Möglichkeit der Beseitigung der Anionenstörung wurde außer von den erwähnten Verfassern auch von Dinnin,[7] West und Cooke,[8] Poluektov und Mitarbeiter,[9] sowie früher von uns studiert.[10,11,12]

Der emissionsvermindernde Einfluß der Anionen ist durch verschiedene Methoden auszuschalten. Es kann die Methode des Strahlungspuffers verwendet werden, wobei man sowohl beim Standard, als auch bei der zu untersuchenden Lösung von dem störenden Anion eine gleiche Menge in Überschuß gebraucht. Dieser Weg ist im Falle des Phosphats nicht zu beschreiten. Nach einem anderen Verfahren wird das störende Anion mittels eines Ionenaustauschers durch ein "nicht störendes" Anion (das Chlorid) ersetzt.

Die Anionenstörung wird in der Literatur auf verschiedene Weise erklärt. Laut einer dieser Erklärungen[13] soll die Anionenstörung als Folge der Gleichgewichtserscheinungen in Gasphase auftreten, wobei die thermische Dissoziation eine entscheidende Rolle spielt. Alkemade, Schuhknecht, sowie Poluektov sind hingegen der Meinung, daß in der Flamme ein schwer sublimierendes Salz mit schlechter Wärmeleitfähigkeit entsteht. Infolgedessen nimmt die Menge der emissionsfähigen Komponenten in dem untersuchten Flammenbereich ab. Diese Meinung beruht auf folgender Feststellung: wenn man die Lösungen mit den störenden Anionen und die Lösung des zu untersuchenden Metalls mittels zweier Zerstäuber getrennt voneinander in die Flamme führt, tritt keine Anionenstörung auf. Deshalb wurde von den erwähnten Verfassern die Erklärung der Anionenstörung auf der Grundlage des Gleichgewichtes abgewiesen.

Nach unserer Meinung kann aus letzterer Untersuchung und aus den mit Änderung der Flammenhöhe durchgeführten Untersuchungen nur in jenem Fall eine eindeutige Schlußfolgerung gezogen werden, wenn die beim thermischen Gleichgewicht entstandenen Komponenten in der Flamme keine weitere Reaktion aufweisen. Deswegen ist es besonders schwer, im Falle von Sulphat und Phosphat weitgehende Schlußfolgerungen zu ziehen. Bei den Letzteren sind nämlich infolge der Temperaturerhöhung Oxyde verschiedenen Zustandes und verschiedener Zusammensetzung stabil. Die Metalloxyde aus der thermischen Dissoziation können also mit den Sulphat- oder Phosphatoxyden keine Gleichgewichtsreaktion eingehen, denn sie zersetzen sich von der Flammentemperatur abhängig in andere Oxyde. Der Verlauf dieser letzteren Reaktion—auch im Falle einer einfachen Bruttoreaktion—kann kinetisch kompliziert sein. Deshalb wählten wir zur Klärung der Anionenstörung die Untersuchung der Aluminiumstörung, da man dabei nicht mit einer Valenzänderung in dem als Anion fungierenden Oxyd rechnen muß.

Bezüglich der Theorie, daß sich die Anionenstörung aus einem Glied der Reaktionsreihe ergibt, die dem Anregungsprozess vorausgeht, haben wir schon früher überzeugende Daten erhalten.[10] Nach diesen Ergebnissen hatte die Qualitätsänderung der Anionen keinen Einfluß auf die qualitative Struktur der Molekülemission von Magnesium, sondern rief nur die Änderung der Intensität seiner Emissionswerte hervor. Die stärkste Emission zeigte das Magnesiumchlorid—welches schon bei niedriger Temperatur zum Magnesiumoxyd hydrolisiert—und die Magnesiamixtur.

In der Literatur kann man auch bezüglich des Strahlungspuffers gegensätzliche Daten finden. Laut Alkemade und Jeuken[2] ist Aluminium als Strahlungspuffer nicht zu gebrauchen, obwohl wir zahlreiche Untersuchungen gemacht haben, bei denen festgestellt wurde, daß sogar bei der Phosphatstörung, die sonst die meisten Probleme verursacht, am günstigsten eben der aluminiumhaltige Strahlungspuffer angewandt werden kann.

Bei der Diskussion der Meßergebnisse müssen die verschiedenen Meßbedingungen in Betracht gezogen werden. Das mit laminarer Flamme arbeitende indirekte Zerstäubungssystem, bei dem sich vor den Flammenreaktionen in der Nebelkammer aus kolloidchemischen Gründen komplizierte Nebenreaktionen abspielen, ist nämlich ganz anders zu betrachten, als das direkte Zerstäubungssystem, bei dem diese Komplikationen entfallen. Die Klärung der Ursachen der Anionenstörung scheint über die theoretisch interessanten Aspekte hinaus auch vom analytischen Gesichtspunkt wichtig.

EXPERIMENTELLER TEIL

Zu unseren Untersuchungen wurde das Beckman Atomabsorptionsgerät mit dem direkten Zerstäuberbrenner angewandt. Weil der Brennerbehälter in Richtung der Flammenachse zu bewegen ist, konnte die Emission alle 10 mm in einem Bereich der Flammenhöhe von 10–70 mm gemessen werden.

Es wurde eine turbulente Wasserstoff-Sauerstoff-Flamme verwendet, mit $H_2:O_2 = 6:1$. Die Zerstäubungsgeschwindigkeit war 2 ml H_2O/Min. Diese Daten entsprachen dem Optimum des vorher festgestellten Zusammenhangs zwischen Emission und Gasdruck. In den einzelnen Meßhöhen wurden die Werte der Flammentemperatur mit der Linieninversionsmethode bestimmt.[1]

Zur Untersuchung der Anionenstörung wurde aus *p.a.* Calciumcarbonat eine 10^{-3} m Calciumchloridlösung—gelöst mit einer äquivalenten *p.a.* Salzsäurelösung—bereitet. Zur Bereitung der Aluminiumchloridlösung wurde Aluminiummetall von 99,99%-iger Reinheit mit *p.a.* Salzsäure um einige % über der Stöchiometrischen Menge in einem Quarzkolben aufgelöst. In den bei den Emissionsmessungen gebrauchten Calcium- und Aluminiumhältigen Lösungen wurde die Konzentration des Aluminiums von 10^{-4} bis $2 \cdot 10^{-2}$ m geändert bei einer konstanten Calciumkonzentration von 10^{-3} m. Die Messungen wurden am Calciumoxyd-Moleküband bei 624 nm durchgeführt.

AUSWERTUNG DER UNTERSUCHUNGSERGEBNISSE

Aus den in der Abb. 1 ersichtlichen Untersuchungsdaten ergibt sich, im Gegensatz zu den Feststellungen von Alkemade,[2,3,4] daß keine eindeutige Verminderung des Anionenstörung mit der Änderung der Flammenhöhe auftritt. Nach der Abbildung scheint das Verhältnis des störenden Anions und des zu untersuchenden Metalls eine viel wichtigere Rolle zu spielen.

Wie sich aus der Tabelle I ergibt, hat die untersuchte Flamme eine viel höhere Temperatur als die in der Publikation von Margoshes und Vallee[6] angegebenen Schmelzpunkte. Könnte die Erscheinung damit erklärt werden, müßte längs der Flammenachse eine bedeutende Abnahme der Störung auftreten. Dies wurde jedoch im Falle der Aluminiumstörung nicht beobachtet. Dieselbe Schlußfolgerung bekommt man, wenn man die Erscheinung mit der Wärmeleitfähigkeit der Kristallite begründen wollte. Weiterhin ist es recht merkwürdig, daß, obwohl die Wärmeleitfähigkeiten von Kaliumchlorid, Kaliumbromid und Kaliumjodid[15] sehr stark voneinander abweichen, trotzdem bei gleicher Konzentration kein flammenphotometrischer Emissionsunterschied gefunden werden kann. Diese Beobachtungen veranlaßten uns, die Ursache der Erscheinung auf das thermische Dissoziationsgleichgewicht von Calciumaluminat zurückzuführen. Wir versuchten die Erscheinung quantitativ auszuwerten.

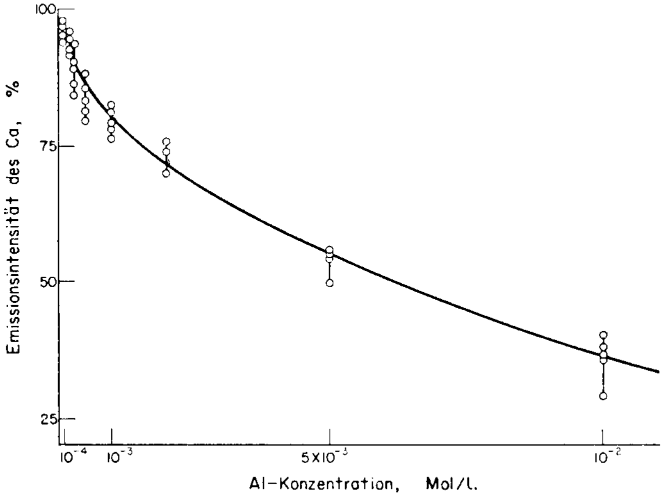

Abb. 1.—Die prozentige Änderung der Emissionsintesität der aluminiumgehaltigen Calcium-Lösungen, bei verschiedenen Flammenhöhen.

Die bei der Ableitung gebrauchten Bezeichnungen sind folgende:

[Ca] = Partialdruck (atm) der Ausgangskonzentration von Calcium im entsprechenden Flammenbereich.

[CaO] = Partialdruck (atm) des in der Flamme tatsächlich vorhandenen Ca, in Oxydform gemessen.

[Al] = Partialdruck (atm) der Ausgangskonzentration von Aluminium im entsprechenden Flammenbereich.

[Al_2O_3] = Partialdruck (atm) des in Oxydform in der Flamme anwesenden Aluminiums.

TABELLE I.—DIE BEI FLAMMENHÖHEN VON 20–75 mm GEMESSENEN EMISSIONWERTE DER ANIONFREIEN UND DER AL-HALTIGEN CA-LÖSUNGEN, UND DIE TEMPERATURWERTE DER ANGEWANDTEN H-O-FLAMME

Flammenhöhe, *mm*	Emissionsintensität (in Skalenteil und in %) der 10^{-3} Ca-Lösungen											Flammentemperatur, °*K*
	ohne Al		mit Al im Vergleich zu Ca									
			1:0,1	1:0,2	1:0,3	1:0,5	1:1	1:2	1:5	1:10	1:20	
20	Skt %	6,4 100	6,0 93,9	5,9 92,3	5,4 84,4	5,1 79,7	4,9 76,5	4,5 76,5	3,0 50,0	1,9 29,7	1,3 20,3	2460
30	Skt %	13,0 100	12,6 97,1	12,5 96,1	11,7 90,0	11,1 85,4	10,6 81,6	9,7 74,4	7,2 55,4	4,8 37,0	3,1 23,8	2900
40	Skt %	15,9 100	15,5 97,5	15,0 94,4	14,9 93,8	14,1 88,7	13,0 81,8	12,2 76,7	9,1 57,0	6,5 40,8	4,0 25,2	3030
50	Skt %	17,3 100	16,9 97,8	16,3 94,4	15,6 90,2	14,8 85,6	14,2 82,1	13,3 77,0	9,6 55,0	6,6 38,2	4,2 24,3	3110
60	Skt %	16,2 100	15,5 95,8	15,4 95,1	14,5 89,5	13,8 85,3	12,8 79,0	12,4 75,6	9,0 55,5	6,5 40,1	3,9 24,1	3100
70	Skt %	12,0 100	11,5 96,0	11,0 91,8	10,4 86,7	10,0 83,4	9,6 80,0	9,1 75,8	6,6 55,0	4,6 38,3	2,9 24,2	3050
75	Skt %	9,6 100	9,2 95,8	8,9 92,7	8,3 86,4	7,8 81,3	7,5 78,1	7,1 74,0	5,2 54,1	3,5 36,5	2,2 22,9	2980

M = Calciummenge, in der Flamme als Aluminat gebunden.

$$M = [\mathrm{Ca}] - [\mathrm{CaO}]$$

in jenem Fall, wenn sich das Aluminium im Vergleich zu Kalzium im Überschuß in der Lösung befindet; bzw. Aluminiummenge, in der Flamme als Aluminat gebunden

$$M = [\mathrm{Al}] - [\mathrm{Al_2O_3}]$$

in jenem Fall, wenn sich das Calcium im Vergleich zu Aluminium im Überschuß in der Lösung befindet.

Im Falle von Aluminiumüberschuß kann das Verhältnis zwischen Calcium und Aluminium bei Vernachlässigung der gebundenen Aluminiummenge in folgender Weise niedergeschrieben werden:

$$\frac{[\mathrm{CaO}]}{[\mathrm{Al_2O_3}]} = \frac{[\mathrm{Ca}] - M}{[\mathrm{Al}]} = \frac{[\mathrm{Ca}] - [\mathrm{Al}] + [\mathrm{Al_2O_3}]}{[\mathrm{Al}]} \sim \frac{[\mathrm{Ca}]}{[\mathrm{Al}]} = V$$

Bei der Untersuchung im Konzentrationsbereich mit Calciumüberschuß kann eine ganz ähnliche Funktion aufgeschrieben werden:

$$\frac{[\mathrm{Al_2O_3}]}{[\mathrm{CaO}]} = \frac{[\mathrm{Al}] - M}{[\mathrm{Ca}]} = \frac{[\mathrm{Al}] - [\mathrm{Ca}] + [\mathrm{CaO}]}{[\mathrm{Ca}]} \sim \frac{[\mathrm{Al}]}{[\mathrm{Ca}]} = V'$$

Das thermische Dissoziationsgleichgewicht ergibt sich aus:

$$K = \frac{[\mathrm{CaO}]\,.\,[\mathrm{Al_2O_3}]}{M} = \frac{[\mathrm{CaO}]\,.\,[\mathrm{Al_2O_3}]}{[\mathrm{Ca}] - [\mathrm{CaO}]}$$

daraus folgt:

$$K\,.\,[\mathrm{Ca}] = K\,.\,[\mathrm{CaO}] + \{[\mathrm{CaO}]\,.\,[\mathrm{Al_2O_3}]\}$$

K = ist die Dissoziationskonstante von $\mathrm{CaAl_2O_4}$ in der Gasphase (atm).
Nach Einführung von V kann das Resultat, auf [CaO] bezogen, mittels nachfolgender Gleichung anschaulich gemacht werden:

$$[\mathrm{CaO}] = \frac{-KV \pm \sqrt{K^2V^2 + 4\,KV\,.\,[\mathrm{Ca}]}}{2}$$

Also

$$[\mathrm{CaO}]^2 \sim K\,.\,V\,.\,[\mathrm{Ca}]$$

daraus folgt:

$$2 \log [\mathrm{CaO}] = \log K + \log V + \log [\mathrm{Ca}]$$

Da die ursprünglich bemessene Calciummenge einen konstanten Wert hat, kann der Funktionzusammenhang zwischen den Werten von [CaO] und V geprüft werden. Ein ähnlicher Zusammenhang findet sich auch im Falle eines Calciumüberschusses. Dann sieht die Endgleichung folgendermaß aus:

$$2 \log [\mathrm{CaO}] = \log K - \log V' + \log [\mathrm{Ca}]$$

wobei man ebenfalls den Zusammenhang zwischen [CaO] und log V' prüfen kann. Die [CaO]-Konzentration wurde mittels der flammenphotometrischen Emission

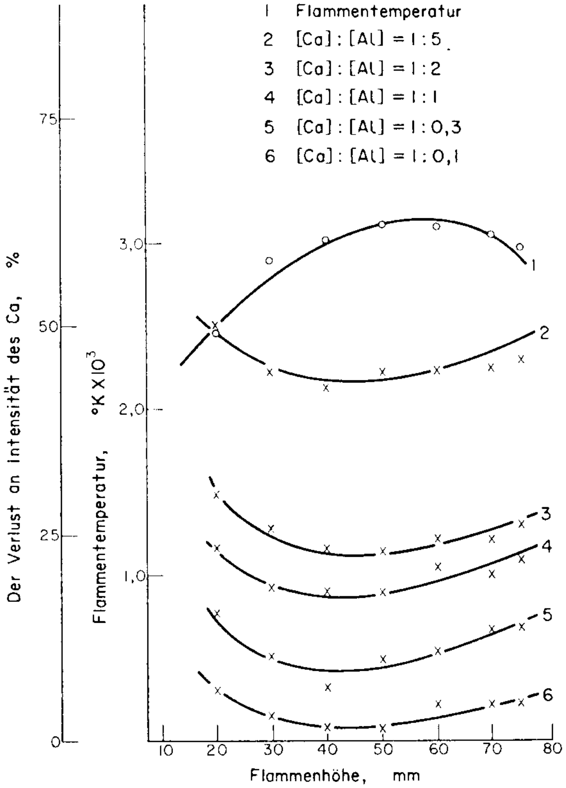

ABB. 2.—Der in Prozent berechnete Verlust an Intensität des Ca und die Änderung der Flammentemperatur, bei verschiedenen Flammenhöhen.

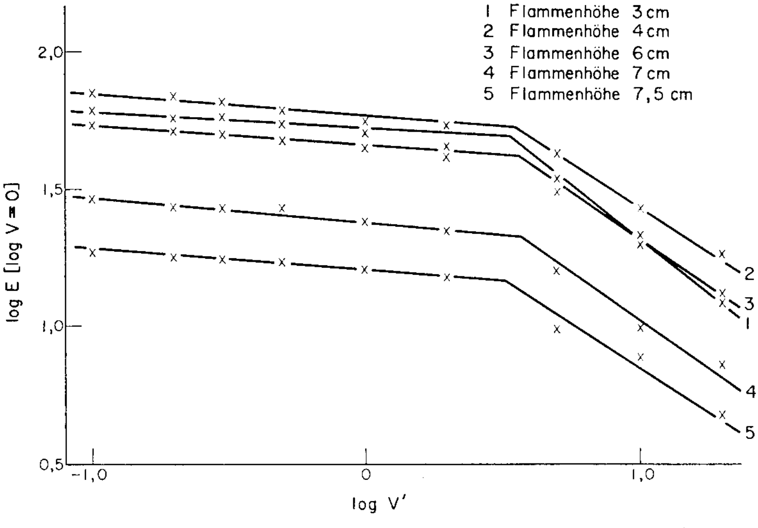

ABB. 3.—Zusammenhang zwischen log [CaO]-Werten (bzw. log *E*) und log *V′* (d.h. log Al : Ca-Verhältnis).

bestimmt und es ergab sich nach unseren Meßerfahrungen mit direkten Zerstäubern, daß die gemessene Emission direkt proportional der Konzentration ist.

Aus unseren in Abb. 2 und 3 gegebenen Ergebnissen ergibt sich die Annahme einer Gleichgewichtsreaktion im Falle von $CaAl_2O_4$.

Aus der Abb. 3 ist es ersichtlich, daß die Bildung eines Ca–Al-Komplexes mit dem Atomverhältnis von 1:2 als bezeugt bis etwa 3–4-facher Aluminiumüberschuß zu Betrachten ist. Über die Lage nach dem Knickpunkt sind noch keine begründeten Erklärungen vorhanden.

Aus der Abb. 2 wird ersichtlich, dass die Änderung der in Prozent angegebenen Differenz zwischen den Emissionswerten der anionfreien bzw. aniongehaltigen Lösungen längs der Flammenachse bei derselben Calcium–Aluminium-Proportion ein Minimum aufweist. Das Mass dieser Emissionsverminderung ist eigentlich mit der in Komplexform gebundenen Calciummenge proportional, und weil sein Minimalwert sich immer bei der Stelle maximaler Flammentemperatur zeigt, darf man die Schlußfolgerung ziehen, wonach die Erscheinung aus der Temperaturänderung längs der Flammenachse zu erklären ist.

Auf Grund unserer Ergebnisse kann der störende Einfluß des Aluminiums im Falle von Calcium—im Gegensatz zu den in der Literatur befindlichen und vorher schon erwähnten Auffassungen—aus dem thermischen Dissoziationsgleichgewicht des Calciumaluminates abgeleitet werden. Daraus erklärt sich auch jene, in der Praxis so oft gemachte Erfahrung, daß man in Flammen gewisser Temperatur (H—O, und darüber hinaus) die Aluminiumstörung mittels eines Aluminiumstrahlungspuffers verhindern kann.

Besonderes Interesse sollte dem Resultat von Alkemade und Mitarbeitern gewidmet werden, das sie bekommen haben, als sie das Aluminium- und Calciumsalz mit Hilfe zweier Zerstäuber getrennt in die Flamme geführt haben. Nach ihren Erfahrungen sinkt die Aluminiumstörung in diesem Fall auf das Minimale. Es muß jedoch beachtet werden, daß die auf diese Weise in die Flamme geratenen Nebelpartikelchen des Aluminiums und Calciums separat mit sich reissen. Bei Aluminium ist es allgemein bekannt, daß sich im Laufe der Trocknung verschiedene Oxokomplexe herausbilden können.[16] Die kinetische Untersuchung ihrer Umsetzung zu Al_2O_3 könnte sehr interessant sein. Wir meinen, durch die Neigung der Aluminiumsalze Isopolybasen zu bilden, können die Ergebnisse der von Alkemade ausgerführten Untersuchungen erklärt werden.

Nicht so eindeutig ist die Lage im Falle der Sulphat- und Phosphatstörung, unsere Untersuchungen auf diesem Gebiete werden in Kürze näher behandelt werden.

Summary—The interference due to aluminium in the flame emission spectroscopic determination of calcium has been investigated, by measurement of the emission intensities at various heights in a turbulent oxy-hydrogen flame. The results suggest the formation of a 1:2 calcium-aluminium compound in the flame. The interference can be explained in terms of an apparent equilibrium in the gas-phase.

Résumé—On a étudié l'interférence dûe à l'aluminium dans le dosage spectroscopique d'émission de flamme du calcium, en mesurant les intensités d'émission à diverses hauteurs dans une flamme turbulente oxygène-hydrogène. Les résultats suggèrent la formation d'un composé calcium-aluminium 1:2 dans la flamme. On peut expliquer l'interférence en fonction d'un équilibre apparent dans la phase gazeuse.

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SHORT COMMUNICATIONS

Absorptiometric determination of traces of iron extracted as ferroin thiocyanate

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THE limitations of the photometric determinations of iron with 1,10-phenanthroline have been pointed out by several investigators. In studies on elimination of interference of various substances, by selective extraction of the ferroin complex, it was found that ferroin can be extracted into chloroform or nitrobenzene only in the presence of perchlorate,[1] cyanide,[2] and iodide or thiocyanate.[3] However, because of the lower selectivity,[3] the extraction of the ferroin–thiocyanate complex has not been exhaustively investigated. In a reinvestigation of these procedures, we have come across some interesting facts. Iron(III) can be determined through extraction as the ferroin–thiocyanate complex without prior reduction with hydroxylamine, if the extraction is carried out at pH 1–2. At this pH, thiocyanate itself functions as a reductant and gives a very stable pink ferroin extract with several solvents. This was found to be a sensitive method for the determination of iron, the complex having a molar absorptivity of $20\cdot5 \times 10^3$ at 525 nm, when pure isobutyl methyl ketone is used as solvent.

EXPERIMENTAL

All reagents used were of analytical-reagent grade. Solutions were prepared with doubly distilled water. Isobutyl methyl ketone (IBMK) was used after double distillation.

Preliminary work showed that the pink complex could be extracted into several hydrocarbons, alcohols, ketones, esters, chloroform and ether, with the exception of carbon tetrachloride, cyclohexane and petroleum ether. However, from the point of immiscibility with water, and intensity of the colour, IBMK was found to be the best, and gives quantitative recovery of iron in a single extraction.

The effect of pH was studied by extracting the iron complex at the appropriate pH with IBMK and measuring the absorbance of the extract against pure solvent after it had been dried over anhydrous sodium sulphate. Figure 1 shows that the absorbance remains constant over the pH range 0·65–2·0.

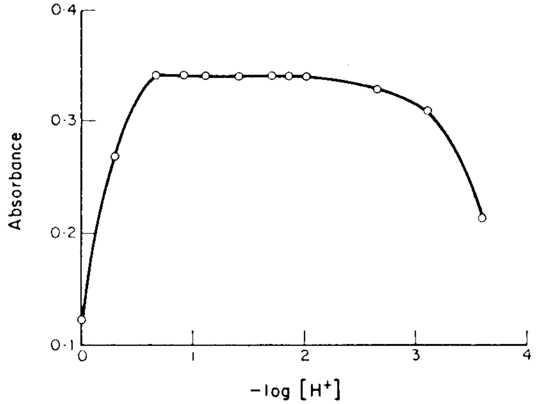

FIG. 1.—Effect of pH on the absorbance of ferroin-thiocyanate. Aqueous phase: 2·5 ml of $2 \times 10^{-4}M$ iron(III) + 0·5 ml of $0\cdot01M$ 1,10-phenanthroline + 1·0 ml of $1M$ KCNS. Total volume adjusted to 25·0 ml after adding the buffer or acid. Organic phase: 25·0 ml of IMBK.

The absorbance does not change with thiocyanate concentration if this is more than 1000 times that of the iron(III), the concentration of 1,10-phenanthroline being 10 times the iron concentration.

With a 2000:1 [SCN$^-$]: [Fe] ratio, a mole-ratio plot of absorbance *vs.* 1,10-phenanthroline (phen) concentration gave a break-point at a 3:1 [phen]:[Fe] ratio, showing that the extracted species is an ion pair [Fe(phen)$_3$$^{2+}$] . (SCN$^-$)$_2$. The complex is stable for at least a day, but care should be taken to prevent evaporation of the solvent.

The absorption spectrum (measured *vs.* a reagent blank) is shown in Fig. 2. The molar absorptivity is 20·5 × 10^3 at 525 nm; this value is the highest reported for 1,10-phenanthroline complexes.

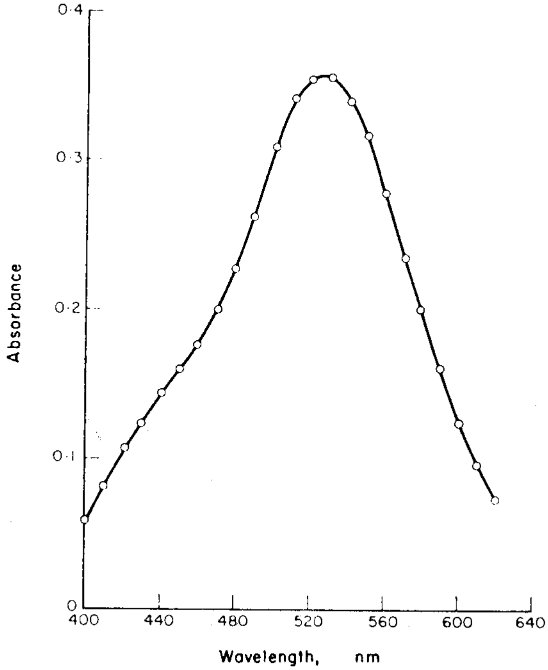

FIG. 2.—Absorption spectrum of ferroin–thiocyanate complex in IBMK. Conditions as for Fig. 1, but 15·0 ml of 0·1*M* hydrochloric acid used.

Procedure

In a 100-ml separating funnel mix an aliquot of iron(III) solution, containing up to 3 ppm of iron, with 15·0 ml of 0·1*M* hydrochloric acid, 0·5 ml of 0·01*M* 1,10-phenanthroline and 1·0 ml of 1·0*M* potassium thiocyanate, and make up the solution to 25·0 ml with doubly distilled water. Equilibrate with 25·0 ml of IBMK for 1 min, separate the organic phase, dry it over anhydrous sodium sulphate and measure its absorbance at 525 nm against a reagent blank. Use filter No. 4 if a Hilger absorptiometer is used. Beer's law is obeyed up to 3 ppm of iron.

Interferences

Citrate, fluoride, oxalate, phosphate and tartrate (100-fold amounts) had no effect on the determination, provided the reagents were added in large excess. EDTA and pyrophosphate interfere seriously, but their interference can be eliminated by first reducing the iron in the mixture at pH 7 with hydroxylamine in the presence of the reagents and then extracting iron with IBMK after adjustment of the pH of the aqueous phase to 1.

Al, As, Ba, Cd, Ce(IV), Cr(III), Hg(II), Mg, Mn(II), Th, Ti(IV), U(VI) and Zr do not interfere even when present in 1000-fold amounts. Zn, Bi(III) (500-fold amounts) and Mo(VI) (100-fold amount) are without interference if a proportionate excess of the reagents is used. There is serious interference from Co(III), Cu(II), Ni, V(V) and W(VI), but this can be eliminated by adapting Luke's procedure[4] for the separation of iron from these species. The final determination is made by shaking the IBMK extract with an aqueous solution of 1,10-phenanthroline and thiocyanate at pH 1.

Applications

The method developed has been used for the determination of iron in commercial grade hydrochloric acid, aluminium alloy (containing 11% of magnesium) and a copper-base alloy (containing 39% of zinc). The results obtained were checked by Přibil's method and the thiocyanate procedure (Table I).

TABLE I

Sample	Iron content		
	Ferroin–thiocyanate procedure	Ferroin–iodide procedure	Thiocyanate procedure
Commercial HCl	32·5 μg/ml	32·9 μg/ml	32·5 μg/ml
Al alloy	0·11%	0·11%	0·11%
Cu-base alloy	0·44%*	0·45%	0·43%†

* Fe separated by Luke's procedure.
† Cu separated by H_2S.

DISCUSSION

The fading of the colour of the iron(III)–thiocyanate complex in solution is attributed to the slow reduction of iron(III) by thiocyanate, at least in part.[5] This reaction should proceed more rapidly and quantitatively in the presence of 1,10-phenanthroline which binds iron(II) strongly and thus increases the potential of the iron(III)–iron(II) couple. This has been confirmed by the fact that when a drop of thiocyanante is added to a mixture of iron(III) and 1,10-phenanthroline at pH 1, the ferroin colour is immediately produced. Thus in the present method no other reductant than thiocyanate is necessary to reduce the iron(III).

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Summary—Iron up to 3 ppm can be absorptiometrically determined by extracting the ferroin–thiocyanate complex at pH 1 into isobutyl methyl ketone (IBMK). At this pH thiocyanate itself reduces iron(III) so reductants such as hydroxylamine are not needed. The complex is very stable and has a molar absorptivity of $20{\cdot}5 \times 10^3$ in IBMK at 525 nm. Most of the substances associated with iron in minerals and alloys do not interfere and methods are suggested for the elimination of the effect of those which do.

Zusammenfassung—Eisen bis herauf zu 3 ppm kann durch Extraktion des Ferroin-Rhodanid-Komplexes bei pH 1 in Isobutylmethylketon (IBMK) absorptiometrisch bestimmt werden. Bei diesem pH reduziert Rhodanid selbst das Eisen(III), sodaß Reduktionsmittel wie Hydroxylamin nicht notwendig sind. Der Komplex ist sehr stabil und hat einen molaren Extinktionskoeffizienten von $20{,}5 \cdot 10^3$ in IBMK bie 525 nm. Die meisten Begleiter von Eisenn in Mineralien und Legierungen stören nicht; Methoden zur Ausschaltung der Störungen von Anderen werden vorgeschlagen.

Résumé—On peut doser le fer par absorptiométrie jusqu'à 3 p.p.m. en extrayant le complexe ferroïne-thiocyanate à pH 1 en méthylisobutylcétone (IBMK). A ce pH, le thiocyanate lui-même réduit le fer(III) de sorte que des réducteurs comme l'hydroxylamine ne sont pas nécessaires. Ce complexe est très stable et a un coefficient d'absorption moléculaire de 20,5 × 10^3 en IBMK à 525 mμ. La majeure partie des substances associées au fer dans les minerais et alliages n'interfère pas et l'on suggère des méthodes pour éliminer l'influence de ceux qui gênent.

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Determination of potassium with alkali-heavy metal cobaltinitrites

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MOST methods[1] for the determination of potassium have application to limited analytical problems only. The chloroplatinate method, although commonly used, is expensive; in the perchlorate method supersaturation causes losses; flame-photometric determination of potassium in the presence of sodium also presents technical inconveniences, chiefly high sensitivity (optimal concentration range 10–20 ppm) necessitating repeated dilutions of practical samples such as those analysed in the potash industry. An accurate method for estimation of potassium is needed in the potash industry.

Tananaye[2] suggested the detection of potassium in the form of "mixed" cobaltinitrites of the type $KMe[Co(NO_2)_6]$, where Me is lead or some other bivalent "heavy" metal ion. In 1912 Burgess and Kamm[3] published a study of the analytical applications of alkali metal–silver cobaltinitrites and proposed a series of qualitative tests based on precipitation of such compounds. The same authors also studied other insoluble alkali metal salts of this type. Indirect determination of potassium by EDTA titration of the cobalt content of sodium potassium cobaltinitrite in the absence of lead has been reported.[4–6]. Přibil and Malik[7] determined potassium in blood colorimetrically by precipitation of sodium potassium cobaltinitrite in the absence of lead, and dissolution of the separated precipitate in EDTA in the presence of hydrogen peroxide.

The object of the present investigation was to examine the possibility of using alkali cobaltinitrites containing lead or other cations for the quantitative determination of potassium, and particularly to find a method suited to the analytical problems of the potash industry.

EXPERIMENTAL

Analytical grade reagents were used throughout. Potassium was also determined with an EEL flame photometer and by the perchlorate method.

Method

The optimal conditions were studied for the quantitative precipitation of potassium as a cobaltinitrite in the presence of lead ions. For this purpose, a series of precipitations was carried out according to the following general scheme. Solution A was prepared by mixing *a* ml of 10% cobalt(II) nitrate hexahydrate solution, *b* ml of 15% sodium nitrite solution, *c* ml of 12% lead nitrate solution and $100 - (a + b + c)$ ml of water. To this mixture *x* ml of potassium chloride solution containing 10–20 mg of K^+/ml were added. The reaction mixture was stirred, 10 ml of 10% hydrogen peroxide solution were added (to assure cobaltinitrite formation) and the suspension obtained was heated. By systematic variation the following optimal working conditions were obtained: 5 ml of a sample solution containing 10–20 mg of K^+/ml are added to 95 ml of a solution containing 11.5 g of lead nitrate, 15 g of sodium nitrite and 10 g of cobalt(II) nitrate hexahydrate, the reaction mixture is stirred for 2 min, 10 ml of 10% hydrogen peroxide are added and the solution is kept at 90° for 5 min;

a dark precipitate of $KPb[Co(NO_2)_6]$ is obtained. Check analyses by other procedures show that this precipitate contains substantially all the potassium initially added. The compound is stoichiometric to within 1%.

The precipitate is filtered off and the filtrate discarded; the precipitate is dissolved in a mixture of 10 ml of 1*M* sodium hydroxide and 20 ml of 5% EDTA solution. The absorbance of the violet solution (CoEDTA) obtained is measured and compared to a standard curve obtained by treating known amounts of potassium by the same procedure.

The proposed procedure can also be used to determine any heavy metal such as Ag, Pd and Pt which replaces the lead and gives an insoluble compound of the type $K_xMe_y[Co(NO_2)_6]$. Another method for determination of the potassium content of the precipitate consists of dissolving the latter, adding a mixture of ammonia and sodium hydroxide and titrating the cobalt complexometrically.[7-10]

Note—Parts of the procedures described here are protected as a patented invention, for extraction and removal of cobalt, heavy metals and potassium for technological purposes, by A.H.I. Ben-Bassat and Yissum Research and Development Co., Israel (*Israel Patent* No. 20747, 5 February 1964).

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Summary—A procedure is proposed for the removal and determination of K^+ by precipitation with $[Co(NO_2)_6]^{3-}$ in the presence of Pb^{2+} and H_2O_2. The whole precipitate is dissolved, the Co^{3+} estimated colorimetrically, and the K^+ content calculated, with a relative error of 1%. The potassium-containing precipitate may also be dissolved in $NaOH + NH_3$ solution, the Co^{3+} titrated complexometrically, and the potassium content deduced. These two procedures may be modified for the removal and determination of Pb^{2+}, Co^{2+}, Co^{3+} and NO_2^-. Na^+ ions do not interfere.

Zusammenfassung—Eine Vorschrift zur Abtrennung und Bestimmung von K^+ durch Fällung mit $[Co(NO_2)_6]^{3-}$ in Gegenwart von Pb^{2+} und H_2O^3 wird vorgeschlagen. Der ganze Niederschlag wird gelost, das Co_2^+ kolorimetrisch bestimmt und der K^+-Gehalt mit einem relativen Fehler von 1% berechnet. Der Kalium enthaltende Niederschlag kann auch in $NaOH + NH_3$-Lösung gelöst, das Co^{3+} komplexometrisch titriert und der Kaliumgehalt berechnet werden. Diese beiden Vorschriften können zur Abtrennung und Bestimmung von Pb^{2+}, Co^{2+}, Co^{3+} und NO_2^- abgewandelt werden. Na^+-Ionen stören nicht.

Résumé—On propose une technique pour l'élimination et le dosage de K^+ par précipitation avec $[Co(NO_2)_6]^{3-}$ en présence de Pb^{2+} et de H_2O_2. La totalité du précipité est dissoute, le Co^{3+} estimé colorimétriquement et la teneur en K^+ calculée avec une erreur relative de 1%. On peut dissoudre le précipité contenant le potassium dans une solution $NaOH + NH_3$, titrer le Co^{3+} par complexométrie et en déduire la teneur en potassium. Ces deux techniques peuvent être modifiées pour l'élimination et le dosage de Pb^{2+}, Co^{2+}, Co^{3+} et NO_2^-. Les ions Na^+ ne gênent pas.

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Microdetermination of iron in plant tissue with 4,7-diphenyl-1,10-phenanthroline

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SINCE its introduction by Smith, McCurdy and Diehl, the reagent 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline, BPT) has been widely used to determine microgram quantities of iron.[1] Diehl and Smith[2] have published an extensive literature survey of its applications. The Fe–BPT complex is intensely coloured (molar absorptivity $>22 \times 10^3$ at 533 mμ)[2] and can be quantitatively extracted into a small volume of organic solvent. Nitrobenzene,[3] isoamyl alcohol,[4] and hexanol[4] have been used. Although dependent on the pH of the aqueous solution, the intensity of the colour is constant over the pH range 3·3–9·0. BPT is soluble below pH 3·5, but within the pH range 3·5–9·0 is precipitated and makes the mixture turbid. This characteristic provides a convenient pH check. Relatively few ions interfere, the most important being cobalt and copper, which compete with the iron for the BPT. Most previous BPT methods are comparatively slow and not well suited for large numbers of routine analyses, though modifications have been made to save time and increase sensitivity, e.g., those by Peterson[5] and Kingsley and Getchell[6] to determine iron in blood serum.

The method reported here was developed for the determination of small amounts of iron in many samples of plant material (tobacco leaves).

EXPERIMENTAL

Reagents

Bathophenanthroline, 0·005*M*. Dissolve 0·1662 g of BPT in about 80 ml of boiling absolute methanol. Cool and dilute to 100 ml with methanol.

Hydroxylamine hydrochloride solution, 10% w/v. Dissolve 100·0 g of reagent grade $NH_2OH{\cdot}HCl$ in about 600 ml of demineralized water in a separatory-funnel. Add 4 ml of 0·005*M* BPT and 20 ml of hexanol, shake, and remove the organic phase; repeat until the organic phase is no longer coloured. Dilute the aqueous phase to 1000 ml with demineralized water.

Sodium acetate solution, 10% w/v. Dissolve 100·0 g of reagent grade $CH_3{\cdot}COONa$ in about 600 ml of demineralized water in a separatory-funnel. Add 5 ml of 10% hydroxylamine hydrochloride solution and extract iron as just described, with 4 ml of 0·005*M* BPT and 20 ml of hexanol. Dilute the aqueous phase to 1000 ml with demineralized water.

Iron standard. Dissolve 0·1000 g of electrolytic iron in 10 ml of 6*M* nitric acid. Boil to expel oxides of nitrogen. Dilute to 1000 ml with demineralized water and dilute again 10-fold. This solution contains 10 μg of Fe/ml.

Digestion

Weigh about 100 ± 0·1 mg of tobacco or other plant material in a 25-ml pyrex volumetric flask. Add 4 ml of concentrated reagent grade sulphuric acid followed by 2·5 ml of concentrated reagent grade nitric acid. Boil the solution gently, without spattering, until all oxides of nitrogen have been expelled and all solid material has been dissolved (1–3 hr). Then cool the flasks, dilute approximately to volume, and mix. After the heat of dilution has subsided, dilute to exact volume.

Analytical procedure

To an aliquot of the sample solution that contains from 0·5 to 10·0 μg or iron (1 ml for most tobaccos), add, in order, 1·00 ml of 10% hydroxylamine hydrochloride solution, 0·40 ml of 0·005*M* BPT in methanol and 10 ml of 10% sodium acetate solution, and mix. If the solution is not turbid, continue adding 1-ml increments of sodium acetate solution until a turbidity appears after mixing. Add 4·00 ml of hexanol, shake well, and allow to settle. Using an automatic dilutor (*e.g.*, Labindustries "Repipet") transfer 2·00 ml of the alcohol extract to a cuvette, followed by 1·00 ml of absolute ethanol to rinse the dilutor. Read the absorbance at 536 nm against a reagent blank. If an automatic dilutor is not available, any convenient means of transfer may be used. The final solution mixes rapidly.

Carry 0·10, 0·20, 0·30, 0·40 and 0·50-ml portions of a 10 μg/ml standard iron solution through this procedure to construct a calibration curve.

Because the amount of iron being determined is so small, all reagents must be made as iron-free as possible by reducing the iron in each reagent solution, complexing it with BPT, and extracting both the complex and the excess of BPT with hexanol.

RESULTS AND DISCUSSION

Iron recovery from the digestion procedure was checked by digesting, for varying lengths of time, samples of cellulose powder to which standard iron solution had been added. The results indicated that a minimum digestion period of 1 hr was necessary. Absorbances were read to 0·001 and were reproducible to ±0·001. Six samples of a homogenized tobacco sample were digested and each was analysed in triplicate. The iron found was 0·025 ± 0·0003%.

The use of 4 ml of extractant instead of the 25 ml used by Smith, McCurdy and Diehl enhances the sensitivity, making the absorbance 0·100 for 1 μg of iron. The method is also more rapid because only a single extraction is required. In this laboratory, an analysis in triplicate by the Smith method took about 1 hr; by the present method, it took about 10 min. Comparison of results for the same samples by the two methods showed no difference in recovery of iron except for the smallest amount, where the greater sensitivity of the present method gave a positive result but the Smith method failed.

The wet digestion procedure is safe, rapid and effective. Use of a volumetric flask as weighing vessel, digestion flask, and means of dilution to volume reduces the chance of sample loss as well as the time required for multiple analyses. The reproducibility of the results is a clear indication that no serious errors result from changes in the volume of the flasks on repeated heating and cooling.

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Summary—A method is described for the wet digestion and colorimetric determination of small amounts of iron in plant tissues. The wet digestion uses a mixture of sulphuric and nitric acids instead of perchloric acid; a volumetric flask is used for weighing, digestion, and dilution. The iron complex with 4,7-diphenyl-1,10-phenanthroline is extracted into hexanol.

Zusammenfassung—Eine Vorschrift zum nassen Aufschluß und zur kolorimetrischen Bestimmung von kleinen Eisenmengen in Pflanzengeweben wird angegeben. Der nasse Aufschluß verwendet ein Gemisch von Schwefel- und Salpetersäure statt Überchlorsäure; zum Einwiegen, Aufschließen und Verdünnen wird ein Meßkolben verwendet. Der Eisenkomplex mit 4,7-Diphenyl-1,10-phenanthrolin wird in Hexanol extrahiert.

Résumé—On décrit une méthode pour la digestion par voie humide et le dosage colorimétrique de petites quantités de fer dans les tissus végétaux. La digestion par voie humide utilise un mélange d'acides sulfurique et nitrique au lieu de l'acide perchlorique une fiole volumétrique est utilisée pour la pesée, la digestion et la dilution. On extrait le complexe du fer avec la 4,7-diphényl 1,10-phénanthroline en hexanol.

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Untersuchungen an Reagenzien für Niob und Tantal—III.

Die Reaktionen der Dibromgallussäure mit Niob(V) und Tantal(V)

(*Eingegangen am* 7. *November* 1967. *Revidiert am* 30. *Juli* 1968. *Angenommen am* 12. *August* 1968)

AUS systematischen Untersuchungen von Brenzkatechinderivaten[1] ergab sich, daß Dibromgallussäure für die photometrische Bestimmung von Niob und Tantal gut geeignet ist, auch wenn beide Erdsäuren nebeneinander vorliegen.

Untersuchungen in Lösungen mit Ligandenüberschuß

Niob(V) reagiert mit Dibromgallussäure* unter Bildung intensiv gefärbter Reaktionsprodukte. In sehr stark saurem Medium entstehen rot-orange Färbungen, die mit abnehmender Acidität in orange bzw. gelb-orange übergehen. Tantal(V) gibt weniger intensive gelbe Lösungen. In stark alkalischem Milieu sind mit beiden Elementen infolge Konkurrenzreaktionen ihrer Kationen nach

$$\mathrm{MeO}_n^{(5-2n)+} + (6\text{–}2n)\mathrm{OH}^- \rightleftharpoons \mathrm{MeO}_3^- + (3\text{–}n)\mathrm{H_2O} \qquad n = 0, 1, 2$$

keine Färbungen mehr zu beobachten.

Die Absorptionsspektren (Abb. 1) der Niob(V)-Lösungen mit überschüssiger DBG haben

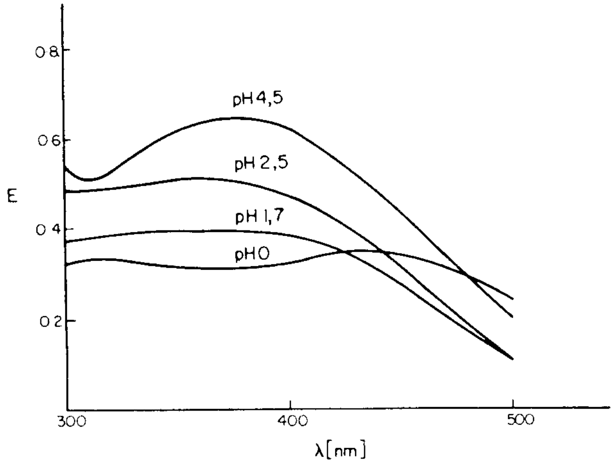

ABB. 1.—Absorptionsspektren der Niob(V)–Dibromgallussäure-Chelate.
$p = C_{\mathrm{DBG}}::C_{\mathrm{Nb}} = 402$; $C_{\mathrm{Nb}} = 7{,}56 \cdot 10^{-5}M$; $\mu = 1{,}0$

deutlich ausgeprägte Maxima, die für pH = 4,5 bei 380 nm und für pH = 0 bei 320 nm und 440 nm liegen. Die entsprechenden Absorptionsspektren der Tantalchelate mit überschüssiger DBG sind in Abb. 2 wiedergegeben. Das Extinktionsmaximum bei 320 nm, das im pH-Bereich von 1,9 bis 4,5 auftritt, weist auf die Existenz nur eines Chelates hin. Messungen bei pH = 0 waren nicht möglich, da sich die zu messende Lösung bereits nach kurzer Zeit trübt. Die Absorptionsspektren zeigen, daß in der Lösung verschiedene Chelate der Erdsäuren mit DBG existieren. Die Ermittlung der Molarkoeffizienten n erfolgte indirekt durch Vergleich einer Reihe von Bildungskonstanten für $n = 1, 2, 3$ und 4 bei verschiedenen Reagenzüberschüssen mit Hilfe der Job-Methode.[2] Die aus den Maxima berechneten Bildungskonstanten sind in den Tabellen I und II zusammengefaßt.

Für Niob ist bei pH = 0 und pH = 3,4 die Übereinstimmung der Werte für log K_1 am besten. Das spricht für ein 1:1-Chelat. Die Übereinstimmung der Konstanten K_2 bei den Tantalchelaten bei pH = 3,4 und pH = 5,0 weisen auf die Bildung eines Chelates mit dem Komponentenverhältnis Ta:DBG = 1:2 hin. Der Verlauf der Job-Kurve bei pH = 0 deutet ebenfalls auf ein 1:2-Chelat hin. Auf eine mathematische Auswertung wurde jedoch wegen zu großer Streuung der Meßwerte (Hydrolyse) verzichtet.

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* Als Kurzform hierfür wird in der vorliegenden Veröffentlichung DBG benutzt.

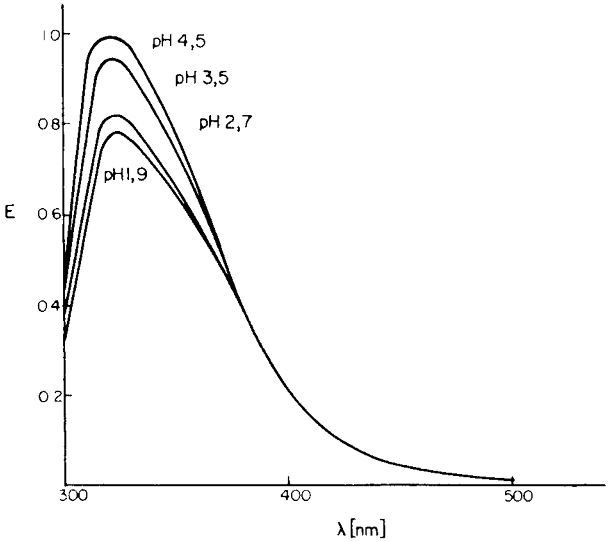

ABB. 2.—Absorptionsspektren der Tantal(V)-Dibromgallussäure-Chelate. $p = C_{DBG}:C_{Ta} = 207$; $C_{Ta} = 1{,}47 \cdot 10^{-4}M$; $\mu = 0$

TABELLE I.—BILDUNGSKONSTANTEN DER NIOBCHELATE FÜR $n = 1$–4

pH	M	p	x	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
0	0,002	5	0,42	2,2	5,9	10,5	*
0	0,002	10	0,31	2,5	5,6	9,2	14,5
0	0,002	15	0,28	2,4	5,3	8,3	11,8
3,4	0,001	3	0,29	4,5	†	8,8	*
3,4	0,001	5	0,23	4,2	—	9,4	—
3,4	0,001	10	0,15	4,2	—	10,2	—

* $x(p + 4) - 4 < 0$
† $x(p + 2) - 2 < 0$
M = Konzentration der Erdsäure
p = Konzentration DBG/Konzentration Erdsäure
x = Molenbruch am Job-Maximum
$K_n = (p - 1)^n [n - x(1 + n)]/M^n p^{n-1} [x(p + n) - n]^{n+1}$

TABELLE II.—BILDUNGSKONSTANTEN DER TANTALCHELATE FÜR $n = 1$–4

pH	M	p	x	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
3,4	0,001	5	0,58	*	4,9	8,4	11,9
3,4	0,001	10	0,50	*	4,8	7,7	10,6
3,4	0,001	15	0,42	1,9	4,9	7,6	10,4
5,0	0,001	5	0,56	*	5,2	8,6	12,3
5,0	0,001	10	0,46	1,7	5,1	8,0	11,1
5,0	0,001	15	0,39	2,0	5,0	7,8	10,7

* $1 - 2x \leqslant 0$

Bei photometrischen Bestimmungsmethoden arbeitet man meistens mit einem mehr oder weniger großen Reagenzüberschuß. Interessant ist deshalb die Stöchiometrie der Chelate unter diesen Bedingungen. Durch Analyse einer sogenannten C_R-Kurve[3] $[E = f(C_{DBG})$ für pH und $C_{Me} =$ konstant$]$ läßt sich der Molarkoeffizient n bei hohen Überschüssen an Reagens angeben. Nach Logarithmierung von K_n für die Reaktion

$$\mathrm{Me} + n\mathrm{DBG} \rightleftharpoons \mathrm{MeDBG}_n + x\mathrm{H}^+$$

gilt für große Überschüsse an DBG

$$\log \frac{E}{E_0 - E} = n \log C_{DBG} + c.$$

Hierin bedeuten E eine Extinktion auf dem ansteigenden Ast der Kurve, E_0 den Grenzwert der Funktion und c eine Konstante. Der Koeffizient n ist dabei der Anstieg einer durch obige Gleichung beschriebenen Geraden. Seine Bestimmung erfolgte aus dem Neigungswinkel. Die Bildungskurven sind in Abb. 3 dargestellt. Die logarithmische Analyse ergibt eine lineare Abhängigkeit des Ausdruckes $\log E/(E_0 - E)$ von C_{DBG} für hohe Überschüsse an Reagens. Der Anstieg der Geraden beträgt 2,1 für Niob bzw. 2,2 für Tantal.

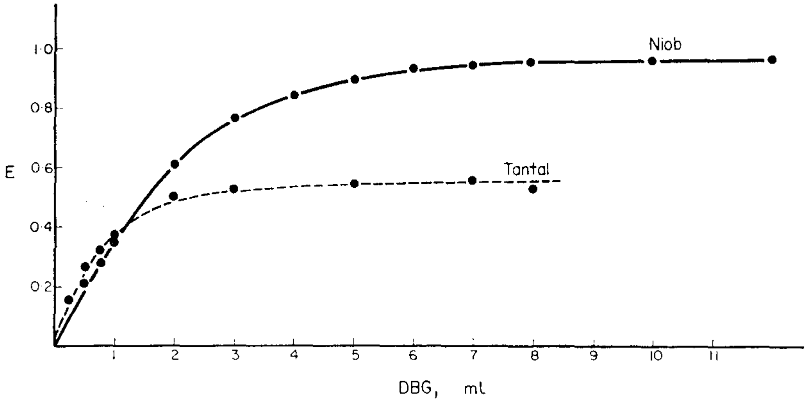

Abb. 3—Abhängigkeit der Extinktion der DBG-Chelate von DBG-Überschüssen bei pH = 5,0.
$\lambda = 400\,\mathrm{nm}$; $\mu = 0{,}1$; $C_{DBG} = 0{,}1M$; $C_{Nb} = 8 \cdot 10^{-5}M$; $C_{Ta} = 3{,}2 \cdot 10^{-4}M$

Untersuchungen in äquimolaren Lösungen

Die Job-Kurven sind infolge von Nebenreaktionen des Niob(V) mit dem Lösungsmittel deformiert. Der aus dem erhaltenen Maximum berechnete gebrochene Molarkoeffizient von $n = 0{,}85$ deutet auf die Existenz eines 1:1-Chelates hin. Die Lage des Maximums ist wellenlängenunabhängig, was nach dem Vosburghschen Kriterium[4] auf die Bildung eines einheitlichen Chelates hinweist.

Die Zusammensetzung des Niobchelates bei pH = 5,0 ermittelten wir mit Hilfe der Methode des molaren Verhältnisses[6] durch photometrische Titration. Die Messungen ergaben, daß auch bei diesem pH-Wert ein 1:1-Chelat vorliegt. Beim Tantal werden Messungen an äquimolaren Systemen durch unübersichtliche Hydrolysereaktionen des Kations unmöglich gemacht.

Papierelektrophorese

Die photometrischen Verfahren lassen keine eindeutigen Aussagen über die Struktur der Chelate zu, da die untersuchten Kationen auch als definierte Hydrolysestufe MeO^{3+} bzw. $\mathrm{MeO_2}^+$ vorliegen können. Nach Arbeiten von Sommer[6-8] über Titan(IV)-Polyphenol-Komplexe muß man erwarten, daß bei den hier untersuchten System mit der Bildung protonisierter Chelate zu rechnen ist. Ergänzend zu den photometrischen Methoden wurden deshalb mit Hilfe der Papierelektrophorese die Ladungen der Chelate bestimmt.[7] Auf Grund dieser Messungen können vorliegen: $[\mathrm{NbO_2H_2R}]$, $[\mathrm{NbO_2HR}]^-$, $[\mathrm{NbO_2R}]^{2-}$, $[\mathrm{NbO_2R_3}]^{8-}$ sowie $[\mathrm{TaO_2R_2}]^{5-}$.

DISKUSSION DER ERGEBNISSE

Niob-Chelate

Wie die spektralphotometrischen Untersuchungen zeigen, bildet Niob(V) mit DBG in äquimolaren Lösungen innerhalb eines breiten pH-Bereiches (0 bis 5) 1:1-Chelate. Nach den durchgeführten elektrophoretischen Messungen existieren

$$[NbO_2H_2R]; \quad [NbO_2HR]^-; \quad [NbO_2R]^{2-}; \quad (DBG = H_3R).$$

Der jeweilige Reaktionsmechanismus wird vom pH-Wert der Lösung bestimmt. In saurer Lösung mit kleinem Ligandenüberschuß ($pH = 1{,}8, p = 20$) liegt ein Gemisch von $[NbO_2H_2R]$ und $[NbO_2HR]^-$ vor. In Lösungen mit höheren pH-Werten verschiebt sich das Gleichgewicht auf die Seite der Dissoziationsprodukte $[NbO_2HR]^{1-}$ bzw. $[NbO_2R]^{2-}$. Bei $pH = 3{,}4$ ($p = 20$) entsteht nur noch $[NbO_2R]^{2-}$. Das Teilchen $[NbO_2H_2R]^{\pm 0}$ mit $\lambda_{max} = 440$ nm bildet sich auch bei einem Ligandenüberschuß von $p = 400$ bei $pH = 0$.

In schwach saurer Lösung ($p = 400$) bildet sich eine Koordinationsverbindung mit $\lambda_{max} = 380$ nm Nach spektrophotometrischen Messungen handelt es sich dabei um ein 1:2-Chelat. Die elektrophoretischen Untersuchungen im pH-Bereich 3,4 bis 5,0 deuten aber auf ein 1:3-Chelat mit der wahrscheinlichen Zusammensetzung $[NbO_2R_3]^{8-}$.

An Hand der vorliegenden Ergebnisse läßt sich nicht entscheiden, ob ein 1:2- oder 1:3-Komplex vorliegt. Zu ähnlichen Resultaten kam auch Sommer und Havel[9] für Niob–Chromotropsäure-Chelate, die gleichfalls bei ihren photometrischen Untersuchungen einen 1:2- und bei elektrophoretischen Messungen einen 1:3-Komplex fanden.

Tantal-Chelate

Der zwischen Tantal(V) und DBG durch spektralphotometrische Methoden nachgewiesene 1:2-Komplex ($\lambda_{max} = 320$ nm) bildet sich unabhängig vom Liganden überschuß in einem großen pH-Bereich (0 bis 5). Das Chelat entsteht wahrscheinlich auch in äquimolaren Lösungen in breiten pH-Grenzen. Elektrophoretische Untersuchungen in schwach saurer Lösung deuten auf die Formel $[TaO_2R_2]^{5-}$ hin. Die Protonisierung dieses Teilchens in stark saurer Lösung kann jedoch nicht ausgeschlossen werden.

EXPERIMENTELLER TEIL

Die spektralphotometrischen Messungen erfolgten mit dem Beckman-Spektralphotometer Modell DU in 10-mm Quarzküvetten.

Zur Elektrophorese der Chelate diente eine Apparatur nach Jokl.[10] Als Träger diente Papier WF 13 des VEB Spezialpapierfabrik Niederschlag/Erzgeb. Das Potentialgefälle betrug 1,3 V/mm, Dauer der Elektrophorese 60–120 min. Als innerer Beweglichkeitsstandard diente Pikrinsäure. Der Grundelektrolyt, mit dem das Papier getränkt wurde, hatte die gleiche Zusammensetzung und gleichen pH-Wert wie die Chelatlösung, nur ohne Niob bzw. Tantal. Zur Stabilisierung der DBG bei $pH = 5{,}0$ wurde Natriumdithionit verwendet.

Etwa 0,3 g Nb_2O_5 (0,5 g Ta_2O_5) wurde mit 1,5 g (2,5 g) Kaliumcarbonat im Platintiegel geschmolzen und die klare Schmelze in 250 ml Wasser bei 60° gelöst. Die Gehaltsbestimmung der filtrierten Lösung erfolgte gravimetrisch mit Kupferron. Die für die Messungen verwendeten verdünnten Lösungen waren nie älter als zwei Tage.

Das Reagens (DBG) wurde nach einer Vorschrift von Hlasiwetz[11] dargestellt.

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Zusammenfassung—Mit Hilfe spektrophotometrischer und elektrophoretischer Methoden werden die Bildungsbereiche der Chelate von Dibromgallussäure mit Niob(V) und Tantal(V) festgelegt und die Strukturen der Reaktionsprodukte bestimmt. Je nach der Konzentration der Komponenten und dem pH-Wert liegen $[NbO_2H_2R]$, $[NbO_2HR]^-$, $[NbO_2R]^{2-}$ und wahrscheinlich $[NbO_2R_3]^{8-}$ sowie $[TaO_2R_2]^{5-}$ vor. (Dibromgallussäure $= H_3R$).

Summary—The nature and structure of the chelates formed between dibromogallic acid and niobium(V) or tantalum(V) have been investigated by spectrophotometric and electrophoretic methods. Depending on the pH and the concentration of the components, the complexes $[Nbo_2H_2R]$, $[Nbo_2HR]^-$, $[Nbo_2R]^{2-}$ and probably $[Nbo_2R_3]^{8-}$ and $[TaO_2R_2]^{5-}$ appear to be formed (H_3R = dibromogallic acid).

Résumé—On a étudié la nature et la structure des chélates formés entre l'acide dibromogallique et le niobium(V) ou le tantale(V) par des méthodes spectrophotométriques et électrophorétiques. Dépendant du pH et de la concentration des composants, les complexes formés se présentent comme (NbO_2H_2R), $(NbO_2HR)^-$, $(NbO_2R)^{2-}$ et probablement $(NbO_2R_3)^{8-}$ et $(TaO_2R_2)^{5-}$ (H_3R = acide dibromogallique).

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Untersuchungen an Reagenzien für Niob und Tantal—IV

Die Reaktionen der Dibromgallussäure mit Niob(V) und Tantal(V) in Gegenwart von Oxalsäure, Weinsäure und Äthylendiamintetraessigsäure

(*Eingegangen am* 22. *November* 1967. *Revidiert am* 26. *April* 1968. *Angenommen am* 12. *August* 1968)

Bei der Bestimmung von Niob und Tantal, sowohl wenn diese getrennt, wie auch, wenn sie im Gemisch vorliegen, werden sogenannte Hilfskomplexbildner benötigt. Diese Substanzen-meist Polycarbonsäuren—haben die Aufgabe einmal unerwünschte Nebenreaktionen, wie Hydrolyse, Polykondensation usw. zu unterdrücken, zum anderen aber auf Grund der verschiedenen Stabilität der Komplexe mit den Erdsäuren eine Nebeneinanderbestimmung zu ermöglichen. Auch bei den früher[1] beschriebenen Untersuchungen setzten wir den Lösungen der Erdsäuren Oxalsäure als Hilfskomplexbildner zu.

Orientierende Versuche zeigten, daß Oxalsäure und Weinsäure bei Verwendung von Dibromgallussäure (DBG) als chromophoren Liganden besonders geeignet sind. Der Einfluß dieser beiden Säuren auf die Chelatbildung bzw. Chelatzusammensetzung der Erdsäuren mit DBG wurde deshalb näher untersucht. Außerdem sollte noch der Einfluß von Äthylendiamintetraessigsäure geprüft werden, weil diese Aminopolycarbonsäure als ein sehr gutes Maskierungsreagens für mehrwertige Metalle bekannt ist.

PHOTOMETRISCHE UNTERSUCHUNGEN

Weinsäure

Das System Tantal–DBG–Weinsäure ist für eine Tantalbestimmung wenig geeignet, da sich beim Lösen des Aufschlusses $Ta_2O_5 \cdot xH_2O$ abscheidet. Auf seine Untersuchung mußte deshalb verzichtet werden.

Niob(V) reagiert auch im tartrathaltigen Medium mit DBG je nach der Wasserstoffionenkonzentration zu orangenen oder rot-orangenen Chelaten. Die Extinktionskurven zeigen mit und ohne Hilfskomplexbildner bei den verschiedenen pH-Werten den gleichen Verlauf (λ_{max} bei 380 nm, 320 nm bzw. 440 nm). Damit ist nachgewiesen, daß die Zusammensetzung dieser Metallchelate in Gegenwart und in Abwesenheit von Tartrat gleich ist.

Oxalsäure

Die bei verschiedenen pH-Werten aufgenommenen Extinktionskurven ($p = 380$, $s = 141$)* identifizieren das auch in Lösung ohne Hilfskomplexbildner nachgewiesene Niobchelat mit $\lambda_{max} =$ 380 nm. Das in reiner Lösung sowie in Anwesenheit von Weinsäure nachgewiesene rot-orangene Chelat ($\lambda_{max} = 440$ nm) wird in Gegenwart von Oxalsäure nicht gebildet.

Tantal(V) bildet mit DBG in Gegenwart von Oxalsäure je nach dem pH-Wert zwei gelbe Chelate unterschiedlicher Zusammensetzung. In schwach saurer Lösung bei $p = 380$ und $s = 141$ entsteht das in reiner Lösung bereits nachgewiesene 1:2-Chelat mit $\lambda_{max} = 320$ nm (Abb. 1), welches mit zunehmender Acidität in eine Koordinationsverbindung anderer Zusammensetzung übergeht. Bei etwa 385 nm durchlaufen die Extinktionskurven (außer bei pH = 0, da unter dieser Bedingung keine vollständige Komplexbildung mit DBG möglich ist) einen isosbestischen Punkt, der den Übergang zweier Chelate ineinander charakterisiert und für den die Extinktionskoeffizienten beider Chelate gleich sein müssen.

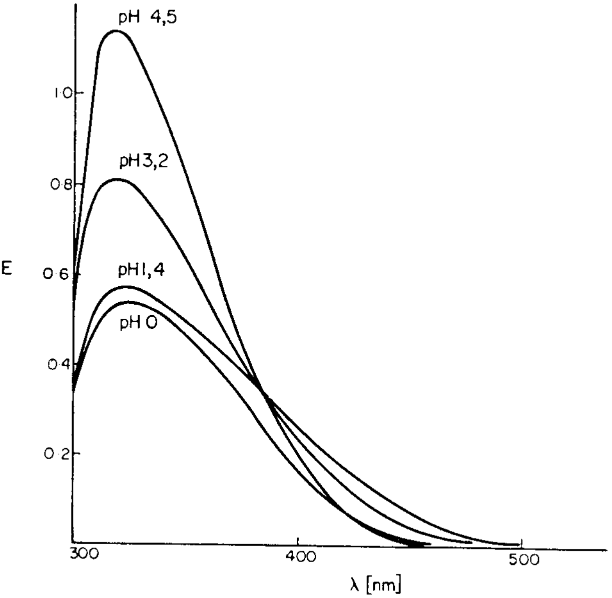

Abb. 1.—Absorptionsspektren der Tantal–DBG-Chelate in Gegenwart von Oxalat.
$c_{Ta} = 8 \cdot 10^{-5} M$; $p = 380$; $s = 141$; $\mu = 1,0$

Das Maximum des zweiten Chelates ist vom Spektrum des ersten Chelates überdeckt. Die Bildung des Chelates III bei $s = 141$ ist nicht quantitativ. Die pH-Kurven bei 330, 360 und 400 nm ($p = 380, s = 141$) (Abb. 2) identifizieren die Existenzbereiche beider Verbindungen. Das 1:2-Chelat bildet sich bei pH = 4,5 vollständig, für das andere ist der optimale pH-Wert 2,0.

Da im System Tantal–DBG nur ein Chelat nachgeweisen werden konnte,[2] lag die Vermutung nahe, daß Oxalsäure beim Chelat III an der Komplexbildung teilnimmt. Um den Einfluß von Oxalsäure deutlich zu machen, wurde ein Spektrum bei pH = 2,0 mit sehr großem Oxalatüberschuß aufgenommen. Wie die Messungen zeigen, tritt für $s = 1550$ im Absorptionsspektrum bei 400 nm ein neues Maximum auf. Damit wird es wahrscheinlich, daß sich das Oxalat als Ligand an der Komplexbildung beteiligt. Das gelbe Chelat mit $\lambda_{max} = 400$ nm war selbst bei einem Verhältnis $C_{Ta}:C_{DBG} = 1:1$ ($s = 141$, pH = 2,0) nachweisbar. Job-Kurven von äquimolaren Lösungen bei $s = 141$ und pH = 2,0 ergeben für DBG einen Molarkoeffizienten von $n = 1$ im ternären Chelat.

Vom zweiten Liganden (Oxalat) ist ein hoher Überschuß nötig, um das ternäre Chelat zu erhalten, da Tantal(V) mit DBG selbst in äquimolarer Lösung ein relativ stabiles 1:2-Chelat bildet. Das Verhältnis Tantal:Oxalat im ternären Chelat wurde deshalb nach einem modifizierten Verfahren zur Analyse von C_R-Kurven bestimmt.

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* s = Verhältnis der Konzentration des Hilfskomplexbildners zur Konzentration der Erdsäure; p = Konzentration DBG/Konzentration Erdsäure.
]

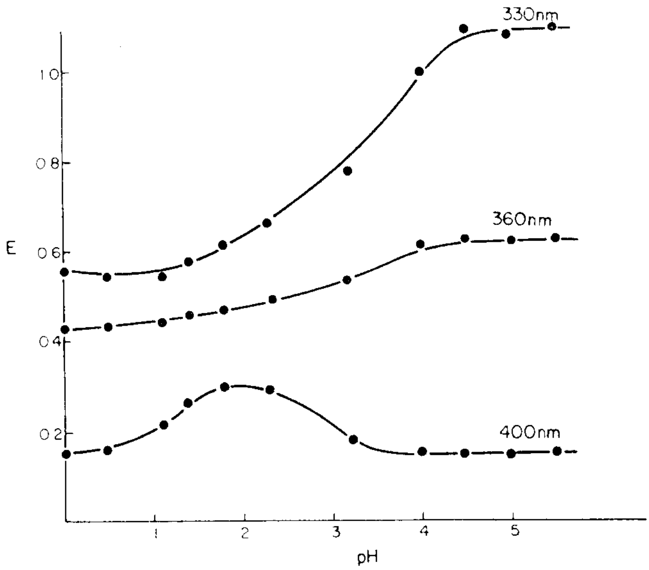

Abb. 2.—Abhängigkeit der Extinktion der Tantal–DBG-Chelate vom pH-Wert in Gegenwart von Oxalat.
$c_{\mathrm{Ta}} = 8\cdot10^{-5}M$; $p = 380$; $s = 141$; $\mu = 1{,}0$

Für die Reaktion des Tantal-DBG-Chelats mit Oxalsäure lautet die Endgleichung zur Analyse der Funktion $E = f\,(C_{\mathrm{HOx}^-})$

$$\log \frac{E' - E}{E - E_0} = n \log C_{\mathrm{HOx}^-} + c$$

Es bedeuten:

E_0 = Extinktionswert bei quantitativer Bildung des ternären Chelates

E' = Extinktionswert bei quantitativer Bildung des binären Chelates

n = Molarkoeffizient für Oxalat im ternären Chelat

c = eine Konstante

Die Bestimmung von n erfolgte aus dem Neigungswinkel der Funktion. Der Wert von E' wurde durch Extrapolation der Funktion $E = f\,(C_{\mathrm{HOx}^-})$ für $C_{\mathrm{HOx}^-} = 0$ zu $E = 0{,}25$ erhalten. Der Molarkoeffizient beträgt $n = 2{,}0$. Die Zusammensetzung des ternären Chelates ist somit (da Ta:DBG = 1:1) Ta:DBG:Ox = 1:1:2.

Äthylendiamintetraessigsäure

Die im Anschluß beschriebenen Versuche sollten entscheiden, ob auch die Äthylendiamintetraessigsäure in der Lage ist, ternäre Komplexe mit DBG und den Erdsäuren zu bilden.

Bei pH = 1,9, $p = 402$ und $s = 106$ bildet sich ein rotes Chelat mit $\lambda_{\max} = 470$ nm, das schon bei pH = 3,1 vollständig zerfallen ist (Abb. 3), denn hier tritt wieder das Spektrum des binären Komplexes auf.

Das Verhältnis Nb:DBG:ÄDTA im Chelat ermittelten wir mit Hilfe der Methode des molaren Verhältnisses.[3] Bei den Untersuchungen wurden jeweils zwei Komponenten konstant gehalten und die Konzentration der dritten variiert. Die photometrischen Titrationskurven (Nb·ÄDTA)–DBG und (Nb·DBG)–ÄDTA haben beim Komponentenverhältnis Nb:DBG = 1:1 bzw. Nb:ÄDTA = 1:1 einen scharfen Knick. Das Verhältnis Nb:DBG:ÄDTA im ternären Chelat muß somit 1:1:1 betragen.

Mit Tantal konnte das entsprechende ternäre Chelat nicht nachgewiessen werden, da nur die Spektren des binären Ta-DBG-Chelats mit $\lambda_{\max} = 320$ nm erhalten wurden.

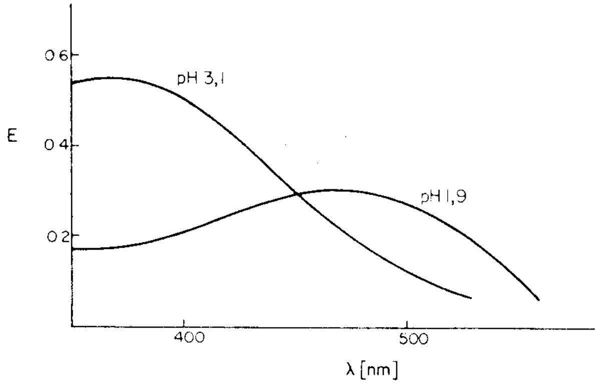

Abb. 3.—Absorptionsspektren des Niob–DBG-Chelats in Gegenwart von ÄDTA. $c_{Nb} = 7{,}56 \cdot 10^{-5} M$; $p = 402$; $s = 106$; $\mu = 1{,}0$

PAPIERELEKTROPHORESE

Die elektrophoretische Bestimmung der Chelat-Ladung erfolgte, wie bereits früher[2] beschrieben. Auf Grund der ermittelten Ladung von -2,8 sind komplexe Niob–DBG–ÄDTA-Ionen der Zusammensetzung $[NbO_2H_3RY]^{3-}$ bzw. $[NbOHRY]^{3-}$ möglich (H_3R = DBG; H_4Y = ÄDTA). Die für den Tantal–DBG–Oxalat-Komplex ermittelte Ladung von -6 entspricht $[TaO_2ROx_2]^{6-}$.

DISKUSSION DER ERGEBNISSE

In Gegenwart von Tartrat- oder Oxalationen bildet Niob die in reiner Lösung nachgewiesenen Verbindungen.[2] Lediglich die Existenzbereiche der einzelnen Chelate sind infolge Konkurrenzreaktionen von Niob mit den Hilfskomplexbildnern verschoben. In schwach saurer Lösung bildet sich bei hohem DBG-Überschuß auch $[NbO_2R_3]^{8-}$. Das Chelat $[NbO_2H_2R]$ entsteht bei pH = 0 auch in Anwesenheit von Tartrat; Oxalationen unterdrücken seine Bildung.

Unter bestimmten Bedingungen kommt es auch zur Bildung ternärer Chelate mit neuen optischen Eigenschaften. Die Reaktionsmechanismen werden hauptsächlich von der Konzentration der Komponenten und vom pH-Wert bestimmt. DBG reagiert mit Niob(V) in Gegenwart von ÄDTA in bestimmten pH-Grenzen zu einem ternären Chelat (λ_{max} = 470 nm) mit einem Verhältnis Nb:DBG:ÄDTA = 1:1:1 mit der wahrscheinlichen Zusammensetzung $[NbO(H)RY]^{3-}$, da der reine Niob–ÄDTA-Komplex in schwach saurer Lösung in der Literatur als $[NbOY]^{-}$ formuliert wird.[4,5] Nach Schwarzenbach[6] lagern die meisten ÄDTA-Komplexe bei pH = 3 ein Proton an. Ähnliche Verhältnisse sind auch bei Mischkomplexen zu erwarten. Andererseits kann aber auch eines der zwei Donatoratome der DBG in Chelaten protonisiert sein. Die Zuordnung des Protons zu einem der zwei Liganden ist deshalb auf Grund des vorliegenden Materials kaum möglich. Interessant ist, daß die analogen 1:1:1-Chelate des Niobs mit Brenzcatechin[7,8] (λ_{max} = 470 nm) und Pyrogallol[5] (λ_{max} = 480 nm) sehr ähnliche optische Eigenschaften besitzen.

Das entsprechende Tantal–DBG–ÄDTA-Chelat konnte nicht nachgewiesen werden, obwohl aus der Literatur die Mischkomplexe mit Pyrogallol und Brenzkatechin bekannt sind.[5,7,8]

Tantal(V) bildet in schwach saurer Lösung (pH = 4,5) auch in Gegenwart von Oxalationen das Chelat $[TaO_2R_2]^{5-}$, λ_{max} = 320 nm.[3] Bei pH = 2 und Oxalatüberschüssen kommt es zur Anlagerung von Oxalationen unter Abspaltung eines DBG-Liganden:

$$[TaO_2R_2]^{5-} + 2\,C_2O_4^{2-} \rightleftharpoons [TaO_2R(C_2O_4)_2]^{6-} + R^{3-}$$

Das Absorptionsmaximum verschiebt sich dabei von 320 nm nach 400 nm.

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Summary—The reactions between niobium(V) or tantalum(V) and dibromogallic acid in the presence of auxiliary complexing agents have been examined spectrophotometrically and electrophoretically. The ternary chelates $[NbO(H)RY]^{3-}$ and $[TaO_2ROx_2]^{6-}$ (H_3R = dibromogallic acid, Ox = oxalate, H_4Y = EDTA) were found.

Zusammenfassung—Mit Hilfe spektrophotometrischer und elektrophoretischer Messungen werden die Reaktionen von Niob(V) und Tantal(V) mit Dibromgallussäure in Gegenwart einiger Hilfskomplexbildner untersucht und die Existenzbereiche der Reaktionsprodukte bestimmt. Dabei konnten die ternären Chelate $[NbO(H)RY]^{3-}$ und $[TaO_2ROx_2]^{6-}$ (Dibromgallussäure = H_3R, Ox = Oxalat, H_4Y = ÄDTA) nachgewiesen werden.

Résumé—On a examiné par spectrophotométrie et électrophorèse les réactions entre le niobium(V) ou le tantale(V) et l'acide dibromogallique en la présence d'agents complexants auxiliaires. On a trouvé les chélates ternaires $[NbO(H)RY]^{3-}$ et $[TaO_2ROx_2]^{6-}$ (H_3R = acide dibromogallique, Ox = oxalate, H_4Y = EDTA).

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SUMMARIES FOR CARD INDEXES

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Summary—The metallochromic indicator Methylthymol Blue was purified chromatographically with cellulose and ion-exchange resin columns. The monosubstituted product of the reaction, Semimethylthymol Blue, was also separated and purified, and can also be used for the colorimetric determination of metals. There are not marked differences between the infrared spectra of Methylthymol Blue and Semimethylthymol Blue. The purities of Methylthymol Blue and Semimethylthymol Blue finally obtained were above 97% and 90% respectively. In acidic medium Methylthymol Blue forms 1:1 greyish blue and 1:2 pure blue chelates with copper(II) whilst Semimethylthymol Blue forms only 1:1 orange chelates with bivalent metals. The molar absorptivities at 435 mμ are 1·89 (±0·03) × 10^4 for Methylthymol Blue at pH 5·00 and 1·76 (±0·03) × 10^4 for Semimethylthymol Blue at pH 5·45.

Automated determination of traces of mercury in biological materials by substoichiometric radioisotope dilution: J. RŮŽIČKA and C. G. LAMM, *Talanta*, 1969, **16**, 157. (Chemistry Department A, The Technical University of Denmark, Building 207, Lyngby.)

Summary—Solid samples (1–2 g) are burned in oxygen in a flask containing radiomercury in dilute hydrochloric acid, in which the non-active mercury to be determined is immediately absorbed. All mercury is subsequently extracted by dithizone in carbon tetrachloride and then re-extracted into dilute hydrochloric acid. This aqueous phase is further analysed automatically (AutoAnalyzer, 20 samples/hr) as previously described. Liquids (up to 100 ml) are analysed in the same way but instead of being burned in oxygen are first oxidized with potassium permanganate in acid medium. Quantities between 2 and 0.00004 ppm Hg were determined in various materials. Results for international biological standards agreed well with values obtained by activation analysis: kale 0.159 ppm Hg (relative standard deviation 2%) and IAEA cereals 0.0435 ppm Hg (±5%). The new method is far more simple and rapid than activation analysis and just as sensitive; it is therefore more suitable for routine work. About 100 samples can be analysed per day.

ИЗУЧЕНИЕ МЕТИЛТИМОЛОВОГО ГОЛУБОГО—I. ВЫДЕЛЕНИЕ И ОЧИЩЕНИЕ МЕТИЛТИМОЛОВОГО ГОЛУБОГО И СЕМИМЕТИЛТИМОЛОВОГО ГОЛУБОГО:

Takashi Yoshino, Harumi Imada, Tadayoshi Kuwano and Katsuya Iwasa, *Talanta*, 1969, **16**, 151.

Резюме—Металлохромный индикатор метилтимоловый голубой очищен хроматографическим методом на колонках целлюлозы и ионообменной смолы. Однозамещенный продукт реакции, семитимоловый голубой также выделен и очищен; им также можно пользоваться для колориметрического определения металлов. Заметные разницы между инфракрасными спектрами метилтимолового голубого и семиметилтимолового голубого не существуют. Получены конечные чистоты больше чем 97% для метилтимолового голубого и 90% для семиметилтимолового голубого, соответсвтенно. В кислой среде метилтимоловый голубой образует 1:1 сероватоголубой и 1:2 чистый голубой хелаты с медью(II), а семиметилтимоловый голубой образует только 1:1 оранжевые хелаты с двувалентными металлами. Молярные поглощения при 435 ммк 1,89(±0,03) × 10^4 для метилтимолового голубого при pH 5,00, а 1,76(±0,03) × 10^4 для семитимолового голубого при pH 5,45.

АВТОМАТИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ РТУТИ В БИОЛОГИЧЕСКИХ ИАТЕРИАЛАХ СУБСТЕХИОМЕТРИЧЕСКИМ МЕТОДОМ РАЗБАВЛЕНИЯ ИЗОТОПОВ:

J. Růžička and C. G. Lamm, *Talanta*, 1969, **16**, 157.

Резюме—Твёрдые пробы (1–2 г) сжигают в кислороде в колбе содержащей радиоактивную ртуть в разбавленной соляной кислоте, в которой определимая неактивная ртуть немедленно абсорбируется. Последовательно всю ртуть извлекают раствором дитизона в тетрахлорметане и снова извлекают разбавленной соляной кислотой. Эту водную фазу анализируют автоматическим методом (АутоАналайзер, 20 проб/час) как раньше описано. Жидкости анализируют тем же образом, но вместо сжигания в кислороде окисляют перманганатом калия в кислой среде. Концентрации в пределах 2 до 0,00004 мг/л Hg определени в разных материалах. Результаты получены на международных биологических эталонах хорошо соглашались с величинами полученными методом радиоактивационного анализа: кудрявая капуста 0,159 мкг (г Hg) относительная стандартная ошибка 2%/ и ИАЕА кушанье 0,0435 мкг/г Hg (±5%). Новый метод значительно простее и быстрее чем метод радиоактивационного анализа, а обладает одинаковой чувствительностью; этим образом метод является подходящим для серийных анализов. Можно провести около 100 проб в день.

Ion-exchange resins in non-aqueous solvents—III. Solvent-uptake properties of ion-exchange resins and related absorbents: Donald J. Pietrzyk, *Talanta*, 1969, **16**, 169. (University of Iowa, Department of Chemistry, Iowa City, Iowa 52240, U.S.A.)

Summary—Solvent-uptake properties for several synthetic resins and common adsorbents were determined by the centrifugation method. Data are reported for eighteen different solvents, which include water and the common polar and non-polar organic solvents. The cation-exchange resins are of two varieties: the microreticular or gel type and the macroreticular or porous type. The latter resin being rigid and porous takes up all types of solvents, whereas the former resin, which relies on swelling of the resin matrix, does not take up the non-polar solvents. Data for the H^+ form and Na^+ form macroreticular resin are compared. Unsulphonated polystyrene-divinylbenzene polymers which possess, similar micro- and macroreticular properties to the cation-exchange resins were also studied in the same solvents. The swelling properties of these non-polar resins are compared with each other and with the polar cation resins. Other adsorbents, which are frequently used as supports in chromatography were also examined in the same solvents. Several of these have large average pore diameters and surface areas like the macroreticular resin.

Coulometric assay of the primary standards potassium dichromate and ammonium hexanitratocerate: John Knoeck and Harvey Diehl, *Talanta*, 1969, **16**, 181. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—The high-precision coulometric titration apparatus of Eckfeldt and Shaffer (Leeds & Northrup Company) has been used for the precision assay of two primary standard materials for oxidation-reduction work. The purity found for NBS 136b Potassium Dichromate, 99.975%, standard deviation 0.002%, checks the earlier value of Marinenko and Taylor. Ammonium hexanitratocerate. if low in thorium, is also an excellent primary standard, two recent commercial preparations having purities of 99.972 and 99.984%, a higher standard deviation, 0.005%, reflecting a minor difficulty in end-point detection, caused by platinum oxide formation on the indicating electrodes.

ИСПОЛЬЗОВАНИЕ ИОНООБМЕННЫХ СМОЛАХ В НЕВОДНЫХ РАСТВОРИТЕЛЯХ—III. ПОГЛОЩЕНИЕ РАСТВОРИТЕЛЕЙ ИОНООБМЕННЫМИ СМОЛАМИ И СВЯЗАННЫМИ АДСОРБЕНТАМИ:

DONALD J. PIETRZYK, *Talanta*, 1969, **16**, 169.

Резюме—Определены методом центрифугирования поглощающие свойства некоторых синтетических смол и обыкнове) Н-ных адсорбентов. Приведены данные для 18 растворителей включая воду и обыкновенные полярные и неполярные органические растворители. Изучены два типа катионообменных смол: микроретикулярный или гельный тип и макроретикулярный или пористый тип. Последная смола является твёрдой и пористой и следовательно поглощает все типы растворителей; первые смолы основываются на набухании матрици смолы и не поглощают неполярные растворители. Сравнены данные для H^+ и Na^+ форм макроретикулярных смол. Также изучено поведение в тех же растворителях несульфонированных полимеров полистиролa-дивинилбензола, обладающих микро- и макроретикулярными свойствами подобными катионообменными смолами. Поглощающие свойства этих неполярных смол сравнены одна с другой и с полярными катионными смолами. Другие часто использованные в хроматографии в качестве носителей адсорбенты также исследованы в тех же растворителях. Некоторые из них обладают большими средными диаметрами пор и поверхностями подобными макроретикулярной смоле.

АНАЛИЗ ПЕРВИЧНЫХ ЭТАЛОНОВ ДИХРОМАТА КАЛИЯ И ГЕКСАНИТРАТОЦЕРАТА АММОНИЯ КУЛОНОМЕТРИЧЕСКИМ МЕТОДОМ:

JOHN KNOECK and HARVEY DIEHL, *Talanta*, 1969, **16**, 181.

Резюме—Высокопрецизионный прибор для кулонометрического титрования Экфельта и Шеффера (фирма Лидс и Нортруп) использован для прецизионного анализа двух первичных эталонов для окислительно-восстановительного анализа. Для дихромата калия NBS 136ь найдена чистота 99,975%, стандартная ошибка 0,002%, которая хорошо соглашается с данными Мариненка и Тейлора. Гексанитратоцерат аммония, если содержает только небольшие преимеси тория, так же является отличным первичным эталоном—два коммерческих препарата дали чистоты 99,972 и 99,984%, стандартная ошибка 0,005%. Высшая ошибка указивает на незначительную трудность определения конца титрования, вызванную образованием окиси платины на индикаторных электродах.

X-Ray fluorescence analysis of titanium alloys: G. L. VASSILAROS and J. P. McKAVENEY, *Talanta*, 1969, **16**, 195. (Crucible Steel Research Laboratories, P.O. Box 988, Pittsburgh, Pennsylvania 15230, U.S.A.)

Summary—An X-ray solution method is proposed for determining major amounts of Mo, Sn and Zr in Ti alloys. The method utilizes adjacent elements in the periodic table as internal standards and has been successfully applied to levels of 3–10% Sn, 11–40% Mo and 6–20% Zr. The procedure involves three steps: dissolving the sample with a suitable acid mixture; adding the suitable internal standard at the concentration levels experimentally found to give optimum accuracy and precision; analysing the resulting solution mixture by X-ray fluorescence. Antimony was found to be a suitable internal standard for its adjacent element tin at a concentration ratio of 3:1 Sb:Sn. Niobium was successfully used for both its adjacent elements, molybdenum and zirconium, at 2:1 concentration ratios, Nb:Mo and Nb:Zr. A number of elements non-adjacent to tin, molybdenum and zirconium (i.e., copper, bromine, titanium, bismuth and tantalum) were experimentally found unsuitable as internal standards. Concentration factors of the internal standard and the adjacent elements sought were found to affect significantly the precision of analysis.

Spectrophotometric extractive titrations—VI. Titrations with 1-(2-pyridylazo)-2-naphthol: AFTANAS GALÍK, *Talanta*, 1969, **16**, 201. (Lachema, N.C., Kaznějov, Pilsen North, Czechoslovakia.)

Summary—The possibility of using PAN as a titrant in spectrophotometric extractive titrations has been investigated. Conditions suitable for the titration of zinc and of cadmium were found, with the aid of equations derived earlier and after investigation of the absorption spectra and pH- and reagent-dependence of the extraction of the chelates involved. For the purpose of spectrophotometric extractive titration of copper with PAN the formation and extraction of ion-association pairs $CuPAN^{+}\cdot Br^{-}$ and $CuPAN^{+}\cdot CNS^{-}$ were studied in detail. This titration was found to be highly selective. Dilute solutions of PAN in ethanol are much more stable than solutions of dithizone.

АНАЛИЗ СПЛАВОВ ТИТАНА МЕТОДОМ РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНЦИИ:

G. L. VASSILAROS and J. P. McKAVENEY, *Talanta*, 1969, **16**, 195.

Резюме—Предложен метод рентгеновской флуоресценции для определения макроколичеств Mo, Sn и Zr в сплавах титана. Метод пользуется соседными элементами в периодической таблице в качестве внутренных стандартов и был успешно применен в пределах 3–10% Sn, 11–40% Mo и 6–20% Zr. Процедура состоится из трех частей: растворения образца в подходящей смеси кислот; добавления подходящего внутренного стандарта в уровнях концентраий при которых опитом определена оптимальная точность и воспроизводимость; анализирования приготовленного раствора методом рентгеновской флуоресценции. Сурьма оказалася подходящим внутренным стандартом для соседного элемента олова при отношении концентраций Sb:Sn = 3:1. Ниобием успешно пользовались для обоих его соседных элементов—молибдена и циркония, при отношении концентраций Nb : Mo и Nb : Zr = 2 : 1. Ряд элементов не соседных олову, молибдену и цирконию (т.е. медь, бром, титан, висмут и тантал) опытом оказались неподходящими в качестве внутренных стандартов. Факторы концентрации внутренного стандарта и анализируемых соседных элементов в значительной мере влияли на точность анализа.

ЗКСТРАКЦИОННО-СПЕКТРОФОТОМЕТРИЧЕСКИЕ ТИТРАЦИИ—VI. ТИТРАЦИИ 1-(2-ПИРИДИЛАЭО)-2-НАФТОЛОМ:

AFTANAS GALÍK, *Talanta*, 1969, **16**, 201.

Резюме—Исследована возможность применения реагента в качестве титрационного агента в спектрофотометрическом экстрактивном титровании. Для простого расчета концентрации реагента была установлена абсолютная величина молярного поглощения реагента в этаноле. Было установлено, что устойчивость очень разбавленых растворов реагента намного выше устойчивости соответствующих растворов дитизона. В результате исследования спектров поглощения и влияния pH и количества реагента на экстракцию цинка и кадмия, применив уравнения выведенные раньше, были установлены оптимальные условия титрования этих элементов. С намерением установить оптимальные условия экстрактивного титрования меди было предпринято тщетное исследование экстракции этого элемента в виде ионных ассоциатов $CuPAN^+ \cdot Br^-$ или $CuPAN^+ \cdot CNS^-$. Это титрование оказалось весьма избирательным.

Application of partially dissociated complexes for spectrophotometric methods of analysis—I: Z. Slovák, J. Fischer and J. Borák, *Talanta*, 1969, **16**, 215. (Institute for Pure Chemicals, Lachema, Brno, Czechoslovakia.)

Summary—The dependence of errors in photometric methods of analysis based on the formation of partially dissociated complexes is discussed, and the range of ligand concentrations for various errors is calculated. It is shown that the highest possible ligand concentration should be used in order to minimize the error in a determination.

On potentiometric titration curves in complexometry: A. Hulanicki and M. Trojanowicz, *Talanta*, 1969, **16**, 225. (Department of Inorganic Chemistry, University, Warsaw, Poland.)

Summary—An equation is given which describes the potential changes during complexometric titration of metals with potentiometric end-point detection. The potential of the indicator electrode (*e.g.*, silver or mercury electrode) depends on the equilibrium of the reaction $MY + W \rightleftharpoons WY + M$, where W represents the indicator metal ion, and M the metal ion determined by titration with the ligand Y, forming 1:1 chelates. Introduction of the conditional stability constants and corresponding side-reaction coefficients facilitates the prediction of the limits of application of this type of titration as well as the optimum conditions for the determination.

Ternary complexes in the spectrophotometric determination of trace amounts of platinum(IV): Mohamed T. El-Ghamry and Roland W. Frei, *Talanta*, 1969, **16**, 235. (Chemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada.)

Summary—A simple, rapid, reproducible, sensitive and selective method is proposed for the spectrophotometric determination of submicrogram amounts of platinum(IV) in aqueous media. The proposed method involves the formation of a ternary complex between the hexa-ammine–platinum(IV) cationic complex, and the counter-ion 2,4,5,7-tetrabromofluorescein ethyl ester. The reaction is instantaneous and the red ternary complex remains stable for *ca.* 1 hr. Beer's law is obeyed over the range 39–1170 ppM with molar absorptivity of *ca.* $8{\cdot}0 \times 10^4$ at 555 nm and pH 10. A relative standard deviation of 1·1% was found for the reproducibility of the method. Even without the use of masking agents, no interference is encountered from other noble metals except rhodium(III). Of 13 other cations and 8 anions tested, only iron(III) interferes.

ПРИМЕНЕНИЕ НЕПОЛНО ДИССОЦИИРОВАННЫХ КОМПЛЕКСОВ В СПЕКТРОФОТОМЕТРИЧЕСКИХ МЕТОДАХ АНАЛИЗА—I.

Z. Slovák, J. Fischer and J. Borák, *Talanta* 1969, **16**, 215.

Резюме—Обсуждено появление ошибок в фотометрических методах анализа основывающихся на неполно диссоциированных комплексах, и рассчитаны пределы концентраций лигандов для различных ошибок. Показано что надо употреблять самые большие концентрации лигандов с целью довести на минимум ошибку в определении.

О ПОТЕНЦИОМЕТРИЧЕСКИХ КРИВЫХ ТИТРОВАНИЯ В КОМПЛЕКСОНОМЕТРИИ:

A. Hulanicki and M. Trojanowicz, *Talanta*, 1969, **16**, 225.

Резюме—Приведено уравнение описывающее перемены потенциала в течении комплексонометрического титрования металлов с потенциометрическим показанием конца титрования. Потенциал индикаторного электрода (на пр. серебряного или ртутного электрода) зависит от равновесия реакции $MY + W \rightleftharpoons WY + M$, где W представляет ион металла-индикатора, а M ион металла определимого с лигандом Y, образующего I:I хелаты. Введение обыкновенных констант устойчивости и соответствующих коэффициентов бочных реакций облегчает предсказание пределов применения этого типа титрования и оптимальных условий определения.

ИСПОЛЬЗОВАНИЕ ТРОЙНИХ КОМПЛЕКСОВ В СПЕКТРОФОТОМЕТРИЧЕСКОМ ОПРЕДЕЛЕНИИ СЛЕДОВЫХ КОЛИЧЕСТВ ПЛАТИНЫ(IV):

Mohamed T. El-Ghamry and Roland W. Frei, *Talanta*, 1969, **16**, 235.

Резюме—Предложен несложный, быстрый, воспроизводимый, чувствительный и селективный метод спект рофотометрического определения субмикрограммовых количеств платины(IV) в водных средах. Предложенный метод основывается на образовании тройного комплекса из катионного комплекса гексаммино-платины(IV) и противоиона этилового эфира 2,4,5,7-тетрабромфлуоресцеина. Реакция мгновенная а красный троной комплекс устойчивый в течение часа. Закон Бера сохраняется в области 39–1170 мг/л, молярная экстинкция составляет $8{,}0 \times 10^4$ при 555 нм и pH 10. Для воспроизводимости метода определена относительная стандартная ошибка 1,1%. Другие благородные металлы за исключением родия(III) не влияют на определение, даже без использования маскирующих агентов. Из испытаных других 13 катионов и 8 анионов только железо(III) влияет на определение.

Spectroscopy in separated flames—V. The argon- or nitrogen-sheathed nitrous oxide–acetylene flame in flame emission spectroscopy: G. F. Kirkbright, M. Sargent and T. S. West, *Talanta*, 1969, **16**, 245. (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The separation of the premixed nitrous oxide–acetylene flame by sheathing with argon or nitrogen is described. The interconal zone of the hot, slightly fuel-rich flame exhibits low background and noise levels and an extended reducing atmosphere, providing better conditions for the excitation of atoms of elements which form refractory oxides. The limits of detection found for nine such elements are greatly superior to those obtainable in the conventional unsheathed flame under similar conditions.

Spectrophotometric determination of tartaric acid with β-naphthol: Gary D. Christian, *Talanta*, 1969, **16**, 255. (Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, U.S.A.)

Summary—Tartaric acid (50–800 μg) is reacted with β-naphthol (5 mg) in 90% sulphuric acid (2 ml) for 30 min on a steam-bath. The solution is cooled and diluted to 25 ml with 90% sulphuric acid and the absorbance is measured at 603 nm. Several absorption maxima are observed and the ratio and intensity of these depend on the concentration of acid during and after the reaction, and on the β-naphthol concentration. All tartaric acid isomers give essentially the same colour and absorbance. Interference studies are reported.

Application of a demountable water-cooled hollow-cathode lamp to atomic-fluorescence spectrometry: G. Rossi and N. Omenetto, *Talanta*, 1969, **16**, 263. (CCR-Euratom Chemistry Department, Ispra (Varese), Italy.)

Summary—A demountable water-cooled hollow-cathode lamp has been investigated as a primary source in atomic fluorescence spectrometry. The discharge current ranged from 300 to 500 mA, and the flowing argon pressure between 0·4 and 4 mbar. Sensitivities ranging from 0·03 to 2 μg/ml were obtained for 12 elements. The performances of the hollow-cathode lamp and those of the customary metal vapour discharge lamps for thallium, indium and gallium are compared. The role of the narrowness of the exciting lines in increasing the signal-to-scattering ratios is stressed.

СПЕКТРОСКОПИЯ В ОТДЕЛЕННЫХ ПЛАМЕНАХ—V. ПРИМЕНЕНИЕ ОТДЕЛЕННЫХ АРГОНОМ ИЛИ АЗОТОМ ПЛАМЕН ЗАКИСИ АЗОТА И АЦЕТИЛЕНА В ПЛАМЕННОЭМИССИОННОЙ СПЕКТРОСКОПИИ:

G. F. Kirkbright, M. Sargent and T. S. West, *Talanta*, 1969, **16**, 245.

Резюме—Описано отделение предварительно смешанного пламени закиси азота и ацетилена аргоном или азотом. Интерконусная зона горячего, незначительно богатого топливом пламени обладает низким фоном и уровнем шума и протянутой восстанавливающей атмосферой; этим образом улучшены условия для возбуждения атомов элементов образующих огнеупорные окиси. Пределы обнаружения девять таких элементов в значительной мере превосходят пределы полученные обыкновенным неотделенным пламенем в подобных условиях.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ВИННОЙ КИСЛОТЫ БЕТАНАФТОЛОМ:

Gary D. Christian, *Talanta*, 1969, **16**, 255.

Резюме—Винную кислоту (50–80 мкг) реагируют с бета-нафтолом (5 мг) в 90%-тной серной кислоте (2 мл) в течение 30 мин. На паровой бане. Раствор охлаждают и разбавливают ло 25 мл с 90%-тной серной кислотой, затем измеряют светопоглощение при 603 нм. Обнаруживнются несколько максимумов, отношение и интенсивность которых зависит от концентрации кислоты во время и после реакции и от концентрации бета-нафтола. Все изомеры дают естественно ту же окраску и светопоглощение. Приведены результаты изучения влияющих на определение веществ.

ИСПОЛЬЗОВАНИЕ В АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОМЕТРИИ СЪЕМНОЙ ЛАМПЫ С ПОЛЫМ КАТОДОМ С ВОДЯНЫМ ОХЛАЖДЕНИЕМ:

G. Rossi and N. Omenetto, *Talanta*, 1969, **16**, 263.

Резюме—Изучено использование в атомно-флуоресцентной спектрометрии съёмной лампы с полым катодом с водяным охлаждением в качестве первичного источника. Разрадный ток составлял 300 до 500 ма, а давление струи аргона 0,4 до 4 мбар. Получены чувствительности 0,03 до 2 мкг/мл для 12 элементов. Сравнены действия лампы с полым катодом и обыкновенных ламп с разрядом пара металла для таллия, индия и галлия. Подчеркнуто влияние узости возбуждующих линий на повышение отношения сигнала и фона.

Prüfung der flammenphotometrischen Anionenstörung—I: Untersuchung der Aluminiumstörung: E. Pungor and Á. Szász, *Talanta*, 1969, **16**, 269. (Institut für Analytische Chemie der Universität für Chemische Technik, Veszprém, Ungarn.)

Summary—The interference due to aluminium in the flame emission spectroscopic determination of calcium has been investigated, by measurement of the emission intensities at various heights in a turbulent oxy-hydrogen flame. The results suggest the formation of a 1:2 calcium-aluminium compound in the flame. The interference can be explained in terms of an apparent equilibrium in the gas-phase.

Absorptiometric determination of traces of iron extracted as ferroin thiocyanate: V. Pandu Ranga Rao, K. Venugopala Rao and P. V. R. Bhaskara Sarma, *Talanta*, 1969, **16**, 277. (Chemistry Department, Andhra University, Waltair, S. India.)

Summary—Iron up to 3 ppm can be absorptiometrically determined by extracting the ferroin–thiocyanate complex at pH 1 into isobutyl methyl ketone (IBMK). At this pH thiocyanate itself reduces iron(III) so reductants such as hydroxylamine are not needed. The complex is very stable and has a molar absorptivity of $20\cdot5 \times 10^3$ in IBMK at 525 nm. Most of the substances associated with iron in minerals and alloys do not interfere and methods are suggested for the elimination of the effect of those which do.

Determination of potassium with alkali–heavy metal cobaltinitrites: A. H. I. Ben-Bassat: *Talanta*, 1969, **16**, 280. (Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.)

Summary—A procedure is proposed for the removal and determination of K^+ by precipitation with $[Co(NO_2)_6]^{3-}$ in the presence of Pb^{2+} and H_2O_2. The whole precipitate is dissolved, the Co^{3+} estimated colorimetrically, and the K^+ content calculated, with a relative error of 1%. The potassium-containing precipitate may also be dissolved in $NaOH + NH_3$ solution, the Co^{3+} titrated complexometrically, and the potassium content deduced. These two procedures may be modified for the removal and determination of Pb^{2+}, Co^{2+}, Co^{3+} and NO_2^-. Na^+ ions do not interfere.

ИЗУЧЕНИЕ ВЛИЯНИЯ АНИОНОВ НА МЕТОД ПЛАМЕННОФОТОМЕТРИЧЕСКОГО АНАЛИЗА:—I: ИССЛЕДОВАНИЕ ВЛИЯНИЯ АЛЮМИНИЯ:

E. Pungor and Á. Szász, *Talanta*, 1969, **16**, 269.

Резюме—Изучено влияние алюминия на определение кальция методом пламенной эмиссионной спектроскопии, измерением интенсивности эмиссии при различных высотах в турбулентной пламени кислорода и водорода. Результаты опытов указивают на образование соединения кальция-алюминия 1:2 в пламени. Влияние можно объяснять кажущимся равновесием в газовой фаэе.

АБСОРБЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ЖЕЛЕЗА ЭКСТРАГИРОВАННЫХ В ФОРМЕ ТИОЦИАНАТА ФЕРРОИНА:

V. Pandu Ranga Rao, K. Venugopala Rao and P. V. R. Bhaskara Sarma, *Talanta*, 1969, **16**, 277.

Резюме—Метод позволяет абсорбциометрическое определение до 3 мг/л железа экстрагированием комплекса ферроинтиоцианата при pH 1 изобутилметилкетоном (ИБМК). При этом pH сам тиоцианат восстанавливает железо(III), поэтому применение восстановителя такого как гидроксиламина излишно. Комплекс является весьма устоьчивым а его молярное светопоглощение равно $20{,}5 \times 10^3$ в ИБМК при 525 ммк. Большинство веществ находящихся вместе с железом в рудах и сплавах не влияют на определение; предложены методы исключения эффекта мешающих веществ.

ОПРЕДЕЛЕНИЕ КАЛИЯ С ИСПОЛЬЗОВАНИЕМ КОБАЛЬТИНИТРИТОВ ЩЕЛОЧНЫХ И ТАЖЁЛЫХ МЕТАЛЛОВ:

A. H. I. Ben-Bassat, *Talanta*, 1969, **16**, 280.

Резюме—Предложен метод удаления и определения K^+ осаждением с $[Co(NO_2)_6]^{3-}$ в присутствии Pb^{2+} и H_2O_2. Целый осадок растворяют, Co^{3+} определяют колориметрическим методом, а содержание K^+ рассчитают с относительной ошибкой 1%. Содержащий калий осадок также можно растворять в растворе NaOH и NH_3, определять CO^{3+} комплексонометрическим титрованием, а содержание калия определять из разницы. Эти две процедуры можно модифицировать для удаления и определения Pb^{2+}, CO^{2+}, Co^{3+} и NO_2^-. Иони Na^+ на мешают определению.

Microdetermination of iron in plant tissue with 4,7-diphenyl-1,10-phenanthroline: DONALD E. QUINSLAND and DONALD C. JONES, *Talanta*, 1969, **16**, 282. (Pacific Southwest Forest and Range Experiment Station Forest Service, U.S. Department of Agriculture, P.O. Box 245, 1960 Addison Street, Berkeley, California 94701, U.S.A.)

Summary—A method is described for the wet digestion and colorimetric determination of small amounts of iron in plant tissues. The wet digestion uses a mixture of sulphuric and nitric acids instead of perchloric acid; a volumetric flask is used for weighing, digestion, and dilution. The iron complex with 4,7-diphenyl-1,10-phenanthroline is extracted into hexanol.

Untersuchungen an Reagenzien für Niob und Tantal—III. Die Reaktionen der Dibromgallussäure mit Niob(V) und Tantal(V): GERHARD ACKERMANN and SIEGFRIED KOCH, *Talanta*, 1969. **16**, 284. (Institut für Anorganische und Analytische Chemie der Berkademie Freiberg, 92 Freiberg (Sachs), D.D.R.)

Summary—The nature and structure of the chelates formed between dibromogallic acid and niobium (V) or tantalum (V) have been investigated by spectrophotometric and electrophoretic methods. Depending on the pH and the concentration of the components, the complexes $[Nbo_2H_2R]$, $[Nbo_2HR]^-$, $[Nbo_2R]^{2-}$ and probably $[Nbo_2R_3]^{8-}$ and $[TaO_2R_2]^{5-}$ appear to be formed (H_3R = dibromogallic acid).

Untersuchungen an Reagenzien für Niob und Tantal—IV. Die Reaktionen der Dibromgallussäure mit Niob(V) und Tantal(V) in Gegenwart von Oxalsäure, Weinsäure und Äthylendiamintetraessigsäure: GERHARD ACKERMANN and SIEGFRIED KOCH, *Talanta*, 1969, **16**, 288. (Institut für Anorganische und Analytische Chemie der Bergakademie Freiberg, 92 Freiberg (Sachs), D.D.R.)

Summary—The reactions between niobium(V) or tantalum(V) and dibromogallic acid in the presence of auxiliary complexing agents have been examined spectrophotometrically and electrophoretically. The ternary chelates $[NbO(H)RY]^{3-}$ and $[TaO_2ROx_2]^{6-}$ (H_3R = dibromogallic acid, Ox = oxalate, H_4Y = EDTA) were found.

МИКРООПРЕДЕЛЕНИЕ ЖЕЛЕЗА В ТКАНИ РАСТЕНИЙ С 4,7-ДИФЕНИЛ-1,10-ФЕНАНТРОЛИНОМ:

Donald E. Quinsland and Donald C. Jones, *Talanta*, 1969, **16**, 282.

Резюме—Описан метод дигерирования и колориметрического определения небольших количеств железа в ткани растений. Дигерирование проводят с смесью серной и азотной кислотах вместо хлорной кислоты; для взвешивания, дигерирования и разбавления пользуются мерной кольбой. Комплекс железа с 4,7-дифенил-1,10-фенантролином экстрагируют гексанолом.

ИЗУЧЕНИЕ РЕАГЕНТОВ ДЛЯ НИОБИЯ И ТАНТАЛА—III. РЕАКЦИИ ДИБРОМГАЛЛОВОЙ С НИОБИЕМ(V) И ТАНТАЛОМ(V):

Gerhard Ackermann and Siegfried Koch, *Talanta*, 1969, **16**, 284.

Резюме—Исследованы природа и строение хелатов образующихся дибромгалловой кислотой и ниобием(V) или танталом(V) с применением спектрофотометрических и электрофоретических методов. В зависимости от pH и концентрации компонентов образуются комплексы $[NbO_2H_2R]$, $[NbO_2HR]^-$, $[NbO_2R]^{2-}$ и вероятно $[NbO_2R_3]^{8-}$ и $[TaO_2R_2]^{5-}$ (H_3R = дибромгалловая кислота).

ИЗУЧЕНИЕ РЕАГЕНТОВ ДЛЯ НИОБИЯ И ТАНТАЛА—IV. РЕАКЦИИ ДИБРОМГАЛЛОВОЙ КИСЛОТЫ В ПРИСУТСТВИИ ЩАВЕЛЕВОЙ, ВИННОЙ И ЭТИЛЕНДИАМИНТЕТРАУКСУСНОЙ КИСЛОТ:

Gerhard Ackermann and Siegfried Koch, *Talanta*, 1969, **16**, 288.

Резюме—Изучены спектрофотометрическими и электрофоретическими методами реакции ниобия(V) или тантала(V) с дибромгалловой кислотой в присутствии вспомогательных комплексообразующих агентов. Обнаружены третичные хелаты $[NbO(H)RY]^{3-}$ и $[TaO_2ROx_2]^{6-}$ (H_3R = дибромгалловая кислота, Ox = оксалат, H_4Y = ЭДТА).

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