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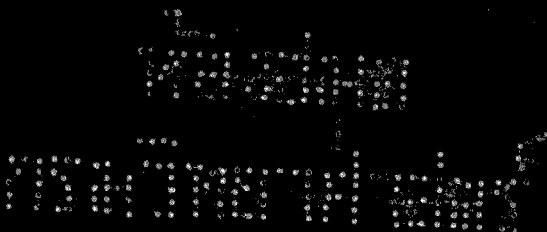
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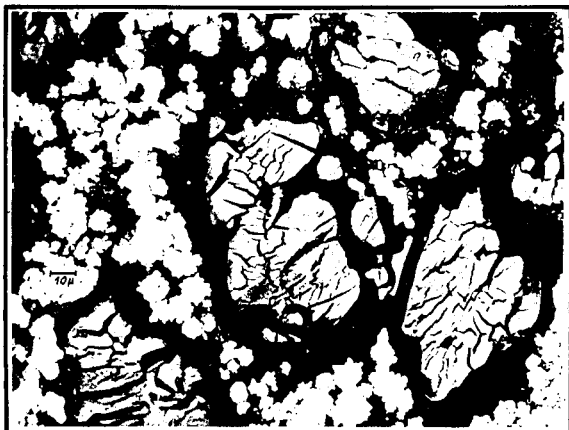
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ELECTROCHIMICA *Acta*

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Microphotograph of a DSK working layer.

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USE OF TETRACYANOPLATINATE(II) FOR THE LUMINESCENT DETECTION OF METAL IONS*

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Summary—The tetracyanoplatinate(II) (TCP) ion forms insoluble fluorescent compounds with many metal ions. This property has not hitherto been exploited for analytical use. The soluble sodium TCP salt has been applied as a reagent for metal ion detection. Fluorescent precipitates useful for detection of the metal ions were obtained with Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) and Th(IV). Limits of detection ranged from 5 to 200 ppm. With ammonium acetate as a masking agent, selective detection of 10 ppm of silver was achieved in the presence of the other metal ions. As little as 20 ppm of zirconium can be detected in the presence of hafnium, which yields a non-fluorescent precipitate.

THE DETECTION and/or determination of metal ions by luminescent methods constitutes an important and growing topic of present-day analytical research. The reagents used are mainly organic chelating molecules, producing characteristic fluorescent solutions with particular metal ions. Some inorganic compounds also possess luminescent properties. Of these, the tetracyanoplatinate(II) (TCP) ion is an unusual example since it is not a metal chelate. The physical properties of the TCP salts have been examined in some detail since the mid-19th century, yet their chemical reactions have received little attention. As far as could be ascertained from the literature the TCP salts have not been previously investigated as analytical reagents.

Many of the crystalline soluble TCP salts are fluorescent in the solid state, or in the frozen state in solution under ultraviolet excitation, and have been studied in some detail in radiation investigations. Apart from this, the applicability of metal-TCP compounds, in particular the insoluble compounds, does not appear to have been studied for metal ion detection. It seemed therefore of interest to study whether the luminescence of the insoluble metal TCP compounds could be exploited to detect metal ions in solution. The results of this study as they apply to detection are reported in this communication. The chemical and physical chemical aspects of the investigation will be reported elsewhere.

As a result of our investigation methods have been developed for the detection of certain metal ions. For example, silver, which is normally difficult to detect directly in the presence of such elements as lead, mercury and noble metals, is easily detected by means of the luminescent precipitate formed; zirconium, virtually indistinguishable chemically from hafnium, is readily detected in the presence of the latter because the zirconium TCP precipitate is luminescent and the hafnium one is not.

This communication describes the preparation and use of the pure barium and sodium TCP salts; the sodium salt is the preferred reagent. Use of sodium TCP as a

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reagent for the gravimetric and titrimetric determination of silver will be described in a later communication.

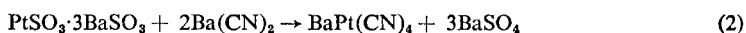
EXPERIMENTAL

Preparation of the tetracyanoplatinate(II) reagents

The barium and sodium TCP salts were prepared. The first recorded preparation of tetracyanoplatinate(II) compounds was by Gmelin¹ in 1822 for the potassium salt. Quadrat² in 1847 made the insoluble copper TCP from which he obtained the soluble barium salt, while Schertel³ made the latter by the fusion of platinum disulphide with barium cyanide. None of these methods appeared to give good yields. Bergsøe⁴ in 1899 synthesized the barium salt by a route involving the formation of an intermediate double salt of $\text{PtSO}_3 \cdot 3\text{BaSO}_3$, formed according to the reaction:



The double salt was then digested with barium cyanide solution at 50° to yield barium TCP as follows:



This method was reported to give good yields of the TCP salt, but it was not clear to what extent the yield was governed by the amount of barium cyanide in excess, the reaction temperature, and the digestion time.

Our first attempts to produce the barium TCP salt by Bergsøe's method, with a moderate excess of barium cyanide, produced rather poor yields. This was finally overcome by using a large excess of barium cyanide (about 5 times the stoichiometric requirements) and digestion for 4 hr at 50°; ~95% yields of pure material were then obtained.

The cyanide digestion temperature was found to be critical. At temperatures above 60° the double sulphite tends to decompose, depositing platinum black in the reaction mixture.

Poor yields were also obtained if in reaction (1) nitrate ion or nitric acid remained in the hexachloroplatinic acid solution, whether this was obtained as a commercial preparation or from dissolution of platinum sponge in *aqua regia*. The chloroplatinic acid solution must be repeatedly evaporated to dryness with hydrochloric acid in order to drive off all the nitric acid.

In the case of the alkali metal TCP salts, Quadrat² described some methods based on the reaction of the insoluble copper TCP with the metal hydroxides, and by treating tetrachloroplatinate salts with the appropriate alkali metal cyanide. These methods were considered too cumbersome as a means of obtaining the pure sodium TCP salt. In recent times Bergsøe *et al.*⁵ (1962) described an ion-exchange method for the preparation of alkali metal TCP salts; a solution of the barium TCP salt was passed down a column of cation-exchange resin to convert the salt into the free tetracyanoplatinic acid, which was then neutralized with the appropriate alkali, or alkaline earth metal oxide or carbonate.

It was considered that the ion-exchange method would provide a purer sample of the sodium TCP, and it was modified by using a cation-exchanger in the sodium form.

Preparation of barium tetracyanoplatinate(II). Platinum sponge of 99.999% purity (2 g) was dissolved in *aqua regia* (20 ml) and the solution of hexachloroplatinic acid reduced to small bulk on a boiling water-bath. The residue was taken up in conc. hydrochloric acid (10 ml, MAR) and the volume of liquid reduced once more by evaporation. This hydrochloric acid treatment was repeated until no more nitric acid was present in the residue.

The residue was taken up in distilled water (10 ml) and transferred to a 500-ml round-bottomed flask with distilled water. The solution was adjusted to pH 9–10 with 0.5M barium hydroxide, and diluted to about 200 ml with distilled water; barium hydroxide (23 g) was then added. The orange mixture was stirred to dissolve most of the barium hydroxide and the flask was placed in a water-bath maintained at 70°. The vessel was provided with a gas-delivery tube and exit, and when the mixture was at about 70° sulphur dioxide was passed slowly through the reaction mixture until the latter was colourless, indicating that all the barium hexachloroplatinate(IV) had been reduced, and was then passed for a further 15 min to ensure complete reduction. The contents of the flask, a mixture of the double sulphite and barium sulphate, were adjusted to pH 9–10 with 0.5M barium hydroxide and then filtered.

The reaction product was collected on a Whatman No. 542 paper in a Büchner funnel and washed with hot distilled water. The precipitate was very fine and difficult to collect, and decantation was impracticable since the precipitate did not settle. The product was sucked dry on the filter, transferred to a 250-ml beaker, and treated with a suspension of barium cyanide (20 g in 50 ml of water). The mixture was heated to 50° and stirred constantly for 4 hr. The precipitate decreased in bulk as reaction (2) proceeded. Carbon dioxide was then passed through the suspension in order to destroy

the excess of barium cyanide. The mixture was filtered and the solution of the barium TCP salt obtained was evaporated to small bulk. Green crystals of the barium TCP tetrahydrate were obtained on cooling the concentrate.

The yield was 4.87 g: 92.6% of the theoretical from the platinum taken. Analysis: found, C 9.3, 9.3%; H 1.6, 1.7%; Ba 26.6, 26.6%; $[\text{Pt}(\text{CN})_4]^{2-}$ 58.6, 58.6%; calculated for $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, C 9.43%; H 1.59%; Ba 27.0%; $[\text{Pt}(\text{CN})_4]^{2-}$ 58.8%.

Notes. 1. Determination of the water content of the product by drying to constant weight was found to be impracticable. The dried salt was extremely hygroscopic.

2. Further purification of the product was attempted by recrystallization from water, the solution being saturated with carbon dioxide. Yellow crystals of barium TCP tetrahydrate were obtained, and did not differ in analytical composition from the green material. This is consistent with the observations of Levy.⁶ Both tetrahydrates gave a green fluorescence under ultraviolet excitation, but the yellow form was much less fluorescent.

Preparation of sodium tetracyanoplatinate(II). A column of Amberlite IR-120 cation-exchange resin, 250 mm long and 20 mm in diameter, was changed into the sodium form by passage of a saturated solution of sodium bromide through it, and then washed free from bromide ions with demineralized water. A solution of the pure barium TCP tetrahydrate (1 g in 25 ml of water) was placed on the column, which was then washed with demineralized water until the effluent no longer gave a precipitate with silver nitrate solution, *i.e.*, all the TCP ion was washed from the resin.

The solution collected from the column was evaporated to small bulk and colourless crystals of the sodium TCP trihydrate were obtained on cooling the concentrate. The product gave a bright blue fluorescence under the ultraviolet lamp. Yield 0.76 g; 96.8% of theoretical. Analysis: found, $[\text{Pt}(\text{CN})_4]^{2-}$ 74.7, 74.8%; H_2O 13.4, 13.4%; calculated for $\text{Na}_2\text{Pt}(\text{CN})_4 \cdot [\text{Pt}(\text{CN})_4]^{2-}$ 74.9%; H_2O 13.5%.

Note. The $[\text{Pt}(\text{CN})_4]^{2-}$ ion was determined by the argentometric potentiometric titration used for the analysis of the barium TCP. The water of crystallization was determined by heating the weighed samples to constant weight at 160°. The anhydrous salt was not hygroscopic.

The reaction of tetracyanoplatinate(II) with metal ions

Quadrat⁷ described the preparation and analysis of some insoluble TCP compounds, and Stokes⁷ in 1853 stated that the precipitates obtained from the heavy metal ions and soluble TCP salts were usually non-fluorescent, but that mercury(II) gave a strongly fluorescent precipitate and silver a very weakly fluorescent precipitate. Since then no other investigators have reported fluorescence of insoluble TCP compounds. Müller,⁸ for example, in 1903 reported the production of coloured precipitates from the addition of a 3% solution of potassium TCP to certain metal salts in solution; no mention was made that any of the precipitates exhibited fluorescence.

A large number of soluble metal tetracyanoplatinate(II) salts have been prepared, mainly because of the interest shown in their fluorescent characteristics in the solid state and their possible use as scintillation materials. Pringsheim⁹ lists a number of soluble TCP salts prepared by various investigators before 1949. Later Tolstoi *et al.*¹⁰ prepared the alkali, alkaline earth and rare earth metal TCP salts in order to measure their fluorescence lifetimes.

In the present investigation, preliminary tests showed which of the metals selected and available gave precipitates with the sodium tetracyanoplatinate(II) reagent. The metals listed in Table I, as 5% w/v aqueous solutions of their nitrates or other soluble metal salts where the nitrates were not available, were treated with an excess of 5% w/v aqueous solution of the reagent.

Since several of the metal ion solutions were naturally acidic, the pH was raised, after the addition of TCP, by addition of 0.1M or 2.5M ammonium solution, the former being used for fine control. A greatly extended range of precipitates was thus obtained but some of these precipitates were evidently the metal hydroxides. However, when a fluorescent precipitate was produced only on addition of the ammonia it was concluded that at least some of the TCP ion had been brought out of solution, and further that either these metal-TCP compounds were soluble in acid and precipitated by ammonia, or that fluorescence was caused by adsorption of the TCP ion onto the metal hydroxide precipitate.

A more detailed study of the precipitation was then carried out under carefully controlled pH conditions. In this series of experiments the usual buffer solutions could not be used to control the pH, because they contained anions which would have given precipitates with some of the metal ions.

Each metal ion solution (0.1 ml) was treated with the sodium TCP reagent (0.1 ml), then adjusted to different pH values with the aid of narrow-range indicator papers and dropwise addition of 0.1M ammonia hydroxide or 0.1M nitric acid. The information obtained narrowed our interest (i) to those precipitates which formed in solutions of pH 6 or less, irrespective of whether they were fluorescent or not; and (ii) those precipitates that were fluorescent and which formed in solutions of pH above 6. The precipitates which formed in alkaline solutions were no longer of particular interest unless they were fluorescent, as some might well have been metal hydroxides.

The results are tabulated in Table I and discussed below.

DISCUSSION

Our investigation of the effect of pH on the formation of insoluble metal TCP precipitates revealed the conditions under which they were obtained. Certain of these precipitates, however, were non-fluorescent (see Table I), particularly those formed in solutions of pH 2, and it was not known whether they were indeed tetracyanoplatinates. It is known that the crystalline alkali and alkaline earth metal TCP compounds are fluorescent in the solid state^{9,10} Hence it seemed reasonable to expect any metal TCP precipitate to fluoresce. Many of the precipitates formed at pH 6–10 were fluorescent, as shown in Table I. Those that did not fluoresce and produced precipitates only in alkaline solution warranted further investigation, but were not of importance in this study of the TCP compounds. It was considered desirable to check that all the precipitates of interest did contain the metal tetracyanoplatinates.

TABLE I.—REACTION OF METAL IONS WITH TETRACYANOPLATINATE(II)

No precipitate	Non-fluorescent precipitate		Fluorescent precipitate		
	From aqueous solution	After addition of NH ₃	From aqueous solution (pH)	After addition of NH ₃ (pH)	
Ba	Co(II)	Au	Mn(VII)	Ag (1–9)	Al (4–6)
Ca	Cr(III)	Be	Nd	Hg(II)(1–5)	Cd (6–9)
Cr(VI)	Cu(II)	Bi(V)	Ni ⁺		La (10–12)
Cs	Fe(II)	Ce(III)	Pr		Pb (7–9)
K	Fe(III)	Ce(IV)	Pt		Th (7–9)
Li	Hg(I)	Co(II)†	Sb(III)		Y (10)
Mo	Ni	Cr(III)*	Sb(V)		Zn (6–9)
Na	Sb(III)	Cu(II)†	Sc		Zr (4–7)
Pd	V	Er	Sn(II)		
Rb		Eu	Sn(IV)		
Re(IV)		Fe(II)*	Tb		
Sr		Fe(III)*	Ti(III)		
Tl(III)		Hf	Ti(IV)		
		Hg(I)‡	Tl(I)		
		Ho	U(IV)		
		In	U(VI)		
		Mg	V		
		Mn(II)			

* Precipitation, pH 1–12.

† Precipitation, pH 1–6.

‡ Precipitation, pH 1–5.

The amounts available were too small for full analysis so we relied on ultraviolet examination, after dissolution of the samples in suitable media, for the peaks at 256 and 280 nm, attributable to the $[\text{Pt}(\text{CN})_4]^{2-}$ ion.¹¹ In all cases the presence of the TCP ion in the precipitates was confirmed.

From the results and consideration of the conditions of precipitation, we believe that those compounds precipitated in acid solution are simple TCP compounds, *e.g.*, $\text{NiPt}(\text{CN})_4$, whereas those obtained from an alkaline solution are probably basic salts, *e.g.*, $\text{Pb}(\text{OH})_2 \cdot x\text{PbPt}(\text{CN})_4$.

The silver, mercury and lead precipitates were found to have certain differences as follows:

Silver TCP. A white precipitate was obtained over the pH range 1–9, but none at pH 9–12, presumably because of ammine formation. The product had a brilliant

bluish-green fluorescence which became less intense on standing, and finally disappeared. Stokes⁷ found that only a weakly fluorescent precipitate was obtained.

Three factors were found to affect the decay time of the fluorescence: the decay time was shortened if the silver concentration was decreased, the excess of sodium TCP increased, or the degree of agitation increased.

When 0.5 ml of silver nitrate solution was treated with one drop of 1% sodium TCP reagent, the times needed for disappearance of the fluorescence were 2700, 600 and 15 sec for 1000, 100 and 10 ppm of silver respectively. The pH of the solutions did not seem to affect these times. The time factor must therefore be taken into account when applying the TCP test for detection of silver. The decay of the fluorescence, which occurs only with silver TCP, may be caused by photodecomposition, especially in ultraviolet light. Stoke's observation of weak fluorescence could have been due to delay in examination.

Mercury(I) TCP. At the mercury(I) concentration used a dark blue non-fluorescent precipitate was obtained over the pH range 1–5. At higher pH values elemental mercury was deposited in the reaction mixture.

When mercury(I) was examined at different dilution levels extremely anomalous results were obtained. At concentrations from 1 part in 10 down to 1 part of Hg(I) in 100, sodium TCP reagent gave a dark blue-non-fluorescent precipitate. From 1 part in 100 down to 1 part of Hg(I) in 200, a pale blue non-fluorescent precipitate was obtained. From 1 part in 200 down to 1 part in 10000 of Hg(I), a yellow precipitate was obtained which gave a blue fluorescence on standing for about 2 min.

With a concentrated solution of mercury(I) acetate dissolved in dilute sulphuric acid, sodium TCP gave a bright yellow precipitate having a blue fluorescence.

Quadrat² reported an analysis of the blue mercury(I) precipitate he had obtained and indicated that it may have contained nitrate ion. This fact was confirmed by us during an infrared study of these different precipitates. The dark blue precipitate gave the characteristic absorption lines of the nitrate ion on the spectrum. Mercury(I) therefore appears to yield under certain conditions a complex TCP nitrate which constitutes a positive interference in the test for the Hg(I) ion.

The test can be applied to detect Hg(I) at pH 1–5 provided the concentration of the metal does not exceed 1000 ppm. At this concentration, nitrate does not interfere with the performance of the test, which relies on the production of the yellow form of precipitate having a blue fluorescence.

The mercury(II) ion, as nitrate, does not yield anomalous precipitates at any concentration.

Lead TCP. Over the pH range 7–9 a white precipitate with a bluish-green fluorescence was obtained. At pH 1–4 there was no precipitation. With excess of ammonia a white non-fluorescent precipitate was obtained. It was found that lead also can form TCP nitrate complexes.

Three distinct varieties of lead TCP were produced: a non-fluorescent pink variety, an orange variety which had a yellow fluorescence, and white variety with a bluish-green fluorescence. The pink and orange forms showed the characteristic absorption lines of the nitrate when subjected to infrared analysis. The pink and orange complexes only occurred when the lead nitrate concentration was extremely high. Concentrations of up to 5% as lead nitrate gave a white variety with the bluish-green fluorescence.

Determination of the limits of identification

Solutions of the metal nitrates were prepared, containing 1000 ppm of the metal ion. A measured volume of the metal solution (0.5 ml) was taken in a micro test-tube, a drop of 1% sodium TCP reagent was added, and the pH of the mixture

TABLE II.—LIMITS OF DETECTION

Metal ion	pH for Precipitation	Colour of precipitate	Colour of fluorescence	Limit of detection ppm
Y(III)	10	White	Bluish-green	100
Zr(IV)	4-7	White	Green	20
Cr(III)	1-12	Blue	None	—
Fe(II)	1-12	White	None	—
Fe(III)	1-12	Brown	None	—
Co(II)	1-6	Pink	None	—
Ni(II)	1-6	Pale-green	None	—
Cu(II)	1-6	Pale-blue	None	—
Ag(I)	1-9	White	Bluish-green	10
Zn(II)	6-9	White	Green	50
Cd(II)	6-9	White	Green	200
Hg(I)	1-5	Blue*	None	—
		Yellow†	Blue	100
Hg(II)	1-5	White	Blue	5
Al(III)	4-6	White	Green	200
Pb(II)	7-9	White	Bluish-green	100
La(III)	10-12	White	Green	10
Th(IV)	7-9	White	Green	20

* Above 1000 ppm [Hg(II)].

† Below 1000 ppm [Hg(II)].

adjusted as indicated in Table II. The precipitate was examined *in situ*, under ultra-violet light. The metal ion solution was then diluted stepwise and treated as above until the dilution was so high that fluorescence under ultraviolet lamp was no longer visible. The concentration at which fluorescence was just visible on the precipitate was noted as the limit of detection for the metal ion.

Of the metal ions forming insoluble TCP compounds at pH 2, only silver, mercury(I) and mercury(II) yielded fluorescent precipitates. This difference provided a possible way of detecting these metal ions in the presence of the others, and in the presence of those metals which form non-fluorescent TCP compounds. However, those metals forming non-fluorescent precipitates are of some importance because they constitute a possible cause of interference by masking the fluorescent TCP to be detected.

The detection of the silver ion was explored first, because the methods for the chemical detection of silver in silver groups (Group I) of the classical qualitative analysis scheme and in metallurgical and geological specimens are laborious and require separation of silver from the other metals. A simple direct test would offer some advantage.

In application of the TCP test for silver in the silver group, lead does not interfere, because it does not give a TCP precipitate at pH 2, but mercury(I) and mercury(II) both yield fluorescent precipitates at pH 2 and do interfere. Metal ions yielding non-fluorescent TCP precipitates at pH 2 may also interfere.

Tests on solutions containing 10 ppm of silver showed that observation of the

fluorescence of the silver compound became impossible in the presence of 2 ppm of mercury(I), 200 ppm of chromium(III), 200 ppm of iron(II), 1 ppm of iron(III), 800 ppm of cobalt(II), 200 ppm of nickel(II) or 40 ppm of copper(II).

Further tests with various silver concentrations showed there was a linear relationship between silver ion concentration and the maximum tolerable interfering metal ion concentration.

Attempts to prevent the interference of other metal ions by addition of conventional masking agents such as EDTA, DCTA and other complexing substances were unsuccessful. These masking agents require buffering of the solution, and, the usual buffer solutions contain anions which themselves give precipitates with many metal ions. The silver ion was also complexed. It was found, however, that only the silver ion gave a fluorescent precipitate in ammonium acetate solution (used to produce a solution buffered at pH 7). The ammonium acetate acted as a complexing agent as well as a buffer.

The blue copper TCP compound dissolved in the ammonium acetate buffer to yield a deep blue solution, indicating that complexing had occurred, although free ammonia could not have been present to form the copper ammine complex.

Investigation showed that in order to detect 10 ppm of silver a final concentration of 10% of ammonium acetate in the precipitation solution was the maximum permissible. The more concentrated the ammonium acetate the more masking effect it would have, but later work on the gravimetric determination of silver as its TCP showed that extremely high concentrations of ammonium acetate dissolved some of the silver TCP precipitate.

The addition of ammonium acetate (1000-fold w/w ratio to silver) was found to raise the interference levels of mercury(I) to 10 ppm, iron(III) to 10 ppm and copper(II) to 250 ppm. The other interfering metal ions were unaffected, and the interference levels were again in linear relationship with the silver concentration, as in the absence of masking agent. As much as 1000 ppm of mercury(II) was masked with ammonium acetate.

Metals yielding precipitates only at pH values well above 2 did not interfere, whether the precipitation was fluorescent or not.

SOME ANALYTICAL APPLICATIONS OF SODIUM TCP REAGENT

The investigation has yielded a direct selective test for silver with many applications. Some of these are given below together with methods for other metal ions.

Reagents

Analytical-grade reagents and demineralized water were used throughout.

Ammonia solution, 0.1M. Prepared by dilution of concentrated ammonia solution.

Nitric acid, 0.1M.

Ammonium acetate solution, 10% w/v.

Sodium tetracyanoplatinate(II) solution, 1% w/v.

Silver in the presence of all metal ions

Place a drop of test solution* containing not less than 10 ppm of silver in a micro test-tube.† Add a drop each of the ammonium acetate and sodium TCP reagent. Flick the tube to mix the contents and place it immediately under an ultraviolet lamp (preferably enclosed in a box with its base and inside walls blackened). A white precipitate, having a bluish-green fluorescence and fading within minutes, indicates the presence of silver.

* Of the nitrates. If halides are present they must be removed by heating with sulphuric acid. Silver halides (except the fluoride) do not react with TCP.

† The preferred vessel. The depressions in a spot-tiler are not deep enough for the fluorescence to be seen.

Silver in galena

Heat 0.1 g of powdered sample with conc. sulphuric acid until fumes of sulphur trioxide are evolved, and repeat this process to remove any chloride present in the ore. Heat the residue to red heat, cool it, add a few drops of conc. nitric acid, warm, cool, centrifuge, separate the supernatant liquid, evaporate it to dryness, and take up the residue in 0.2 ml of 2.5M nitric acid. Treat one drop of the solution with 1 drop each of the ammonium acetate and sodium TCP reagents.

An ore analysed by emission spectroscopy and found to contain the elements Pb, As, Sb, Al, sI, Ca, Fe, Cu, Sn, Ni and Ag, was tested and a faintly green fluorescent precipitate was obtained.

Lead in the presence of mercury(II)

Take a drop of test solution containing about 100 ppm of lead in a micro test-tube, adjust the pH to 9 with 0.1M ammonia solution and add a drop of TCP reagent. A white precipitate having a bluish-green fluorescence indicates the presence of lead. Lead is distinguishable from silver by the fact that the fluorescence of the silver TCP fades within minutes, whereas that of lead TCP is quite stable. Up to 1000 ppm of mercury(II) can be tolerated in the test solution.

Lead in the presence of silver and mercury(II)

To a drop of test solution containing about 100 ppm of lead add a drop of 5% sodium chloride and warm to coagulate the silver chloride. Cool the mixture, adjust the pH to 9 with solution of ammonia and add a drop of sodium TCP reagent. A bluish-green fluorescent precipitate indicates the presence of lead. Up to 1000 ppm of silver and mercury(II) can be tolerated in the test solution.

Mercury(II) in the presence of lead

Adjust a drop of test solution [containing not less than 5 ppm of mercury(II)] to pH 2, in the micro-tube. Add a drop of sodium TCP reagent. A blue fluorescent precipitate indicates the presence of mercury(II).

Zirconium in the presence of hafnium

Take a drop of the test solution, containing not less than 20 ppm of zirconium, preferably as the nitrate, in the tube and adjust the pH to 6. Add a drop of the sodium TCP reagent. A green fluorescent precipitate indicates the presence of zirconium. Up to 100 ppm of hafnium can be tolerated in the solution.

Thorium in the presence of cerium

Adjust a drop of the test solution, containing not less than 20 ppm of thorium, to pH 9 and add a drop of the TCP reagent. A green fluorescent precipitate indicates the presence of thorium.

CONCLUSIONS

The tetracyanoplatinate(II) ion in the form of its sodium salt has proved a useful and versatile reagent for the detection of silver and some other metal ions, and for the determination of silver. Its application in the detection of zirconium in the presence of hafnium is of some interest because of the lack of suitable direct chemical methods for detecting zirconium. We have reported only on the preliminary work in this study of the zirconium-hafnium system, which is being continued to establish methods for the analysis of zirconium-containing materials. Systems involving other metal ions which yield fluorescent precipitates are also being examined.

The original aim of the investigation to produce a fluorescent titrimetric reagent based on a square planar complex ion of platinum is still being considered. It is felt that there may exist a complex of this metal with π -acceptor ligands which does exhibit strong fluorescence in solution. The possibility of this aspect is being explored.

The possibility of determination of metal ions by means of fluorescence of their TCP compounds has not been overlooked. It is considered that analysis by means of a modified spectrofluorophotometric technique may prove more fruitful than either gravimetric or titrimetric methods.

Zusammenfassung—Das Tetracyanoplatination (TCP) bildet unlösliche fluoreszierende Verbindungen mit vielen Metallionen. Diese Eigenschaft wurde bisher analytisch noch nicht ausgenutzt. Das lösliche Natrium-TCP-Salz wurde als Reagens zum Metallionen-Nachweis verwendet. Zum Nachweis geeignete fluoreszierende Niederschläge wurden mit Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I)-Hg(II), Al(III), Pb(II), La(III) und Th(IV) erhalten. Die Nachweisgrenzen lagen bei 5–200 ppm. Mit Ammoniumacetat als Maskierungsmittel wurde ein selektiver Nachweis von 10 ppm Silber in Gegenwart anderer Metallionen erzielt. 20 ppm Zirkonium können in Gegenwart von Hafnium nachgewiesen werden; Hafnium gibt eine nicht fluoreszierende Fällung.

Résumé—L'ion tétracyanoplatinate(II) (TCP) forme des composés fluorescents insolubles avec de nombreux ions métalliques. Cette propriété n'a pas été exploitée jusqu'ici à des fins analytiques. Le sel de sodium soluble du TCP a été appliqué comme réactif pour la détection d'ions métalliques. On a obtenu des précipités fluorescents utiles pour la détection d'ions métalliques avec Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) et Th(IV). Les limites de détection se sont situées entre 5 et 200 ppm. Avec l'acétate d'ammonium comme agent de dissimulation on a réalisé la détection sélective de 10 ppm d'argent en la présence des autres ions métalliques. Des quantités aussi faibles que 20 ppm de zirconium peuvent être détectées en la présence de hafnium qui donne un précipité non fluorescent.

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L'AUTOMATISATION EN ANALYSE PAR ACTIVATION NEUTRONIQUE ET SES APPLICATIONS A LA PRODUCTION INDUSTRIELLE

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Résumé—On tente d'expliquer pour quelles raisons l'analyse par activation n'a pratiquement pas encore réussi à sortir du domaine du laboratoire. On donne les conditions pour qu'une méthode analytique puisse être appliquée en cours de production industrielle et on étudie comment l'analyse par activation pourrait s'adapter à ces conditions. On présente enfin un cas de réussite d'une telle adaptation: l'analyse automatique de l'oxygène dans les aciers.

LA DÉCOUVERTE de ce procédé d'analyse élémentaire date de plus de trente ans. On connaît bien ses divers avantages: grande sensibilité, bonne précision, utilisation d'étalons primaires, bonne représentativité (gros échantillons, analyse dans la masse), conservation souvent possible de l'échantillon.^{1,2} Et pourtant la radio-activation n'est encore pratiquement utilisée que par les laboratoires très spécialisés de l'énergie atomique, des universités ou de quelques rares industries.

Cette diffusion, qui semble limitée à la recherche, tient principalement à deux caractères propres à l'analyse par activation.

(a) Il faut d'abord irradier l'échantillon à analyser au moyen de neutrons dont la principale source est constituée par la réaction de fission. C'est pourquoi l'analyse par activation s'est primitivement développée à proximité des centres nucléaires équipés de réacteurs.

(b) Le résultat du comptage de la radio-activité induite dans l'échantillon par l'irradiation se traduit le plus souvent par des histogrammes donnant l'intensité du rayonnement gamma en fonction de son énergie. Or, ces spectres sont en général très complexes; leur dépouillement est long et nécessite un personnel très qualifié.

Si les qualités de précision et de représentativité sont particulièrement appréciables pour les industriels, il n'en demeure pas moins que l'activation ne pourra s'imposer comme méthode d'analyse en cours de production que si elle répond à trois autres impératifs dont l'importance est primordiale: un temps de réponse assez bref, un grand débit de dosages et un coût rendant son utilisation rentable. Ceci a été longtemps impossible, du fait de la dépendance vis-à-vis des réacteurs et du dépouillement manuel des résultats; le développement récent des générateurs de neutrons et des petites calculatrices a changé les données du problème.

C'est ce qui explique que, en dehors des recherches sur le dosage des traces ultimes, il existe maintenant une nouvelle tendance très dynamique de l'analyse par activation dont le but est de rendre cette méthode applicable dans l'industrie.

ADAPTATION DE L'ANALYSE PAR ACTIVATION A L'INDUSTRIE

Développement des générateurs de neutrons

Le premier point était de s'affranchir des réacteurs. Cela a été rendu possible par le développement des petits accélérateurs de particules peu coûteux qui, équipés de cibles

tritiées, permettent d'obtenir des débits de l'ordre de 10^{11} à 10^{12} neutrons par seconde.³ Il s'agit de neutrons de 14 MeV et des études^{4,5} ont montré qu'on pouvait ainsi, avec ou sans thermalisation, doser plusieurs dizaines d'éléments avec une sensibilité qui atteint souvent la partie par million.

De plus, de nombreux dispositifs ont été imaginés^{6,7} pour obtenir des irradiations uniformes malgré la grande hétérogénéité des flux produits.⁸ Il en résulte une reproductibilité proche de la limite théorique et un écart-type relatif individuel inférieur à 2% est courant.

Automatisation du dépouillement

Le second point était de rendre automatique le dépouillement des comptages. L'utilisation d'une petite calculatrice électronique dans ce but n'est pas nouvelle.⁹ Mais il est, par contre, très rare de voir cette calculatrice montée en ligne, directement à la sortie de l'ensemble de spectrométrie.

En fait, le problème se pose différemment suivant la complexité du spectre gamma obtenu.²

(a) Si l'irradiation de l'échantillon ne donne naissance qu'à un seul radio-isotope ou bien si le radio-isotope choisi pour le dosage émet un rayonnement plus énergétique que ceux émis par les autres, il suffit d'utiliser un sélecteur à un seul canal que l'on centre sur le photopic gamma à mesurer. Le résultat du comptage se lit alors directement sur une échelle après une simple soustraction du bruit de fond.

(b) Si, par contre, le radio-isotope choisi pour le dosage ne produit pas le photopic le plus énergétique du spectre ou bien si on veut doser simultanément plusieurs éléments, on a le choix entre deux solutions.

1. On peut faire autant de comptages avec un sélecteur monocanal qu'il y a d'éléments à doser, en laissant l'échantillon refroidir entre chaque comptage de façon à faire disparaître les activités gênantes ou bien, au contraire, à obtenir certaines activités par différence. Le temps de réponse est alors relativement long mais il est possible d'augmenter le débit d'analyses par l'imbrication des séquences successives et par leur commande automatique au moyen d'un programmeur.

2. On peut utiliser un sélecteur multicanal qui permet d'enregistrer l'ensemble du spectre gamma. Ces informations sont ensuite traitées par une calculatrice qui, au moyen d'un programme appliquant la méthode des moindres carrés,^{10,11} reconstitue le spectre de l'échantillon à partir des spectres de ses éléments constitutifs. Les quantités de ces derniers se déduisent alors des coefficients de pondération.

Dans tous les cas, il faut évidemment rapporter les activités mesurées à un poids d'échantillon donné et à un flux de neutrons bien déterminé.¹²

Les petites calculatrices électroniques permettent d'envisager maintenant une automatisation complète de tous ces calculs, d'où une grande rapidité d'analyse accompagnée d'une économie de personnel.

CAS DU DOSAGE DE L'OXYGENE DANS LES ACIERS

Le dosage de l'oxygène est très important dans de nombreuses industries, surtout en métallurgie. Plusieurs procédés tels que la fusion réductrice sous vide ou sous gaz inerte peuvent fournir rapidement des résultats précis mais les masses ainsi analysées sont très faibles par rapport à la méthode par activation; de plus, lorsqu'un grand

nombre de dosages doit être effectué, l'activation ajoute l'avantage d'être économique grâce à la possibilité qu'elle offre de rendre l'analyse entièrement automatique.

Principe

On utilise une réaction qui ne se produit d'ailleurs qu'avec les neutrons très rapides donnés par les petits accélérateurs :



L'azote-16 ainsi formé décroît avec une période de 7,4 s, ce qui permet une mesure rapide, et il émet principalement des rayons gamma de 6,1 MeV. Or, ce radio-isotope est pratiquement le seul à émettre un rayonnement aussi énergétique. Il est donc facile d'automatiser le comptage en utilisant un sélecteur monocanal dont la fenêtre est réglée entre 4,5 et 6,5 MeV.¹³

Appareillage

L'équipement décrit ici a été mis au point par le Professeur Hoste à l'Université de Gand;^{14,15} il est à présent commercialisé par la S.A.M.E.S. à Grenoble. Il comprend trois parties.¹⁶

Un *générateur de neutrons* du type D (150 kV, 1,5 mA) peut fournir, avec les cibles tritiées actuelles, un débit constant de neutrons de $2 \cdot 10^{10}$ n/s pendant 10 heures environ. Une irradiation de 5 s étant suffisante, il est possible de faire 5000 dosages par cible, ce qui est donc très économique. Les irradiations sont commandées par le mouvement d'un écran escamotable en tantale. Ce générateur est entièrement blindé, ce qui permet de l'installer dans une salle de 3 m² seulement. Il est cependant nécessaire de l'entourer de protections importantes contre les neutrons rapides,¹⁷ de l'ordre de 1,20 à 1,50 m de béton.

Le *système de transfert* présente la particularité d'être constitué d'un double pneumatique de façon à pouvoir irradier ensemble, l'un derrière l'autre et pendant le même temps, l'échantillon et un étalon d'oxygène.^{18,19} Ainsi, même s'il y a des variations du débit de neutrons pendant l'irradiation, l'échantillon et l'étalon reçoivent des flux qui restent toujours proportionnels. Ce double pneumatique relie la double station d'irradiation, placée contre la cible, aux deux stations départ-arrivée, l'une étant pour l'étalon et l'autre pour l'échantillon. Cette dernière est équipée d'une glissière pour récupérer l'échantillon ou en introduire un nouveau. Par contre, le même étalon peut servir indéfiniment. Un chronoscope à temps fixes de 5, 10 et 15 s permet de sélectionner le temps d'irradiation en fonction de la teneur à déterminer et de l'usure de la cible. Un second chronoscope à temps fixe de 30 s donne le temps de comptage. Deux paires de cellules photo-résistantes n'autorisent l'une le déclenchement de l'irradiation et l'autre le démarrage du comptage que si échantillon et étalon sont tous les deux en place. Le programmeur assure automatiquement le va-et-vient des échantillons et des étalons par la commande de vannes à air comprimé. Il permet un fonctionnement manuel "coup par coup" ou bien automatique, les échantillons stockés dans le magasin étant alors analysés l'un après l'autre, une, deux ou trois fois chacun (ce qui est possible puisque l'analyse est non-destructive).

La *spectrométrie gamma* est faite au moyen de deux chaînes identiques comprenant chacune un détecteur à iodure de sodium, un sélecteur monocanal et une échelle qui a la particularité d'être remise à zéro sur le complément du bruit de fond lors de l'introduction d'un nouvel échantillon; un muret en plomb sépare les deux détecteurs.

Echantillon et étalon sont ainsi comptés séparément mais simultanément. A la fin du comptage, les nombres d'impulsions obtenus avec chacune des deux chaînes sont envoyés dans une petite calculatrice. Celle-ci fait le rapport entre ces deux nombres puis affecte ce rapport d'un coefficient tenant compte de la quantité d'oxygène contenue dans l'étalon, du poids de l'échantillon et d'un facteur *k* dû aux différences entre les conditions opératoires pour l'échantillon et pour l'étalon. Ces différences proviennent des efficacités de comptage, qui peuvent être différentes pour les deux chaînes, et du fait que l'étalon est irradié derrière l'échantillon; il est facile de déterminer ce facteur *k* en utilisant un échantillon identique à l'étalon. Le résultat du dosage est imprimé directement en nombre de ppm d'oxygène.

Résultats

Une telle installation est en fonctionnement depuis décembre 1966 dans une aciérie de la Société Cockerill-Ougree-Providence, juste au pied des convertisseurs

L.D.²⁰ Les résultats obtenus en exploitation de routine peuvent être résumés par le tableau suivant.^{21,22}

poids de l'échantillon	37 g
sensibilité limite	environ 5 ppm
précision au niveau de 50 ppm	10 %
au niveau de 500 ppm	4 %
au niveau de 1000 ppm	2 %
temps de réponse sans tenir compte du prélèvement	45 s
compte-tenu du prélèvement	3 mn
nombre de dosages actuellement effectués (3 par échantillon)	75000/an
prix de revient du dosage (amortissement sur 5 ans)	3,20 F

Cette installation répond donc parfaitement aux besoins des aciéristes qui doivent connaître très rapidement l'état d'oxydation des bains de métal à affiner.

DOSAGE AUTOMATIQUE DES AUTRES ELEMENTS

Le cas des autres éléments se présente de façon généralement beaucoup plus complexe. Cependant, comme on l'a signalé plus haut, le dosage automatique peut être possible par décroissance sélective ou par la méthode des moindres carrés, à condition bien entendu que l'élément à doser se transmute en un radio-isotope émettant un rayonnement gamma suffisamment intense.⁵ On peut citer quelques exemples d'applications dont certaines sont en cours de réalisation :

- dosage du silicium dans les aciers²³
- dosage de Fe, Si et Al dans les minerais de fer²⁴
- dosage de l'azote dans les engrais
- dosage du phosphore dans les scories Thomas
- dosage du hafnium dans les produits nucléaires
- dosage du baryum dans les huiles.

Nous n'avons jusqu'à présent envisagé que les analyses séquentielles par prélèvement mais il est évident que la prochaine étape du développement industriel de l'analyse par activation sera constituée par le dosage en continu qui permettra de contrôler la production directement sur bande transporteuse ou sur tuyauterie.^{25,26,27}

Summary—Reasons are given for the applications of activation analysis being generally confined to laboratory use. Conditions are given for application of analytical methods to industrial process control, in particular for automatic determination of oxygen in steels.

Zusammenfassung—Es werden Gründe dafür angegeben, daß die Anwendung der Aktivierungsanalyse im allgemeinen auf das Laboratorium beschränkt ist. Es werden die Bedingungen dafür angegeben, daß analytische Methoden auf die industrielle Prozeßüberwachung angewandt werden können, speziell auf die automatische Sauerstoffbestimmung in Stählen.

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A STUDY OF SOME MATRIX EFFECTS IN THE DETERMINATION OF BERYLLIUM BY ATOMIC-ABSORPTION SPECTROSCOPY IN THE NITROUS OXIDE-ACETYLENE FLAME

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Summary—A study has been made of a number of interferences observed in the trace determination of beryllium by atomic-absorption in the nitrous oxide-acetylene flame. The major negative interference caused by the presence of excess of aluminium salts may be overcome by the use of 8-hydroxyquinoline. Magnesium and silicon also depress the Be signal, but most other metals cause enhancement. In most instances the enhancements may be made uniform by the addition of potassium ions to the sample solution.

IN CONTINUATION of previous work in this laboratory on the determination of trace elements in a matrix of alumina or in the presence of large amounts of aluminium salts,^{1,2} it was decided to investigate the behaviour of beryllium atoms in the long-path (50 mm) nitrous oxide-acetylene flame when nebulized from solutions containing high concentrations of aluminium and various other elements.

Beryllium, being an element capable of forming highly refractory compounds, cannot be atomized efficiently in low-temperature flames, *e.g.*, a sensitivity of 300 ppm for 1% absorption has been quoted for 120-mm long air-acetylene flame,³ but the introduction of the high-temperature, highly reducing, nitrous oxide-acetylene flame enabled Amos and Willis⁴ to determine trace levels of beryllium by atomic-absorption spectroscopy (AAS). These authors reported a 10% depression of sensitivity caused by 500 ppm of aluminium, but observed no interference from 2.5*N* (*ca.* 12% w/v) sulphuric acid, though 1000 ppm of phosphorus (as phosphoric acid) caused a 2% enhancement. In the same paper it was shown that 1000 ppm of aluminium caused 10–20% enhancement in magnesium absorption. These and subsequent workers^{5,6} have investigated the effects of potassium as an ionization suppressant on calcium, barium, *etc.*, and several other significant interference effects in the nitrous oxide-acetylene flame have since been reported. In this work, the enhancement or depressant effects of many metal ions, acids and other compounds on the AAS determination of beryllium have been studied with special reference to aluminium interference.

EXPERIMENTAL

Apparatus

Techtron AA4 atomic-absorption spectrophotometer, with an A.S.L. beryllium hollow-cathode lamp and detector modulated at 285 Hz, fitted with an R213 photomultiplier and a 50-mm slot burner head for premixed nitrous oxide-acetylene. The wavelength was set at the most sensitive beryllium absorption line at 234.86 nm; the lamp current was 6 mA, slitwidth 100 nm (0.33-nm optical slit-width), nitrous oxide pressure 110 kN/m², acetylene pressure sufficient to give a red-zone of *ca.* 20 mm height; position of measurement in the flame usually 10–15 mm above the burner head.

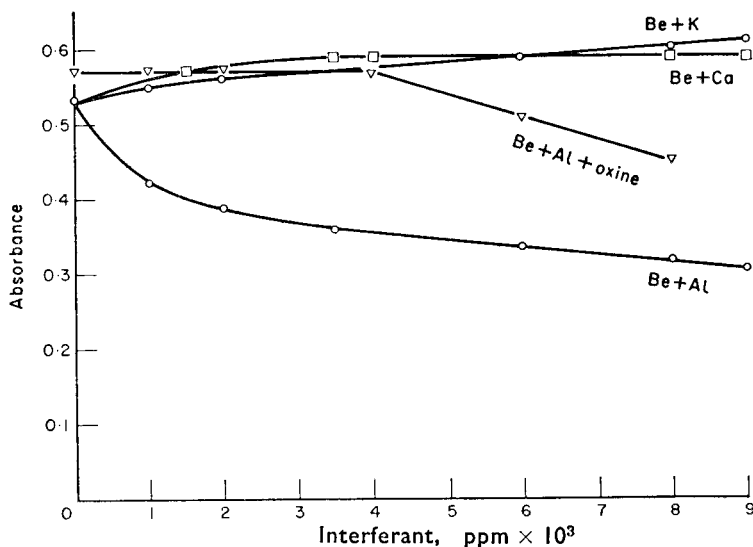


FIG. 1.—Effect of various interferents on 4 ppm of beryllium atomic absorption.

Reagents

Stock beryllium solution, 100 ppm. Prepared by dissolving 1.9656 g of analytical-grade $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ in water and diluting to 1 litre. Test solutions were prepared by dilution from this stock solution.

Aluminium chloride solution, 50000 ppm. Prepared by dissolving 50 g of aluminium foil in excess of hydrochloric acid (1 + 1) and diluting to 1 litre.

8-Hydroxyquinoline solution, 10% w/v. Prepared by dissolving 100 g of 8-hydroxyquinoline in hydrochloric acid (1 + 1) and diluting to 1 litre with water.

Potassium solution, 100000 ppm. Prepared by dissolving 25.9 g of potassium nitrate in water and diluting to 100 ml.

All solutions used were prepared from analytical-grade reagents except where stated.

Experiments on solutions containing high concentrations of aluminium and other metals

The direct determination of trace amounts of beryllium in aluminium alloys or alumina by atomic absorption in the nitrous oxide-acetylene flame, after simple dissolution in hydrochloric acid, would be desirable, but previous work⁴ suggested that considerable interference would be caused by as little as 500 ppm of aluminium. On continued addition of aluminium chloride to solutions containing 4 ppm of beryllium, a continuously increasing depression of signal was noticed and above about 5000 ppm of aluminium the depression became approximately linear with respect to aluminium concentration (see Fig. 1). At the 4000- and 9000-ppm aluminium levels depressions of 32% and 42.5% respectively were observed. It is clear that this is a very serious effect, the rapid variation of signal with aluminium concentration in the region 0–2500 ppm of the interferent obviously being the source of considerable error in the determination of traces of beryllium. It is well known that aluminium salts can cause major negative interferences in the atomic-absorption determination of many elements in the cooler air-propane and air-acetylene flames, owing to the formation of refractory alumina clotlets which are not readily dissociated, thereby entrapping the trace elements present.

In the nitrous oxide-acetylene flame, however, both enhancement and depression of sensitivity have been observed, *e.g.*, aluminium has been shown to enhance the AAS signal for magnesium,⁴ titanium,⁷ and vanadium,⁸ whereas there is a depression in the AAS signal for beryllium,⁴ strontium⁴ and cobalt.² It is clear, therefore, that several factors are involved (see Discussion), one of which may still be the formation of refractory clotlets which are not dissociated completely.

Previously it has been reported that the addition of 5% of oxine (8-hydroxyquinoline) to solutions containing magnesium and 200 ppm of aluminium could overcome their depressant effects in a low-temperature flame⁹. The reduction of interference is presumed to be caused by more efficient dissociation of the aluminium-containing clotlets in the presence of the organic compound. In this respect the atomization of beryllium in the flame would also be expected to be improved by the presence of oxine. A study of the effect of increasing oxine concentration in the AAS signal for 4 ppm of beryllium showed that up to 2% of oxine gave maximal enhancement of *ca.* 8%, but if the

TABLE I.—THE EFFECT OF HIGH CONCENTRATIONS OF VARIOUS METAL IONS ON THE ATOMIC-ABSORPTION SENSITIVITY OF BERYLLIUM*

Ion	Compound added	Concentration ppm	Effect on Be signal %
K	KNO ₃		+17.0
Pb	Pb(NO ₃) ₂		+17.0
Sn(II)	SnCl ₂		+17.0
Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄		+17.0
Sr	Sr(NO ₃) ₂		+15.1
Cd	CdSO ₄		+15.1
Zr	ZrCl ₄	10000	+15.1
Hg(II)	Hg(NO ₃) ₂		+13.2
Co(II)	CoCl ₂		+13.2
U(VI)	UO ₂ (NO ₃) ₂		+13.2
Ca	Ca(NO ₃) ₂		+11.3
Cu(II)	CuSO ₄		+11.3
Th	Th(NO ₃) ₄		+9.4
V(V)	NH ₄ VO ₃	4000	+9.4
Na	NaNO ₃		+7.5
Bi	Bi(NO ₃) ₃		+7.5
Fe(III)	FeCl ₃		+7.5
Cr(III)	CrCl ₃		+7.5
Se(IV)	H ₂ SeO ₃	10000	+6.6
Zn	ZnSO ₄		+5.7
Mn(II)	MnSO ₄		+5.7
Te(IV)	Te in HNO ₃ /HCl		+1.9
Nb(V)	Nb in HF	4000	+1.9
Ti(IV)	Ti in HF		+1.0
Ni	NiSO ₄		0.0
Mg	Mg(NO ₃) ₂	10000	-3.8
Si	H ₂ SiF ₆		-18.9
Al	AlCl ₃		-43.4

* All solutions contained 4 ppm beryllium, which in pure aqueous solution gave an absorbance of 0.53.

concentration was increased above *ca.* 6% of oxine, the absorption fell off again, presumably because of increased viscosity and reduction of nebulizer efficiency. The effect of adding 2.5% of oxine to solutions containing up to 4000 ppm of aluminium and from 1 to 4 ppm of beryllium, was to overcome the depression completely and to obtain a linear calibration curve exactly similar to that of a pure aqueous beryllium solution containing 2.5% of oxine (see Fig. 1). It was necessary to acidify the solutions with hydrochloric acid in order to obtain complete dissolution of the oxine and to prevent precipitation of the Al(C₉H₆ON)₃ complex. Unfortunately the "masking" of aluminium by oxine falls off steadily if concentrations of the metal are increased to above 4000 ppm, and a corresponding increase in oxine concentration to, say, 5% could not offset this.

Although beryllium atoms have been reported to be completely un-ionized in the nitrous oxide-acetylene flame,⁴ it was decided to test the effect of ionization suppressants and it was found that the presence of 9000 ppm of potassium and calcium produced enhancements of 15% and 11.3% respectively (Fig. 1). Subsequent investigations showed that many other metals, when added in large amounts, could cause significant enhancements of sensitivity for beryllium (see Table I).

From Table I it can be seen that the maximal enhancement of 17% was caused by the presence of 10000 ppm of potassium, lead, tin(II) or molybdenum (VI) whilst the other metal ions tested produced a steadily decreasing series of enhancements down to titanium(IV) and nickel, which exhibited little or no enhancement. Apart from magnesium which caused a depression of 3.8%, the only depressants encountered were silicon and aluminium.

It was found that linear calibration curves could be constructed for 0.5–4 ppm beryllium in the presence of excess of potassium, uranium, copper, *etc* and virtually no further enhancement of sensitivity was achieved by changing from 10000 to 20000 ppm of potassium. For all these minor enhancement interferences, it is clearly undesirable to have to construct a different calibration curve to account for the presence of each individual element, or group of elements, and it was discovered that if the metal ions of Sr, Cd, Zr(IV), Hg(II), Co(II), U(VI), Ca, Cu(II), Th, V(V), Na, Bi, Fe(III),

TABLE II.—THE EFFECT OF ORGANIC SOLVENTS ON THE ABSORPTION OF 4 ppm OF BERYLLIUM

Solvent added, 20% v/v	Interference, %
Methanol	+11.3
Ethanol	+13.2
Propan-2-ol	+20.8
Glycerol	-17.0
Acetone	+15.1
Acetic acid	+15.1

Cr(III), Se(IV), Zn, Mn(II), Te(IV), Nb(V), Ti(IV) and Ni were present in concentrations up to 4000 ppm the enhancement could be raised to the maximum produced by potassium, simply by making the solutions 10000 ppm in potassium by addition of 25.9% w/v potassium nitrate solution (equivalent to 100000 ppm of potassium). This procedure was also effective for masking up to 4000 ppm of magnesium. At concentrations greater than *ca.* 5000 ppm of the original interferent the addition of excess of potassium nitrate could not always be relied upon to bring the enhancement up to the required level, but for many of the elements producing enhancement as great or nearly as great as that by potassium [*e.g.*, U(VI), Mo(VI)], up to 10000 ppm of the original interferent plus 10000 ppm of potassium could be tolerated.

A 4000-ppm concentration of aluminium caused a 32% depression for 4 ppm of beryllium and this was reduced to a 21% depression by the addition of 10000 ppm of potassium; this may be considered as an enhancement effect on the absorption of the free beryllium atoms existing in the presence of aluminium, in which case it would represent a 17% enhancement—the same value produced by potassium for pure beryllium. A similar effect was predicted for silicon, but the precipitation of K_2SiF_6 prevented further investigation.

A study of the effect of position of measurement in the flame for a solution containing 4 ppm of beryllium, 4000 ppm of aluminium and 10000 ppm of potassium showed that optimal absorption occurred at a height of *ca.* 10 mm above the burner head, *i.e.*, the same as for pure solutions of beryllium.

Experiments on solutions containing acids, ammonium salts and organic compounds

Because some of the solutions previously described contained free hydrochloric acid, it was decided initially to test the effect of this acid on beryllium absorption, but no interference was noticed when solutions were made 1M with respect to hydrochloric acid. Subsequently 4-ppm beryllium solutions were prepared which contained orthophosphoric, sulphuric, hydrochloric and nitric acids at the 10000-ppm level with respect to Cl, S, N and P (*i.e.*, 3.16, 3.06, 1.03 and 4.50 w/v, respectively, of the pure acids).

Sulphuric acid caused a 5.7% enhancement, but the other acids showed no interference, nor did hydrofluoric acid at the 2 and 4% w/v levels. A systematic study of the enhancement caused by sulphuric acid revealed a steady increase in signal up to *ca.* 2.75% w/v sulphuric acid (7.5% enhancement) followed by a gradual decline until no effect at all was observed when the test solution contained *ca.* 9.2% w/v sulphuric acid. A similar reduction in the enhancement was noticed when solutions containing beryllium and aluminium were made more than *ca.* 6% w/v in oxine, and this could be caused by reduction of nebulizer efficiency in more viscous solutions. An attempt to verify the viscosity effect was made by making gradual additions of sucrose to solutions, the results being closely similar to those obtained with sulphuric acid, *i.e.*, a maximal enhancement of *ca.* 7% was observed at 2–3% w/v of sucrose, followed by a gradual decline. Ammonium chloride and ammonium nitrate, when added in the range 1–10% w/v, caused enhancements very similar to those obtained with potassium in the range 1000–10000 ppm and the ammonium radical may therefore, be grouped in Table I, with the metals causing optimal enhancement.

The effect of organic solvents can be seen in Table II; the results are predictable with the possible exception of acetic acid, where such a large enhancement was not expected. In each case the fuel flow-rate was adjusted to give the best flame conditions.

Finally the effect of a powerful surface active agent was investigated. The addition of 0.5% cetyltrimethylammonium bromide caused no interference.

DISCUSSION

Of the interference effects observed in AAS in the nitrous oxide-acetylene flame some may be explained by direct extension of the theories available to account for the

interferences in lower temperature flames, *e.g.*, organic solvent enhancement, which is primarily due to increased efficiency of nebulization.

In the high-temperature flame, ionization assumes greater importance and in many cases the addition of an ionization suppressant is valuable. In other cases, the ability of this flame to dissociate and reduce refractory oxides may cause a complete reversal of an interference effect, *e.g.*, in the air-propane flame the presence of aluminium severely depresses absorption sensitivity for magnesium whereas the opposite effect is observed in the nitrous oxide-acetylene flame. The presence of aluminium and titanium has been shown to give a maximal enhancement of *ca.* 25% in the AAS determination of vanadium^{8,10} and similar results were obtained for molybdenum.¹¹ In these cases, it has been proposed that a competition mechanism has been operating by which aluminium and titanium atoms preferentially remove atomic oxygen from the flame plasma, allowing a higher concentration of the test element in its atomic form, this process being favoured by a large excess of the interferent. It has also been reported that a number of refractory elements, especially aluminium, have a major enhancement effect in the determination of titanium.^{6,7} However, aluminium depresses the absorption of strontium⁶ and experiments on the AAS of calcium in the nitrous oxide-acetylene flame (in connection with the present work) showed that the presence of excess of aluminium could almost completely eliminate the calcium absorption signal.

For beryllium, it has been shown that the major depression caused by aluminium could be overcome by the addition of oxine. This would tend to indicate that the formation of refractory particles in the base of the flame is still of major importance even in a high-temperature reducing flame, and if this is the case, it becomes difficult to explain the enhancements previously noted. That the formation of refractory clots is not a generally valid assumption to account for depression of sensitivities in this flame medium is further suggested by the observation that other elements potentially capable of forming such high melting point oxides (*e.g.*, Mo, Zr, U, Th, Nb) cause *enhancement* of beryllium absorption. Bearing this in mind, it was noted that the only three elements, of those investigated, to cause negative interference were magnesium, aluminium and silicon, of which magnesium could scarcely be considered as capable of forming refractory particles in the flame. Furthermore in the periodic table magnesium and silicon flank aluminium, being elements of atomic number 12, 14 and 13 respectively. It is well known that beryllium and aluminium present what is probably the best example of the "diagonal relationship", there being many chemical similarities; there are also certain chemical similarities between beryllium and silicon (*e.g.*, see F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1962, pp. 168-177). In addition the ability of aluminium to replace silicon in silicate lattices to form the important group of aluminosilicate minerals illustrates further the close relationship of these elements. It is pertinent here to note that the major source of beryllium is the mineral beryl, $3\text{BeO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$, and considering these facts it is clear that a special case of refractory compound formation in the flame may well be responsible for the major depressant effects of aluminium and silicon, while the minor depression due to magnesium may also be the result of a chemical interaction causing reduction in atomic population. There are other examples of specific chemical interference in atomic absorption in the nitrous oxide-acetylene flame, *e.g.*, the enhancement caused by hydrofluoric acid and iron on

titanium, zirconium, hafnium and tantalum^{4,7} and the recently reported enhancement effect of nitrogen-containing compounds on the atomic absorption of zirconium, which has been utilized in the indirect determination of these substances.¹²

Before commenting further on the table of enhancement interferences, it is necessary to consider the possibility of ionization. From the very high first ionization potential of the beryllium atom (9.32 eV) it is evident that even in the nitrous oxide-acetylene flame the degree of ionization of beryllium will be very low and the magnitude of the effect will not be significant in this work.

The problem of explaining the majority of the enhancements is very complex. In work reported to date the effect of added sulphuric acid has been to cause enhancements for absorption of calcium, aluminium and zinc,¹³ and titanium⁶ but at the 5% v/v level sulphuric acid causes a 25% depression of the molybdenum signal.¹¹ Orthophosphoric acid has been shown to give enhancement of sensitivity for a number of elements; in the cases of calcium and barium the increases in signal caused by 10000 ppm of phosphorus (as phosphoric acid) were attributed to an improvement in dissociation rate.⁵ Koirtzohann and Pickett¹³ have recently reported 10% enhancements of calcium and barium atomic emissions from a nitrous oxide-acetylene slot flame upon making the samples 0.3M (ca. 2.9% w/v) with respect to phosphoric acid, also a 15% enhancement was observed for the AAS of 1 ppm of Aluminium. Similar results were obtained with sulphuric and perchloric acids (0.3–1M), ammonium orthophosphate and sodium chloride (1–2%) and a theory was developed involving the spatial distribution of the sample within the flame. According to this explanation, the particles, after they have dried in the base of the flame, will be heavier in the presence of an involatile salt or high-boiling acid and will therefore diffuse more slowly towards the edges of the flame, giving a higher concentration in the centre of the flame (*i.e.*, along the axis of the burner slot).

In the present work it was found that orthophosphoric acid (4.5% w/v) produced no enhancement of beryllium absorption and, when considered with the marked depression of molybdenum sensitivity by sulphuric acid, this theory does not appear to be generally satisfactory. Similarly, organic materials, including sucrose, were stated to produce no effect on the atomic emission of Ca, Sr, Ba, Li, Na, K, Al, and Ga or atomic absorption of Ca, Al and Zn, whereas it has been observed here that there are major interferences from organic compounds in the AAS of beryllium, sucrose behaving in a very similar fashion to sulphuric acid (over a similar % w/v range). Beryllium absorption is also enhanced by the presence of 1–2% of ammonium compounds and sodium chloride, but it is not thought valid to refer to sodium chloride as an involatile salt at the temperatures encountered in the nitrous oxide-acetylene flame. Further, a comparison of the interference effects on the absorption of beryllium produced by the same weight concentrations of different metal ions, leads inevitably to the conclusion that spatial distribution is only one of a number of important factors involved.

It is not easy to apply the "oxygen competition" theory developed by Sachdev, Robinson and West⁸ to such a wide range of metal ion interferences. Moreover, the two elements, aluminium and titanium, which enhance sensitivity for vanadium and molybdenum do not have this effect on beryllium. The major depression by aluminium may be explained by compound formation, but this seems unlikely to be an important cause of interference between titanium and beryllium. The refractory

elements which, in large excess, would be expected to cause significant reduction in atomic oxygen concentration, occur in various positions in the table of enhancements from Mo (maximal enhancement of 17%) to Ti (minimal enhancement of 0.95%), and it is difficult to consider these effects as being in any way separate from the similar effects of the other metals in the table.

Because no simple coherent theory can be invoked to explain all the observed effects, it is necessary to consider most of the metallic interferents individually; however, certain factors do appear to be common to a number of determinations, e.g., the addition of hydrochloric or nitric acid usually produces no significant variation of signal, and the expected organic solvent effects are usually observed. In the determination of beryllium the gradual building up of the enhancement with increasing concentration of interferant material, followed by a steady decline, is probably the result of the enhancement effect being gradually overcome by reduction of nebulizer efficiency as the solutions become denser and more viscous.

For some of the interferences noted it is possible to postulate a specific chemical action which could improve atomization in the flame (e.g., the formation of the $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ ion from oxy- or hydroxy-species as sulphuric acid is added), but in most instances it is not easy to conceive of simple explanations for these "releasing" effects.

CONCLUSION

The enhancement effects observed cannot be accounted for by ionization suppression or ascribed to any other *single* phenomenon. In all cases both physical and chemical interactions occur which may be additive or subtractive. The theories of chemical releasing and complexation reactions, of oxygen competition and chemical change of the flame conditions, of spatial distribution in the flame and nebulization effects must all be considered and it is, therefore, extremely difficult, if not impossible, to attempt accurate prediction of an interference effect.

However, for the interference of aluminium and silicon in beryllium AAS, it has been suggested that a strong chemical action is the predominant cause, and in the case of aluminium, accurate analyses may be performed after addition of 8-hydroxyquinoline reagent.

For many metallic enhancements it has been shown that their interferences are not additive, with certain limitations, and accurate analyses may therefore be performed by making addition of excess of potassium nitrate in order to give maximal enhancement.

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Zusammenfassung—Es wurde eine Untersuchung einer Anzahl Interferenzen vorgenommen, die in der Spurenermittlung von Beryll bei atomischer Absorption in der Nitrooxyd-Azetylenflamme beobachtet wurden. Die grössere, negative Interferenz, die durch Vorhandensein von übermässigen Aluminiumsalzen verursacht wird, kann durch Verwendung von 8-Hydroxyquinoline vermieden werden. Magnesium und Silizium drücken auch das Be Signal herab, aber die meisten anderen Metalle verursachen Verstärkung. In den meisten Fällen kann die Verstärkung durch Zufügen von Kalium Ionen zu der Musterlösung gleichförmig gemacht werden.

Résumé—On a effectué une étude sur un certain nombre d'interférences observées dans la détermination de traces de béryllium par absorption atomique dans la flamme protoxyde d'azote-acétylène. L'interférence négative majeure causée par la présence d'excès de sels d'aluminium peut être surmontée par l'emploi de 8-hydroxyquinoléine. Le magnésium et le silicium abaissent aussi le signal de Be mais la plupart des autres métaux causent une exaltation. Dans la plupart des cas, les exaltations peuvent être rendues uniformes par l'addition d'ions potassium à la solution échantillon.

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DETERMINATION OF MICROGRAM AMOUNTS OF METALS BY CHRONOMETRIC ANALYSIS

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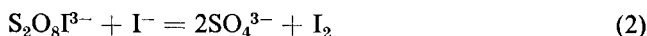
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Summary—The reaction between peroxodisulphate and iodide, modified by the addition of thiosulphate to show the Landolt effect, has been used for the determination of copper and iron in the range 1–100 $\mu\text{g/ml}$, based on the catalytic effect of these ions. The procedure is rapid and simple, and the errors are less than 10%. The interference from iron in the determination of copper may be overcome by the addition of a masking reagent such as fluoride.

LANDOLT reactions were first used for catalytic microdeterminations by Erdey and Svehla^{1–3} who used the slow reaction between hydrogen peroxide and iodide, accelerated by molybdate ions. Ascorbic acid was used to change the reaction to one showing the Landolt effect, since it reduces instantaneously the free iodine formed by oxidation by the peroxide. Free iodine is then only detectable in solution after all the ascorbic acid has been consumed. Variamine Blue was added as an indicator for free iodine.

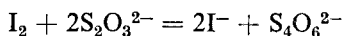
Erdey and Svehla later suggested that the peroxodisulphate–iodide–ascorbic acid system might be used for the determination of some metal ions.⁴

The reaction between peroxodisulphate and iodide proceeds in two steps, as follows:⁵



The second step is fast, but the first is slow and is accelerated in the presence of copper and iron ions, the former having the greater effect.

Sodium thiosulphate was used to change the reaction to one with the Landolt effect, as it reacts with the free iodine:



Free iodine occurring after consumption of the thiosulphate was indicated by the appearance of the blue colour in the presence of starch.

EXPERIMENTAL

Reagent solutions

(1) *Oxidizing solution*, containing 7 g of potassium peroxodisulphate and 10 ml of 1M sulphuric acid in 500 ml.

(2)–(7) *Reducing solutions*: see Table I.

All reducing solutions contained 6.8 g of sodium acetate, 10 ml of 1M sulphuric acid and 5 g of starch, and were diluted to 500 ml with distilled water.

(8) *Copper(II) stock solution* contained 3.93 g of copper sulphate pentahydrate in 1 l. (copper concentration = 1 mg/ml).

(9) *Iron(II) stock solution* contained 1.404 g of ammonium iron(II) sulphate and 10 drops of concentrated sulphuric acid, in 1 l. (iron concentration = 0.2 mg/ml).

TABLE I.—REDUCING SOLUTIONS

No.	Purpose	Potassium iodide, g	Sodium thiosulphate, g	Copper sulphate, g
(2)	Investigation	1.65	0.13	—
(3)	Investigation with copper	1.65	0.63	0.0589
(4)	Determination of 1–10 $\mu\text{g/ml}$ of copper	1.65	0.4	—
(5)	Determination of 10–100 $\mu\text{g/ml}$ of copper	1.3	1.2	—
(6)	Determination of 1–10 $\mu\text{g/ml}$ of iron	1.3	0.08	—
(7)	Determination of 10–1000 $\mu\text{g/ml}$ of iron	1.65	0.2	—

Procedure

Test-tubes were thoroughly cleaned with chromic acid, washed with distilled water, and dried before use. Known, and equal, quantities of one of the solutions (2)–(7) were transferred to a number of test-tubes to each of which were added equal quantities of water and of solutions containing different concentrations of catalyst. Into each test-tube was put a glass rod with a flattened end (for stirring) and the test-tubes were put in a water-bath controlled at $25 \pm 0.5^\circ$. The oxidizing solution (1) was also put into the water-bath, and all solutions were left for 2 hr to reach constant temperature. A known volume of solution (1) was added to the first test-tube, the stop-watch was started, the solution stirred, and the time taken for the blue colour to appear was recorded. This procedure was repeated for each test-tube.

The uncatalysed reaction between peroxodisulphate and iodide is second-order. This was checked experimentally both for the uncatalysed and the catalysed reaction. Equal portions (2 ml) of reducing solution (2) were transferred to a series of test-tubes containing increasing amounts of water. The procedure as described was then followed, with the same volume of oxidizing solution (1) in each test-tube. In a second series of experiments, reducing solution (3) was used, which contained 75 μg of copper per ml. For each series, a plot of recorded reaction time against total volume gave a straight line passing through the origin, verifying that the reaction was in each case second-order. From the known concentrations of the reacting species, the rate constants were calculated, and found to be, at 25° , $2.32 \times 10^{-1} \text{ l.mole}^{-1}.\text{min}^{-1}$ uncatalysed, and $1.79 \times 10^3 \text{ l.mole}^{-1}.\text{min}^{-1}$ when catalysed by copper(II).

Procedure for the determination of copper or iron

Determination of copper in the range 1–10 $\mu\text{g/ml}$. Into each of 36 test-tubes transfer 5 ml of reducing solution (4) then add 5 ml of distilled water to each of the first three, 5 ml of solution containing 1 μg of copper per ml to each of the next three, 5 ml of 2 $\mu\text{g/ml}$ copper solution to the next three, and so on up to 10 $\mu\text{g/ml}$ of copper. Then to each of the last three add 5 ml of the unknown solution, and follow the described procedure for each test-tube, calculating the average of the three time measurements obtained for each concentration. The reciprocal time values are proportional to the concentration of catalyst.

We have found that results obtained from plots of reciprocal time are not as reliable as those obtained from plots of t_0/t values (where t_0 is the time measured in the absence of catalyst), and hence the latter are to be preferred.

Other concentrations, and determination of iron. For the determination of copper in the range 10–100 $\mu\text{g/ml}$ and of iron in the ranges 1–10 and 10–100 $\mu\text{g/ml}$, the reducing solutions (5)–(7) are

used, respectively, and the concentrations of the standard catalyst solutions are chosen suitably. The data for the calibration graphs as obtained are reproduced in Table II. The error of the determinations was within the limits $\pm 10\%$ for both ions.

TABLE II.—DATA FOR CALIBRATION CURVES

Element	Range of concentration $\mu\text{g/ml}$	Graph of t_0/t vs. concentration		Std. devn. of t_0/t
		Intercept	Slope	
Copper	1-10	1.206	0.524	0.46
	10-100	1.208	0.696	1.64
Iron	1-10	0.962	0.157	0.06
	10-100	0.967	0.079	0.08

The effect of other ions on the reaction was also investigated. Since the reproducibility of the measurements is about 10%, the interference due to a given ion may be neglected at a given catalyst concentration if the t_0/t value is within 10% of the value in the absence of that ion. Expressed in these terms, it was found that lithium, sodium, potassium, calcium, zinc and molybdate do not interfere at concentrations below 0.1M, strontium, barium, silver, chromium(III), manganese(II), cobalt, nickel and vanadate at concentrations below $10^{-2}M$, aluminium and lead in concentrations below $10^{-3}M$, and arsenic, antimony, cerium and mercury in concentrations below $10^{-4}M$. Of the last-mentioned, As(III), Sb(III) and Hg(I) give rise to negative errors because they are themselves oxidized.

The possibility of masking iron in solution, and hence of determining copper in its presence, was investigated, using fluoride as masking reagent.

Three series of solutions were prepared, containing, in the first, increasing amounts of copper(II), and sodium fluoride (5 g/l); in the second, the same concentrations of copper and fluoride and also iron(II) ($10^{-3}M$); and in the third series, copper, fluoride and iron(III) (also $10^{-3}M$). The concentration of iron was therefore from 5 to 50 times that of the copper. The calibration graphs, prepared as described under *Procedure* were the same within experimental error, supporting the use of fluoride as masking reagent, and making possible the determination of copper in the presence of iron.

The chronometric method described has been successfully applied to the determination of traces of copper present as an activator in zinc sulphide luminescent powder.

Zusammenfassung—Bei der Reaktion zwischen Peroxydisulfat und Jodid wurde Thiosulfat zugegeben, um den Landolteffekt zu erzielen. Diese Reaktion wurde zur Bestimmung von Kupfer und Eisen im Bereich 1-100 $\mu\text{g/ml}$ auf Grund ihrer katalytischen Wirkung verwendet. Das Verfahren geht schnell und einfach und die Fehler sind kleiner als 10%. Die Störung durch Eisen bei der Bestimmung von Kupfer kann durch Zugabe eines Maskierungsmittels wie Fluorid beseitigt werden.

Résumé—On a utilisé la réaction entre le peroxydisulfate et l'iode, modifiée par l'addition d'hyposulfite pour montrer l'effet Landolt, pour la détermination du cuivre et du fer dans le domaine 1-100 $\mu\text{g/ml}$, en se basant sur l'influence catalytique de ces ions. La technique est rapide et simple, et les erreurs sont inférieures à 10%. L'interférence du fer dans le dosage du cuivre peut être éliminée par l'addition d'un agent de dissimulation comme le fluorure.

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VERWENDUNG MÄßIG DISSOZIIERTER KOMPLEXE BEI SPEKTRALPHOTOMETRISCHEN BESTIMMUNGEN—II.

REAKTIONEN VON ARSENAZO III MIT URANYL UND THORIUM(IV)

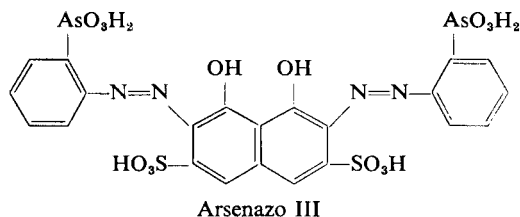
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Zusammenfassung—Bei Reaktion von Uranylionen mit Arsenazo III entstehen in sauren Lösungen zwei dissoziierte Komplexe des Typus ML. Ihr Konzentrationsverhältnis in der Lösung ist von der Acidität abhängig. Die Werte der differentiellen molaren Extinktionskoeffizienten dieser Komplexe beim Absorptionsmaximum 565 nm betragen $5,3 \cdot 10^3$ bzw. $8,8 \cdot 10^3$ l.mole⁻¹.mm⁻¹. Auf Grund der festgelegten Beständigkeitskonstanten wurden die bisherigen empirischen Kenntnisse über die Empfindlichkeit der Reaktion erklärt. Thorium(IV) bildet mit Arsenazo III in sauren Lösungen M₂L₂- und zwei ML-Komplexe. Der in analytischer Praxis verwendete mäßig dissoziierte Komplex ML₂ entsteht vorwiegend in stark sauren Lösungen bei einem hohen Reagensüberschuß. Der differentielle molare Extinktionskoeffizient des Komplexes ML₂ im Absorptionsmaximum 658 nm beträgt $12,8 \cdot 10^3$ l.mole⁻¹.mm⁻¹.

ARSENAZO III (2,7-Bis[azo-2- arsonphenyl]chromotropsäure) ist das meist benutzte Reagens aus der Reihe der symmetrischen Bisazoderivaten der Chromotropsäure. Es wurde erstmals im Jahre 1959 für die Bestimmung einer Reihe von Elementen durch Savvin¹ vorgeschlagen. Eine breite Anwendung fand das Reagens insbesondere bei Uran-²⁻⁹ und Thoriumbestimmungen.¹⁰⁻¹⁹ Weitere Verwendungsmöglichkeiten wurden in der Monographie²⁰ von Savvin angegeben.



Trotz der großen Bedeutung von Arsenazo III in der analytischen Chemie wurden bisher die grundlegenden Fragen der Komplexbildung nicht befriedigend erklärt. In der Mehrzahl der Veröffentlichungen^{1-9,20} wurde bei der Reaktionen von Uranylionen mit Arsenazo III die Bildung eines ML-Komplexes nachgewiesen. Nach Buděšinský²¹ entsteht ein Komplex des Typus M₂L₂. Auch die Möglichkeit der Bildung eines ML₂-Komplexes ist erwähnt²² worden. Für die Extinktionskoeffizienten bei Absorptionsmaximum wurden folgende Werte angegeben: $5,3 \cdot 10^3$ l.mole⁻¹.mm⁻¹ bei pH 2,²³ $6,0 \cdot 10^3$ in 6M Salpetersäure⁶ und $7,5 \cdot 10^3$ in 5,6M Perchlorsäure.⁹ Auch bei der Anwendung des Reagens bei Thoriumbestimmungen¹⁰⁻¹⁹ wurden die Fragen der

Komplexbildung bisher nicht eindeutig gelöst. Arsenazo III–Thorium(IV)-Komplexe folgender Typen wurden beschrieben: ML , ML_2 , ML_3 und sogar ML_4 .^{16,20,24} Nach Buděšínský²¹ entsteht ein M_2L_2 -Komplex.

Es kann erwartet werden, daß die Komplexe von Arsenazo III bei einer hohen Acidität zu bedeutendem Teil dissoziieren werden. Darauf zeigt die Abhängigkeit der molaren Extinktionskoeffizienten von der Ligandkonzentration⁶ sowie der publizierte Wert der Beständigkeitskonstante eines Arsenazo III–Uranyl-Komplexes ($K = 1 \cdot 10^4$ in 6M Salpetersäure). In der ersten Mitteilung dieser Reihe²⁵ wurde gezeigt, daß die Bestimmung der Beständigkeitskonstanten der Komplexe und somit auch ihrer Zusammensetzung für die Auswertung einer für die spektralphotometrische Analyse dienenden Reaktion unerlässlich sind.

Im Weiteren geben wir einen Überblick über die Komplexbildung von Arsenazo III mit Uranylionen und Thorium(IV) bei Bedingungen der analytischen Verwendung, d.h. in mäßig und stark sauren Lösungen. Die grundlegende Methode der Untersuchung war die Auswertung photometrischer Titrationskurven. Bei der Bildung von dissoziierten Komplexen wurden die Titrationskurven nach den von uns beschriebenen Methoden analysiert.²⁶

Verwendete Symbole und Bezeichnungen

c_M ; c_L	totale Metall- bzw. Ligandkonzentration, molar
$[M_aL_b]$	Gleichgewichtskonzentration des Komplexes M_aL_b
K	Beständigkeitskonstante;

$$K_{M_aL_b} = \frac{[M_aL_b]}{(c_M - a \cdot [M_aL_b])^a \cdot (c_L - b \cdot [M_aL_b])^b}$$

ΔA	Extinktionsmodul, gemessen gegen gleiche c_L
ΔA_0	Extinktionsmodul bei einem großen Titrantüberschuß (horizontaler Ast einer photometrischen Titrationskurve)
ϵ_L ; ϵ_{ML}	molarer Extinktionskoeffizient des Liganden bzw. Komplexes ML (gegen Wasser)
$\Delta \epsilon_{ML}$	differentieller molarer Extinktionskoeffizient des Komplexes ML ²⁶
$\Delta \epsilon_{ML, \text{eff}}$	effektiver differentieller molarer Extinktionskoeffizient des Komplexes ML (Steigung des Anfangsteiles einer photometrischen Titrationskurve) ²⁶
H_0	Acidität nach Hammettscher Funktion; die H_0 -Werte für HNO_3 und $HClO_4$ aus ^{27,28} entnommen.

EXPERIMENTELLER TEIL

Lösungen

Uranylnitrat-Stammlösung, $1,45 \cdot 10^{-3}M$. Der UO_2^{2+} -Gehalt wurde gravimetrisch bestimmt. *Thorium(IV)-Nitrat-Lösung*, $1,00 \cdot 10^{-3}M$. Die Thorium(IV)-Konzentration wurde chelatometrisch²⁹ bestimmt.

Die Acidität der Lösungen wurde durch konz. Perchlorsäure *p.a.* bzw. Salpetersäure *p.a.* eingestellt. Jeweils 100 ml der konz Salpetersäure wurden zwecks Beseitigung der salpetrigen Säure 1 g Harnstoff zugesetzt.¹⁶

Zur Herstellung der Ligandenstammlösung wurden 90–100 mg chromatographisch reines Arsenazo III in 10 ml Wasser gelöst. Die Lösung wurde durch eine kleine Säule mit Dowex 50 \times 8 (H^+ -Form) laufen gelassen und schließlich auf 100 ml aufgefüllt. Die Konzentration der Stammlösung wurde coulometrisch³⁰ bestimmt. Die Arsenazo III-Lösungen waren mindestens 2 Monate beständig.

Reinigung von Arsenazo III

Es wurden 1–2 g des Ausgangsproduktes (Spolana Neratovice) in 15–25 ml 5%-iges Ammoniumhydroxid gelöst. Nach Filtration der Lösung wurde das Arsenazo III durch eine Zugabe von 10 ml Salzsäure (1:1) ausgefällt. Die Umfällung wurde noch einmal wiederholt, und 0,5 g des auf diese Weise vorgereinigten Präparates wurde in 7 ml eines Gemisches n-Propanol-NH₄OH konz.-H₂O (1:1:1, Volumenverhältnis) bei 50° aufgelöst. Nach dem Erkalten wurde filtriert und das Filtrat auf eine Säule (ϕ 25 mm, Höhe 120 mm) von mikrokristallinischer Zellulose (Lachema, Brno) gegeben. Die Säule wurde vorher mit dem Laufmittel, bestehend aus n-Propanol-NH₄OH konz.-H₂O (Volumenverhältnis 3:1:1), durchgespült. Die Elutionsgeschwindigkeit betrug 1,5 ml/Min. Nachdem die blau gefärbte Zone von Arsenazo III die Mündung der Kolonne erreicht hatte, wurden 10 ml-Fractionen des Eluats entnommen. Die Reinheit der einzelnen Fractionen wurde chromatographisch am Papier Whatman 4 mit 1M Salzsäure als Laufmittel kontrolliert. Als Verunreinigung des Ausgangsproduktes wurden auf dem Papierchromatogramm ein roter (Arsenazo I, $R_f \sim 0,35$) und ein brauner Fleck ($R_f \sim 0,05$) sichtbar. Arsenazo III ergab einen langgezogenen rotviolettten Fleck ($R_f \sim 0,25$).

Die chromatographisch einheitlichen Fractionen wurden vereinigt und bei maximal 80° auf 10–15 ml eingedampft. Dann wurde das Arsenazo III mit 10 ml konz. Salzsäure und schließlich mit wenig Äthanol gewaschen. Das Präparat wurde an der Luft bei Zimmertemperatur getrocknet.

Bei der papierchromatographischen Reinheitskontrolle wurde nur ein einziger Fleck von Arsenazo III erhalten.

Die Spektren der Lösungen von reinem Arsenazo III und der maximale Wert von $\epsilon_L = 3,6 \cdot 10^3$ l.mole⁻¹.mm⁻¹ bei 540 nm sind in guter Übereinstimmung mit den meisten publizierten Arbeiten, mit Ausnahme von B. Buděšinský.²¹ Im Absorptionsspektrum von Arsenazo III treten im Bereich der Wellenlängen 400–700 nm in Abhängigkeit von der Acidität der Lösung (von pH 2,8 bis H_0 –2,5) praktisch keine Änderungen auf. Bei einer größeren Acidität als $H_0 - 3$ macht sich die Protonisierung von Azogruppen²⁰ in den Absorptionskurven deutlich bemerkbar.

Photometrische Titrationen

Die Titrationen wurden unmittelbar in den Meßküvetten mit Hilfe einer Agla-Mikrodosierungsspritze durchgeführt. Das Volumen der titrierten Lösung blieb während der Titration praktisch unverändert und betrug in der 10-mm Küvette 2,5 ml und in der 20-mm Küvette 5,0 ml. Das maximal zugesetzte Volumen der Titerlösung betrug weniger als 1–2% des Gesamtvolumens. Nach jeder Zugabe von 0,001–0,005 ml der Titerlösung wurde die Lösung in der Küvette mit einem Teflon-Stäbchen durchgemischt. Anschließend wurden entweder die Absorptionsspektren im Wellenbereich 580–720 nm registriert oder es wurde nur bei der Wellenlänge des Absorptionsmaximums gemessen. Bei dem Studium der Reaktionen von Thorium(IV) mit Arsenazo III wurden zwei Arten von Titrationskurven aufgenommen:

(a) Titration des Liganden mit dem Kation. ΔA wurde direkt gemessen.

(b) Titration des Kations mit dem Liganden. In diesem Fall wurde als Vergleichslösung Wasser benutzt. Vom Meßwert wurde die Extinktion einer reinen Arsenazo III-Lösung gleicher Konzentration abgezogen.

Bei der Untersuchung der Reaktion von Arsenazo III mit Uranyl wurden nur Titrationen mit Kation ausgeführt.

MEßERGEBNISSE

Reaktionen von Uranyl

Photometrische Titrationskurven von Arsenazo III-Lösungen mit Uranyl bei pH 2,8 (0,1M Essigsäure) weisen einen scharfen Knick auf, der einem Molverhältnis Arsenazo III:UO₂²⁺ = 1:1 genau entspricht. Die Steigungen der Anfangsteile der Kurven sind c_L -unabhängig ($\Delta \epsilon_{ML, \text{eff}} \equiv \Delta \epsilon_{ML} = 5,3 \cdot 10^3$ l.mole⁻¹.mm⁻¹ bei λ_{max} 656 nm).

Bei höheren Aciditäten (ab pH 1) wurde eine c_L -Abhängigkeit der $\Delta \epsilon_{\text{eff}}$ -Werte festgestellt. Eine Übersicht der Ergebnisse ($\Delta \epsilon_{\text{eff}}$ bei $\lambda = 656$ nm) und der gewählten experimentellen Bedingungen (c_L , H_0) ist in Tab. I gegeben. Nach jeder Titration wurde noch der Extinktionsmodul ΔA_0 bei einem großen UO₂²⁺-Überschuß durch Zugabe kleiner Kriställchen von Uranylnitrat bzw. Uranylperchlorat in die Meßküvette ermittelt.

TABELLE I.—AUSWERTUNG PHOTOMETRISCHER TITRATIONSKURVEN VON ARSENAZO III MIT URANYL

Acidität	$c_L \cdot 10^3 M$	$\Delta \epsilon_{\text{eff}} \cdot 10^{-3}$ $l.mole.^{-1}mm^{-1}$	$\Delta \epsilon_{ML} \cdot 10^{-3}$ $l.mole.^{-1}mm^{-1}$		$K \cdot 10^{-4}$	
			(a)	(b)	(a)	(c)
0,5M HNO ₃ pH 0,2	1,37	0,75				
	2,74	1,39				
	6,85	2,55	6,1	6,0	1,04	1,07
	13,7	3,58				
1,0M HNO ₃ $H_0 - 0,2$	22,1	4,45				
	1,37	0,39				
	2,74	0,75	6,5	6,4	0,49	0,48
	6,85	1,52				
1,12M HClO ₄ $H_0 - 0,3$	13,7	2,56				
	1,52	0,70				
	4,36	1,65	7,1	7,1	0,71	0,81
	10,9	3,10				
5,8M HNO ₃ $H_0 - 1,75$	2,74	1,20				
	6,85	2,48	8,3	8,15	0,63	0,66
	13,7	3,85				
	5,5M HClO ₄ $H_0 - 2,6$	1,52	4,80			
11,5M HNO ₃ $H_0 - 3,0$	4,36	6,60	8,2	8,3	10,0	10,5
	10,9	7,40				
	2,74	0,72				
	5,48	1,26	9,0	8,9	0,32	0,32
	10,9	2,33				

(a) aus der c_L -Abhängigkeit der $\Delta \epsilon_{\text{eff}}$ -Werte bestimmt(b) aus ΔA_0 bestimmt

(c) bei der logarithmischen Analyse der Titrationskurven ermittelt

Reaktionen von Thorium(IV)

Eine Titrationskurve von Arsenazo III durch Thoriumnitratlösung in 0,1M Essigsäure (pH 2,8) bei 662 nm ist in Abb. 1 dargestellt. Die Steigung der Kurve ist c_L -unabhängig und wird durch die Zahl $4,6 \cdot 10^3 l.mole^{-1}.mm^{-1}$ ($\equiv \Delta \epsilon$) charakterisiert. Bei der Titration des Kations mit Arsenazo III bei den gleichen Bedingungen bei 672 nm ($= \lambda_{\text{max}}$) wurde keine Abhängigkeit der Steigungen der Anfangsteile der Titrationskurven von c_M festgestellt. Die Steigung ($\equiv \Delta \epsilon$) beträgt $2,6 \cdot 10^3 l.mole^{-1}.mm^{-1}$. Die Titrationskurven von Thorium(IV) mit dem Liganden weisen einen S-förmigen Verlauf auf.

Meßergebnisse und gewählte experimentelle Bedingungen (c_L, H_0) für die Titrationsen von Arsenazo III mit Thorium(IV) in stark sauren Lösungen sind in Tab. II zusammengestellt. Tabelle III enthält die Meßergebnisse und die gewählten experimentellen Bedingungen für Titrationsen von Thorium(IV) mit Arsenazo III in stark sauren Lösungen.

AUSWERTUNG UND DISKUSSION

Die Komplexbildung wurde aus dem Gesichtspunkt der analytischen Verwendung der Reaktionen untersucht. Bei der Bildung von wenig dissoziierten Komplexen wurde deshalb lediglich das Verhältnis M:L aus der Form der Titrationskurve ermittelt. Die für die spektralphotometrische Anwendung wichtige Konstante $\Delta \epsilon_{M_a L_b}$ ist in diesem Fall unmittelbar durch die Steigung der Eichkurve gegeben.

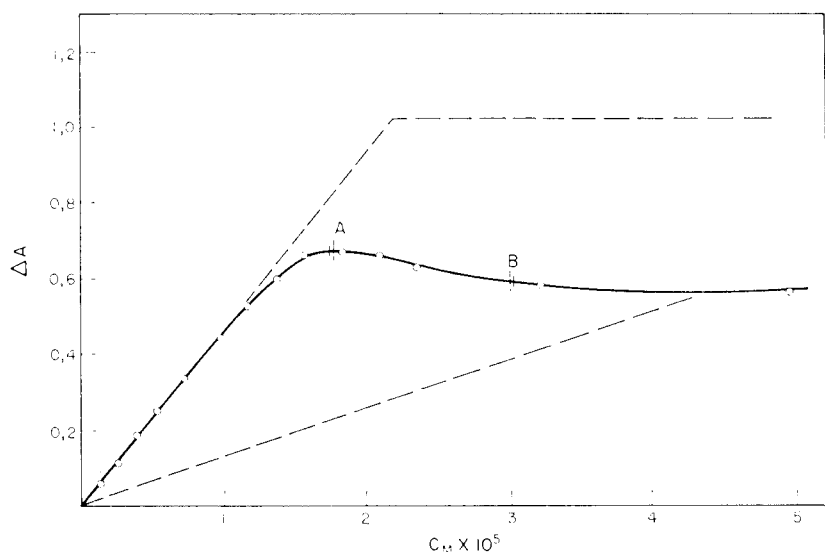


ABB. 1.—Photometrische Titration von Arsenazo III mit Thorium(IV). 0,1M Essigsäure, pH 2,8; $c_L = 2,21 \cdot 10^{-5}M$; $\lambda = 662 \text{ nm}$.

TABELLE II.—AUSWERTUNG PHOTOMETRISCHER TITRATIONSKURVEN VON ARSENAZO III MIT THORIUM(IV)

Acidität	$c_L \cdot 10^5 M$	$\Delta \epsilon_{\text{eff}} \cdot 10^{-3}$ $l.\text{mole.}^{-1}\text{mm}^{-1}$	$\Delta \epsilon_{ML_2} \cdot 10^{-3}$ $l.\text{mole.}^{-1}\text{mm}^{-1}$ (a)	$K \cdot 10^{-9}$ (a)	(b)
2,8M HNO ₃ $H_0 - 1,0$	1,20	9,50			
	2,40	11,0	12,8	10,0	
	4,80	12,0			
	7,20	12,6			
0,44	1,31				
5,6M HNO ₃ $H_0 - 1,75$	1,50	8,37			
	2,21	9,97	12,8	8,6	8,9
	11,05	12,4			
	15,05	12,4			
	22,1	12,7			
3,96	4,54				
11,3M HNO ₃ $H_0 - 3,05$	7,92	7,84	12,7	0,26	0,34
	19,8	11,4			

(a) aus der c_L -Abhängigkeit der $\Delta \epsilon_{\text{eff}}$ -Werte bestimmt

(b) bei der logarithmischen Analyse der Titrationskurven ermittelt

Die Grundlagen der Auswertung von photometrischen Titrationskurven bei der Bildung von dissoziierten Komplexen wurden früher abgeleitet:²⁶

1. Trägt man die für gleiche Reaktionsbedingungen (Acidität) gewonnenen $\Delta \epsilon_{\text{eff}}$ -Werte bei Bildung eines einkernigen Komplexes (ML_b oder M_aL) in geeigneten Koordinaten auf, so erhält man Geraden, deren Steigung den differentiellen molaren Extinktionskoeffizienten ($\Delta \epsilon_{ML_b}$ bzw. $\Delta \epsilon_{M_aL}$) angibt. Die Wahl der richtigen Koordinaten hängt vom vermuteten Komplextyp ab. Aus derselben Beziehung läßt sich der Wert der Beständigkeitskonstante K ermitteln. Aus den Werten von $\Delta \epsilon$ der Komplexe kann man die ΔA_0 -Werte berechnen. Das hat besondere Bedeutung für

TABELLE III.—AUSWERTUNG PHOTOMETRISCHER TITRATIONSKURVEN VON THORIUM(IV) MIT ARSENAZO III

Acidität	$c_M \cdot 10^5 M$	$\Delta \epsilon_{\text{eff}} \cdot 10^{-3}$ $l.mole.^{-1}mm^{-1}$	$\Delta \epsilon_{ML} \cdot 10^{-3}$	$K \cdot 10^{-4}$	
			$l.mole.^{-1}mm^{-1}$ (a)	(a)	(b)
2,8M HNO ₃ $H_0 - 1,0$	2,0	4,8			
	4,0	5,5	6,7	14	
	10,0	6,1			
	50,0	6,6			
5,6M HNO ₃ $H_0 - 1,75$	0,99	3,3			
	1,98	4,6	8,1	6,8	8,0
	4,95	6,1			
	9,90	7,0			
99,0	7,8				
11,3M HNO ₃ $H_0 - 3,05$	0,99	0,9			
	1,98	1,45	7,3	1,2	1,4
	3,96	1,65			
	9,90	3,9			
	19,8	5,05			
99,0	6,6				

(a) aus der c_M -Abhängigkeit der $\Delta \epsilon_{\text{eff}}$ -Werte bestimmt

(b) bei der logarithmischen Analyse der Titrationskurven ermittelt

die logarithmische Analyse, wenn sich die ΔA_0 -Werte experimentell nicht bestimmen lassen.

2. Die bei gleichen Reaktionsbedingungen (Acidität) experimentell erhaltenen Titrationskurven lassen sich bei bekannten ΔA_0 -Werten innerhalb bestimmter, vom Komplextyp abhängiger Koordinaten, in eine Gerade transformieren. Zur Ermittlung der Zusammensetzung des in der Lösung vorliegenden Komplexes sind diejenigen Koordinaten zu wählen, bei denen die transformierten Titrationskurven, die bei verschiedenen Konzentrationen der titrierten Lösung erhalten wurden, in einer Geraden zusammenfallen ("logarithmische Analyse der Titrationskurven"). Außerdem muß die Steigung dieser Geraden mit der theoretisch berechneten Steigung übereinstimmen. Die Koordinaten für die einzelnen Komplextypen (M_aL_b) für die photometrischen Titrationsen von Kation durch Ligand und umgekehrt sowie die theoretischen Steigungen der resultierenden Geraden folgen aus Gl. (1) und (2):

$$\log \frac{1}{b \cdot \frac{c_M}{c_L} \Delta A_0 - a \cdot \Delta A} = -\frac{1}{a} \cdot \log \frac{\Delta A}{(\Delta A_0 - \Delta A)^b} + \frac{1}{a} \cdot \log \frac{K \cdot b^b}{\Delta \epsilon_{M_aL_b}^{a+b-1}} \quad (1)$$

für $c_L = \text{Konst.}$

$$\log \frac{1}{a \cdot \frac{c_L}{c_M} \Delta A_0 - b \cdot \Delta A} = -\frac{1}{b} \cdot \log \frac{\Delta A}{(\Delta A_0 - \Delta A)^a} + \frac{1}{b} \cdot \log \frac{K \cdot a^a}{\Delta \epsilon_{M_aL_b}^{a+b-1}} \quad (2)$$

für $c_M = \text{Konst.}$

Diese Gleichungen wurden analog wie bereits für den ML-Komplex angegeben²⁶ berechnet. Aus dem Ordinatenabschnitt bei einem bekannten $\Delta \epsilon_{M_aL_b}$ -Wert läßt sich die Beständigkeitskonstante berechnen. Man setzt bei diesem Verfahren nach Möglichkeit immer die experimentell ermittelten ΔA_0 -Werte und die daraus berechneten $\Delta \epsilon_{M_aL_b}$ ein. Nur wenn die ΔA_0 -Werte experimentell nicht zugänglich sind (z.B.

wegen Bildung eines anderen Komplexes bei größeren Titrantüberschüssen), müssen die bei der Auswertung der Konzentrationsabhängigkeiten von $\Delta\epsilon_{\text{eff}}$ erhaltenen differentiellen molaren Extinktionskoeffizienten und die daraus berechneten (Ref. 26, Gl. (5)) ΔA_0 -Werte eingesetzt werden.

Reaktion von Arsenazo III mit Uranylionen

In mäßig saurer Lösung (pH 2,8) wird ein fester Komplex des Typus ML gebildet. Der ermittelte $\Delta\epsilon_{\text{ML}}$ -Wert bei λ_{max} 656 nm, $5,3 \cdot 10^3 \text{ l.mole}^{-1} \cdot \text{mm}^{-1}$, stimmt mit der Literaturangabe überein.²³

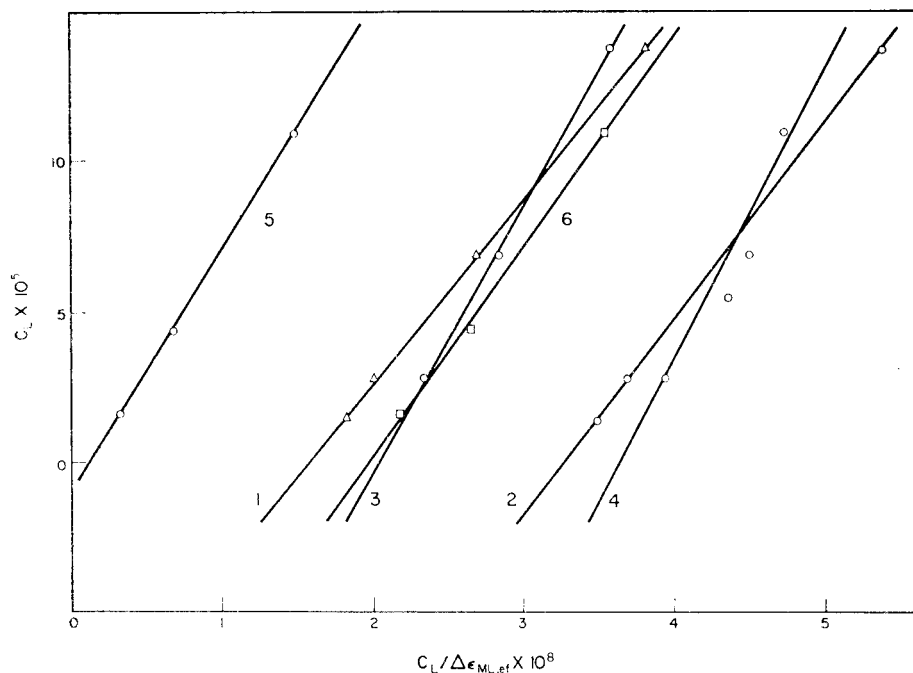


ABB. 2.—Auswertung der c_L -Abhängigkeit von $\Delta\epsilon_{\text{eff}}$ bei Titration von Arsenazo III mit Uranyl.

1 0,5M HNO₃; 2 1,0M HNO₃; 3 5,6M HNO₃; 4 11,6M HNO₃; 5 1,1M HClO₄; 6 5,6M HClO₄.

In sauren Lösungen werden dissoziierte Komplexe gebildet. Abbildung 2 zeigt die Auswertung der Konzentrationsabhängigkeit der $\Delta\epsilon_{\text{eff}}$ -Werte für einen vermuteten Typ ML. Die hieraus ermittelten $\Delta\epsilon_{\text{ML}}$ -Werte stimmen gut mit jenen $\Delta\epsilon_{\text{ML}}$ -Werten überein, die aus den experimentell ermittelten ΔA_0 -Werten bei einem großen Uranylüberschuß berechnet wurden (Tab. 1).

Abbildung 3 zeigt die transformierten Titrationskurven. Alle Geraden besitzen innerhalb der für einen ML-Komplex gültigen Koordinaten die Steigung $-1,00 \pm 0,03$. Damit ist das Vorliegen eines 1:1 Komplexes eindeutig bewiesen. Die aus dem Ordinatenabschnitt ermittelten K -Werte sind in guter Übereinstimmung mit jenen, die bei der Auswertung der Konzentrationsabhängigkeit der $\Delta\epsilon_{\text{ML,eff}}$ -Werte festgestellt wurden (Tab. 1).

Mit Hilfe der transformierten Titrationskurven läßt sich auch zeigen, daß in sauren Lösungen bei keinem Konzentrationsverhältnis c_M/c_L Komplexe des Typus

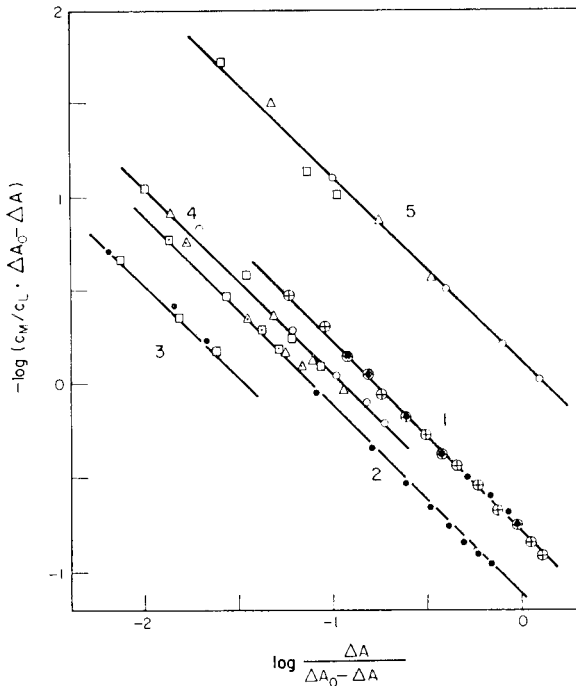


ABB. 3.—Logarithmische Analyse der Titrationskurven von Arsenazo III mit Uranyl (vorausgesetzter Komplex ML).

1. 0,5M HNO₃; $c_L = 2,65 \cdot 10^{-5}M$ ● und $2,21 \cdot 10^{-4}M$ ⊕
2. 5,8M HNO₃; $c_L = 2,74 \cdot 10^{-5}M$ ●, $6,85 \cdot 10^{-5}M$ △ und $13,7 \cdot 10^{-5}M$ □
3. 11,6M HNO₃; $c_L = 5,48 \cdot 10^{-5}M$ □ und $10,96 \cdot 10^{-5}M$ ●
4. 1,1M HClO₄; $c_L = 1,52 \cdot 10^{-5}M$ ○, $4,36 \cdot 10^{-5}M$ △ und $10,9 \cdot 10^{-5}M$ □
5. 5,6M HClO₄; c_L und Bezeichnungen wie bei 4.

M_2L_2 entstehen. Abbildung 4 zeigt die Transformation von zwei bei gleicher Acidität, jedoch verschiedenen c_L gewonnenen Titrationskurven innerhalb der für einen M_2L_2 -Komplex gültigen Koordinaten. Die Steigungen der beiden *getrennten* Linien (etwa $-0,75$) weichen erheblich von der geforderten Steigung $-0,5$, vgl. Gl. (1), ab.

Die Abhängigkeit der $\Delta\varepsilon_{ML}$ -Werte der Uranyl-Arsenazo III-Komplexe von der Acidität der Lösung (H_0) wird in Abb. 5 dargestellt. Es ist ersichtlich, daß bei gleicher Acidität dieselben Ergebnisse ($\Delta\varepsilon_{ML}$) erzielt werden, unabhängig von der Art der benutzten Säure. Auch das Verhältnis von ΔA -Werten bei verschiedenen Wellenlängen ist bei gleicher Acidität von dem Charakter der Säure unabhängig. Aus dem Verlauf der in Abb. 5 dargestellten Kurve, mit Rücksicht auf die Ergebnisse der logarithmischen Analyse, folgt, daß in dem System zwei (oder mindestens zwei) ML-Komplexe entstehen. Ihr Konzentrationsverhältnis in der Lösung hängt von der Acidität ab. Die Wellenlängen der Absorptionsmaxima beider Komplexe sind im Rahmen der Meßgenauigkeit identisch (656 ± 2 nm). Bei kleineren Aciditäten als pH 1 entsteht überwiegend ein ML-Komplex mit einem $\Delta\varepsilon_{ML}$ -Wert von $5,3 \cdot 10^3$ l.mole⁻¹.mm⁻¹ bei 656 nm. Bei höheren Aciditäten als H_0 -2 kann praktisch die ausschließliche Bildung eines weiteren ML-Komplexes (Bezeichnung ML*) mit $\Delta\varepsilon_{ML*} = 8,8 \cdot 10^3$ bei 656 nm vorausgesetzt werden. Eine vollständige Beschreibung des Gleichgewichtes zwischen den beiden Komplexen, d.h. die Erklärung ihrer

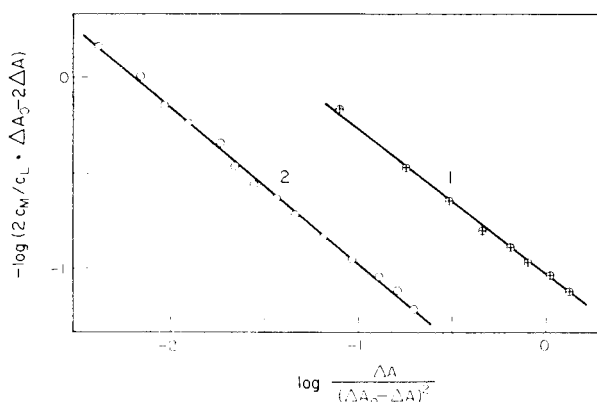


ABB. 4.—Logarithmische Analyse der Titrationskurven von Arsenazo III mit Uranyl
 (vorausgesetzter Komplex M_2L_2).
 $0,5M HNO_3$; 1. $c_L = 2,65 \cdot 10^{-3}M$; 2. $c_L = 2,21 \cdot 10^{-4}M$.

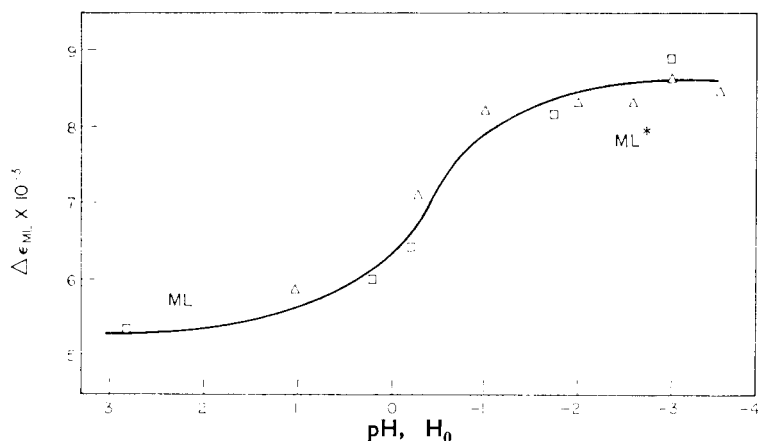


ABB. 5.—Differenzielle Extinktionskoeffizienten der Komplexe von Arsenazo III mit
 Uranyl in Abhängigkeit von der Acidität.
 Δ bestimmt bei Anwesenheit von HNO_3
 \square bestimmt bei Anwesenheit von $HClO_4$
 \square bestimmt bei Anwesenheit von CH_3COOH .

Struktur, übersteigt den Rahmen dieser Arbeit. Die Spektren beider Komplexe (umgerechnet auf $\Delta\epsilon_{ML}$ bzw. $\Delta\epsilon_{ML^*}$) sind in Abb. 6 dargestellt.

Die früher veröffentlichten unterschiedlichen Beziehungen zwischen den ΔA -Werten der Uranyl-Arsenazo III-Komplexe und der Säurekonzentration^{6,9} lassen sich somit leicht erklären. Die Autoren haben lediglich die $\Delta\epsilon_{ML,eff}$ -Werte gemessen. Die Abhängigkeit dieser Werte weist mit Aciditätserhöhung ein Minimum auf, bedingt einerseits durch die wachsende Dissoziation des ML-Komplexes ($\Delta\epsilon_{ML} = 5,3 \cdot 10^3$) und andererseits durch Erhöhung der $\Delta\epsilon_{ML,eff}$ -Werte ab bestimmten Säurekonzentrationen in Zusammenhang mit der bevorzugten Bildung des Komplexes ML^* ($\Delta\epsilon_{ML^*} = 8,8 \cdot 10^3$).

Aus einem Vergleich der $\Delta\epsilon_{ML,eff}$ -Werte bei entsprechenden c_L -Werten und gleicher Acidität (eingestellt durch Salpetersäure bzw. Perchlorsäure) wird für die

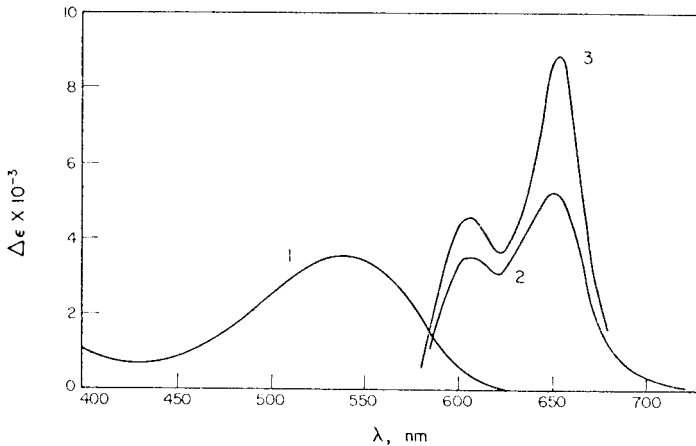


ABB. 6.—Spektren von Arsenazo III (als ϵ_L) und von Arsenazo III-Uranylkomplexen (als $\Delta\epsilon_{ML}$ und $\Delta\epsilon_{ML^*}$).

1. Arsenazo III, pH 2,8; 2. Komplex ML (pH 2,8); 3. Komplex ML* (11M HNO₃).

analytische Praxis die große Bedeutung für die richtige Auswahl der Säure ersichtlich. Bei Verwendung von Salpetersäure wurden stets niedrigere K -Werte und somit²⁶ auch $\Delta\epsilon_{ML,eff}$ -Werte gefunden als bei Anwesenheit von Perchlorsäure (vgl. Tab. 1). Es muß angenommen werden, daß bei Anwesenheit von Salpetersäure neben der Komplexbildung Arsenazo III-Uranyl (Komplexe ML und ML*) noch eine Konkurrenzreaktion der Salpetersäure mit Uranyl verläuft. Daher ist zwar das Konzentrationsverhältnis der Komplexe ML und ML* bei gleicher Acidität von der Art der Säure unabhängig, die Gleichgewichtskonzentrationen dieser Komplexe sind jedoch bei Anwesenheit von Salpetersäure wesentlich kleiner als in einem Reaktionsmedium mit Perchlorsäure. Die Existenz von Komplexen des Uranyls mit Nitrationen ist bekannt.³¹

Reaktionen von Arsenazo III mit Thorium(IV)

Bei höheren Aciditäten ($H_0 - 1$; 2,8M Salpetersäure) wurde bei Titrations von Arsenazo III mit Thorium eine merkliche c_L -Abhängigkeit ($c_L = 10^{-5}$ bis $10^{-4}M$) der effektiven Extinktionskoeffizienten festgestellt (Tab. 2). Die graphische Auswertung der gemessenen $\Delta\epsilon_{eff}$ -Werte in den Koordinaten c_L^2 gegen $c_L^2/\Delta\epsilon_{eff}$ deutete auf die Anwesenheit eines dissoziierten ML_2 -Komplexes. Der Wert von $\Delta\epsilon_{ML_2} = 12,8 \cdot 10^3 \text{ l.mole}^{-1}.\text{mm}^{-1}$ bei 658 nm ist im Bereich $-1 > H_0 > -3$ von der Acidität der Lösung unabhängig. Für die transformierten Titrationskurven (Abb. 7) wurden die benötigten ΔA_0 -Werte mit Hilfe dieser Zahl ($12,8 \cdot 10^3$) berechnet. Unmittelbar experimentell lassen sich die ΔA_0 -Werte nicht bestimmen, da bei großen Überschüssen von c_M andere Komplexe entstehen (vgl. unten). Die Geraden 1 und 2 in Abb. 7 bestätigen das Vorliegen eines ML_2 -Komplexes. Dagegen wird durch die Geraden 2' und 2'' der Abb. 7 das Nichtvorhandensein eines ML-Komplexes bei diesen Reaktionsbedingungen eindeutig bewiesen.

Bei Titrations von Thorium(IV) mit Arsenazo III, also bei Bedingungen eines c_M -Überschusses, ist die Beziehung zwischen c_M und $c_M/\Delta\epsilon_{eff}$ linear—es kann die Bildung von ML-Komplexen vorausgesetzt werden. Die aus den Steigungen

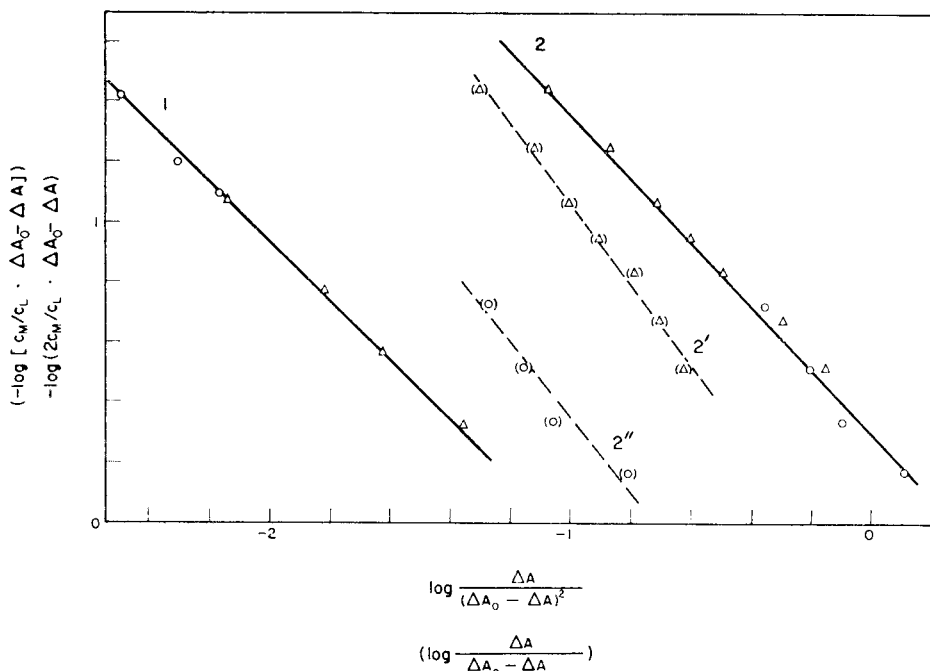


ABB. 7.—Logarithmische Analyse der Titrationskurven von Arsenazo III mit Thorium(IV). Vorausgesetzter Komplex ML_2 (1 und 2) oder ML (2' und 2'').

1. $11,6M HNO_3$; $c_L = 7,92 \cdot 10^{-5}M$ Δ und $19,8 \cdot 10^{-5}M$ \circ

2. $5,8M HNO_3$; $c_L = 0,44 \cdot 10^{-5}M$ \circ und $2,21 \cdot 10^{-5}M$ Δ

2' wie 2, $c_L = 2,21 \cdot 10^{-5}M$; 2'' wie 2, $c_L = 0,44 \cdot 10^{-5}M$.

ermittelten $\Delta\epsilon_{ML}$ -Werte sind wie bei den Uranylkomplexen von der Acidität der Lösung abhängig. Deshalb nehmen wir an, daß mindestens zwei Thorium(IV)-Arsenazo III-Komplexe des Typs ML gebildet werden, weiter ML und ML^* bezeichnet. Die transformierten Titrationskurven (Geraden 1 und 2 in Abb. 8) bestätigen die Bildung von ML -Komplexen. Die benötigten ΔA_0 -Werte wurden aus den Werten von $\Delta\epsilon_{ML}$ berechnet. Durch die Geraden 1' und 1'' wird das Nichtvorhandensein eines M_2L -Komplexes bei diesen Reaktionsbedingungen bewiesen.

Die Abweichung eines Teiles der Kurve 2 (Abb. 8) von der theoretischen Steigung kann durch gleichzeitige Anwesenheit des ML_2 -Komplexes bei einem kleineren Überschuß von c_M erklärt werden. Ähnliche Abweichungen wurden auch bei der Bildung des ML_2 -Komplexes bei kleineren c_L ($c_L \leq 2 \cdot 10^{-5}M$) und einer höheren Acidität ($H_0 \approx 3,05$) beobachtet während der Titration von Arsenazo III mit Thorium(IV). Sie lassen sich durch Bildung von ML -Komplexen erklären. Aus den angeführten Ergebnissen geht aber hervor, daß in stark sauren Lösungen bei einem genügenden Reagensüberschuß vorwiegend der ML_2 -Komplex, bei einem großen Thorium(IV)-Überschuß praktisch nur die ML - und ML^* -Komplexe entstehen.

Die Zusammensetzung der Thorium-Arsenazo III-Komplexe, die bei kleinen Säurekonzentrationen entstehen, kann nicht mit Hilfe der oben erwähnten Methoden bestimmt werden, da es keine Konzentrationsabhängigkeit der Steigungen der Anfangsteile von photometrischen Titrationskurven gibt. Man kann jedoch auf sie schließen aus dem Verlauf der photometrischen Titrationskurven, sowie aus einem

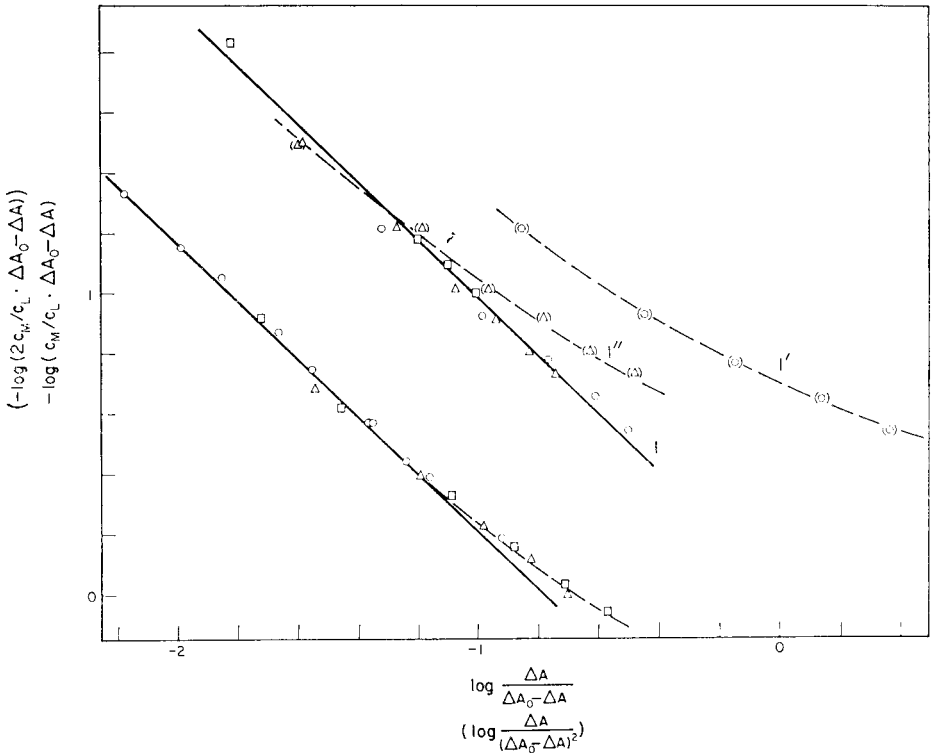


ABB. 8.—Logarithmische Analyse der Titrationskurven von Thorium(IV) mit Arsenazo III. Vorausgesetzter Komplex ML (*I* und 2) oder M_2L (*I'* und *I''*).

1. 5,8M HNO₃; $c_M = 1,98 \cdot 10^{-5}M$ ○, $4,95 \cdot 10^{-5}M$ △ und $9,9 \cdot 10^{-5}M$ □

2. 11,6M HNO₃; $c_M = 1,98 \cdot 10^{-5}M$ ○, $3,96 \cdot 10^{-5}M$ △ und $9,9 \cdot 10^{-5}M$ □
I' wie *I*; $c_L = 1,98 \cdot 10^{-5}M$; *I''* wie *I*; $c_L = 4,95 \cdot 10^{-5}M$.

Spektrvergleich mit Komplexen, deren Zusammensetzung bei einer höheren Acidität eindeutig festgestellt wurde. Aus Abb. 1 ist ersichtlich, daß bei der Titration von Arsenazo III mit Thorium(IV) bei pH 2,8 nacheinander zwei Komplexe entstehen. Der gefundene Wert des differentiellen Extinktionskoeffizienten bei großen Reagensüberschüssen (Steigung des Anfangsteiles der Titrationskurve, $4,6 \cdot 10^3 \text{ l.mole}^{-1} \cdot \text{mm}^{-1}$ bei λ_{max} 662 nm) sowie das ganze Spektrum sind mit dem Wert $\Delta \epsilon_{ML}$ und dem Absorptionsspektrum des ML-Komplexes identisch, der bei größeren Säurekonzentrationen ($H_0 - 0,1$) bei einem Metallüberschuß entsteht.

Bei Titrations von Thorium(IV) mit Arsenazo III bei pH 2,8 wird bei λ_{max} 672 nm eine c_M -unabhängige Steigung der Anfangsteile der Titrationskurven, die einem differentiellen Extinktionskoeffizienten $2,6 \cdot 10^3$ entspricht, beobachtet. Diese Zahl entspricht dem bei 662 nm gefundenen Wert von $2,5 \cdot 10^3$, der durch den horizontalen Ast der Titrationskurve (Abb. 1) gegeben wird. Die erwähnte S-förmige Form der Titrationskurve von Thorium(IV)-Lösungen mit Arsenazo III läßt sich durch gleichzeitige Bildung des ML-Komplexes bei kleiner werdenden Metallüberschüssen erklären.

Die beschriebenen Tatsachen, die bei Titrations bei pH 2,8 festgestellt wurden, können nicht durch gleichzeitige Bildung von zwei Komplexen eines gleichen Typs,

z.B. ML, erklärt werden, da ihr Konzentrationsverhältnis in der Lösung von dem Verhältnis der reagierenden Komponenten ($c_L:c_M$) unabhängig sein müßte. Eine schrittweise Bildung von Komplexen ML und M_2L_2 ist durch die Form beider Titrationskurven ebenfalls ausgeschlossen. Deshalb muß man neben dem ML-Komplex mit $\Delta\epsilon_{ML}$ $4,6 \cdot 10^3$, der bei einem Ligandenüberschuß bei pH 2,8 entsteht, noch die Existenz eines M_2L -Komplexes bei Bedingungen eines Metallüberschusses annehmen ($\Delta\epsilon_{M_2L} = 2,6 \cdot 10^3$ bei λ_{max} 672 nm). Bei der schrittweisen Bildung der wenig dissoziierten Komplexen ML und M_2L bei der photometrischen Titration von Arsenazo III mit Thorium(IV) (Abb. 1) entspricht dem Punkt A die Zusammensetzung 86,5 % mol. ML und 13,5 % mol. M_2L , und dem Punkt B 9 % mol. ML und 91 % M_2L .

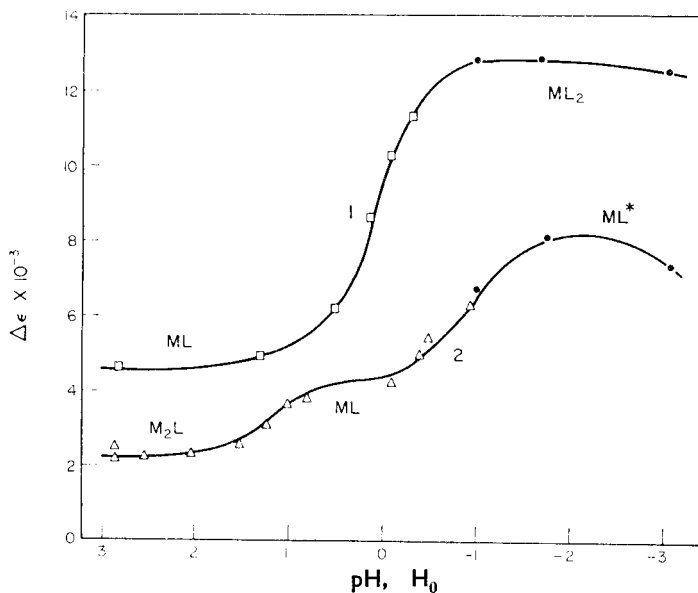


ABB. 9.—Differenzielle Extinktionskoeffizienten der Komplexe von Arsenazo III mit Thorium(IV) in Abhängigkeit von der Acidität.—1 bei $c_L \gg c_M$; 2 bei $c_M \gg c_L$; ● extrapolierte Werte aus den Konzentrationsabhängigkeiten von $\Delta\epsilon_{eff}$.

In Abb. 9 sind Abhängigkeiten der differentiellen molaren Extinktionskoeffizienten von der Acidität der Lösung bei einem solchen c_L -oder c_M -Überschuß dargestellt, bei welchem praktisch keine Konzentrationsabhängigkeit der $\Delta\epsilon_{eff}$ -Werte bemerkbar ist. Die Werte sind stets für das Maximum bei längeren Wellenlängen (vgl. Abb. 10) angegeben. Kurve 1 (Abb. 9) charakterisiert die Komplexe ML und ML_2 , die bei Bedingungen eines Arsenazo III-Überschusses gebildet werden. Die Komplexe M_2L , ML und ML^* werden in Abhängigkeit von der Acidität der Lösung bei großen Metallüberschüssen vorwiegend gebildet, Kurve 2, Abb. 9. Differentielle Absorptionsspektren (als $\Delta\epsilon$) der vier Arsenazo III-Thorium(IV)-Komplexe sind in Abb. 10 angeführt. Es ist beachtlich, daß die λ_{max} der beiden 1:1-Komplexe (ML, $\Delta\epsilon_{ML}$ $4,6 \cdot 10^3$ und ML^* , $\Delta\epsilon_{ML^*}$ $8,1 \cdot 10^3$) gleich wie im Fall der Uranylkomplexe im Rahmen der Meßgenauigkeit identisch sind (662 ± 2 nm).

Bei den untersuchten Bedingungen (c_M , c_L , Acidität) entstehen keine Komplexverbindungen anderer Typen (M_2L_2 ,²¹ ML_3 und ML_4 ¹⁶).

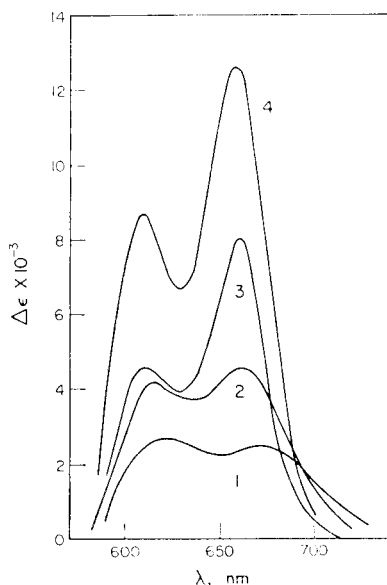


ABB. 10.—Spektren von Arsenazo III-Thorium(IV)-Komplexen (als $\Delta\epsilon_{M_aL_b}$).
1 Komplex M_2L ; 2 Komplex ML ; 3 Komplex ML^* ; 4 Komplex ML_2 .

FOLGERUNGEN FÜR DIE ANALYTISCHE PRAXIS

Bei der spektralphotometrischen Uranylbestimmung mit Arsenazo III ist es günstig, die bevorzugte Bildung des ML^* -Komplexes mit $\Delta\epsilon_{ML^*} = 8,8 \cdot 10^3$ (656 nm) in stark sauren Lösungen bei $H_0 < -1$ auszunutzen. Als Reaktionsmedium bewährte sich Perchlorsäure besser als Salpetersäure. Bei $c_L \geq 1 \cdot 10^{-4}M$ und $-1 > H_0 > -2,5$ ist es dann möglich, die Bestimmung bei Bedingungen, die einer vollständigen Komplexbildung nahe kommen, zu verwirklichen weil $\Delta\epsilon_{ML^*,eff}$ ändert sich kaum mit c_L und nähert sich dem Wert von $\Delta\epsilon_{ML^*}$.

Die Bestimmung von Thorium(IV) in stark salpetersauren Lösungen beruht auf der Bildung eines ML_2 -Komplexes. Bei einem genügenden Ligandenüberschuß ($c_L \geq 1 \cdot 10^{-4}M$) sind die Steigungen der Eichkurven praktisch c_L -unabhängig und sie nähern sich dem Wert von $\Delta\epsilon_{ML_2} = 12,8 \cdot 10^3$.

SCHLUßBETRACHTUNG

Die Ergebnisse des Studiums der Komplexbildung von Arsenazo III mit Uranyl und Thorium(IV) weisen darauf hin, daß die vollständige Analyse der photometrischen Titrationskurven eindeutige Resultate auch in komplizierten Fällen bei Entstehung von mehreren dissoziierten Komplexen liefern kann. Die allgemeinen Fragen der Auswertung von photometrischen Titrationskurven beim Studium der Gleichgewichte (Komplextyp, K) und Eigenschaften ($\Delta\epsilon_{M_aL_b}$) dissoziierter Komplexe wollen wir noch einmal später ausführlich behandeln.

Für die erwiesene Interesse und Unterstützung sind wir Herrn Prof. Dr. Lumír Sommer, Dr.Sc., aus der Universität UJEP Brno zu Dank verpflichtet.

Summary—The reaction of uranyl ion with Arsenazo III in acid solution gives rise to the formation of two complexes of the type ML, the proportions of these two being dependent on the acidity. The molar absorptivities of the complexes at 565 nm are 5.3×10^3 and 8.8×10^3 l.mole⁻¹.mm⁻¹. The formation constants have been determined, and the apparent variation in the sensitivity of the reaction is explained. In acid solution thorium forms complexes with Arsenazo III of the types M₂L, ML (two), and ML₂, the last of which is analytically useful, although partially dissociated. It predominates in strongly acid solution containing a large excess of reagent, and has a molar absorptivity at 658 nm of 12.8×10^3 l.mole⁻¹.mm⁻¹.

Résumé—La réaction de l'ion uranyle avec l'Arsenazo III en solution acide engendre la formation de deux complexes du type ML, leurs proportions dépendant de l'acidité. Les coefficients d'absorption moléculaire des complexes à 565 nm sont $5,3 \times 10^3$ et $8,8 \times 10^3$ l. mole⁻¹. mm⁻¹. On a déterminé les constantes de formation, et l'on explique la variation apparente dans la sensibilité de la réaction. En solution acide, le thorium forme avec l'Arsenazo III des complexes des types M₂L, ML (deux) et ML₂, ce dernier étant analytiquement utile, quoique partiellement dissocié. Il prédomine en solution fortement acide contenant un grand excès de réactif, et a un coefficient d'absorption moléculaire à 658 nm de $12,8 \times 10^3$ l.mole⁻¹.mm⁻¹.

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SHORT COMMUNICATIONS

2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid as a new acid-base indicator

(Received 11 June 1969. Accepted 20 September 1969)

IN RESEARCH on 2,4-bis(nitrobenzazo)resorcinol-6-sulphonic acid (BRS) as a selective qualitative reagent for magnesium, the substance was found suitable as an acid-base indicator, capable of filling a gap in the series of alkaline region indicators.

The substance was prepared according to Podstata and Allan,¹ and purified by a two-stage reprecipitation. The purity at each step was checked by paper chromatography, and the final purity was verified by means of elementary analysis.

Two colour transitions were found, at pH 6.8-8.2 (yellow → red), and at pH 10.5-13 (red → blue-violet). The dissociation constant values pK_1 7.64 and pK_2 11.64 correspond to these transitions, and were obtained as described elsewhere.²

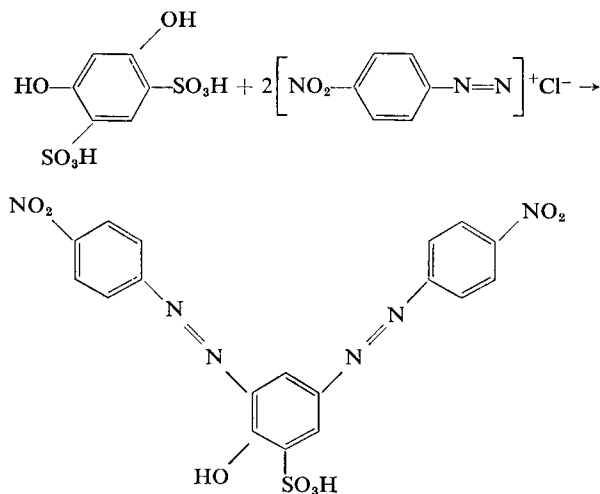
The polarographic behaviour of the substance was investigated and the problem of its possible structures discussed. The use of BRS as a new acid-base indicator was tested by a series of determinations of weak and strong acids. It proved very suitable for the determination of *p*-hydroxybenzoic acid, permitting, in contrast to the commonly used indicators, the carboxyl group to be titrated without simultaneous titration of the labile proton of the hydroxyl group.

The literature shows that the use of resorcinol azo dyes as acid-base indicators is rare (Tropaeolin O and Azo Violet^{3,4}); no mention has been made of bisazo dyes derived from resorcinol.

EXPERIMENTAL

Preparation

Heat resorcinol with conc. sulphuric acid for about 90 min at 140-160°.⁵ Cool the mixture, and quickly collect the precipitate on a sintered porcelain dish by suction. Moisten the product with a little conc. sulphuric acid and subject it to suction for 30 min.



Treat *p*-nitroaniline (2.76 g) with 5 ml of 2*M* hydrochloric acid and quickly add (all at once, in order to prevent formation of amino-azo dye)⁶ the theoretical quantity of solid sodium nitrite (1.38 g) cooled with ice. Then dissolve resorcinol-4,6-disulphonic acid (9 g) in boiling water (about 200 ml) and add sodium acetate (30 g). Cool with ice (100 g), and then add the 0.02 mole of diazonium salt. As the coupling is slow, heat the reaction mixture to 30° after an hour. Collect the precipitated dye rapidly under suction and wash it with a small quantity of water.

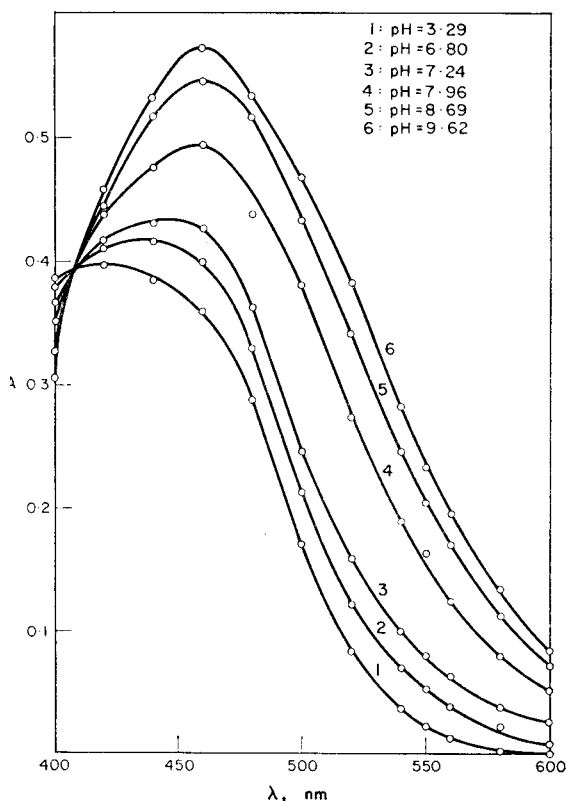


FIG. 1.—Absorption spectra of $2.4 \times 10^{-5}M$ indicator solution, pH 3.29–9.62.

Dissolve the purified substance in boiling water (200 ml) and add sodium carbonate (about 10 g) till alkaline. Salt out the sodium salt by adding about 5% w/v of solid sodium chloride, cool, dilute the solution to twice its volume and collect the brown-red precipitate by suction. In the second stage of purification dissolve the precipitate in 400 ml of water, filter hot, and add 2M hydrochloric acid to the hot filtrate till it is acid to Congo Red, collect, wash and dry the amorphous red precipitate. Test the product chromatographically, with Whatman No. 4 paper and (a) 20% ammonia-isopentanol-pyridine, (1:1:1), (b) 20% ammonia, and by elementary analysis. (The R_f value of the product is 0.6, and of the impurities, 0.07.)

For use as an indicator the purified product is precipitated again as the sodium salt.

Spectrophotometric studies

Measurements were made of the absorption spectra of $2.4 \times 10^{-5}M$ indicator solutions buffered at pH values from 3.29 to 13.30, and (except for the pH 13.3 solution) kept at constant ionic strength with sodium perchlorate (Figs. 1 and 2). The dissociation constants of the indicator were calculated from the equation

$$\log \frac{\alpha_1}{1 - \alpha_1} = \text{pH} - \text{p}K_1 \quad (1)$$

where α_1 is the degree of dissociation, and were verified by a graphical method² (from the dependence of the absorbance on pH) and by a linear regression method,³ and were found to be $\text{p}K_1 = 7.64$; $\text{p}K_2 = 11.64$.

Applications

The indicator was found suitable for most acid-base titrations (*e.g.*, benzoic and phthalic acids dissolved in 70% ethanol, malonic, tartaric, acetic acids in water, mineral acids, *p*-hydroxybenzoic acid, titrated with sodium hydroxide) but not for phosphoric acid because of the mismatch of $\text{p}K$ values for the acid and the indicator. Some results are given in Table I.

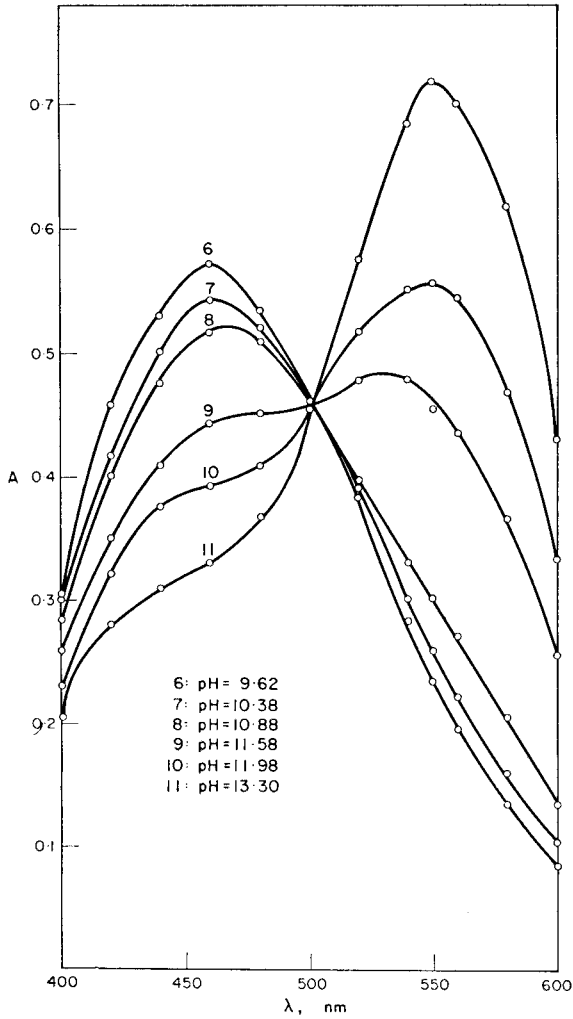


Fig. 2.—Adsorption spectra of $2.4 \times 10^{-5}M$ indicator solution, pH 9.62–13.30.

TABLE I.—ACID-BASE TITRATIONS WITH THE NEW INDICATOR

Acid	0.02M NaOH, ml		Acid	0.02M NaOH, ml	
	theory	found		theory	found
Hydrochloric	7.46	7.46	Malonic	8.40	8.40
		7.48			8.40
Tartaric	6.72	7.46	<i>p</i> -Hydroxybenzoic	5.66	8.38
		6.70			5.68
		6.70			5.66
Benzoic	4.80	4.84	Acetic	7.36	7.34
		4.80			7.36
		4.80			7.34
Phthalic	8.22	8.22			
		8.22			
		8.22			

In non-aqueous media, *e.g.*, acetic acid, pyridine, acetone and methanol, the indicator gave no distinct colour transition.

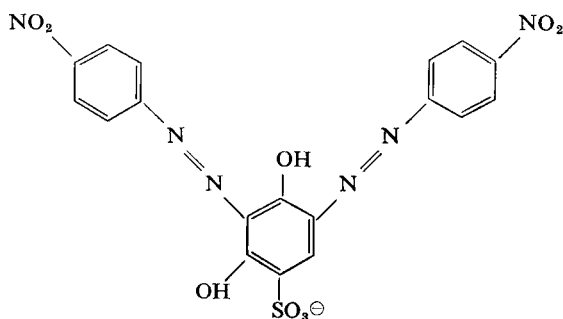
It was found experimentally that the most suitable quantity of indicator for visual titrations is 0.01–0.05 ml of 0.1% indicator solution (*i.e.*, a saturated solution) in 25 ml of titration solution.

DISCUSSION

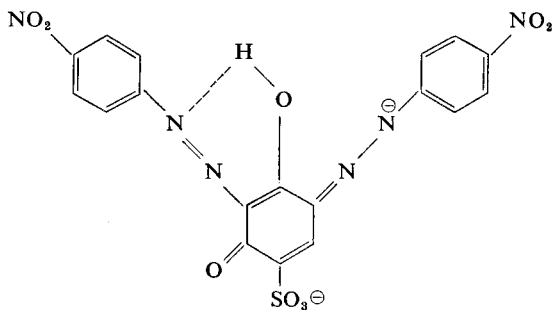
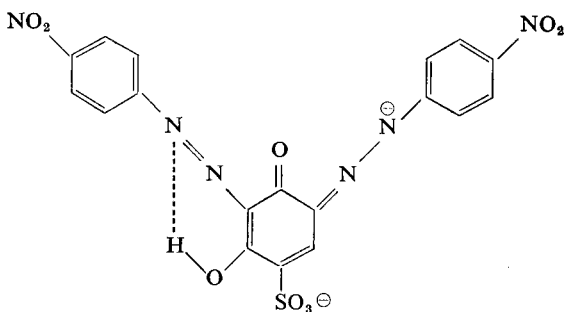
The indicator is polarographically active, giving an anodic wave, most probably because it forms a complex with mercury (a more detailed explanation will be given elsewhere), and a cathodic reduction wave, common in azo-substances.

The most probable cause of the strong bathochromic shift with increasing pH is associated with the quinonoid groups. As the indicator is derived from resorcinol, the orthoquinone structure is energetically most suitable, and therefore most likely to be produced in the first dissociation, with quinone formation between the second hydroxy group and the second azo group in the second dissociation. However, the paraquinone structure cannot be completely left out of account.

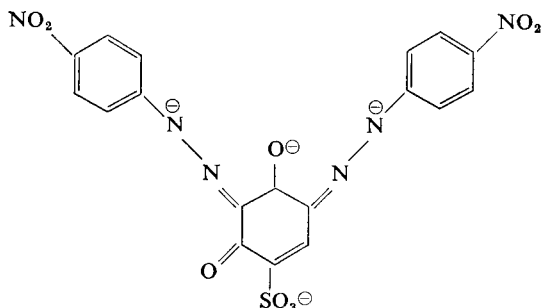
An attempt to determine the structures by means of infrared spectra was unsuccessful. On the basis of common structural relationships in organic chemistry it can be supposed that in acid medium (yellow form of the indicator) the structure is:



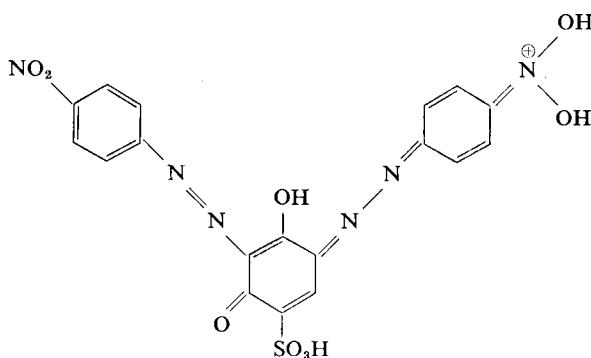
with dissociation of one proton to give the red forms:



and loss of another proton in strongly alkaline medium to give the violet-red form:



In strongly acidic medium (70% sulphuric acid), a red form is produced:



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Summary—2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid is suggested as a new visual acid-base indicator, which because of its colour sharpness and other qualities is useful in titrations of weak acids. There are two colour transitions, one from yellow to red at pH 6.8–8.2, the other from red to blue-violet at 10.5–13.0. The corresponding dissociation constants are pK_1 7.64, and pK_2 11.64.

Zusammenfassung—2,4 - Bis(4 - nitrobenzazo)resorcinol - 6 - sulphonic Säure wird als neue sichtbare Anzeige auf Säuregrundlage vorgeschlagen, welches wegen der Farbschärfe und anderer Eigenschaften nützlich bei Titrierung schwacher Säuren ist. Es gibt zwei Farbübergänge, einer von gelb auf rot bei pH 6,8–8,2, der andere von rot auf blau-violett bei 10,5–13,0. Die entsprechenden Dissoziationskonstanten sind pK_1 7,64, und pK_2 11,64.

Résumé—On suggère l'acide 2,4-bis(4-nitrobenzazo) résorcinol 6-sulfonique comme un nouvel indicateur visuel acide-base qui, par suite de sa netteté de coloration et d'autres qualités, est utile dans les titrages d'acides faibles. Il y a deux transitions de coloration, l'une du jaune au rouge à pH 6,8–8,2 l'autre du rouge au bleu-violet à pH 10,5–13,0. Les constantes de dissociation correspondantes sont $pK_1 = 7,64$ et $pK_2 = 11,64$.

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Silver (III) as an oxidative titrant Determination of some sugars, carboxylic acids and inorganic ions

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THE EVIDENCE for the existence of silver(III) was obtained by Jirsa¹ who made a mixed oxide of silver(II) and silver(III) by the anodic oxidation of silver(I) salts. A pure variety of silver(III) was obtained by Carmon² by the oxidation of silver(I) with ammonium persulphate. Subsequently stable compounds of silver(III) were obtained by complexation. Malaprada³ complexed silver(III) with periodate and the sparingly soluble sodium diperiodatoargentate(III) $\text{Na}_7[\text{Ag}(\text{IO}_6)_2]$ was prepared. Malatesta⁴ used tellurate as complexing agent for preparing a ditelluratoargentate(III) compound $\text{Na}_6\text{H}_3[\text{Ag}(\text{TeO}_6)_2] \cdot 18\text{H}_2\text{O}$. Ray⁵ isolated a number of 4-co-ordinated silver(III) ethylenebiguanide (enbg) salts of the type $[\text{Ag}^{\text{III}}(\text{enbg})_2] \cdot \text{X}_3$ where X is $\frac{1}{2}\text{SO}_4^{2-}$, NO_3^- , ClO_4^- or OH^- . In spite of the interesting behaviour of silver(III) compounds, no attempts appear to have been made for their use as oxidizing titrants and the present work is directed towards this end.

EXPERIMENTAL

Materials

All the chemicals used were of reagent grade.

Silver(III) solution. Malatesta's procedure⁴ was employed with some modification for the preparation of silver(III) solution. Silver nitrate (1.36 g), potassium tellurite (3.8 g), potassium persulphate (6.5 g) and potassium hydroxide (9 g) were added to about 250 ml of water. The order of addition was not important. The mixture was shaken thoroughly and heated on a hot-plate for about 30 min. It became greenish and finally a light red solution mixed with black oxides of silver was obtained. After cooling, the black precipitate was filtered off on a porosity-4 sintered-glass crucible.

The persulphate used is just sufficient to oxidize silver(I) and tellurite to silver(III) and tellurate respectively and is therefore completely removed during boiling. If an excess of persulphate is used, boiling for a longer time is necessary for its complete decomposition. The removal of persulphate is necessary because of its interference in the oxidation of substrate compounds and in the estimation of silver(III) by the iodimetric method. The absence of persulphate in the prepared solution can be ascertained by acidifying about 1 ml of solution with dilute sulphuric acid till the red colour is completely discharged [silver(III) is then reduced to silver(I)], adding 5 ml of 0.5M sodium bicarbonate and 1 ml of 10% potassium iodide solution, letting stand for 2 min, then adding starch. Absence of a blue colour shows the absence of persulphate.

The prepared solution was diluted to 250 ml. The silver(III) concentration was found to be $\sim 1.26 \times 10^{-2}M$. From the amount of silver(I) taken, the silver(III) solution should have been $3.2 \times 10^{-2}M$. The divergence may be due to loss of silver by precipitation as oxide. The final concentration of potassium hydroxide in the prepared solution was $\sim 0.5M$. The solution obtained was fairly stable (for at least 3 months).

Procedure

For standardization of silver(III) solution, treat 5 ml of it with 10 ml of 0.02M arsenite solution, let stand for 1 min and then acidify with $\sim 1N$ sulphuric acid till the colour disappears. Then add 5 ml of 0.5M sodium bicarbonate and 1 ml of 10% potassium iodide solution. Back-titrate the unconsumed arsenite with standard iodine solution (0.006N), using starch as indicator. Run a blank.

For determinations, to 25 ml of silver(III) solution add an amount of sample that will reduce less than half the silver(III) and keep it at 75–80° for the time shown in Table I. Determine the excess of silver(III) as described for standardization. If the temperature is >80° erratic results are obtained. Run a blank.

TABLE I

Sample	Amount μ mole	Ag(III) consumed, equiv/mole of sample	Duration, hr
Glucose	1.55	23.90	4
Fructose	2.51	24.05	4
Sucrose	1.24	47.90	4
Xylose	2.26	20.13	4
Maltose	0.825	48.23	4
Lactose	1.16	48.20	4
Arabinose	1.86	20.08	4
Mannose	1.82	24.10	4
Potassium tellurite	16.1	2.01	4
Thiosulphate	5.33	8.05	$\frac{1}{2}$
Sulphite	14.9	2.01	1
Hydrogen peroxide	24.3	1.99	1
Chromium(III)	3.80	3.01	1
Potassium ferrocyanide	7.25	1.005	$\frac{1}{2}$
Sulphide	1.33	7.98	3
Tartaric acid	6.78	10.05	1
Citric acid	1.61	18.10	1
Salicylic acid	0.692	28.10	1
Ascorbic acid	1.41	20.02	1
Formic acid	16.5	2.01	1

DISCUSSION

From the results (which were reproducible within 0.5%), it is clear that the sugars and organic acids are oxidized to carbon dioxide and water by heating at 80° for an appropriate time with an excess of silver(III) solution. Arabinose and xylose, which are pentoses, require 20 equivalents of Ag(III) for complete oxidation. The hexoses such as glucose, fructose, mannose, consume 24 equivalents, whereas sucrose, maltose, and lactose require 48 equivalents. Organic acids, *viz.*, formic, tartaric, citric, ascorbic and salicylic, take 2, 10, 18, 20, 28 equivalents respectively. Inorganic compounds such as potassium hexacyanoferrate(II), sodium sulphite, hydrogen peroxide, chromium sulphate, sodium sulphide, and sodium thiosulphate require 1, 2, 2, 3, 8, 8 equivalents respectively. It shows that thiosulphate, sulphite and sulphide ions are converted into sulphate, hydrogen peroxide into water and oxygen, chromium(III) to chromium(VI) and $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$. If the amount of silver(III) added is less than twice that required, complete oxidation is uncertain; this may be due to the fact that in such cases solid silver(II) oxide formed in the system oxidizes the substrate very slowly. This was found to happen with potassium tellurite, glucose, fructose, sucrose, xylose, maltose, lactose, arabinose, mannose, sodium sulphide, tartaric acid, citric acid and salicylic acid, but not with the other compounds tested. Tellurate does not interfere as an oxidant, since silver(III), being a stronger oxidant, reoxidizes any tellurite that may be formed in the reaction mixture.

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Summary—Silver(III) has been stabilized as its tellurato complex and used for the oxidation of sugars, organic acids, ferrocyanide, sulphide, peroxide and thiosulphate, the excess of oxidant being measured by reducing it with an excess of arsenite and then titrating the surplus arsenite with iodine.

Zusammenfassung—Silber(III) wurde als Telluratkomplex stabilisiert und zur Oxidation von Zuckern, organischen Säuren, Ferrocyanid, Sulfid, Peroxid und Thiosulfat verwendet. Der Überschuß an Oxidationsmittel wird mit überschüssigem Arsenit reduziert und dessen Überschuß mit Jod titriert.

Résumé—L'argent(III) a été stabilisé sous forme de son complexe tellurique et utilisé pour l'oxydation de sucres, acides organiques, ferrocyanure, sulfure, peroxyde et thiosulfate, l'excès d'oxydant étant mesuré en le réduisant avec un excès d'arsénite puis en titrant l'excès de celui-ci à l'iode.

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The volumetric determination of nitrite with chloramine T

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THE METHOD most frequently used for the volumetric determination of nitrite seems to be the titration with permanganate. Disadvantages of the method are the low reaction-rate, and the decomposition and air-oxidation of the nitrous acid during the titration. As a consequence complicated procedures are often given, and the results obtained are not satisfactory.¹

The application of chloramine T (sodium salt of *p*-toluenesulphochloramide, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-NCINa} \cdot 3\text{H}_2\text{O}$) as an oxidimetric reagent has been described frequently in the literature. It is cheap, may be obtained in a rather pure state, and its solution is rather stable. Literature surveys are given by Bishop and Jennings,² Kolthoff and Belcher³ and Berka, Vulterin and Zýka.⁴

The direct titration of nitrite with chloramine T has been described, but does not give satisfactory results.⁴ An indirect method is possible,³ but no detailed information seems available on the scope and limitations of the method. In this paper some information on this point is therefore given. In the procedure used, a modification of the earlier procedure,³ the sample is oxidized to nitrate with chloramine T, then iodide is added and oxidized to iodine by the excess of the reagent, and the iodine is titrated with thiosulphate solution.

EXPERIMENTAL

Reagents

A chloramine T solution, about 0.05*M*, was prepared by dissolving as far as possible about 25 g of the reagent, filtering into a 2-litre volumetric flask, and diluting to the mark. The solution was stored in an amber bottle. A cation-exchanger, 20–50 mesh, dry capacity 4.8 mequiv/g was used.

Procedure

In a 500-ml stoppered conical flask take 25 ml of chloramine T solution (or 50 ml if more than 30 mg of nitrite are present), add the sample, dilute to about 150 ml, add 10 ml of 9*M* acetic acid and after 2 min add 10 ml of 10% potassium iodide solution. Place the flask in the dark for 5 min and titrate in the usual way with thiosulphate solution and starch indicator.

Perform a blank in the same way. From the difference in the quantities of thiosulphate added, calculate the nitrite content of the sample.

RESULTS AND DISCUSSION

Stock solutions were prepared with the products of two different manufacturers. The pH of both solutions was about 10, in agreement with Berka *et al.*⁴ Bishop gives the value 7.7 however.² The titre of one solution decreased 0.3% in 5 weeks and 0.7% in 10 weeks, the other solution had a

constant titre for 3 weeks. More stable solutions have been described in the literature.^{2,4} The purities of the two chloramine T, samples, (calculated from the thiosulphate titre, standardized against iodate) were 98 and 98.5% respectively. This is in agreement with Bishop.²

The repeatability of the method was checked in two series of five experiments with 25 mg of nitrite. In both cases the relative standard deviation was about 0.1%.

Interferences were investigated by adding the foreign compound immediately after the sample had been added and then completing the procedure described above. The foreign compounds were added in quantities of 1, 2, 5, 10, 25, 50 and 125 mg. The maximum permissible amount (error below 0.3% when 25 mg of nitrate were present) was found to be less than 1 mg for S^{2-} , NH_4^+ and SCN^- , 1 mg for $Fe(CN)_6^{4-}$, 5 mg for Cu^{2+} , 50 mg for I^- , and 125 mg (or more) for Br^- , $Fe(CN)_6^{3-}$, Hg^{2+} , Pb^{2+} , and ClO_3^- .

Iodide interferes if present in too large amounts because it consumes too much chloramine T, and not enough is left for the oxidation of nitrite. Theoretically, bromide should not interfere, because the bromine formed also oxidizes nitrate.

Cu^{2+} reacts slowly with iodide $Fe(CN)_6^{4-}$, S^{2-} , NH_4^+ and SCN^- react about quantitatively with chloramine T; the reaction products do not react appreciably with iodide under the experimental conditions. Hg^{2+} and Pb^{2+} react with part of the I^- , but presumably this does not interfere with the reaction with chloramine T. ClO_3^- probably has no oxidizing properties under the experimental conditions. $Fe(CN)_6^{3-}$ possibly oxidizes nitrite to some extent, but the $Fe(CN)_6^{4-}$ formed in this way consumes an equivalent amount of chloramine T, and no error results.

It should be noted that the interfering compounds investigated had not been in contact with nitrite for a long time before the analysis was performed. If the contact had taken place for a longer time, some interfering reaction might have taken place in some cases, before the analysis itself was started. Investigations of this point have not been performed because the prevailing conditions during storage (such as pH and concentration) may considerably influence the extent to which the interfering reaction takes place.

Several attempts have been made to eliminate some of the interferences. Solutions containing NH_4^+ were boiled at high pH, but high results were obtained probably because of incomplete removal of ammonia, which consumes more reagent than nitrite does. Sodium tetraphenylborate forms an insoluble salt with NH_4^+ , but the interference could not be prevented by this reaction because the reagent was found to react with chloramine T. EDTA also reacts with chloramine T and therefore the interference of copper could not be eliminated by the addition of this complexing agent.

Application of a cation-exchange column gave satisfactory results; 35 ml of a solution containing 25 mg of nitrite and variable amounts of Cu^{2+} and NH_4^+ were passed through the column (about 50×10 mm) into the titration flask, the column was rinsed with about 50 ml of water, and the resulting solution was diluted to 150 ml and treated as described under *Procedure*. Results of 13 experiments with 25 mg of nitrite and 10 mg of Cu^{2+} (3 experiments), 10 mg of NH_4^+ (3), 125 mg of Cu^{2+} (2), 125 mg of NH_4^+ (2), and no foreign compound (3) all gave results about 0.10 mg of nitrate low, an error of 0.4%. The error is probably caused by oxidation of nitrite by air, during the run through the column (45 min). The error was not considered serious but possibly may be further reduced if a smaller column is used.

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Summary—Nitrite may be determined by oxidation with chloramine T, reaction of the excess of chloramine T with excess KI, and titration of I_2 formed, with thiosulphate. The reproducibility and some interferences are discussed.

Zusammenfassung—Nitrit kann bestimmt werden durch Oxidation mit Chloramin T, Reaktion des überschüssigen Chloramin T mit überschüssigem KI und Titration des gebildeten I_2 mit Thiosulfat. Die Reproduzierbarkeit und einige Störungen werden diskutiert.

Résumé—On peut déterminer le nitrite par oxydation avec la chloramine T, réaction de l'excès de chloramine T avec un excès de KI et titrage de I_2 formé avec le thiosulfate. On discute de la reproductibilité et de quelques interférences.

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Exchange reactions of ternary ion-association complexes directly in the organic phase

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A NEW approach has been developed that combines the advantages of solvent extraction with the inherently high sensitivities afforded through the incorporation of large organic dye cations into ternary ion-association complexes containing the metal ion of interest. Basically, the new technique involves the formation of a complex, $[ML_x^-]R^+$, where R^+ initially is either a non-coloured or a non-fluorescent organic cation. Following extraction of $[ML_x^-]R^+$ a second cation, R_1^+ , which is capable of exchanging with the first R^+ group, is added directly to the organic phase. In this instance, however, R_1^+ is purposely selected to be highly coloured or fluorescent, thereby yielding the highly coloured or fluorescent complex $[ML_x^-]R_1^+$. Unreacted R_1^+ is readily back-extracted, leaving only the dye-complex in the organic phase. In the present paper the determinations of gold and uranium are described to illustrate the advantages of the new technique.

EXPERIMENTAL

Reagents

A uranium stock solution (1.00 mg/ml) was prepared by dissolving 1.180 g of triuranium octaoxide in 10 ml of concentrated nitric acid and diluting to 1 litre with distilled water.

A 1.00 mg/ml gold solution was prepared by dissolving 1.000 g of gold rod in 5 ml of *aqua regia*, evaporating to incipient dryness and diluting to 1 litre with 0.1M hydrochloric acid.

Working solutions were prepared by further dilution.

Dye solutions were prepared by dissolving 30 mg of Brilliant Green (C.I. No. 42040, bisulphate salt) or Rhodamine 6G (C.I. No. 45160, chloride salt) in 100 ml of absolute ethanol.

The following aqueous solutions were used: 1M ammonium thiocyanate, 0.1M sodium benzoate and 0.01M tetraphenylarsonium chloride.

Apparatus

Absorption spectra were obtained with a dual-beam recording spectrophotometer whereas measurements at a fixed wavelength were made on a single-beam instrument. Matched 10-mm absorption cells were used in all instances.

Fluorescence measurements were obtained with a single-beam, uncorrected spectrofluorometer.

Extractions were carried out in 60-ml separatory funnels equipped with all-Teflon fittings. A large, industrial-type centrifuge was used to hasten the separation of phases.

Procedures

Gold-thiocyanate system. The aqueous phase, containing $\leq 20 \mu\text{g}$ of gold(III), is made 0.02M in thiocyanate, 0.002M in tetraphenylarsonium chloride and 0.01M in hydrochloric acid. Following extraction with 5.00 ml of benzene for 1 min (vigorous shaking), the sample is centrifuged and the aqueous layer is discarded. Approximately 0.5 ml of alcoholic dye solution is added to the benzene fraction and mixed, and the resulting solution is back-washed with an equal volume of 0.01N hydrochloric acid to remove unreacted dye (30-sec shaking time is ample). The extract is then analysed either spectrophotometrically or spectrofluorometrically, depending on the choice of dye. Beer's law is obeyed over the range 1–20 μg of gold. For Brilliant Green, maximum absorbance is at 640 nm; for Rhodamine 6G the excitation maximum is 525 nm and the emission maximum is 550 nm.

Uranium(VI)-benzoate system. This is similar to the gold-thiocyanate system except that instead of being 0.02M in thiocyanate, the aqueous phase is 0.05M in sodium benzoate and has a pH in the range 2–5. There is one other significant difference. The complex, [Brilliant Green⁺] [UO₂(C₆H₅COO)₃⁻], decomposes with time but can be stabilized by the addition of acetone. At least 40% by volume is necessary. This composition is achieved most readily by diluting 2.00 ml of acetone, previously added to a dry 5-ml volumetric flask, to the mark with the benzene extract.

In the procedures above, the various reagent concentrations cited are not necessarily optimum values but are sufficient for demonstrating the advantages of the extraction-exchange approach. Preliminary pH studies, however, have shown that acidity definitely does not need to be closely controlled. In practice, any value in the range 2–9 is satisfactory. Above about pH 5 some difficulty may be encountered with emulsion formation.

DISCUSSION AND RESULTS

From a 0.01M thiocyanate solution at pH 2 thiocyanate ion can be quantitatively extracted into benzene as the binary complex [R⁺] [CNS⁻] with either Brilliant Green or Rhodamine 6G as the R⁺ group. Consequently, in ternary complex reactions based on metal-thiocyanate-dye systems, the anion dye side-reaction can cause excessively high blank values since the R⁺ group is solely responsible for the colour and/or fluorescence in both the binary and ternary complexes.

To investigate the possible advantages of the present approach in minimizing the [R⁺] [CNS⁻] side-reaction the gold-thiocyanate system was selected for initial study. The absorbances obtained for 10 μg of gold were 0.902, 0.884 and 0.887 for three independent determinations. Most important, however, the corresponding blank was only 0.003. If the same amount of Brilliant Green had been added directly to the 0.01M thiocyanate, the corresponding blank value would have been approximately 0.9, *i.e.*, approximately the same as the sample signal. Thus, instead of a sample-to-background ratio of 1:1, the exchange approach gave a ratio of about 300:1.

Attempts to extract microgram amounts of uranium(VI) as the complex, [ϕ_4 As⁺] [UO₂(CNS)₃⁻], were not as successful as the gold experiments. Although various thiocyanate concentrations up to 1M were investigated, the maximum net absorbance obtained for 100 μg of uranium was only about 0.3 with a corresponding blank that was also about 0.3 (for 1M thiocyanate), indicating that significant amounts of thiocyanate were being extracted as [ϕ_4 As⁺] [CNS⁻] in the initial extraction and remaining in the benzene phase as [Brilliant Green⁺] [CNS⁻] following the exchange reaction. Attempts to lower the amount of binary-bound thiocyanate by back-extracting with iron(III) solutions (1 mg/ml; 10 ml taken for phase equilibration) met with moderate success. In this instance the blank was reduced from 0.3 to 0.09 with an average deviation of ±0.01 for four runs.

The formation and extraction of the red ternary complex, [Rhodamine B⁺] [UO₂(C₆H₅COO)₃⁻], was first reported by Feigl¹ and later used by Anderson and Hercules² for the quantitative determination of trace amounts of uranium. In the latter work complete extraction of uranium(VI) was obtained only when the aqueous:organic volume ratio was 1:10. In the exchange approach, however, uranium is completely extracted at aqueous:organic phase ratios of 2:1 and indications are that much larger ratios can be tolerated. As pointed out previously, the benzene extracts of the uranyl-benzoate-dye complexes are unstable and both their absorbance and fluorescence decrease rapidly with time. In the case of the Brilliant Green complex, the rate of decrease in absorbance was found to vary from about 8% per min at the 5-μg uranium level to approximately 3% per min at the 20-μg level. Stabilizing with a minimum of 40% v/v of acetone, however, yielded extracts with absorbances which were constant for several hours and decreased only about 2% overnight.

Although Růžička and Starý³⁻⁵ have recently described the analytical implications of chelate exchange in the organic phase, apparently the present work is the first report of exchange reactions involving ternary ion-association complexes. Because much larger concentrations of intermediate ligand, L, can be utilized effectively when coupled with an exchange reaction a number of interesting and potentially useful analytical systems are now open for study. Furthermore, since the initial (tetraphenylarsonium) extraction can be carried out at a lower acidity than normally employed with the triphenylmethane and rhodamine dyes, the possibility of using masking agents to increase selectivity further is also greatly enhanced. Finally, dye purity and light-fastness appear to cause considerably fewer problems in the proposed technique and much smaller quantities of dye are needed.

Summary—The analytical implications of exchanging a highly coloured or fluorescent group R for a non-coloured or non-fluorescent one directly in the organic phase are discussed for ternary ion association complexes of the type $[ML_x^-]R^+$. Several examples are given to illustrate the approach.

Zusammenfassung—Die analytischen Gesichtspunkte beim Austausch einer stark gefärbten oder fluoreszierenden Gruppe R in ternären Ionenassoziationskomplexen des Typs $[ML_x^-]R^+$ gegen eine farblose oder nicht fluoreszierende in der organischen Phase werden diskutiert. Mehrere Beispiele werden zur Erläuterung des Vorgehens angegeben.

Résumé—On discute des incidences analytiques de l'échange d'un groupe R hautement coloré ou fluorescent par un autre non coloré ou non fluorescent directement dans la phase organique pour les complexes d'association d'ions ternaires du type $(ML_x^-)R^+$. On donne plusieurs exemples pour illustrer cette voie.

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The structure of primary nickel dithizonate

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ALTHOUGH a considerable volume of work has been published on the structure of diphenylthiocarbazonate (dithizone, H_2Dz) complexes,^{1,2} the crystal structures of only $Hg(HDz)_2$ and $Cu(HDz)_2$ have been determined.^{3,4} Both these complexes were shown to co-ordinate through sulphur and nitrogen. Several authors have grouped the complexes according to various properties. All have concluded that the nickel, palladium and platinum compounds are unusual, and are characterized by multiple visible absorption bands,⁵ a high formation constant⁶ and a strong absorption band at 1220 cm^{-1} in the infrared.⁷ On the basis of these results, Math, Fernando and Freiser⁸ proposed that the dithizone ligand was bonded through two nitrogen atoms in the nickel complex. These workers seem to have assumed that they had a 1:1 complex; however, they used the term "octahedrally co-ordinated" in their discussion.

We have reacted nickel and dithizone at various pH values from 1 to 11 and with metal:ligand ratios from 1 to 100 without finding evidence of any complex other than $Ni(HDz)_2$, nor has a secondary complex been reported elsewhere. The visible and infrared spectra published by Math *et al.* are identical to those found for our $Ni(HDz)_2$. We have also prepared fourteen other dithizone complexes and the powder diffraction patterns of $Ni(HDz)_2$, $Pd(HDz)_2$ and $Pt(HDz)_2$ show that they are closely isostructural and, in fact, constitute the only group of isomorphs among the complexes investigated. Surprisingly it was found that $Ni(HDz)_2$ is paramagnetic, with a magnetic moment of 3.15 BM.

Recrystallization of $Ni(HDz)_2$ from chloroform yielded black needles which are triclinic, space group $P\bar{1}$; $a = 0.462\text{ nm}$, $b = 1.099\text{ nm}$, $c = 1.250\text{ nm}$; $\alpha = 88.8^\circ$, $\beta = 97.4^\circ$, $\gamma = 99.1^\circ$; $Z = 1$, $D_0 = 1.50$, $D_c = 1.51$. The structure was determined from a Patterson projection down the a axis, and refined by observed and difference Fourier syntheses to yield $R = 0.15$ for the 338 OkI data (250 observed with Ni-filtered $Cu\ K\alpha$ radiation).

The molecule is centrosymmetric with a planar configuration about the nickel that is essentially the same as that found for the copper complex (Fig. 1). The dithizone moiety is bonded to the nickel atom through one nitrogen and one sulphur atom and definitely not as suggested by Math *et al.*⁸

The unit cell dimensions of $Ni(HDz)_2$ are very similar to those of $Cu(HDz)_2$ but with the exception that a is longer (0.462 *vs.* 0.429 nm) and c is shorter (1.250 *vs.* 1.336 nm). This suggests that the $Ni(HDz)_2$ molecule is tilted further out of the basal plane of the unit cell than is $Cu(HDz)_2$, thus

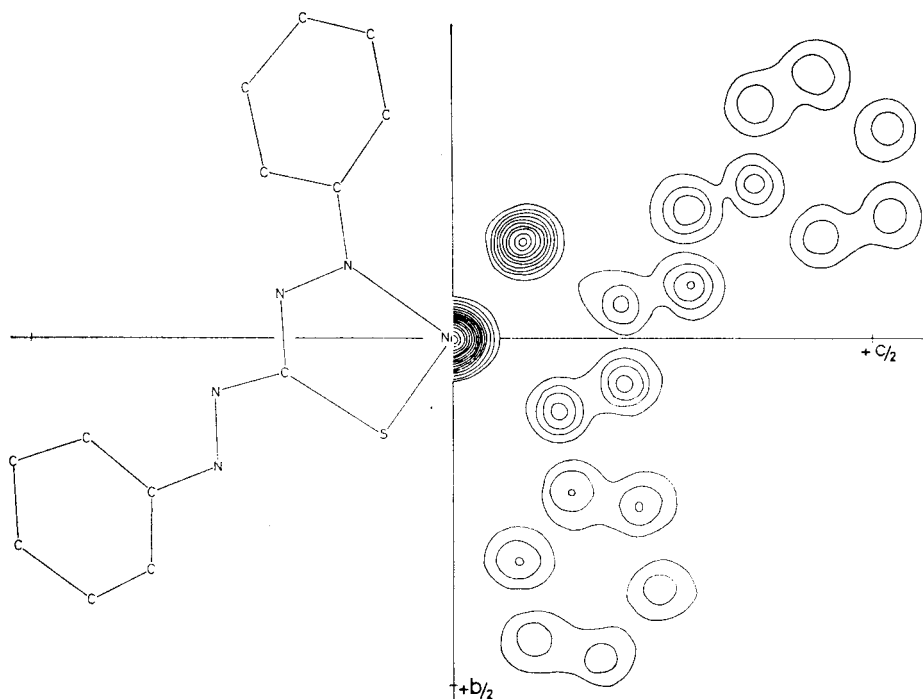


FIG. 1.—Structure of the nickel complex.

possibly allowing pseudo-octahedral co-ordination of the nickel atom with either sulphur or nitrogen atoms in the neighbouring molecules above and below it. Such a configuration would account for the paramagnetic susceptibility of the nickel complex, which cannot be explained by a simple planar arrangement.

A three-dimensional structure analysis is being done to determine in detail the co-ordination around the nickel atom. This will be reported later.

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Summary—Primary nickel dithizonate is found to be isostructural with the palladium and platinum complexes, and the nickel dithizonate molecule is shown to contain nickel in an approximately square planar configuration bonded to the organic ligand through both sulphur and nitrogen atoms.

Zusammenfassung—Primäres Nickel-Dithizonat ist isostrukturell mit den Palladium- und Platinkomplexen. Es wird gezeigt, daß das Nickeldithizonatmolekül Nickel in ungefähr quadratisch planarer Konfiguration enthält. Es ist sowohl über Schwefel als auch über Stickstoff an den organischen Liganden gebunden.

Résumé—On a trouvé que le dithizonate de nickel primaire est isostructural avec les complexes du palladium et du platine, et l'on montre que la molécule de dithizonate de nickel contient le nickel dans une configuration plane carrée approximativement, liée au coordinaat organique par l'intermédiaire à la fois des atomes de soufre et d'azote.

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Determination of dicyclohexylamine in sodium cyclamate

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FOR THE past two years or so colorimetric methods for the determination of mono and dicyclohexylamine in cyclamates have been in regular use in Nobel Division of I.C.I. Ltd. That for the mono compound is the same as that of Bradford and Weston¹ except that benzene is used instead of chloroform as extractant, and considerable demand has been evident for the method used for the dicyclo compound. The method described here is a colorimetric procedure based on the use of Bromophenol Blue, but before it was chosen a number of possible techniques were explored.

The possibility of using a colorimetric procedure in which the amine is reacted with carbon disulphide to form a dithiocarbamate² was first examined. A yellow colour is obtained when the method is used for secondary amines, but lack of sensitivity in the microgram range precludes its use for dicyclohexylamine. Thin-layer chromatographic procedures,³ although sensitive and useful for exploratory work, were not suitable for routine work. Likewise, gas chromatography, although useful for preparative work, is unsuitable for the many different users of cyclamate.

During a literature search for a colorimetric method appropriate for dicyclohexylamine, it was noted that Bromophenol Blue has been used as a complexing agent for the determination of cationic surfactants.⁴ In the titration of sodium oleyl sulphate with cetyltrimethylammonium bromide solution, the end-point is detected by forming the complex of cetyltrimethylammonium bromide with Bromophenol Blue, which is soluble in chloroform, and it was considered that it might be possible that dicyclohexylamine would react in the same way, since dicyclohexylamine has itself been recommended as a cationic surfactant.⁵ Moreover it is claimed⁶ that complexes are formed by reaction of Methyl Orange with fatty amines, but the authors could not identify the complexes by infrared spectroscopy. However, the yellow colour of the complex indicated that the cationic form of the Methyl Orange predominated and hence the complex may be a salt of the cationic amine. Preliminary experiments with Methyl Orange gave inconsistent results so the Bromophenol Blue reaction was explored.

A 10- μ g amount of dicyclohexylamine gave a measurable colour in the presence of excess of monocyclohexylamine in sodium cyclamate.

The method described is applicable to samples of sodium cyclamate for the determination of dicyclohexylamine down to the order of 1 ppm in the presence of as much as 600 ppm of monocyclohexylamine.

EXPERIMENTAL

Reagents

Bromophenol Blue solution. Add 0.075 g of solid Bromophenol Blue to 60 ml of water in a 100-ml beaker followed by 10 ml of 0.1M sodium bicarbonate and stir continuously for about 15 min until dissolution is complete. Add 0.2M hydrochloric acid and adjust the pH of the solution to 4.0 (pH meter). Transfer the solution to a 100-ml volumetric flask and make up to volume with water.

Acetic acid-hydrochloric acid reagent. Mix 200 ml of 1M hydrochloric acid with 166.6 ml of glacial acetic acid in a 1-litre volumetric flask and dilute to the mark with water.

Sodium hydroxide, 0.1M.

Standard dicyclohexylamine solution. Dissolve 0.5 g of dicyclohexylamine in 100 ml of chloroform. Dilute 1 ml of this solution to 200 ml with chloroform (1 ml contains 25 μ g of dicyclohexylamine).

Procedure

Dissolve 10 g of the sodium cyclamate sample in 100 ml of water and transfer the solution to a separating-funnel. Add 10 ml of 0.1M sodium hydroxide and extract the mixture three times with 10-, 5- and 5-ml quantities of chloroform. Combine the chloroform extracts in a second separating-funnel, add 100 ml of water followed by 3 ± 0.2 ml of the acetic acid-hydrochloric acid reagent and 1 ml of the Bromophenol Blue reagent. Shake the mixture for 3 min and at the end of this time set it aside for 30 min, protecting it from sunlight.

Open the tap of the separating-funnel momentarily to disperse any entrapped water, dry the stem of the funnel with filter paper, run off the chloroform layer into a graduated flask and dilute it to 25 ml with chloroform. Entrapped water may also be removed by passing the chloroform solution through a dry filter paper. Prepare a blank in the same way, omitting only the sample. Measure the absorbance of the test solution and of the blank against chloroform in 40-mm cells at 410 nm.

Purify sodium cyclamate by making it just alkaline and then extracting with chloroform. Dissolve 10-g portions in water and add known amounts of up to 75 μg of dicyclohexylamine, dilute each solution in turn to 100 ml and carry out the test described, to obtain a calibration curve, which should be linear.

DISCUSSION

An absorbance of 0.110 was found to be equivalent to 1 ppm of dicyclohexylamine. Amounts of 3 or 6 mg of monocyclohexylamine in 10-g samples of sodium cyclamate did not interfere with the determination of 10–75 μg of dicyclohexylamine. Samples of sodium cyclamate taken from various sources were tested and found to contain from less than 1 up to 2.5 ppm of dicyclohexylamine.

Should some impurity other than dicyclohexylamine be present in the cyclamate and produce a small amount of yellow colour, the apparent amount of dicyclohexylamine found would be incorrect but it would be certain that not more than this amount of dicyclohexylamine was present.

The purity of the dicyclohexylamine used in this work was checked by testing fractions obtained by preparative gas chromatography. Traces of 5 other compounds, including monocyclohexylamine, were present but the yellow colour due to the Bromophenol Blue was only obtained from the fraction corresponding to the dicyclohexylamine peak.

The conditions for the preparation of the dicyclohexylamine fraction were as follows.

Column	6 m \times 13 mm
Stationary phase	SE 30 (30% on Chromosorb W)
Column temperature	250°
Nitrogen flow-rate	300 ml/min
Amount of commercial dicyclohexylamine	50- μl portions injected at repeated intervals

Thin-layer chromatography (TLC) can be used as an alternative method for the separation and determination of small amounts of dicyclohexylamine. A known weight (about 10 g) of sodium cyclamate is dissolved in 100 ml of water and, after being made alkaline, the solution is extracted four times with 10-, 5-, 5- and 5-ml quantities of chloroform. The combined chloroform extracts are evaporated to 0.5 ml in a specially designed graduated tube, at room temperature, by means of a jet of air. With a Hamilton syringe 0.05 ml of the solution is applied as a single spot on a Kieselgel G thin-layer plate. Standards (0.05 ml of chloroform containing 2.5–10 μg of dicyclohexylamine) are put on the plate at the same time. The chromatogram was developed with a mixture of ammonia, acetone and petroleum ether (b.p. 40–60°) (17:833:400). After development, the plate is sprayed with a 1:1 mixture of 0.1N iodine and 10% sulphuric acid and the size of the spots compared. It is easy to differentiate between 25-, 50-, 75- and 100- μg amounts of dicyclohexylamine added to 10-g amounts of sodium cyclamate dissolved in 100 ml of water. Samples of sodium cyclamate, when tested by this method, gave results comparable to those obtained by the colorimetric procedure, but we would not recommend a TLC procedure for routine work, because it is more time-consuming and less suited to plant control work than the relatively simple colorimetric method.

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Summary—Dicyclohexylamine is determined in sodium cyclamate at levels of concentration down to the order of 1 ppm by measurement of the yellow colour of the chloroform extract of its Bromophenol Blue complex.

Zusammenfassung—Dicyclohexylamin wird in Mengen bis herunter zu 1 ppm in Natriumcyclamat durch Messung der gelben Farbe des Chloroformextraktes seines Komplexes mit Bromphenolblau bestimmt.

Résumé—On dose la dicyclohexylamine dans le cyclamate de sodium à des niveaux de concentration descendant jusqu'à l'ordre de 1 ppm par mesure de la coloration jaune de l'extrait chloroformique de son complexe avec le Bleu de Bromophénol.

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Coulometrische Titration von Hypochloriten und Chloraten

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HYPOCHLORIT und Chlorat wurden coulometrisch bei Generator-stromstärken von 0,2 bis 100 mA titriert. Die Messungen fanden in einer offenen "H-Zelle" statt. Der Meßraum hatte ein Volumen von 100 ml. Als Hilfselektrode diente ein Platinblech in 1N Natriumsulfatlösung. Die Elektrodenräume waren durch eine Salzbrücke aus Gelatine/1N Natriumsulfatlösung getrennt. Die Endpunkte wurden biamperometrisch an einem Platin-Drahtpaar bzw. amperometrisch an einer rotierenden Platinelektrode indiziert. Der Meßraum wurde mit einem Magnetrührer gerührt.

Bestimmung von Hypochlorit

Elektrolyt. Eisen(III) sulfat, 0,1M; Natriumacetat, 1M; pH-Wert auf 4,3 bis 4,7 eingestellt.

Die Generatormethode war eine Platindrahtspirale mit einer Oberfläche von ca. 600 mm². Die Potentialdifferenz zwischen den Indikatorelektroden für biamperometrische Indikation betrug 700 mV.

Die Elektrolytlösung (30 bis 50 ml) wird vor und während der Messung mit Stickstoff gespült. Nach Einschalten des Generatorstroms wird bei laufender Registrierung des Indikationsstroms die Probe zugegeben. Die biamperometrische Indikation ergibt am Endpunkt ein scharfes Minimum.

Sehr kleine Konzentrationen werden besser nach dem indirekten amperometrischen Verfahren von Christian¹ bestimmt. Die Probe wird zu überschüssigem Eisen(II) gegeben und der Gehalt aus dem Anstieg der Indikationskurve ermittelt.

Chlorverflüchtigung aus der Lösung ist vermeidbar, wenn vor Probezugabe bereits soviel Eisen(II) erzeugt wurde, daß nur ein kleiner Rest von Hypochlorit austitriert werden muß.

Chloride, Perchlorate, Chlorate und Sulfate in sehr hoher Konzentration sowie Nitrate in max. zehnfachem Überschuß stören die Bestimmung nicht. Chlorite werden mittitriert.

Probepbestimmungen wurden mit Natriumhypochloritlösung² ausgeführt, deren Gehalt durch Titration mit Arsenit³ kontrolliert wurde.

TABELLE I.—BESTIMMUNG VON HYPOCHLORIT

Einwaage, μMol	Durchschnittsergebnis von n Bestimmungen, μMol	Strom, mA	n	Fehler, %
93,6	93,2	28,66	4	-0,4
17,61	17,58	4,64	11	-0,2
9,084	9,093	2,50	11	+0,1
1,018	1,021	0,266	4	+0,3
0,2119	0,2119	0,265	5	0,0*
0,1033	0,1021	0,247	5	+1,2*

* Indirekte amperometrische Bestimmung.¹

Bestimmung von Chlorat

Elektrolyt. Titan-tetrachlorid, 0.1*M*; Kaliumrhodanid, 0.08*M*; Salzsäure, 2*M*. Die Generator-kathode war eine nach Slovák und Příbyl⁴ präparierte Kupferamalgamelektrode mit einer Oberfläche um ca. 1400 mm². Zur Indikation diente eine auf +25 mV gegen SCE polarisierte rotierende Platinelektrode. Diese Elektrode bestand aus einem Platindraht, der in das Ende eines L-förmig gebogenen Glasrohrs eingeschmolzen war. Sie rotierte mit 1000 Umdrehungen pro Minute und diente gleichzeitig zum Rühren der Lösung.

Unter strömendem Stickstoff wird bei laufender Registrierung des Indikationsstroms Titan(III) erzeugt (Indikationsstrom steigt linear an), bis die Titan(III)-Konzentration mindestens äquivalent der zu erwartenden Probemenge an Chlorat ist. Danach wird die Probe ohne Stromunterbrechung zugegeben und weiter elektrolysiert, bis der Indikationsstrom erneut linear ansteigt, nachdem er zunächst stark abgesunken war. Die Zeitdifferenz der linearen Kurventeile ergibt den Gehalt an Chlorat. Das Absinken des Indikationsstromes rührt von der Bildung von Hypochlorit während der Messung her. Ammoniumsalze, Chloride, Perchlorate und Sulfate stören die Bestimmung nicht. Probebestimmungen wurden mit gereinigtem und getrocknetem Natriumchlorat ausgeführt.

TABELLE II.—BESTIMMUNG VON CHLORAT

Einwaage, μMol	Durchschnittsergebnis von n Bestimmungen, μMol	Strom, mA	n	Fehler, %
1243,0	1243,1	100,0	4	+0,09
235,4	235,6	28,9	6	+0,08
46,88	47,29	28,9	4	+0,85
11,453	11,453	11,1	4	0,0
1,395	1,385	1,43	4	+0,7

Zur Analyse von Gemischen kann in einer ersten Probe Hypochlorit bestimmt werden. In einer weiteren Probe wird Chlorat bestimmt, nachdem zuvor Hypochlorit durch Kochen mit Wasserstoffperoxid in alkalischer Lösung ausgetrieben worden ist. In einer dritten Probe können Verunreinigungen, die mit Titan(III) reduzierbar sind, bestimmt werden, indem man vorher alle oxydierenden Chlorverbindungen durch Kochen mit konz. HCl in Chlor umwandelt und mit Luft austreibt.

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Summary—Hypochlorite was determined by direct coulometric titration with iron(II) in an acetate buffered solution. Chlorate was titrated with titanium(III) in 2*M* hydrochloric acid. Amperometric indication with one and two electrodes, respectively, was used. Mixtures of hypochlorites and chlorates, *e.g.*, in industrial electrolytes, may be analysed.

Zusammenfassung—Hypochlorit wurde durch direkte coulometrische Titration mit Eisen(II) in acetathaltiger Lösung bestimmt. Chlorat kann mit Titan(III) in 2*M* salzsäure coulometrisch titriert werden. Die Äquivalenzpunkte wurden durch amperometrisch Indikation mit einer bzw. mit zwei polarisierten Elektroden angezeigt. Hypochlorit und Chlorat können in Mischungen z.B. in technischen Elektrolyselaugen, bestimmt werden.

Résumé—On a déterminé l'hypochlorite par titrage coulométrique direct avec le fer(II) dans une solution tamponnée à l'acétate. On a titré le chlorate avec le titane(III) en acide chlorhydrique 2*M*. On a utilisé l'indication ampérométrique une et deux électrodes respectivement. On peut analyser des mélanges d'hypochlorites et de chlorates, par exemple dans des électrolytes industriels.

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3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
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SUMMARIES FOR CARD INDEXES

Use of tetracyanoplatinate(II) for the luminescent detection of metal ions: B. C. CAPELIN and G. INGRAM, *Talanta*, 1970, 17, 187. (Department of Chemistry and Geology, Portsmouth Polytechnic, Portsmouth, Hampshire, England.)

Summary—The tetracyanoplatinate(II) (TCP) ion forms insoluble fluorescent compounds with many metal ions. This property has not hitherto been exploited for analytical use. The soluble sodium TCP salt has been applied as a reagent for metal ion detection. Fluorescent precipitates useful for detection of the metal ions were obtained with Y(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) and Th(IV). Limits of detection ranged from 5 to 200 ppm. With ammonium acetate as a masking agent, selective detection of 10 ppm of silver was achieved in the presence of the other metal ions. As little as 20 ppm of zirconium can be detected in the presence of hafnium, which yields a non-fluorescent precipitate.

L'automatisation en analyse par activation neutronique et ses applications à la production industrielle: J. PERDION, *Talanta*, 1970, 17, 197. (Centre d'Études Nucléaires de Grenoble, Rue des Martyrs, 38-Grenoble, France.)

Summary—Reasons are given for the applications of activation analysis being generally confined to laboratory use. Conditions are given for application of analytical methods to industrial process control, in particular for automatic determination of oxygen in steels.

A study of some matrix effects in the determination of beryllium by atomic-absorption spectroscopy in the nitrous oxide-acetylene flame: B. FLEET, K. V. LIBERTY and T. S. WEST, *Talanta*, 1970, 17, 203. (Chemistry Department, Imperial College, London, S.W. 7.)

Summary—A study has been made of a number of interferences observed in the trace determination of beryllium by atomic-absorption in the nitrous oxide-acetylene flame. The major negative interference caused by the presence of excess of aluminium salts may be overcome by the use of 8-hydroxyquinoline. Magnesium and silicon also depress the Be signal but most other metals cause enhancement. In most instances the enhancements may be made uniform by the addition of potassium ions to the sample solution.

ИСПОЛЬЗОВАНИЕ ТЕТРАЦИАНОПЛАТИНАТА(II)
ДЛЯ ОБНАРУЖЕНИЯ ИОНОВ МЕТАЛЛОВ
МЕТОДОМ ЛЮМИНЕСЦЕНЦИИ:

V. C. CARPIN and G. INGRAM, *Talanta*, 1970, 17, 187.

Резюме—Тетрацианоплатинат(II) ион (ТЦП) образует нерастворимые флуоресцирующие соединения с рядом ионов металлов. Этой характеристикой до сих пор не пользовались для аналитических целей. Растворимую натриевую соль ТЦП применили в качестве реагента для обнаружения ионов металлов. Флуоресцирующие осадки, используемые для обнаружения ионов металлов получены с У(III), Zr(IV), Ag(I), Zn(II), Cd(II), Hg(I), Hg(II), Al(III), Pb(II), La(III) и Th(IV). Чувствительность составляла 5 до 200 мг/л. С использованием ацетата аммония в качестве маскирующего агента получено селективное определение 10 мг/л серебра в присутствии других ионов металлов. Определено до 20 мг/л циркония в присутствии гафния, который образует нефлуоресцирующий осадок.

АВТОМАТИЗАЦИЯ НЕЙТРОННОАКТИВАЦИОННОГО
АНАЛИЗА И ЕГО ПРИМЕНЕНИЕ В
ПРОМЫШЛЕННОМ ПРОИЗВОДСТВЕ:

J. PERDION, *Talanta*, 1970, 17, 197

Резюме—Обсуждено применение активационного анализа, который в принципе использован только в лаборатории. Даны условия для применения аналитических методов в регулировании промышленных процессов, в частности в автоматическом определении кислорода в сталях.

ИЗУЧЕНИЕ НЕКОТОРЫХ МАТРИЧНЫХ
ЭФФЕКТОВ В ОПРЕДЕЛЕНИИ БЕРИЛЛИЯ
МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ
СПЕКТРОСКОПИИ В ПЛАМЕНИ ЗАКИСИ АЗОТА
И АЦЕТИЛЕНА:

V. FLEET, K. V. LIBERTY and T. S. WEST, *Talanta*, 1970, 17, 203.

Резюме—Изучен ряд мешающих эффектов обнаруженных в определении следов бериллия методом атомно-абсорбционной спектроскопии в пламени закиси азота и ацетилена. Главное мешающее действие, вызвано присутствием избытка солей алюминия можно избежать использованием 8-оксихинолина. Магний и кремний также снижают сигнал бериллия но большинство других металлов повышают этот сигнал. В большинстве случаев добавление к раствору ионов калия выравнивает эти повышения.

Determination of microgram amounts of metals by chronometric analysis: A. PALL, G. SVEHLA and L. ERDEY, *Talanta*, 1970, 17, 211. (Institute for General and Analytical Chemistry of the Technical University, Budapest, Hungary.)

Summary—The reaction between peroxodisulphate and iodide, modified by the addition of thiosulphate to show the Landolt effect, has been used for the determination of copper and iron in the range 1–100 $\mu\text{g/ml}$, based on the catalytic effect of these ions. The procedure is rapid and simple, and the errors are less than 10%. The interference from iron in the determination of copper may be overcome by the addition of a masking reagent such as fluoride.

Verwendung mäßig dissoziierter Komplexe bei spektralphotometrischen Bestimmungen—II. Reaktionen von Arsenazo III mit Uranyl und Thorium(IV): J. BORÁK, Z. SLOVÁK und J. FISCHER, *Talanta*, 1970, 17, 215. (Institut für reine Chemikalien, Lachema Brno, Tschechoslowakei.)

Summary—The reaction of uranyl ion with Arsenazo III in acid solution gives rise to the formation of two complexes of the type ML, the proportions of these two being dependent on the acidity. The molar absorptivities of the complexes at 565 nm are 5.3×10^3 and $8.8 \times 10^3 \text{ l.mole}^{-1}.\text{mm}^{-1}$. The formation constants have been determined, and the apparent variation in the sensitivity of the reaction is explained. In acid solution thorium forms complexes with Arsenazo III of the types M_2L , ML (two), and ML_2 , the last of which is analytically useful, although partially dissociated. It predominates in strongly acid solution containing a large excess of reagent, and has a molar absorptivity at 658 nm of $12.8 \times 10^3 \text{ l.mole}^{-1}.\text{mm}^{-1}$.

2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid as a new acid-base indicator: J. JENÍK and F. RENGGER, *Talanta*, 1970, 17, 231. (Department of Analytical Chemistry, College of Chemical Technology, Pardubice, Slov. povstání 565, Czechoslovakia.)

Summary—2,4-Bis(4-nitrobenzazo)resorcinol-6-sulphonic acid is suggested as a new visual acid-base indicator, which because of its colour sharpness and other qualities is useful in titrations of weak acids. There are two colour transitions, one from yellow to red at pH 6.8–8.2, the other from red to blue-violet at 10.5–13.0. The corresponding dissociation constants are $\text{p}K_1$ 7.64, and $\text{p}K_2$ 11.64.

ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ
КОЛИЧЕСТВ МЕТАЛЛОВ МЕТОДОМ
ХРОНОМЕТРИЧЕСКОГО АНАЛИЗА:

A. PALL, G. SVENLA and L. ERDEY, *Talanta*, 1970, 17, 211.

Резюме—Реакция пероксидисульфата с иодидом, изменена добавлением тиосульфата для получения эффекта Ландольта, применена в определении меди и железа в пределах 1–100 мкг/мл на основе каталитического действия этих ионов. Метод является быстрым и несложным, а ошибки меньше чем 10%. Влияние железа в определении меди избегнуто добавлением маскирующего агента, на пример фторидона.

ПРИМЕНЕНИЕ УМЕРЕННО ДИССОЦИИРОВАННЫХ
КОМПЛЕКСОВ В АНАЛИЗЕ СПЕКТРОФОТОМЕТР-
ИЧЕСКИМ МЕТОДОМ—II. РЕАКЦИИ АРСЕНАЗО
III С УРАНИЛОМ И ТОРИЕМ(IV):

J. BORÁK, Z. SLOVÁK and J. FISCHER, *Talanta*, 1970, 17, 215.

Резюме—В реакции уранилиона с арсеназо III в кислом растворе образуются два комплекса типа ML, отношение которых зависит от кислотности раствора. Дифференциальные молярные светопоглощения комплексов при 565 нм равны $5,3 \times 10^3$ и $8,8 \times 10^3$ л.моль⁻¹.мм⁻¹. Определены константы образования и разъяснено видимое колебание чувствительности реакции. В кислом растворе торий образует комплексы с арсеназо III типа M₂L, ML (два) и ML₂; последним можно пользоваться в анализе хотя он частично диссоциирован. Этот комплекс преобладает в сильнокислом растворе в присутствии большего избытка реагента, его дифференциальное молярное светопоглощение равно, при 658 нм, $12,8 \times 10^3$ л.моль⁻¹.мм⁻¹.

2,4-БИС(4-НИТРОБЕНЗАЗО)РЕЗОРЦИНОЛ-6-
СУЛЬФОНОВАЯ КИСЛОТА В КАЧЕСТВЕ НОВОГО
КИСЛОТНО-ЩЕЛОЧНОГО ИНДИКАТОРА:

J. JENÍK and F. RENGGER, *Talanta*, 1970, 17, 231.

Резюме — 2,4-Бис(4-нитробензазо)резорцинол-6-сульфоновая кислота предложена в качестве нового визуального кислотно—щелочного индикатора, который является полезным в титровании слабых кислот вследствие его острой перемены цвета и других характеристик. Имеются две перемены цвета, одна из желтого в красный при pH 6,8–8,2, другой—из красного в сине-фиолетовый при 10,5–13,0. Соответствующие константы диссоциации равны pK₁ 7,64 и pK₂ 11,64.

Silver(III) as an oxidative titrant. Determination of some sugars, carboxylic acids and inorganic ions: P. K. JAISWAL and K. L. YADAVA, *Talanta*, 1970, **17**, 236. (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—Silver(III) has been stabilized as its tellurato complex and used for the oxidation of sugars, organic acids, ferrocyanide, sulphide, peroxide and thiosulphate, the excess of oxidant being measured by reducing it with an excess of arsenite and then titrating the surplus arsenite with iodine.

The volumetric determination of nitrite with chloramine T: J. AGTERDENBOS, *Talanta*, 1970, **17**, 238. (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands.)

Summary—Nitrite may be determined by oxidation with chloramine T, reaction of the excess of chloramine T with excess KI, and titration of I_2 formed, with thiosulphate. The reproducibility and some interferences are discussed.

Exchange reactions of ternary ion-association complexes directly in the organic phase: R. W. BURKE, *Talanta*, 1970, **17**, 240. (Institute for Materials Research, National Bureau of Standards, Washington, D.C., U.S.A. 20234.)

Summary—The analytical implications of exchanging a highly coloured or fluorescent group R for a non-coloured or non-fluorescent one directly in the organic phase are discussed for ternary ion-association complexes of the type $[ML_x^-]R^+$. Several examples are given to illustrate the approach.

СЕРЕБРО(III) В КАЧЕСТВЕ ОКИСЛИТЕЛЬНОГО
ТИТРОВАННОГО РАСТВОРА. ОПРЕДЕЛЕНИЕ
НЕКОТОРЫХ САХАРОВ, КАРБОНОВЫХ КИСЛОТ
И НЕОРГАНИЧЕСКИХ ИОНОВ:

P. K. JAISWAL and K. L. YADAVA, *Talanta*, 1970, 17, 236.

Резюме—Серебро(III) стабилизировано в форме его теллурато-комплекса и использовано для окисления сахаров, органических кислот, ферроцианида, сульфида, перекиси и тиосульфата. Избыток окислительного реагента определяли его восстановлением с избытком арсенита и оттитровыванием избыточного арсенита с иодом.

ТИТРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИТРИТА
ХЛОРАМИНОМ Т:

J. AGTERDENBOS, *Talanta*, 1970, 17, 238.

Резюме—Нитрит определяли окислением с хлораминном Т, реактированием избытка хлорамина Т с избытком KI и титрованием образующегося I_2 с тиосульфатом. Обсуждены воспроизводимость результатов и некоторые мешающие действия.

РЕАКЦИИ ОБМЕНА ТРОЙНЫХ
ИОНОАССОЦИАЦИОННЫХ КОМПЛЕКСОВ
НЕПОСРЕДСТВЕННО В ОРГАНИЧЕСКОЙ ФАЗЕ:

R. W. BURKE, *Talanta*, 1970, 17, 240.

Резюме—Рассмотрено аналитическое значение замены сильноокрашенной флуоресцирующей группы R за неокрашенную или нефлуоресцирующую группу непосредственно в органической фазе для случая тройных ионоассоциационных комплексов типа $[ML_2]R^+$. Приведено число примеров для объяснения вопроса.

The structure of primary nickel dithizonate: MICHAEL LAING and P. A. ALSOP, *Talanta*, 1970, 17, 242. (Department of Chemistry, University of Natal, Durban, and Department of Chemistry, University College of Rhodesia, Salisbury.)

Summary—Primary nickel dithizonate is found to be isostructural with the palladium and platinum complexes, and the nickel dithizonate molecule is shown to contain nickel in an approximately square planar configuration bonded to the organic ligand through both sulphur and nitrogen atoms.

Determination of dicyclohexylamine in sodium cyclamate: J. W. ERSKINE and A. F. WILLIAMS, *Talanta*, 1970, 17, 244. (Research and Development Department, I.C.I., Nobel Division, Stevenston, Ayrshire.)

Summary—Dicyclohexylamine is determined in sodium cyclamate at levels of concentration down to the order of 1 ppm by measurement of the yellow colour of the chloroform extract of its Bromophenol Blue complex.

Coulometrische Titration von Hypochloriten und Chloraten: PETER GRÜNDLER and HEINZ HOLZAPFEL, *Talanta*, 1970, 17, 246. (Sektion Chemie, Karl-Marx-Universität, Liebigstrasse 18, 701 Leipzig, D.D.R.)

Summary—Hypochlorite was determined by direct coulometric titration with iron(II) in an acetate buffered solution. Chlorate was titrated with titanium(III) in 2M hydrochloric acid. Amperometric indication with one and two electrodes, respectively, was used. Mixtures of hypochlorites and chlorates, *e.g.*, in industrial electrolytes, may be analysed.

КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА ПЕРВИЧНОГО
ДИТИЗОНАТА НИКЕЛЯ:

MICHAEL LAING and P. A. ALSPO, *Talanta*, 1970, 17, 242.

Резюме—Первичный дитизонат никеля является изоструктурным с комплексами палладия и платины, а никель в молекуле дитизоната никеля присутствует в приблизительно квадратической планарной конфигурации связанной с органическим лигандом через атомы серы и азота.

ОПРЕДЕЛЕНИЕ ДИЦИКЛОГЕКСИЛАМИНА В
ЦИКЛАМАТЕ НАТРИЯ:

J. W. ERSKINE and A. F. WILLIAMS, *Talanta*, 1970, 17, 244.

Резюме—Дидициклогексиламин определен в цикламате натрия до концентраций величины I части на Миллион измерением желтого цвета хлороформового экстракта его комплекса с бромфеноловым голубым.

КУЛОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ
ГИПОХЛОРИТОВ И ХЛОРАТОВ:

PETER GRÜNDLER and HEINZ HOLZAPFEL, *Talanta*, 1970, 17, 246.

Резюме—Гипохлорит определяли непосредственным кулонометрическим титрованием с железом(II) в растворе, буферизованном ацетатным буфером. Хлорат титровали с титаном(III) в 2*M* соляной кислоте. Использовано амперометрическое индицирование с одним или двумя электродами, соответственно. Метод позволяет анализировать смеси гипохлоритов и хлоратов, на пример промышленные электролиты.

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PARTIAL CONTENTS OF A RECENT ISSUE

H. Baker MD MRCP Experimental studies on the influence of vehicles on percutaneous absorption

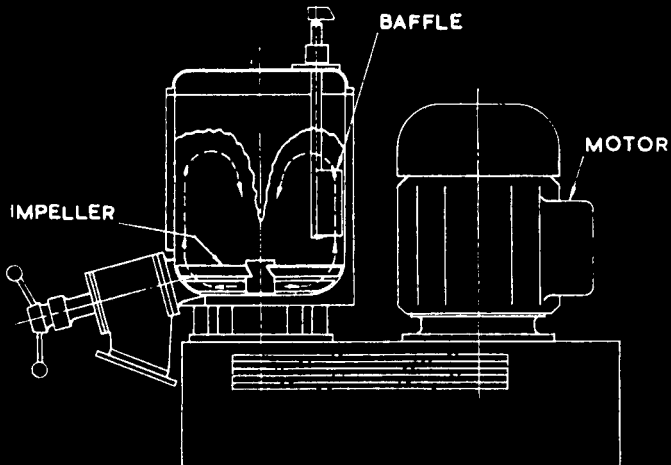
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P. R. Bunkall and M. Quinn Instrumental colour measurement and control

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Contents

B.C.CAPELIN and G.INGRAM: Use of tetracyanoplatinate(II) for the luminescent detection of mercury ions

J.PERDIJON: L'automatisation en analyse par activation neutronique et ses applications à la production industrielle

B.FLEET, K.V.LIBERTY and T.S.WEST: A study of some matrix effects in the determination of beryllium by atomic-absorption spectroscopy in the nitrous oxide-acetylene flame

A.PÁLL, G.SVEHLA and L.FRÉDY: Determination of microgram amounts of metals by chronometric analysis

J.BORÁK, Z.SLOVÁK and J.FISCHER: Verwendung mäßig dissoziierter Komplexe bei spektralphotometrischen Bestimmungen—II. Reaktionen von Arsenazo III mit Uranyl und Thorium(IV)

Short Communications

J.JENÍK and F.RENGER: 2,4-Bis(4-nitrobenzoyl)resorcinol-6-sulphonic acid as a new acid-base indicator

P.K.JAISWAL and K.L.YADAVA: Silver(III) as an oxidative titrant. Determination of some sugar carboxylic acids and inorganic ions

J.AGTERDENBOS: The volumetric determination of nitrite with chloramine T

R.W.BURKE: Exchange reactions of ternary ion-association complexes directly in the organic phase

MICHAEL LAING and P.A.ALSOP: The structure of primary nickel dithizonate

J.W.ERSKINE and A.F.WILLIAMS: Determination of dicyclohexylamine in sodium cyclamate

PETER GRÜNDLER und HEINZ HOLZAPFEL: Coulometrische Titration von Hypochloriten und Chloraten

Papers Received

Notes for Authors

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